

## Synthesis and Characterization of Cobalt Complexes of 2-Hydroxy-1-Naphthaldehyde-Morpholine-N-Thiohydrazone (H<sub>2</sub>-Hnmthon)

**Dr.Naresh Pratap**

Associate Professor

Applied Science K.N.G.D.M.E.C.

Modinagar, Ghaziabad

**Dr.Pragati Singh**

Associate Professor

Deptt of Chemistry

IIMT Ghaziabad

**Barkha Rani**

Research Scholar

Dr. K.N.Modi University

Newai (Rajasthan)

### ABSTRACT

Schiff base constitute a very important group of N, O-donor chelating ligands<sup>(1-4)</sup>. Another group of ligands containing the azomethine grouping (-C=N-) found in Schiff bases is constituted by hydrazones which have also been used as ligand though they are not widely studied<sup>(5-9)</sup> as the Schiff bases. Hydrazine is widely used as a strong reducing agent for corrosion control in boilers and hot water heating systems, also for metal plating and for reducing noble metal catalysts and unsaturated bonds in organic compounds. It is the starting material for many derivatives like antioxidants polymers, plant growth regulators and pesticides. Besides this hydrazine is used in the synthesis of pharmaceuticals such as hydralazine, hydrocarbazine, mebanazine, isoniazide etc.

### INTRODUCTION:

Aroyl hydrazone Schiff bases because of their ambiprotic and flexidentate behaviour provide a wide range of stereochemistry with various metal ions. In highly diluted solution monomeric nature of the complexes may be assumed. Ligand behaviour of aroyl hydrazone Schiff bases viz o-hydroxy naphthalidene benzoyl hydrazone and o-hydroxy naphthalidene salicyloyl hydrazone have been studied with metal ions. Both the ligands behave as monoprotic and bidentate (NO) donors complexation is favoured both by enthalpy and entropy changes. Hydrazides and hydrazones have interesting ligational properties due to the presence of several potential coordination sites and transition metal complexes of these ligands have been studied extensively<sup>(10-12)</sup>. Hydrazones also exhibit pharmacological activity and analytical applications.

Here we report the reactions of 2-hydroxy-1-naphthaldehyde morpholine-N-thiohydrazone (abbreviated to (H<sub>2</sub> hnmthon) with different salts/complexes of Cobalt (II and III) leading to isolation of many new Cobalt (II and III) complexes. [Co(hnmthon) (H<sub>2</sub>O)<sub>3</sub>], isolated in this study, react further with a number of donors to form many new mixed ligand complexes of Cobalt (II and III) including several heterochelates of Cobalt (III).

### Preparation of 2 hydroxy-1-Naphthaldehyde -Morpholine-N-Thiohydrazone-(H<sub>2</sub>hnmthon):

Morpholine-N-thiohydrazone was prepared via the preparation of potassium morpholine dithioacetate by a published method<sup>(13)</sup> and its subsequent treatment with 85% hydrazine hydrate. 2-OH-1-naphthaldehyde (0.01 mol) was treated with ethanolic solution (80 ml) of morpholine-N-thiohydrazone (0.01 mol) under reflux for a period of two hour. The solution on concentration at reduced pressure yielded a light coloured compound.

**(H<sub>2</sub>-hnmthon):** Light cream, m.p.-170<sup>0</sup> C Found: C-60.80, H-5.27, N-13.25 calculated for (C<sub>16</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub>S) C-(60.95), H-(5.40) and N- (13.33).

### Preparation of the metal complexes

1. **[Co(II) (H-hnmthon) (NO<sub>3</sub>) (H<sub>2</sub>O)<sub>2</sub>]:** To a methanolic solution (20 ml) of H<sub>2</sub> nmthon (3.15 g, 0.01mol) a methanolic solution (20 ml) of Co(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O (2.91 g, 0.01mol) was added and the brownish solution was allowed to reflux on a steam bath for three hour (pH ~4) and filtered. A red crystalline compound was obtained from the filtrate on cooling. It was recrystallised from methanol and dried in vacuo, yield 70%.

2. **[Co(II) (H-hnmthon) (Cl) (H<sub>2</sub>O)<sub>2</sub>]:** The dark red coloured compound was isolated in a good yield by a similar procedure when equimolar solutions of (0.01 mol) CoCl<sub>2</sub>.6H<sub>2</sub>O and (H<sub>2</sub>-nmthon) were allowed to react in hot methanol for 3-hour (pH~5). The precipitated compound was collected by filtration and recrystallised from methanol and dried in vacuo, yield ~55%
3. **[Co(II) (hnmthon)]<sub>2</sub>: Co(CH<sub>3</sub>COO)<sub>2</sub>.4H<sub>2</sub>O** was dissolved in 20 ml dry methanol a freshly prepared solution of 2-hydroxy-1-naphthaldehyde morpholine-N-Thiohydrazone (0.01 mol) in equimolar amount in 20 ml dry methanol was added to the above solution with stirring under an atmosphere of nitrogen to get a blue coloured solution. After the addition was complete, it was refluxed for two hours on water bath. The bluish compound obtained was filtered washed with water, methoanol and finally with diethyl ether.
4. **[C(III) (H-ynmthon) (acac)<sub>2</sub> (H<sub>2</sub>O)]:** To a methanolic solution (20 ml) of (H<sub>2</sub>nmthon) (3.15 g, 0.01 mol), a methanolic solution 30 ml of Co(acetyl acetone)<sub>3</sub> (3.56g, 0.01 mol) was added, contents were heated under reflux on a steam bath for three hour (pH~7) and filtered. The filtrate was concentrated to 25 ml which on standing gave dark green solid compound. It was filtered off, washed with methanol and dried in vacuo yield 70%
5. **[Co(II) (hnmthon) (H<sub>2</sub>O)<sub>3</sub>]:** The sodium salt of the ligand 2-Hydroxy-1-naphthaldehyde morpholine-N-Thiohydrazone (3.15 g, 0.01 mol) was prepared by treating the ligand with metallic sodium in methanol (20 ml) under nitrogen. To this yellow solution CoCl<sub>2</sub>.6H<sub>2</sub>O (2.38 g, 0.01 mol) in methanol (20 ml) was added and contents were heated under reflux fo about 3-hour, followed by filtration. On cooling brown coloured solid precipitated out. It was filtered off, washed with cold methanol and dried in vacuo, yield 65%.
6. **[Co(III) (hnmthon) (H<sub>2</sub>O)<sub>2</sub> (NO<sub>3</sub>)<sub>3</sub>]:** This reddish brown compound was prepared similiary by the reaction of Na<sub>2</sub>-Hnmthon (prepared in situ) and Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O (1:1) molar ratio in methanol. Oxygen passed continuously for about two hour. The same reaction however when carried out under dry nitrogen atmosphere afforded a Cobalt(II) complex of the type [Co(II) (H-Hnmthon) (NO<sub>3</sub>) (H<sub>2</sub>O)]<sub>2</sub>,<sup>(7)</sup> where NO<sub>3</sub> function as a bidentate donor. Yield 75%.
7. **[Co(III) (hnmthon) (Cl) (H<sub>2</sub>O)<sub>2</sub>]:** The reaction between Na<sub>2</sub>-Hnmthon and CoCl<sub>2</sub>.6H<sub>2</sub>O in methanol under reflux in 1 : 1 molar ratio, afforded a brown powdery compound. It was recrystallised from methanol and petrollum ether, Yield 60%
8. **Some reactions of Co(II) (hnmthon) (H<sub>2</sub>O)<sub>3</sub> with Pyridine:** The compound [Co(II) (hnmthon) (H<sub>2</sub>O)<sub>3</sub>] was dissolved in freshly distilled pyridine to prepare a saturated solution. It was filtered and the clear filtrate was kept in 0-50C, for 3-4 days when deep brown crystals of [Co(II) (hnmthon) (Py) (OH) (H<sub>2</sub>O)] separated out, which ware filtered off and recrystallised from ethanol. Yield 50%.
9. **With triphenyl phosphine:** To a solution of [Co(II) (hnmthon) (H<sub>2</sub>O)<sub>3</sub>] (2.12 g, 0.005 mol) in acetonitrile (10 ml) was added a solution of triphenyl phosphine (1.31g, 0.005 mol) and the mixture was heated under reflux on steam bath for 3-hour. The separated dark brown solid [Co(II) (hnmthon) (Ph<sub>3</sub>P) (H<sub>2</sub>O)<sub>2</sub>] was filtered off, washed with methanol ether mixture and dried in vacuo, yield 50%.
10. **With pyridine in the presence of NaClO<sub>4</sub>:** To a solution of [Co(II) (hnmthon) (H<sub>2</sub>O)<sub>3</sub>] (2.12 g, 0.005 mol) in acetonitrile (10 ml), solid NaClO<sub>4</sub> (0.61 g, 0.005 mol) and dipyridine(0.78 g, 0.005 mol) were added. Air was then drawn through this mixture for 10-12 hour and solution filtered. After reducing its volume to half, whole contents were kept in ice (0-5) for two days. The dark brown crystals of [Co(II) (hnmthon) (Py)<sub>2</sub> (H<sub>2</sub>O) ClO<sub>4</sub>,] so obtained were filtered off and recrystallised from ethanol. Yield 60%
11. **With dipyridine (in the presence of NaClO<sub>4</sub>):** To a solution of [Co(II) (hnmthon) (H<sub>2</sub>O)<sub>3</sub>] 2.12 g, 0.005 mol in acetonitrile 10ml, solid NaClO<sub>4</sub> (0.61 g, 0.005 mol) and dipyridine (0.78 g, 0.005 mol)

were added. Air was then drawn through this mixture for 10-12 hour and solution filtered. The volume of the filtrate was reduced under low pressure and it was kept in ice (0-5<sup>0</sup>C) for two days.

The dark brown crystals of [Co(III) (hnmthon) (dip) (H<sub>2</sub>O)] ClO<sub>4</sub> separated out. It was filtered, washed with methanol and dried in vacuo.

With acetyl acetone (Hacac), glycine (H.gly) N,N-bis acetophenone ethylene imine (bape) N-phenyl salicylalimine (H Salan). N-phenyl ortho hydroxy acetophenone imine (H hapan); N-carboxy methyl salicylalimine (H<sub>2</sub> salgly); N-2-hydroxy phenyl salicylalimine (H<sub>2</sub> saloap), anthranilic acid (H ana) and N-2-carboxy phenyl salicylalimine (H<sub>2</sub>-Salana). An equimolar mixture (1:1 molar ratio) of the complex [Co(II) (hnmthon) (H<sub>2</sub>O)<sub>3</sub>] and the ligands acetyl acetone, glycine, N, N-bis acetiphenone ethylele-imine, N-phenyl salicylalimine, N-phenylortho-hydroxy acetophenone imine, N-2 carboxy phenyl salicylalimine anthramilic acid in methanol-acetonitrile (50:50 v/v) mixture was refluxed for two hour in excess of oxygen at pH-9 (NH<sub>4</sub>OH) and filtered while hot. The filtrate gave the following coloured cobalt(III) complexes in good yield.

12. [Co(III) (hnmthon) (acac) (H<sub>2</sub>O) Yield 65%]
13. [Co(III) (hnmthon) (gly) (H<sub>2</sub>O) Yield 65%]
14. [Co(III) (hnmthon) (bapei) (OH) Yield 75%]
15. [Co(III) (hnmthon) (Salan) (H<sub>2</sub>O) Yield 70%]
16. [Co(III) (hnmthon) (Ohapan) (H<sub>2</sub>O) Yield 75%]
17. [NH<sub>4</sub>(III) (hnmthon) (Salgly) (H<sub>2</sub>O) Yield 70%]
18. [NH<sub>4</sub>(III) (hnmthon) (Saloap) (H<sub>2</sub>O) Yield 70%]
19. [Co(III) (hnmthon) (ana) (H<sub>2</sub>O) Yield 65%]
20. [NH<sub>4</sub>(III) (hnmthon) (Salana) (H<sub>2</sub>O) Yield 75%]

**TABLE 1. – ELEMENTAL ANALYSIS, MOLECULAR WEIGHTS AND MELTING POINTS OF THE COMPLEX**

S. No.	Complexes	Mol. Wt. Found (Calcd.)	M.P. °C	Found (calculated)%			
				C	H	N	Co
1.	Co(II) (H-hnmthon) (NO <sub>3</sub> )(H <sub>2</sub> O) <sub>2</sub> (C <sub>16</sub> H <sub>20</sub> N <sub>4</sub> O <sub>7</sub> S)Co	460.80(470.93)	175(d)	40.66(40.77)	4.19(4.25)	11.80(11.89)	12.36(12.51)
2.	Co(II) (H-hnmthon) (Cl)(H <sub>2</sub> O) <sub>2</sub> (C <sub>16</sub> H <sub>20</sub> N <sub>3</sub> O <sub>4</sub> SCl)Co	436.10 (444.43)	162(dec)	43.10(43.20)	4.20(4.50)	9.35 (9.45)	13.14 (13.25)
3	Co(II) (H-hnmthon) <sub>2</sub> (C <sub>16</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> S)2Co	670.22 (684.93)	> 340	55.98(56.06)	4.28(4.28)	12.14 (12.26)	8.45 (8.60)
4.	Co(II) (H-hnmthon) (acac) <sub>2</sub> (H <sub>2</sub> O) (C <sub>26</sub> H <sub>32</sub> N <sub>3</sub> O <sub>7</sub> S)Co	580.33 (588.93)	146d	52.75(52.98)	5.34(5.43)	7.70(7.13)	9.83(10.01)
5.	Co(II) (H-hnmthon) (acac) <sub>2</sub> (H <sub>2</sub> O) (C <sub>16</sub> H <sub>21</sub> N <sub>3</sub> O <sub>5</sub> S)Co	412.70(425.93)	> 330	45.0(45.07)	4.80(4.93)	9.73(9.86)	13.74(13.84)
6.	Co(II) (H-hnmthon) (acac)(H <sub>2</sub> O) <sub>2</sub> (NO <sub>3</sub> ) (C <sub>16</sub> H <sub>19</sub> N <sub>4</sub> O <sub>7</sub> S)Co	456.10(469.93)	152(d)	40.73(40.85)	4.0(4.04)	11.82(11.92)	12.44(12.45)
7.	Co(II) (H-hnmthon) (acac) <sub>3</sub> (H <sub>2</sub> O) (C <sub>16</sub> H <sub>18</sub> N <sub>4</sub> O <sub>6</sub> S)Co	452.93	165dec	42.26(42.39)	3.85(3.97)	12.25(12.36)	12.94(13.01)

**TABLE 2. – ELEMENTAL ANALYSIS, MOLECULAR WEIGHTS AND MELTING POINTS OF THE COMPLEX**

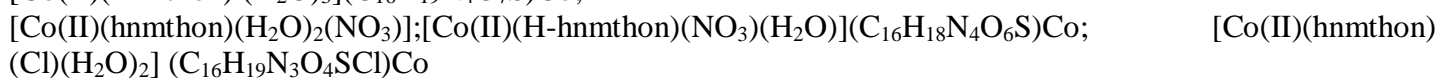
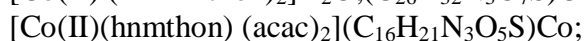
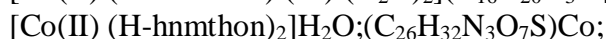
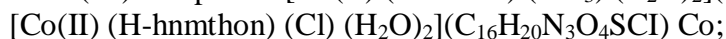
S. No.	Complexes	Mol. Wt. Found (Calcd.)	M.P. °C	Found (calculated)%			
				C	H	N	Co
8.	Co(III) (hnmthon) (H <sub>2</sub> O) <sub>2</sub> (C <sub>16</sub> H <sub>19</sub> N <sub>3</sub> O <sub>4</sub> SCI)Co	443.43	327(d)	43.18(43.30)	4.17(4.28)	9.35(9.47)	13.13(13.27)
9.	Co(III) (hnmthon) (Py)(H <sub>2</sub> O) (C <sub>21</sub> H <sub>23</sub> N <sub>4</sub> O <sub>4</sub> SCI)Co	473.16(485.93)	140(d)	50.84(51.18)	4.62(4.73)	11.41(11.52)	12.0(12.13)
10.	Co(II) (hnmthon)(Ph <sub>3</sub> P) (H <sub>2</sub> O) <sub>2</sub> (C <sub>34</sub> H <sub>34</sub> N <sub>3</sub> O <sub>4</sub> S)2Co	650.13(669.93)	> 310	60.75(60.90)	5.0(5.07)	6.15(6.27)	8.61(8.79)
11.	Co(III) (hnmthon)(Py) <sub>2</sub> (H <sub>2</sub> O)ClO <sub>4</sub> (C <sub>26</sub> H <sub>27</sub> N <sub>5</sub> O <sub>7</sub> SCI)Co	635.10(647.43)	168(d)	48.10(48.19)	4.03(4.17)	10.68(10.81)	9.0(9.09)
12.	Co(III) (hnmthon) (dip)(H <sub>2</sub> O)ClO <sub>4</sub> (C <sub>26</sub> H <sub>23</sub> N <sub>5</sub> O <sub>7</sub> S)Co	630.89(643.43)	192(d)	48.34(48.49)	3.43(3.57)	10.72(10.87)	9.01(9.15)
13.	[Co(III) (hnmthon) (acac)(H <sub>2</sub> O)] (C <sub>21</sub> H <sub>24</sub> N <sub>3</sub> O <sub>5</sub> S)Co	470.33(489.93)	212(d)	51.33(51.43)	4.75(4.89)	8.42(8.57)	11.93(12.02)
14.	[Co(III) (hnmthon) (gly) (H <sub>2</sub> O)] (C <sub>18</sub> H <sub>21</sub> N <sub>4</sub> O <sub>5</sub> S)Co	453.68(463.93)	198(d)	46.42(46.55)	4.39(4.52)	12.0(12.07)	12.55(12.70)

**TABLE 3. – ELEMENTAL ANALYSIS, MOLECULAR WEIGHTS AND MELTING POINTS OF THE COMPLEX**

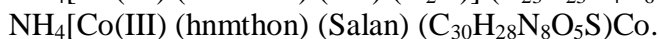
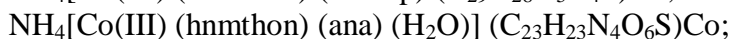
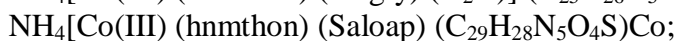
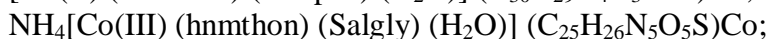
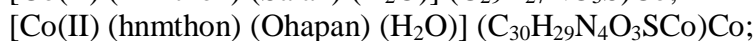
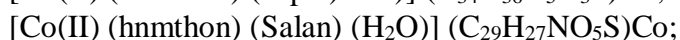
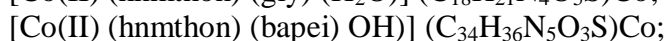
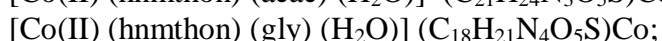
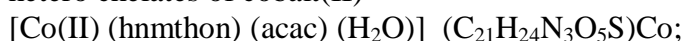
S. No.	Complexes	Mol. Wt. Found (Calcd.)	M.P. °C	Found (calculated)%			
				C	H	N	Co
15.	Co(III) (hnmthon)(baci) (H <sub>2</sub> O) <sub>2</sub> (C <sub>34</sub> H <sub>36</sub> N <sub>5</sub> O <sub>3</sub> S)Co	(652.93)640.34	292(d)	62.35(62.49)	5.40(5.51)	10.62(10.72)	8.93(9.02)
16.	Co(III) (hnmthon)(salan) (H <sub>2</sub> O) (C <sub>29</sub> H <sub>27</sub> N <sub>3</sub> O <sub>5</sub> S)Co	(587.93)570.85	200(d)	59.05(59.19)	4.50(4.59)	7.02(7.14)	9.95(10.02)
17.	[Co(III) (hnmthon)(ohapan) (H <sub>2</sub> O)] (C <sub>30</sub> H <sub>29</sub> N <sub>4</sub> O <sub>3</sub> S)Co	(583.93)572.12	218(d)	61.52(61.65)	4.86(4.96)	9.52(9.59)	9.98(10.09)
18.	NH <sub>4</sub> [Co(III) (hnmthon)(Saloap) (C <sub>25</sub> H <sub>26</sub> N <sub>5</sub> O <sub>5</sub> S)Co	(566.93)556.76	228(d)	52.78(52.91)	4.49(4.58)	12.23(12.34)	10.30(10.39)
19.	NH <sub>4</sub> [Co(III) (hnmthon)(Saloap)] (C <sub>29</sub> H <sub>28</sub> N <sub>5</sub> O <sub>4</sub> S)Co	(600.93)590.66	248(d)	57.80(57.91)	4.57(4.65)	11.56(11.64)	9.70(9.80)
20.	NH <sub>4</sub> [Co(III) (hnmthon)(ana) (H <sub>2</sub> O)] (C <sub>23</sub> H <sub>23</sub> N <sub>4</sub> O <sub>6</sub> S)Co	(541.93)530.72	185(d)	50.80(50.92)	4.14(4.24)	10.24(10.93)	10.77(10.87)
21.	NH <sub>4</sub> [Co(III) (hnmthon)(Saloap)] (C <sub>30</sub> H <sub>28</sub> N <sub>8</sub> O <sub>5</sub> S)Co	(670.93)660.20	240(d)	53.58(53.66)	4.10(4.17)	16.60(16.69)	8.70(8.78)

**RESULTS AND DISCUSSION:**

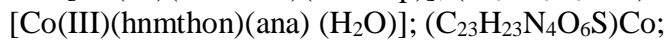
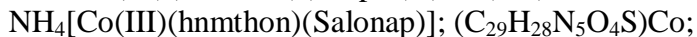
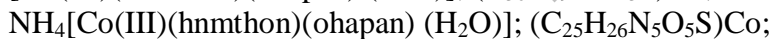
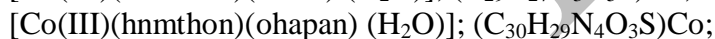
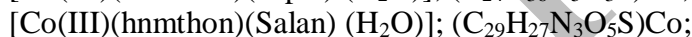
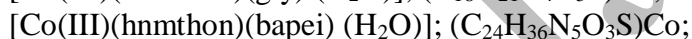
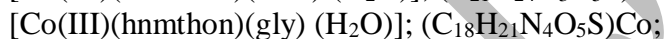
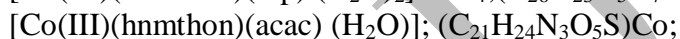
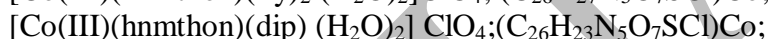
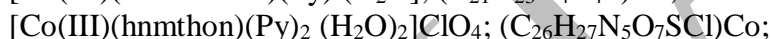
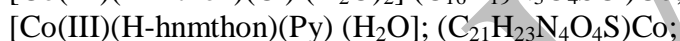
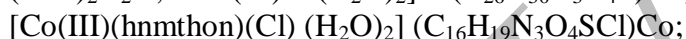
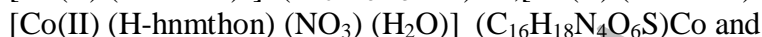
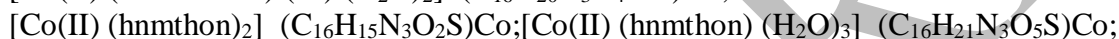
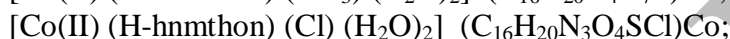
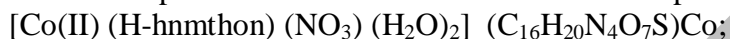
The reaction of 2-Hydroxy-1-naphthaldehyde morpholine-N-Thiohydrazone ( $H_2$ -hnmthon) with  $CoCl_2 \cdot 6H_2O$ ;  $Co(NO_3)_2 \cdot 6H_2O$ ;  $Co(CH_3COO)_2 \cdot 4H_2O$  and  $Co(acac)_2$  under different conditions gave coloured cobalt(II) and cobalt(III) complexes  $[Co(II)(hnmthon)(NO_3)(H_2O)_2](C_{16}H_{20}N_4O_7S)Co$ ;



Depending on the reaction conditions and the reactants the complex  $[Co(II)(hnmthon)(H_2O)_3](C_{16}H_{21}N_3O_5S)Co$  smoothly reacts with pyridine in absence and in the presence of  $NaClO_4$ , triphenyl phosphine and dipyridine in the presence of  $NaClO_4$  affords new complexes  $[Co(III)(hnmthon)(Py)(OH)(H_2O)](C_{21}H_{23}N_4O_4S)Co$ ;  $[Co(II)(hnmthon)(Ph_3P)(H_2O)_2](C_{34}H_{34}N_3O_4SP)Co$ ;  $[Co(II)(hnmthon)(Py)_2(H_2O)ClO_4](C_{26}H_{27}N_5O_7S)Co$ ;  $[Co(II)(hnmthon)(dip)(H_2O)ClO_4](C_{26}H_{23}N_5O_7S)Co$ . N/P It also reacts with monobasic bidentate dibasic tridentate and neutral bidentate ligands to the synthesis of interesting hetero chelates of cobalt(II) –



All the complexes are stable and coloured. The compound



$NH_4[Co(III)(hnmthon)(Salan)]; (C_{30}H_{28}N_8O_5S)Co$  are diamagnetic in nature. The compounds were characterised by elemental analysis, molar conductance values molecular weights and spectroscopic data. The elemental analysis data support the proposed molecular formulae. The physico chemical data for the complexes suggest that the 2-hydroxy-1-naphthaldehyde-morpholine-N-Thiohydrazone  $H_2(hnmthon)$  behaves as a dibasic tridentate (ONS) donor in the complexes:



[Co(III)(hnmthn)(H<sub>2</sub>O)<sub>2</sub>(NO<sub>3</sub>);(C<sub>16</sub>H<sub>19</sub>N<sub>4</sub>O<sub>7</sub>S)Co;  
 [Co(III)(hnmthn)(Cl)(H<sub>2</sub>O)<sub>2</sub>] (C<sub>16</sub>H<sub>19</sub>N<sub>3</sub>O<sub>4</sub>SCl)Co;  
 [Co(III)(hnmthn)(Py)(OH)(H<sub>2</sub>O)] (C<sub>21</sub>H<sub>23</sub>N<sub>4</sub>O<sub>4</sub>S)Co;  
 [Co(III)(hnmthn)(Ph<sub>3</sub>P)(H<sub>2</sub>O)<sub>2</sub>] (C<sub>34</sub>H<sub>34</sub>N<sub>3</sub>O<sub>4</sub>S)Co;  
 [Co(III)(hnmthn)(Py)<sub>2</sub>(H<sub>2</sub>O) ClO<sub>2</sub>] (C<sub>26</sub>H<sub>27</sub>N<sub>5</sub>O<sub>7</sub>SCl)Co;  
 [Co(III)(hnmthn)(dip)(H<sub>2</sub>O)] ClO<sub>4</sub>; (C<sub>26</sub>H<sub>23</sub>N<sub>5</sub>O<sub>7</sub>SCl)Co;  
 [Co(III)(hnmthn)(acac)(H<sub>2</sub>O)];(C<sub>21</sub>H<sub>24</sub>N<sub>3</sub>O<sub>5</sub>S)Co;  
 [Co(III)(hnmthn)(gly)(OH)]; (C<sub>29</sub>H<sub>27</sub>N<sub>3</sub>O<sub>5</sub>S)Co;  
 [Co(III)(hnmthn)(Salan)(H<sub>2</sub>O)]; (C<sub>21</sub>H<sub>24</sub>N<sub>3</sub>O<sub>3</sub>S)Co;  
 [Co(III)(hnmthn)(ohapan)(H<sub>2</sub>O)]; (C<sub>30</sub>H<sub>29</sub>N<sub>4</sub>O<sub>3</sub>S)Co;  
 NH<sub>4</sub>[Co(III)(hnmthn)(Saloap)]; (C<sub>25</sub>H<sub>26</sub>N<sub>5</sub>O<sub>5</sub>S)Co;  
 NH<sub>4</sub>[Co(III)(hnmthn)(acac)]; (C<sub>21</sub>H<sub>28</sub>N<sub>5</sub>O<sub>4</sub>S)Co;  
 [Co(III)(hnmthn)(ana)(H<sub>2</sub>O)]; (C<sub>23</sub>H<sub>23</sub>N<sub>4</sub>O<sub>6</sub>S)Co;  
 NH<sub>4</sub>[Co(III)(hnmthn)(Salan)]; (C<sub>30</sub>H<sub>28</sub>N<sub>8</sub>O<sub>5</sub>S)Co monobasic tridentate (ONS) (thioketo form) in the complexes Co(II) (H-hnmthn) (NO<sub>3</sub>) (H<sub>2</sub>O)<sub>2</sub> (C<sub>16</sub>H<sub>20</sub>N<sub>4</sub>O<sub>7</sub>S) Co. [Co(II)(H-hnmthn)(Cl)(H<sub>2</sub>O)<sub>2</sub>]; (C<sub>16</sub>H<sub>20</sub>N<sub>4</sub>O<sub>7</sub>S)Co and [Co(II)(H-hnmthn) (NO<sub>3</sub>) (H<sub>2</sub>O)] (C<sub>16</sub>H<sub>18</sub>N<sub>4</sub>O<sub>6</sub>SCl)Co and monobasic bidentate (SN) donor in the complex [Co(II)(hnmthn)(acac)<sub>2</sub>(H<sub>2</sub>O)] (C<sub>26</sub>H<sub>30</sub>N<sub>3</sub>O<sub>4</sub>S)Co in which phenolic – OH group of the ligand remains free.

### MOLAR CONDUCTANCE

The molar conductance of 10<sup>-3</sup> M- molar solutions of the complexes have been measured and the values are given in table 4&5 The value show that the cobalt complexes [Co(III)(hnmthn)]; [Co(III)(H-hnmthn)(acac)<sub>2</sub>](H<sub>2</sub>O)]; [Co(III)(hnmthn)(H<sub>2</sub>O)<sub>3</sub>]; [Co(III)(hnmthn)(py)(OH)(H<sub>2</sub>O)]; [Co(III)(hnmthn)(Ph<sub>3</sub>P)(H<sub>2</sub>O)<sub>3</sub>]; [Co(III)(hnmthn)(Ohopan)(H<sub>2</sub>O)]; and [Co(III)(hnmthn)(ana)(H<sub>2</sub>O)] are non electrolytes in DMSO (ohm-4-16cm<sup>2</sup>ohm<sup>-1</sup> mole<sup>-1</sup>)<sup>(14)</sup>. The compounds [Co(III)(hnmthn)(Py)<sub>2</sub> (H<sub>2</sub>O)]ClO<sub>4</sub>; [Co(III)(hnmthn)(dip)<sub>2</sub>(H<sub>2</sub>O)]ClO<sub>4</sub>; NH<sub>4</sub>[Co(III)(hnmthn)(Salgly)] NH<sub>4</sub>[C(III)(hnmthn) (Saloap)] and NH<sub>4</sub>[Co(III)(hnmthn)(Salan)] behaves as 1:1 electrolytes in the same solvent (ΩM=50-75 cm<sup>2</sup> ohm<sup>-1</sup> mol<sup>-1</sup>)<sup>(15)</sup>.

The ΩM-values observed for the complexes Co(II) (H-hnmthn) (NO<sub>3</sub>) (H<sub>2</sub>O)<sub>2</sub>, Co(II) (H-hnmthn) (Cl) (H<sub>2</sub>O)<sub>2</sub>, Co(II) (hnmthn) (H<sub>2</sub>O)<sub>2</sub>(NO<sub>3</sub>), Co(III) (hnmthn) (NO<sub>3</sub>) H<sub>2</sub>O, Co(II) (H-hnmthn) (Cl) (H<sub>2</sub>O)<sub>2</sub>, also suggest 1:1 electrolytic nature in solution although their formulations as shown in table (6.4 and 6.5) based on analytical data are non electrolytic in nature. This behaviour may be explained on the basis of solvolysis of complexes in Dimethyl sulfoxide.

### MAGNETIC SUSCEPTIBILIT

The diamagnetic nature of the complexes [Co(III)(hnmthn)(acac)<sub>2</sub>](H<sub>2</sub>O)]; [Co(III)(hnmthn)(H<sub>2</sub>O)(NO<sub>3</sub>)], [Co(III)(hnmthn)(Cl)<sub>2</sub>](H<sub>2</sub>O)<sub>2</sub>]; [Co(III)(hnmthn)(Py)(OH)(H<sub>2</sub>O)], [Co(III)(hnmthn)(Py)<sub>2</sub>](H<sub>2</sub>O)]ClO<sub>4</sub>], [Co(III)(hnmthn)(dip)<sub>2</sub>(H<sub>2</sub>O)]ClO<sub>4</sub>], [Co(III)(hnmthn)(acac)H<sub>2</sub>O]; [Co(III)(hnmthn)(gly)](H<sub>2</sub>O)]; [Co(III)(hnmthn)(baei)(HO); [Co(III)(hnmthn)(salan)<sub>2</sub>(H<sub>2</sub>O)]; [Co(III)(hnmthn)(Ohapan)(H<sub>2</sub>O)]; [Co(III)(hnmthn)(Salgly); NH<sub>4</sub>[Co(III)(hnmthn)(Saloap)]; [Co(III)(hnmthn)(ana)(H<sub>2</sub>O)]; NH<sub>4</sub>[Co(III)(hnmthn)(Salan)]; suggest the formation of octahedral Cobalt(III) complexes. The other complexes [Co(III)(hnmthn)(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>]; [Co(III)(hnmthn)(Cl)(H<sub>2</sub>O)<sub>2</sub>]; [Co(III)(hnmthn)(PH<sub>3</sub>P)(H<sub>2</sub>O)] are paramagnetic showing room temperature magnetic moment values between 4.2 and 4.6 B.M. The observed magnetic moment value of these complexes are with in the range of octahedral cobalt(II) complexes<sup>(16)</sup>.

The observed magnetic moment value of 4.0 B.M. for the complex [Co(III)(hnmthn)]<sub>2</sub> is slightly lower than that expected for the tetrahedral complexes<sup>(17)</sup>. This may be due to the formation of a dicobalt(II) complex with the ligand 2-hydroxy-1-naphthaldehyde morpholine-N-thiohydrazone functioning as a dibasic tridentate ONS-donor ligand. The magnetic moment in the complex may occur through overlap of cobalt-cobalt orbitals or through ligand participation. The molecular weight indicate the dimeric nature of the complex.

S.No.	Complexes	$\chi^1 M \times 10^{-6}$	$\mu$ -effective (B.M.)	$\Omega M \text{ cm}^2 \text{ ohm}^{-1}$
1.	[Co(II)(H-hnmthon)(NO <sub>3</sub> )(H <sub>2</sub> O)]	8960.697	4.64	40.82
2.	[Co(II)(H-hnmthon)(Cl)(H <sub>2</sub> O) <sub>2</sub> ]	8057.72	4.40	35.45
3.	[Co(II)(H-hnmthon)] <sub>2</sub>	6659.258	4.0	6.80
4.	[Co(III)(H-hnmthon)(acac) <sub>2</sub> (H <sub>2</sub> O)]	253.218	0.78	7.85
5.	[Co(II)(H-hnmthon)(H <sub>2</sub> O) <sub>3</sub> ]	8654.372	4.56	12.44
6.	[Co(III)(H-hnmthon) (H <sub>2</sub> O) <sub>2</sub> (NO <sub>3</sub> )]	279.855	0.82	55.10
7.	[Co(III)(H-hnmthon) (NO <sub>3</sub> ) (H <sub>2</sub> O)]	8503.206	4.52	32.42
8.	[Co(III)(H-hnmthon) (Cl) (H <sub>2</sub> O) <sub>2</sub> ]	227.913	0.68	15.75
9.	[Co(III)(H-hnmthon) (Py) (OH)(H <sub>2</sub> O)]	192.452	-	-
10.	[Co(III)(H-hnmthon) (Ph <sub>3</sub> P)(H <sub>2</sub> O) <sub>2</sub> ]	7624.184	4.28	6.70
11.	[Co(III)(H-hnmthon) (Py) <sub>2</sub> (H <sub>2</sub> O)]ClO <sub>4</sub>	121.364	0.54	62.42

TABLE 5. – MAGNETIC MOMENTS AND CONDUCTIVITY DATA OF THE COMPLEXES

S.No.	Complexes	$\chi^1 M \times 10^{-6}$	$\mu$ -effective (B.M.)	$\Omega M \text{ cm}^2 \text{ ohm}^{-1}$
12.	[Co(II)(hnmthon)(dip)(H <sub>2</sub> O)]ClO <sub>4</sub>	80.577	0.44	62.21
13.	[Co(II)(hnmthon)(acac)(H <sub>2</sub> O)]	149.833	0.60	12.20
14.	[Co(II)(hnmthon)(gly)(H <sub>2</sub> O)]	125.901	0.55	12.50
15.	[Co(III)(hnmthon)(bapei)(HO)]	60.099	0.38	10.30
16.	[Co(II)(hnmthon)(Salan)(H <sub>2</sub> O)]	73.418	0.42	9.80
17.	[Co(III)(hnmthon) (ohapan)](H <sub>2</sub> O)]	66.592	0.40	10.20
18.	NH <sub>4</sub> [Co(III)(hnmthon) (Salgly) (H <sub>2</sub> O)]	186.833	0.67	75.06
19.	NH <sub>4</sub> [Co(III)(hnmthon) (Salgly)]	130.521	0.56	70.84
20.	[Co(III)(hnmthon) (ana)(H <sub>2</sub> O)]	140.01	0.58	9.86
21.	NH <sub>4</sub> [Co(III)(hnmthon) (Salan)]	159.988	0.62	67.10

**Electronic Spectra:** Electronic spectra of the Co(II) and Co(III) complexes have been recorded in dimethyl sulfoxide. The electronic of the present complexes Co(II) (hnmthon)(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>; Co(II) (hnmthon) (Cl)(H<sub>2</sub>O)<sub>2</sub>; Co(II) (Hnmthon) H<sub>2</sub>O)<sub>3</sub>; Co(II) (hnmthon) (NO<sub>3</sub>) (H<sub>2</sub>O) and Co(II) (H-hnmthon) (Ph<sub>3</sub>P) (H<sub>2</sub>O)<sub>2</sub> show bands around 480-510 nm with a shoulder around 580-610 nm assignable to <sup>4</sup>T<sub>1g</sub> – <sup>4</sup>T<sub>1g</sub> (P) (v<sub>3</sub>) and T<sub>1g</sub> (F) – <sup>4</sup>A<sub>2g</sub> transitions respectively. This shows the psuedo octahedral nature of the complexes <sup>(18)</sup>.

The electronic spectra of the complexes [Co(III)(H-hnmthn)(acac)<sup>2</sup>](H<sub>2</sub>O), [Co(III)(hnmthn)(H<sub>2</sub>O)(NO<sub>3</sub>)]; [Co(III)(hnmthn)(H<sub>2</sub>O)(NO<sub>3</sub>)]; [Co(III)(hnmthn)(C1)(H<sub>2</sub>O)]; [Co(III)(hnmthn)(Py)(H<sub>2</sub>O)]; [Co(III)(hnmthn)(Py)(H<sub>2</sub>O)]C1O<sub>4</sub>; [Co(III)(hnmthn)(dip)(H<sub>2</sub>O)]C1O<sub>4</sub>; [Co(III)(hnmthn)(acac)(H<sub>2</sub>O)]; [Co(III)(hnmthn)(gly)(H<sub>2</sub>O)]; [Co(III)(hnmthn)(baei)(OH)]; [Co(III)(hnmthn)(salan)(H<sub>2</sub>O)]. [Co(III)(hnmthn)(ohapan)(H<sub>2</sub>O)]; NH<sub>4</sub>[Co(III)(hnmthn)(salgly)]; [Co(III)(hnmthn)(saloap)]; [Co(III)(hnmthn)(ana)(H<sub>2</sub>O)]; NH<sub>4</sub>[Co(III)(hnmthn)(salan)] exhibit three bands in the range 510-590 nm 445-510, and 340 – 410 nm. The two bands around 510 and 445 nm may tentatively assigned as the split components of the <sup>1</sup>A<sub>1g</sub> – <sup>1</sup>T<sub>1g</sub> transitions<sup>(19)</sup> (i.e. <sup>1</sup>A<sub>1g</sub> – E<sub>g</sub> and <sup>1</sup>A<sub>1g</sub> – <sup>1</sup>A<sub>2g</sub> respectively. The higher energy bands at about 370 nm is probably due to <sup>1</sup>A<sub>1g</sub> – <sup>1</sup>T<sub>2g</sub> transition mixed up with metal to ligand (azomethine linkage) (t<sub>2g</sub> – π\*) transitions.

The electronic spectrum of the complex [Co(II)(hnmthn)]<sub>2</sub> consists of three band at 8525, 17200 and 20600 cm<sup>-1</sup> which can be assigned to the transition <sup>4</sup>A<sub>1g</sub>(F)–<sup>4</sup>T<sub>1g</sub>(P) respectively these bands suggest an octahedral stereochemistry for the Co(II) chelate.

### Infrared and Far Infrared Spectra:-

The spectrum of the ligand showed medium to strong bands suggests presence of hydrogen bonding. The free ligand exhibit bands around 3070 and 2800 cm<sup>-1</sup> also assignable to νNH and ν(C = S) modes. The ν(CH = N) hydrazone linkage in the ligand appeared at 1625 cm<sup>-1</sup> while the amide-III band was observed at 1575 cm<sup>-1</sup>. These data suggest that the free ligand exists in the thione form.<sup>(22)</sup>

The infra red spectra of the compounds Co(II)(H-hnmthn)(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>, Co(II)(H-hnmthn)(C1)(H<sub>2</sub>O)<sub>2</sub> and Co(II)(H-hnmthn)(H<sub>2</sub>O) showed νNH at 3000-3050 cm<sup>-1</sup> along with the following changes in thioamide group vibrations; thioamide-II increased in frequency (1530-1550 cm<sup>-1</sup>) and thio amide-III split into two components at 1180-1200 cm<sup>-1</sup> and 1340-1360 cm<sup>-1</sup>. These changes in thioamide group vibrations suggest amide sulphur coordination of the ligand in thio keto form<sup>(23,24)</sup>. The coordination of thio amide sulphur is supported by the appearance of a band at 400-410 cm<sup>-1</sup> which may be assigned to ν(CO-S).

The disappearance of the band due to νOH at 3200-3280 cm<sup>-1</sup> in the complexes Co(II)(H-hnmthn)(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>; Co(II)(H-hnmthn)(C1)(H<sub>2</sub>O)<sub>2</sub> and Co(II)(H-hnmthn)(NO<sub>3</sub>)(H<sub>2</sub>O) indicates the involvement of phenolic oxygen in coordination after deprotonation. The appearance of new band at 480-490 cm<sup>-1</sup> suggests metal-oxygen phenolic coordination<sup>(25,26)</sup>. The band observed at 450-470 cm<sup>-1</sup> is assigned to ν(CO-N) vibration. The frequency due to –CH=N got lowered by – 20 cm<sup>-1</sup> suggesting coordination of nitrogen of the azomethine group –CH=N to the metal ion. It is therefore concluded that the ligand in the above complexes coordinate in a monobasic tridentate fashion. The bands at 3300-3600, 1620-1630 and 840-860 cm<sup>-1</sup> in the chelates Co(II)(H-hnmthn)(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>; Co(II)(H-hnmthn)(C1)(H<sub>2</sub>O)<sub>2</sub> and Co(II)(H-hnmthn)(NO<sub>3</sub>)(H<sub>2</sub>O) indicate the presence of coordinate water molecule<sup>(27)</sup>.

In the complexes [Co(II)(H-hnmthn)(acac)<sub>2</sub>](H<sub>2</sub>O) and [Co(II)(H-hnmthn)(acac)(H<sub>2</sub>O)] presence of oxygen bonded chelating acetyl acetonate anion has been inferred from the IR-spectra, which in the present complexes showed ν(C-O) around 1570 cm<sup>-1</sup>, while 1520 cm<sup>-1</sup>. Besides, the free ligand band for ν(OH) remained unaltered, while νNH band disappeared. It is thus clear that phenolic OH group of the ligand remains free in the complexes and the ligand acts as a monobasic bidentate ligand in the complexes.

Complexes [Co(II)(hnmthn)]<sub>2</sub>; [Co(II)(hnmthn)(H<sub>2</sub>O)<sub>3</sub>]; [Co(III)(hnmthn)(H<sub>2</sub>O)<sub>2</sub>(NO<sub>3</sub>)]; [Co(III)(hnmthn)(C1)(H<sub>2</sub>O)<sub>2</sub>]; [Co(III)(hnmthn)(Py)(OH)(H<sub>2</sub>O)]; [Co(III)(hnmthn)(Ph<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>]; [Co(III)(hnmthn)(Py)<sub>2</sub>(H<sub>2</sub>O)]; C1O<sub>4</sub>; [Co(III)(hnmthn)(dip)(H<sub>2</sub>O)]; C1O<sub>4</sub>; [Co(III)(hnmthn)(aca)(H<sub>2</sub>O)]; [Co(III)(hnmthn)(gly)(H<sub>2</sub>O)]; [Co(III)(hnmthn)(baei)(OH)]; [Co(III)(hnmthn)(salan)(H<sub>2</sub>O)]; [Co(III)(hnmthn)(ohapan)(H<sub>2</sub>O)]; NH<sub>4</sub>[Co(III)(hnmthn)(saloap)]; [Co(III)(hnmthn)(ana)(H<sub>2</sub>O)] and NH<sub>4</sub>[Co(III)(hnmthn)(salan)] do not show any characteristic band of amide and amino groups suggesting that the ligand was coordinated in enol form assigned to skeleton >C – N – N = C<. The characteristic band observed in the infra red spectra of the compound at – 2540 cm<sup>-1</sup> is probably due to ν(S – H) vibrations<sup>(28)</sup>. The bands at – 3070 and 2540 cm<sup>-1</sup> in the spectra of the ligands are found to be absent in the spectra of the



complexes. Instead strong and sharp bands are observed at  $3400\text{ cm}^{-1}$  indicating the presence of coordinated water molecules. Absence of bands due to phenolic  $\nu(\text{OH})$  and  $\nu(\text{S}-\text{H})$  in the spectra of complexes suggest deprotonation of these groups and coordination of the oxygen and sulphur atoms respectively to the metal ion.

The azomethine  $\nu(\text{CH}=\text{N})$  and  $\nu(\text{C}-\text{S}-\text{C})$  vibrations observed in the spectra of ligands at  $1650$  and  $700\text{ cm}^{-1}$  respectively suffer negative shift on complex formation suggesting coordination of the azomethine nitrogen and sulphur atoms to the metal ions. However the cyclic  $\nu(\text{C}=\text{N})$  and  $\nu(\text{N}-\text{N})$  vibrations observed in the spectra of the compound at  $1580$  and  $1065\text{ cm}^{-1}$  almost remain intact on complexation indicating non involvement of the ring nitrogen in coordination through oxygen nitrogen and sulphur atoms is further supported by the appearance of few additional bands in the spectra of the complexes in the regions  $530-510$ ,  $460-430$  and  $430-410\text{ cm}^{-1}$  which are assigned to  $\nu(\text{M}-\text{O})$ ,  $\nu(\text{M}-\text{N})$  and  $\nu(\text{M}-\text{S})$  vibrations respectively<sup>(29-30)</sup>.

Complexes  $[\text{Co(III)}(\text{hnmthn})(\text{Py})_2(\text{H}_2\text{O})]\text{ClO}_4$ , and  $[\text{Co(III)}(\text{hnmthn})(\text{dip})(\text{H}_2\text{O})]\text{ClO}_4$ , exhibit three bands in the  $1090-1100$  (vs),  $925-930$ (w) and  $620-650\text{ cm}^{-1}$  regions which indicate presence of ionic perchlorate group in these complexes<sup>(31)</sup>. The coordination of pyridine in the complexes  $[\text{Co(III)}(\text{hnmthn})(\text{Py})_2(\text{H}_2\text{O})]\text{ClO}_4$  was indicated by the band in the region  $760-770\text{ cm}^{-1}$ <sup>(32)</sup>. The bands observed at about  $4130-1460\text{ cm}^{-1}$  and  $1230\text{ cm}^{-1}$  in the complexes  $[\text{Co(III)}(\text{hnmthn})(\text{H-hnmthn})(\text{NO}_3)(\text{H}_2\text{O})_2]$  and  $[\text{Co(III)}(\text{hnmthn})(\text{H}_2\text{O})(\text{NO}_3)]$  are assignable to the  $\nu_1(\text{NO}-\text{stretching})$  and  $\nu_4(\text{NO}_2-\text{asymmetric stretching})$  vibrations respectively<sup>(33)</sup>. Thus it may be inferred that  $\text{NO}_3^-$  is present in these complexes as unidentate ligand. On the other hand appearance of two (N-O) stretching at about  $1490$  and  $1285\text{ cm}^{-1}$  indicates the bidentate nature of  $\text{NO}_3^-$  group<sup>(34)</sup> in the  $\text{Co(II)}(\text{H-hnmthn})(\text{NO}_3)(\text{H}_2\text{O})$  complex. Coordination of the chloride ion in the complexes  $\text{Co(II)}(\text{H-hnmthn})(\text{Cl})(\text{H}_2\text{O})_2$  and  $\text{Co(III)}(\text{hnmthn})(\text{Cl})(\text{H}_2\text{O})_2$  is indicated by the identification of  $\nu(\text{Co}-\text{Cl})$  at  $340-360\text{ cm}^{-1}$ . The presence of  $\nu(\text{Co}-\text{O})$  and  $\nu(\text{Co}-\text{N})$  is inferred from appearance of bands at  $450$  and  $380\text{ cm}^{-1}$  respectively<sup>(33)</sup>.

The presence of anionic bidentate hetero ligands in the complexes  $[\text{Co(III)}(\text{hnmthn})(\text{gly})(\text{H}_2\text{O})]$ ;  $[\text{Co(III)}(\text{hnmthn})(\text{baei})(\text{OH})]$ ;  $[\text{Co(III)}(\text{hnmthn})(\text{salan})(\text{H}_2\text{O})]$ ;  $[\text{Co(III)}(\text{hnmthn})(\text{ohapan})(\text{H}_2\text{O})]$ ;  $\text{NH}_4[\text{Co(III)}(\text{hnmthn})(\text{Sal-gly})]$ ;  $\text{NH}_4[\text{Co(III)}(\text{hnmthn})(\text{Saloap})]$ ;  $[\text{Co(III)}(\text{hnmthn})(\text{ana})(\text{H}_2\text{O})]$  and  $\text{NH}_4[\text{Co(III)}(\text{hnmthn})(\text{Salan})]$  has been inferred from the interpretation of the infra red spectra of free ligands and their metal complexes.

All the complexes reveal modified infra red absorptions of both the starting complexes and the hetero ligands indicating the formation of mixed ligand complexes. A band assignable to  $\nu(\text{C}=\text{C})$  is observed at  $1615-1639\text{ cm}^{-1}$  for the ligands and at  $1605-1610\text{ cm}^{-1}$  for the parent as well as mixed ligand complexes indicating nitrogen coordination to the metal ion. The free ligands exhibit broad and weak absorption bands in the region  $3050-3200\text{ cm}^{-1}$  due to  $\nu(\text{OH})$  and strong bands at  $1280-1290\text{ cm}^{-1}$  due to  $\delta(\text{OH})$ .

The latter band is replaced by one at higher frequency ( $1330-1335\text{ cm}^{-1}$ ) in both the parent and mixed ligand complexes indicating that the hydrazone coordinate to the metal ion as deprotonated species. The disappearance of the bands at  $3050-3200\text{ cm}^{-1}$  in the complexes confirms that the O-hydroxy group takes part in the complex formation through phenolic oxygen<sup>(34,35)</sup>. All the complexes exhibit  $\nu(\text{C}=\text{C})$  in the region  $1595-1600\text{ cm}^{-1}$ . The phenyl ring vibrations appear at  $1475-1550\text{ cm}^{-1}$ . The presence of an O-disubstituted benzene ring in the ligand as well as in the complexes is indicated by strong and sharp bands around  $730-750\text{ cm}^{-1}$ . Bands at  $2950-3040\text{ cm}^{-1}$  for the complexes are assigned to  $\nu(\text{C}-\text{H})$  vibrations of the aromatic system<sup>(36)</sup>.

The pyridyl deformation modes appears at  $1600$  and  $1578\text{ cm}^{-1}$  and the (C-H) out of plane deformation mode gives rise to two bands at  $778$  and  $766\text{ cm}^{-1}$ , all these frequencies overlap with the phenyl ring vibrations. The pyridyl deformation modes occur at position ( $430, 455\text{ cm}^{-1}$ ) similar to those observed in the coordinated pyridyl groups<sup>(39)</sup> and hence the nitrogen of 2, 21-bipyridyl are inferred to be coordinated to the metal ion. The coordination of the pyridyl ring is further corroborated by the new bands at  $630$  and  $434\text{ cm}^{-1}$  in the spectra of mixed ligand complexes. Non ligand bands in the far IR-regions ( $365-390$  and  $465-480\text{ cm}^{-1}$ ) are assigned to  $\nu(\text{M}-\text{N})/\nu(\text{M}-\text{O})$  modes respectively<sup>(40)</sup>.

## REFERENCES

1. Campbell M.J.M. – Coord. Chem. Rev; 15 (1975) 279.
2. Padhye S and Kanffman G.B. – Coord. Chem. Rev. 63 (1985) 127.
3. West D.X., Padhye S. and Sonawane P.B. – Struct. and bonding – Berlin 76 (1991) 4.
4. West D.X., Liberta A.E., Padhye S., Chilate, R.C., Sonawane, P.B., Kumbhar A.S. and Yerande R.G. – Coord. Chem. Rev. 123 (1993) 49.
5. Casas J.S., Castellano E.E., Macias A., Rodrigulz M.C. – Arguelles, Sanchez A and Sordo J. – J. Chem. Soc. Dalton Trans. (1993) 353.
6. Ferrari M.B., Fava G.G., Lanfranchi M., Pelizzi C. an Tara Sconi P. – J. Chem. Soc. Dalton Trans. (1989) 361.
7. Ferrari M.B., Fava G.G., Lanfranchi M., Pelizzi C. and Tara Sconi P. – J. Chem. Soc. Dalton Trans. (1991) 1951.
8. Ferrari M.B. and Fava G.G. – Inorg. Chim. Acta 181 (1992) 253.
9. Holloway C.E. and Melnik M. – J. Organometal Chem; 495 (1995) 1.
10. Foye V.O. and Duvall R.N. – J. Am. Pharm. Assoc. Sci. Edvet. 47 (1958) 285.
11. Dilworth J.R. – Coord. Chem. Rev; 21 (1976) 29.
12. Alcock J.P., Baker H.J. and Diamatis A.A. – Aust. J. Chem; 25 (1972) 269.
13. Baner D.J. and Sadler P.W. – Chem. Abstr. 65 (1966) 2224e.
14. Nonayama N., Tomit S. and Yamaski K. – Inorg. Chim. Acta 12 (1975) 33.
15. Geary W.J. – Coord. Chem. Rev; 7 (1971) 81.
16. Kumar D., Syamal A. and Singh A.K. – Ind. Jour. of Chem; 42A (2003) 280.
17. Bhawe N.S., Bahad P.J., Sonaporote P.M. Aswar A.S. – J. Ind. Chem. Soc. 79 (2002) 342
18. Nita A.L., Derek A.T., Goutam K.P., Jnan P.N. and Dipankar D. – Ind. J. Chem; 39A (2000) 400.
19. Lever A.B.P. – Inorganic electronic spectroscopy – 2<sup>nd</sup> Edition Elsevier, Amsterdam (1984).
20. Boucher L.J. – Inorg. Chim. Acta 6 (1972) 443.
21. Fumitchev D.V., McLauchlan C.C. and Holm R.H. – Inorg. Chem. 41 (2002) 958.
22. Fosterloh, Chim C.A. and Holm R.H. – Inorg. Chem 40 (2001) 224.
23. Baker P.K. and Meechan M.M. – Inorg. Chim. Acta 303 (2000) 17.
24. Hille R. – Chem. Rev. 96 (1996) 2757.
25. Szilagyi R.K. Musaev D.G. and Morokuma K. – Inorg. Chem. 40 (2001) 766.
26. Jones R.M. Inscore F.E., Hille R. and Kirk M.L. – Inorg. Chem. 38 (1999) 49
27. Nakamoto K. – Infrared spectra of Inorganic and Coordination compound 2<sup>nd</sup> edition (John Wiley New York) (1963).
28. Bayly S., Mccleverty J.A., Ward M.D., Gatteschi D. and Tolle F. – Inorg. Chem. 39 (2002) 1288.
29. Huheey J.E., Keiter E.A. and Keiter R.L. – Inorganic Chemistry – Principles of Structure and reactivity, 4<sup>th</sup> edition (Wesley, New Delhi) 2000.
30. Nagaraja K.S. and Udupa M.R. – Trans. Met. Chem; 9 (1984) 290; Polyhedron 3 (1984) 907.
31. Torihara N., Okawa H. and Kida S. – Bull. Chem. Soc. Japan 51 (1978) 3256.
32. Smith J.N. and Brown T.M. – Inorg. Chem. 11 (1972) 2697.
33. Lever A.B.P. – Inorg. Chem. 4 (1965) 1042.
34. Lu J., Paliwala T., Lim S.C., Yu C., Niu T. and Jacobson A.J.- Inorg. Chem. 36 (1997) 923.
35. Beyon J.C., Claver C. and Masdeu Bulto – Coord. Chem. Rev. 193. – 195 (1999) 73.
36. Singh N.K., Kushwaha S.K. and Ayyagari A. – Trans. Met. Chem. 26 (2001) 140.
37. Devy R., Vittal J.J. and Dean P.A.W. – Inorg. Chem. 37 (1988) 6339.
38. Baranwal B.P., Gupta Takeshwar and Singh A.K. – Ind. Jour. of Chem; 42A (2003) 1905.
39. James S. and Nagraja K.S. – Ind. Jour. of Chem. 42A (2003) 1900.
40. Howlader M.B.H., Islam M.S. and Karim M.R. – Ind. J. Chem. 39A (2000) 407.