

● CHAPTER-V ●

CHAPTER V

ELECTROPHILIC SUBSTITUTION REACTIONS OF  
METAL COMPLEXES - PART - III  
 (Chemical Reactions)

1. Introduction

Among the electrophilic substitution reactions of coordinated aromatic and pseudoaromatic ligands, halogenation is a common reaction. Liquid bromine as a brominating agent is found to be successful in brominating acid stable metal complexes such as  $\text{Cr}(\text{An})_3\text{Cl}_3$ ,  $\text{M}(\text{oxine})_n$  [  $\text{M}(n) = \text{Cr}(\text{III})$ ,  $\text{Fe}(\text{III})$ ,  $\text{Co}(\text{III})$ ,  $\text{Cu}(\text{II})$ ,  $\text{Al}^{3+}$  and  $\text{M}(\text{ptdn})_3$   $\text{M}(\text{III}) = \text{Cr}(\text{III})$ ,  $\text{Co}(\text{III})$  ]. For the acid labile complexes such as  $\text{M}(\text{ptdn})$  and  $\text{M}(\text{sal})_2$  and  $\text{M}(\text{N-R-salim})_2$ ; NBS is used as a successful brominating agent.

The bromination reaction of  $\text{M}(\text{sal})_2$ , Fig. 1

$\text{M}(\text{II}) = \text{Co}(\text{II})$ ,  $\text{Ni}(\text{II})$ ,  $\text{Cu}(\text{II})$  in chloroform using NBS yields a mixture of  $\text{M}(\text{5-Br,sal})_2$  and  $\text{M}(\text{3,5-Br}_2\text{,sal})_2$ <sup>1</sup>.

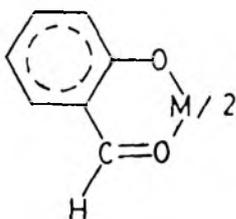


Fig. 1

The acid hydrolysis of the product obtained from the bromination reaction of  $\text{Cu}(\text{sal})_2$  gives 5-Br,sal (60 %) and 3,5-Br,sal (40 %). The corresponding reaction product of  $\text{M}(\text{sal})_2$  [M(II) = Co(II), Ni(II)] gives mainly 3,5-Br<sub>2</sub>,sal upon acid hydrolysis. A change of the reaction medium from chloroform to DMF gives the quantitative yield of  $\text{M}(3,5\text{-Br}_2,\text{sal})_2$  [M(II) = Co(II), Ni(II), Cu(II)] .

However the chlorination and iodination reaction of  $\text{M}(\text{sal})_2$  [M(II) = Co(II) and Cu(II)] could not be achieved by NCS and NIS respectively. The reaction of ICl in DMF with  $\text{M}(\text{sal})_2$  results into the degradation of the complex yielding 3,5-I<sub>2</sub>,sal. The iodination of  $\text{Cu}(3\text{-OCH}_3,\text{sal})_2$  using NIS was successful.

In the bromination reaction of  $\text{Ni}(\text{N-n-but salim})_2$  using NBS the mole ratio of M:NBS seems to decide the nature of the product. When this ratio was 1:2 in chloroform the formation of pure  $\text{Ni}(5\text{-Br, N-n-but salim})_2$  was reported while when the ratio was 1:4, pure  $\text{Ni}(3,5\text{-Br}_2, \text{N-n-but salim})_2$  was formed. A similar reaction with  $\text{M}(\text{sal})_2$  yielded a mixture of  $\text{M}(5\text{-Br,sal})_2$  and  $\text{M}(3,5\text{-Br}_2,\text{sal})_2$ .

The use of  $(\text{SCN})_2$ , synthesised by the reaction of KSCN with liquid bromine is reported to thiocyanate  $\text{M}(\text{ptdn})_n$ . The reaction of  $\text{Cu}(\text{oxine})_2$  with  $(\text{SCN})_2$  in  $\text{CCl}_4$  gives a sticky

mass. An acid hydrolysis of this product with HCl (10 N) followed by the treatment with  $H_2S$  gives a mixture of 5-SCN, oxine (70 %) and 5,7-(SCN)<sub>2</sub>,oxine (30 %). There is no positive report of thiocyanation reaction of  $M(\text{salim})_2$  and  $M(\text{N-R-salim})_n$ .

These reactions suggested that the position of incoming electrophile remains unchanged upon coordination in the halogenation reaction. Literature survey gave an unconvincing report of the formation of only one product,<sup>3-6</sup>  $Ni(5\text{-Br},N\text{-n-butylsalim})_2$  or  $Ni(3,5\text{-Br}_2, N\text{-n-butylsalim})_2$  depending on the molar ratio of the reactants.

Another unconvincing report is that NBS is a successful brominating reagent while it could not give any definite product during a reaction with  $M(\text{sal})_2$ . There is also no positive report of the thiocyanation reaction of  $M(\text{sal})_2$  and  $M(\text{N-R-salim})_2$ . We have therefore undertaken the systematic study of these reactions and our results are summarised in this chapter.

## 2. Experimental

### (1) Materials

1.  $M(\text{N-n-butylsalim})_2$   
bis (N-n-butylsalicylaldiminato) nickel (II) - A
2. bis(5-I,N-n-butylsalicylaldiminato) nickel (II) - E
3. bis(salicylaldehydato)nickel(II) - F
4. bis(5-I, salicylaldehydato) nickel (II) - H

Metal salicylaldehyde and imine complexes of nickel(II) were synthesised using the literature procedure. NIS was synthesised in the laboratory by literature procedure<sup>7</sup> with slight modification. The solvents used for this work were purified by literature methods<sup>8</sup>. NBS was purified by recrystallisation from hot water.

#### I. Bromination reactions

(i) Role of brominating agents in the bromination reaction of  $\text{Ni}(\text{N-n-butylsalim})_2$

All the bromination reactions were carried in daylight under normal atmosphere.

##### (a) Liquid bromine in chloroform

To a stirred solution of A (0.410 g, 0.001 M) in chloroform (10 ml) was added liquid bromine (0.30 g, 0.0019 M) in chloroform (15 ml); a sticky mass was obtained which on treatment with HCl (1 M) gave a yellow residue. TLC of the residue on silica gel using a mixture of benzene and petroleum ether (60-80<sup>o</sup>) (2:1 v/v) as the eluent showed two distinct spots. The two compounds b' and c' were separated on silica gel packed column (100-200 mesh) using a mixture of benzene and petroleum ether (60-80<sup>o</sup>) (2:1 v/v) as the eluent. b' was identified as 3,5-Br<sub>2</sub> sal (0.10 g, 18 %) and c' was identified as 5-Br,sal (0.30 g, 75 %).

Product : b' is yellow needle shaped crystals, m.p. 83.00-83.5°, (lit.<sup>1,2</sup> 81-84°), found C, 30.5; H, 1.10; Br, 56.8;  $C_7H_4O_2Br_2$  requires C, 30.0; H, 1.4; Br, 57.1 %;

$\nu_{max}$  : 3228 (bm), 1678 (s), 1663 (s), 1599 (w), 1486 (w), 1465 (s), 1420 (s), 1385 (s), 1339 (m), 1294 (m), 1206 (s), 1160 (m), 1139 (w), 927 (s), 917 (m), 878 (s), 872 (s), 741 (s), 720 (s), 696 (w), 682 (s)  $cm^{-1}$

Product : c' is yellow crystalline solid, m.p. 106.0-107.0° (lit.<sup>8</sup> 105°), found : C, 41.6; H, 2.8; Br, 4.0;

$C_7H_5O_2Br$  requires C, 41.8; H, 2.5; Br, 39.8 %

$\nu_{max}$  : 3302 (bm), 1678 (s), 1658 (s), 1602 (m), 1552 (m), 1450 (s), 1408 (m), 1362 (w), 1330 (w), 1220 (w), 1180 (s), 1162 (s), 1125 (m), 1077 (w), 902 (vs), 895 (s), 882 (m), 841 (w), 832 (s), 768 (s), 710 (s)  $cm^{-1}$ .

(b) Liquid Br<sub>2</sub> in 1,4-dioxane :

To a stirred solution of A (0.410 g, 0.001 M) in 1,4-dioxane (50 ml) was added liquid Br<sub>2</sub> (0.30 g, 0.0019 M) in 1,4-dioxane (30 ml). TLC of the residue on silica gel using a mixture of benzene and petroleum ether (60-80°) (2:1 v/v) as the eluent showed one spot. It was crystallised from methanol to give yellow crystalline needles whose analytical data was similar to b' (0.42 g, 72 %).

(c) NBS in chloroform :

A mixture of A (0.410 g, 0.001 M) and NBS (0.34 g, 0.0019 M) in chloroform (30 ml) was stirred for 90 minutes at room temperature. The product was isolated by precipitation with petroleum ether (60-80<sup>o</sup>), separating succinimide by vacuum sublimation at 110.0<sup>o</sup>, and purifying the crude product from carbon tetrachloride. TLC of the residue on silica gel using benzene eluent showed two distinct spots. These two components were separated on silica-gel packed column (100-200 mesh). Elution with benzene gave dark green crystals of B which was characterised as Ni(3,5-Br<sub>2</sub>, N-n-butsalim)<sub>2</sub> (0.08 g, 10 %). The column on further elution with a mixture of benzene and acetone (1:1 v/v) gave dark green crystals of C which was characterised as Ni(5-Br, N-n-butsalim)<sub>2</sub> (0.30 g, 50 %).

Product: B is green needle shaped crystalline, m.p. 212.0 - 213.0<sup>o</sup> (lit.<sup>3</sup> 214-216<sup>o</sup>), found : C, 36.4; H, 3.5;

Br, 44.3; Ni, 8.02; C<sub>22</sub>H<sub>24</sub>O<sub>2</sub>N<sub>2</sub>Br<sub>4</sub>Ni requires C, 36.3;

H, 3.3; Br, 44.0; Ni, 8.1 %;  $\gamma_{\max}$  : 2948 (w),

2937 (w), 2884 (w), 1735 (w), 1620 (vs), 1610 (m), 1582 (m),

1525 (w), 1440 (vs), 1421 (s), 1353 (w), 1325 (vs), 1225 (m),

1176 (s), 1060 (w), 982 (w), 950 (w), 872 (vs), 750 (m),

723 (vs), 692 (w) cm<sup>-1</sup>.

Product: C is green crystalline, m.p. 193.0 - 194.0°  
 (lit.<sup>3,4</sup> 193-195°); found : C, 46.1; H, 4.9; Br, 27.9;  
 Ni, 10.4;  $C_{22}H_{26}O_2N_2Br_2Ni$  requires C, 46.5; H, 4.6;  
 Br, 28.1; Ni, 10.3 %;  $\nu_{max}$  : 2968 (w), 2945 (w), 2890 (w),  
 1623 (s), 1602 (s), 1540 (m), 1660 (s), 1428 (m), 1390 (m),  
 1336 (m), 1252 (w), 1230 (m), 1209 (m), 1191 (m), 1141 (m),  
 1121 (w), 1080 (m), 1046 (w), 1026 (w), 1001 (w), 982 (w),  
 970 (w), 880 (w), 820 (s), 797 (w), 761 (w), 738 (w),  
 710 (m), 684 (w)  $cm^{-1}$ .

The ligand separation reactions of B and C by treating them with KCN in 1,4-dioxane gave 3,5-Br<sub>2</sub>, N-n-butsalim, b (0.60 g, 90 %) and 5-Br, N-n-butsalim, c (0.450 g, 94 %) respectively.

Product b : is yellow low melting solid, m.p. 12.0 - 13.0°,  
 found : C, 39.6; H, 3.7; Br, 48.05;  $C_{11}H_{13}CNBr_2$  requires  
 C, 39.4; H, 3.9; Br, 47.7 %  $\nu_{max}$  : 3405 (bm), 2970 (m), 2925 (m),  
 2852 (m), 1637 (s), 1587 (m), 1556 (m), 1446 (s), 1362 (w),  
 1338 (w), 1278 (m), 1216 (s), 1172 (s), 1122 (w), 1100 (w),  
 1072 (m), 1032 (m), 1008 (w), 980 (m), 950 (w), 866 (s),  
 830 (w), 740 (m), 722 (w), 690 (vs),  $cm^{-1}$ .

Product c : is yellow liquid, b.p.\* 220.0° dec.  
 found : C, 51.7; H, 5.8; Br, 31.5;  $C_{11}H_{14}ONBr$  requires  
 C, 51.6; H, 5.5; Br, 31.2 %  $\nu_{max}$  : 3304 (bm), 2962 (m),

\* The exact b.p. of imines could not be determined as they decompose even under high vacuum.

2945 (m), 2872 (m), 1638 (s), 1622 (m), 1578 (m), 1492 (s),  
1450 (m), 1372 (m), 1350 (w), 1288 (s), 1238 (w), 1197 (m),  
1180 (m), 1152 (w), 1120 (m), 1082 (m), 1037 (m), 1008 (w),  
978 (m), 947 (w), 896 (m), 880 (m), 858 (m), 825 (s),  
785 (m), 762 (w), 697 (s), 691 (s), 673 (s)  $\text{cm}^{-1}$ .

## II. Iodination reactions

(i) Role of iodinating agents in the iodination of metal  
salicylaldehyde and imine complexes

(a) By using iodine in chloroform, ICl in chloroform and NIS  
in chloroform, the compounds obtained were sticky and could  
not be characterised.

All the iodination reactions were carried out in  
daylight under normal atmosphere. The effect of oxygen and  
light on the iodination reaction was also studied.

(b) Synthesis of N-iodosuccinimide

The various methods of synthesis of N-iodosuccinimide<sup>7</sup>  
were tried in our laboratory. The procedure which gave the  
better yield in a clean reaction was as follows.

To a solution of succinimide (3.92 g) in boiling  
water (120 ml) was added freshly precipitated silver oxide  
(5.10 g) and the mixture was stirred for 30 minutes at 60°.

It was filtered using <sup>a</sup> hot filtered funnel. The crystalline salt of succinimide (4.5 g) was obtained on cooling. The supernatant liquid was repeatedly stirred with the unreacted silver oxide at 60°. The crystals were washed with cold water (20 ml). It was then powdered (2.0 g) and was added in portions with stirring to a solution of iodine (2.54 g) in acetone (30 ml) at 5 to 10°. After decolourisation (30 min) of the iodine solution, the precipitated silver oxide was filtered and the filtrate was reduced to a small volume under vacuo at room temperature. The residue was washed with ether, and was crystallised from 1,4-dioxane-carbon tetrachloride mixture (1:2 v/v) yielding the colourless needles of N-iodo-succinimide (1.8 g, 80 %), m.p. 202° (lit.<sup>7</sup> 200°), found C, 21.6; H, 2.1; N, 6.0; I, 56.1; C<sub>4</sub>H<sub>4</sub>O<sub>2</sub>IN requires C, 21.4; H, 1.8; N, 6.2; I, 56.4 %.

(c) NIS in 1,4-dioxane / ethanol

The iodination reaction of M(sal)<sub>2</sub> or M(N-Rsalim)<sub>2</sub> (for M(II) = Ni(II), R=n-but) by NIS in 1,4-dioxane / ethanol gives pure M(5-I, salicylaldehyde)<sub>2</sub> and M(5-I, N-butساليم)<sub>2</sub> when the mole ratio of compound : NIS :: 1:2, while pure M(3,5-I<sub>2</sub> sal)<sub>2</sub> and M(3,5-I<sub>2</sub>, N-Rساليم)<sub>2</sub> is obtained when the mole ratio of compound : NIS :: 1:4.

(d) NIS in chloroform : Iodination of A

A mixture of A (0.0410 g, 0.001 M) and NIS (0.45 g, 0.002 M) in chloroform (30ml) was stirred for 90 minutes at room temperature. The product was isolated by precipitation with petroleum ether (60-80<sup>o</sup>) separating succinimide by vacuum sublimation at 110.0<sup>o</sup> and purifying the crude product from carbon tetrachloride. TLC of the residue on silica gel using benzene eluent showed two distinct spots. These two components were separated on silica gel packed column (100 - 200 mesh). Elution with benzene gave dark green crystals of D which was identified as Ni(3,5-I<sub>2</sub>, N,n-butyalim)<sub>2</sub> (0.09 g, 10 %). The column on further elution with a mixture of benzene and acetone (1:1 v/v) gave dark green crystals of E which was characterised as Ni(5-I, N,n-butyalim)<sub>2</sub> (0.30 g, 45 %). The ligand separation reactions of D and E by treating them with KCN gave 3,5-I<sub>2</sub>, N-n-butyalim, d (0.80 g, 93 %) and 5-I, N-n-butyalim, e (0.55 g, 91 %) respectively.

Product D : is green crystalline, m.p. 220.0 - 221.0<sup>o</sup>,  
 found : C, 28.6; H, 3.2; I, 55.2; Ni, 6.7; C<sub>22</sub>H<sub>24</sub>O<sub>2</sub>N<sub>2</sub>I<sub>4</sub>Ni  
 requires C, 28.9; H, 2.6; I, 55.5; Ni, 6.4 %.  $\nu_{\max}$ : 2935 (w),  
 2880 (w), 2848 (w), 1749 (w), 1644 (s), 1625 (s), 1611 (m),  
 1576 (m), 1530 (w), 1515 (w), 1472 (w), 1450 (s), 1445 (s),  
 1415 (s), 1387 (m), 1326 (s), 1235 (m), 1180 (m), 1122 (w),  
 1045 (w), 1028 (w), 972 (w), 950 (w), 895 (w), 876 (s),  
 865 (m), 755 (s), 737 (w), 693 (m) cm<sup>-1</sup>.

Product E : is dark green crystalline, m.p. 193.0 - 194.5<sup>o</sup>  
 found C, 39.4; H, 3.6; I, 38.1; Ni, 9.3;  $C_{22}H_{26}O_2N_2I_2Ni$   
 requires C, 39.8; H, 3.9; I, 38.3; Ni, 8.8 %.

$\nu_{max}$  : 2948 (w), 2880 (w), 2848 (w), 1750 (m), 1620 (s),  
 1609 (s), 1493 (s), 1472(vs), 1445 (m), 1390 (s), 1368 (w),  
 1328 (s), 1210 (m), 1185 (w), 1140 (m), 1075 (m), 1026 (w),  
 975 (w), 878 (m), 830(vs), 760 (w), 740 (w), 708 (m)  $cm^{-1}$ .

Product d : is yellow crystalline, m.p. 96.0 - 97.0<sup>o</sup>,  
 found : C, 30.4; H, 3.3; I, 59.4;  $C_{11}H_{13}ONI_2$  requires  
 C, 30.8; H, 3.0; I, 59.2 %;  $\nu_{max}$  : 3404 (bm), 2965 (m),  
 2920 (m), 2852 (m), 1644 (s), 1585 (s), 1444(m), 1341 (w),  
 1242 (w), 1218 (m), 1162 (m), 1130 (m), 1120(m), 1110 (w),  
 1018 (m), 945 (m), 902 (w), 865 (s), 822 (w), 797 (w),  
 758 (w), 736 (m), 720 (m)  $cm^{-1}$ .

Product e : is yellow liquid, b.p. > 250.0<sup>o</sup> dec. found :  
 C, 42.9; H, 4.3; I, 42.1;  $C_{11}H_{14}ONI$  requires C, 43.6; H, 4.6;  
 I, 41.9 %;  $\nu_{max}$  : 3404 (bm), 2968 (m), 2935 (m), 2879 (m),  
 1633 (vs), 1613 (m), 1575 (m), 1475(vs), 1435 (w), 1360 (m),  
 1335 (w), 1280(vs), 1240 (w), 1195 (m), 1180 (m), 1145 (w),  
 1122 (w), 1075 (m), 1030 (w), 980 (w), 942 (w), 900 (w),  
 872 (w), 850 (m), 820 (s), 775 (w), 735 (w), 692 (m),  
 675 (s)  $cm^{-1}$ .

### III. Iodination of F

A mixture of F (0.3 g, 0.001 M) and NIS (0.45 g, 0.002 M) was stirred in chloroform (30 ml) for 90 minutes. The iodinated product was fractionated into two pure components by a similar procedure used for the fractionation of the iodo derivatives of A. The first fraction was identified as  $\text{Ni}(3,5\text{-I}_2, \text{sal})_2$ ; G (0.052 g, 10 %) and the second fraction was characterised as  $\text{Ni}(5\text{-I}, \text{sal})_2$ , H (0.40 g, 50 %).

Product G : is green crystalline, m.p.  $276.0^\circ\text{-}278.0^\circ$ ;  
 found : C, 21.1; H, 1.1; I, 6.3; Ni, 7.78;  $\text{C}_{14}\text{H}_6\text{O}_4\text{I}_4\text{Ni}$  requires  
 C, 20.87; H, 0.74; I, 63.12; Ni, 7.29 %;  $\nu_{\text{max}}$  : 3285 (bm),  
 2935 (w), 2882 (w), 2850 (w), 1625 (s), 1585 (bw), 1532 (w),  
 1515 (w), 1472 (w), 1390 (m), 1310 (s), 1240 (m), 1190 (m),  
 1067 (w), 1030 (w), 897 (w), 755 (s), 705 (m)  $\text{cm}^{-1}$

Product H : is dark green crystalline, m.p.  $257.0 - 259.0^\circ$ ;  
 found, C, 29.7; H, 2.1; I, 45.6; Ni, 10.57;  $\text{NiC}_{14}\text{H}_8\text{O}_4\text{I}_2$   
 requires C, 30.39; H, 1.44; I, 45.95; Ni, 10.61 %.

$\nu_{\text{max}}$  : 3285 (bs), 1646 (s), 1585 (bw), 1535 (w), 1513 (w),  
 1458 (s), 1396 (m), 1368 (m), 1305 (s), 1246 (s), 1210 (m),  
 1197 (m), 1170 (m), 1155 (s), 1140 (w), 1123 (s), 1067 (w),  
 1032 (w), 900 (s), 830 (m), 780 (m), 755 (w), 700 (s),  
 660 (s), 530 (bs)  $\text{cm}^{-1}$ .

Ligand isolation from G and H

Reaction G (0.804 g, 0.001 M) and H (0.552 g, 0.001 M) with HCl (1 M) gave f and g respectively. f was identified as 3,5-I<sub>2</sub>,sal (0.45 g, 90 %) and was characterised as 5-I,sal<sup>6</sup> (0.40 g, 80 %). Analytical data of f and g are summarized below.

Product f : is yellow needle shaped crystalline, m.p. 109.0 - 109.5°, (lit.<sup>5</sup> 108.0°), found C, 22.8; H, 1.3; I, 67.1;

C<sub>7</sub>H<sub>4</sub>O<sub>2</sub>I<sub>2</sub> requires C, 22.5; H, 1.1; I, 67.9 %.

ν<sub>max</sub> : 3332 (bm), 1725 (w), 1667 (s), 1612 (m), 1485 (w), 1440 (m), 1391 (w), 1350 (w), 1302 (m), 1291 (m), 1218 (s), 1175 (w), 1150 (w), 1125 (s), 1070 (m), 900 (s), 880 (m), 815 (m), 776 (s), 737 (s), 706 (m) cm<sup>-1</sup>.

Product g : is yellow crystalline, m.p. 103.0° (lit.<sup>6</sup> 102.0°),

found : C, 33.4; H, 2.3; I, 51.5; C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>I requires, C, 33.9;

H, 2.0; I, 51.2 %; ν<sub>max</sub> : 3200 (bm), 1667 (s), 1610 (w),

1570 (w), 1472 (s), 1370 (s), 1340 (w), 1310 (w), 1287 (s),

1220 (w), 1205 (w), 1165 (m), 1115 (w), 895 (s), 838 (w),

835 (s), 770 (s), 700 (m) cm<sup>-1</sup>.

#### IV. Thiocyanation reaction

A mixture of H (0.552 g, 0.001 M) and KSCN (0.19 g, 0.002 M) in acetone (40 ml) and 1,4-dioxane (10 ml) was refluxed for 24 h. The reaction mixture was reduced to small

volume in vacuo. The product was loaded on silica gel packed column and eluted with benzene gave I (0.165 g, 30 %). The ligand separation reaction of I by treating it with HCl (1 M) gave h (0.132 g, 20 %). The compound I was characterised as  $\text{Ni}(\text{C}_8\text{H}_3\text{O}_2\text{INS})_2$  and h was characterised as  $\text{C}_8\text{H}_4\text{INO}_2\text{S}$ .

Product I : is green crystalline, m.p.  $225.0 - 226.0^\circ$ , found : C, 29.1; H, 1.1; I, 38.4; 8.92;  $\text{C}_{16}\text{H}_6\text{O}_4\text{S}_2\text{N}_2\text{I}_2$  requires C, 28.79; H, 0.899, I, 38.09; Ni, 8.8 %,  $\nu_{\text{max}}$  : 3280 (bs), 1651 (s), 1582 (bw), 1538 (w), 1515 (w), 1450 (m), 1383 (m), 1368 (m), 1305 (s), 1250 (s), 1195 (m), 1170 (m), 1145 (w), 1125 (s), 1035 (w), 905 (s), 830 (m), 780 (m), 755 (w), 705 (m), 665 (m)  $\text{cm}^{-1}$ .

Product h : is yellow crystalline, m.p.  $90.0^\circ - 91.5^\circ$ , found : C, 31.72; H, 1.56; I, 42.1;  $\text{C}_8\text{H}_4\text{INO}_2\text{S}$  requires C, 31.47; H, 1.31; I, 41.63 %;  $\nu_{\text{max}}$  : 3050 (w), 2400 (m), 1665 (s), 1575 (m), 1416 (w), 1282 (m), 1200 (m), 1170 (s), 1145 (s), 1130 (bw), 970 (w), 897 (m), 880 (m), 870 (m), 800 (bw), 730 (s), 700 (m), 693 (s), 647 (s)  $\text{cm}^{-1}$ .

#### V. Acetoxylation reaction of H with silver acetate :

A mixture of H (0.55 g, 0.001 M) and silver acetate (0.334 g, 0.002 M) in acetone (30 ml) and 1,4-dioxane (10 ml) was stirred at  $25^\circ\text{C}$  for 24 h. The reaction product was extracted with water and chloroform. The chloroform extract

was reduced to small volume in vacuo which gave J (0.165 g, 30 %) and the ligand separation reaction with HCl (1 M) gave i. The compound J was characterised as Ni(5-acetoxy-sal) and i as 5-acetoxy-sal.

Product J : Pale green crystalline, m.p. 320.0°,  
 found : C, 56.3; H, 3.9; Ni, 15.6;  $C_{18}H_{14}O_6Ni$  requires  
 C, 56.14; H, 3.63; Ni, 15.25 %.  $\nu_{max}$  : 3380 (bm), 1740(s),  
 1700 (s), 1650 (s), 1525 (m), 1450 (m), 1330 (m), 1190 (w),  
 1150 (s), 1125 (m), 1035 (w), 900 (s), 850 (w), 780 (w),  
 750 (m)  $cm^{-1}$ .

Product i : is colourless crystalline; m.p. 155.0 - 156.5°;  
 found : C, 60.3; H, 4.9;  $C_9H_8O_4$  requires C, 60.00;  
 H, 4.44 %;  $\nu_{max}$  : 3150 (bm), 1760 (s), 1740 (s), 1700 (s),  
 1670 (w), 1650 (m), 1600 (w), 1580 (w), 1450 (m), 1400 (w),  
 1375 (s), 1370 (s), 1305 (w), 1280 (s), 1245 (m), 1210 (s),  
 1205 (s), 1190 (bs), 1180 (w), 1157 (m), 1115 (s), 1095 (s),  
 1060 (w), 1045 (w), 1010 (s), 915 (m), 875 (m), 850 (m),  
 810 (m), 790 (s), 720 (m), 665 (m)  $cm^{-1}$ .

### 3. Results

The bromination reaction of Ni(N,n-butsalim)<sub>2</sub> (A) gave two products, B and C, separated on silica gel packed column eluting with benzene and benzene-acetone mixture

(1:1 v/v) respectively. The elemental analysis of B suggested that it was a Ni(II) complex with dibromo derivative  $\text{Ni}(3,5\text{-Br}_2, \text{N-n-butyalim})_2$  and the complex C was a nickel complex with monobromoderivative  $\text{Ni}(5\text{-Br}, \text{N-n-butallim})_2$ . The ligands b and c were separated from these complexes respectively by treating them with KCN in 1,4-dioxane. The  $^1\text{H}$  n.m.r. spectrum of b in the aromatic region was a typical of AB system with A and B in meta position ( $\delta$  4, C-H, 7.11 ppm (d,d),  $\delta$  6, C-H, 7.50 ppm (d,d)  $J_{4,6} = 2.2$  Hz). The signal observed at 8.07 ppm was associated with azomethine proton and broad signal observed at 13.4 ppm was due to hydroxy proton. The typical spectrum associated with n-butyl group was observed between 3.52 ppm and 0.88 ppm ( $\delta$   $\text{CH}_3$ , 0.8 ppm (triplet),  $\delta$   $\gamma\text{CH}_2$ , 1.3 ppm (m),  $\delta$   $\beta\text{CH}_2$ , 1.56 ppm (m),  $\delta$   $\alpha\text{-CH}_2$ , 3.52 ppm (t);  $J_{\alpha,\beta} = J_{\text{CH}_3} \gamma = 7$  Hz). Its infrared spectrum displayed a strong band at  $1637\text{ cm}^{-1}$  due to  $\nu_{\text{C=N}}$ . Since the coordinated metal atom is not expected to change the relative magnitude of polarisation at different positions in the coordinated aromatic ligand. This compound was characterised as 3,5-dibromo-N-n-butyalim.

The  $^1\text{H}$  NMR spectrum of the compound c in the aromatic region was typical of AA'B system. It displayed a doublet at 6.77 ppm, another doublet at 7.24 ppm and a doublet of doublet at 7.3 ppm due to  $\delta$  3, C-H,  $\delta$  6, C-H and  $\delta$  4, C-H

respectively. ( $J_{3,4} = 8 \text{ Hz}$ ,  $J_{4,6} = 2 \text{ Hz}$ ). The signal due to azomethine proton was observed at 8.16 ppm. A broad signal observed at 12.9 ppm was due to  $\delta\text{OH}$  and the typical spectrum due to n-butyl group was observed between 3.56 ppm to 0.92 ppm. These observations suggested that ~~from~~ from the polarization model the compound c was 5-Br, N-n-butساليم.

The authenticity of sample b and c was analysed by preparing separately these imines, using 3,5-Br<sub>2</sub>, salicylaldehyde and 5-Br, salicylaldehyde.

The direct bromination reaction of N-n-butساليم using liquid bromine affords a mixture of 3-5, Br<sub>2</sub>, salicylaldehyde and 5,Br-salicylaldehyde. The hydrobromic acid (HBr) formed during the bromination reaction hydrolyses the imine group. The reaction between N-n-butساليم with N-bromosuccinimide (NBS) did give an oily product which could not be characterised. Thus it is possible by using a metal complex to obtain the bromo derivative of N-n-butساليم, which otherwise would be prepared by using bromosalicylaldehyde.

The above analysis suggested that the complex B was a Ni(II) complex with 3,5-Br<sub>2</sub>, N-n-butساليم and the complex C was a Ni(II) complex with 5-Br, N-n-butساليم.

The bromination reaction of complex A was carried out by using different ratios of the complex and NBS in chloroform.

From all these reactions we always obtained a mixture of the nickel complex with 5-Br, N-n-butylsalim and 3-5, Br<sub>2</sub>, N-n-butylsalim even at the ratio of 1:2 and of 1:4. The proportion of 5-Br, N-n-butylsalim was more at the lower ratio and the relative concentration of 3-5, Br<sub>2</sub>, N-n-butylsalim was higher at the higher concentration of NBS. This observation is different from that reported from the literature. An anomalous solvent effect was observed on the bromination reaction. In 1,4-dioxane the reaction is comparatively fast and high amount of 3-5, Br<sub>2</sub>-N-n-butylsalim was obtained under similar experimental condition as compared in chloroform. The effect of light and oxygen was also observed on these reactions.

The treatment of complex A with iodine monochloride (ICl) gave a sticky acid degradable product which could not be characterised. NIS (N-iodosuccinimide) was therefore used as a iodinating agent for complex A using chloroform as a solvent. The separation of the product using a silica packed column gave complex D with benzene and the product E in benzene and acetone (1:1 v/v) as the eluent. The elemental analysis of D suggested that it was a Ni(II) complex with disubstituted N-n-butylsalim and the complex E was a Ni(II) complex with monosubstituted N-n-butylsalim (it was assumed that both the coordinated ligands were identical). For the characterization of these complexes the ligands were separated by treating them

with KCN. The ligand separated from complex D was identified as 3-5, I<sub>2</sub>, N-n-butylsalim d. Its <sup>1</sup>H NMR spectrum displayed a typical AB pattern in the aromatic region (δ 4 C-H, 7.35 ppm (doublet) δ 6, C-H, 7.90 ppm (doublet), J<sub>4,6</sub> = 1.5 Hz). The signal associated with azomethine proton was observed at 8.03 ppm; and signal due to hydroxyl proton was broad at 14 ppm. The signals in the high field region between 3.55 ppm to 0.90 ppm was typical of n-butyl group (δ CH<sub>3</sub> = 0.90 ppm (triplet), δ βCH<sub>2</sub> = 1.59 ppm (multiplet) δ γCH<sub>2</sub> = 1.28 ppm (multiplet), δ α-CH<sub>2</sub> = 3.55 ppm (triplet), J<sub>α,β</sub> = 6Hz, J<sub>γ-CH<sub>3</sub></sub> = 7 Hz. Its infrared spectrum displayed a strong band at 1644 cm<sup>-1</sup>, due to C=N group. Thus similar to bromination reaction using NBS, complex D was characterized as 3-5, I<sub>2</sub>, N-n-butylsalim.

The <sup>1</sup>H NMR spectrum of compound e in the aromatic region was typical of AA'B system. A doublet was observed at 6.71 ppm and another doublet at 7.18 ppm a doublet of doublet was observed at 7.36 ppm. If we assume as the iodo group enters at position 5, a coupling constant J<sub>3,4</sub> was 3.0 Hz and J<sub>4,6</sub> was 2.6 Hz. The signal associated with azomethine proton was observed at 8.18 Hz and the hydroxyl proton displayed a broad signal at 12.75 ppm. The typical pattern associated n-butyl group was observed in the region 3.54 ppm and 0.91 ppm.

The comparison of this spectrum with that of the

authentic sample prepared separately by using 5-I, salicylaldehyde was identical with that of NMR spectrum of compound e. Its infra red spectrum displayed a very strong band at  $1633\text{ cm}^{-1}$  due to C=N group. A similar iodination reaction of salicylaldehyde complex using NIS, yielded a mixture of complex G and H, which were separated on silica gel packed column. The elemental analysis of G suggested that it was a Ni(II) complex with 3-5, diiodo-salicylaldehyde and H was a Ni(II) complex of monoiodosalicylaldehyde. The ligand from these complexes was separated by treating the complex with HCl. The  $^1\text{H}$  NMR spectra of f separated from the complex G showed a typical AA' pattern in the aromatic region ( $\delta$  4 C-H, 7.74 ppm (doublet);  $\delta$  6, C-H, 8.16 ppm (doublet);  $J_{4,6} = 1.5\text{ Hz}$ ). The signal observed at 0.66 was associated with CHO proton and a singlet signal observed at 11.58 ppm was due to OH proton. These observations suggested that the compound f was 3-5,  $\text{I}_2$ , salicylaldehyde. Its infra red spectrum displayed a strong band at  $1667\text{ cm}^{-1}$  due to C=O group. These observations suggested that the compound f was 3-5,  $\text{I}_2$ , salicylaldehyde and the complex g was a Ni(II) complex with 3-5,  $\text{I}_2$ , salicylaldehyde.

The  $^1\text{H}$  NMR spectrum of g displayed a typical pattern of AA'B. A doublet was observed at 7.55 ppm a doublet of a doublet was observed at 7.53 ppm and a doublet was observed at

6.82 ppm. The signal due to CHO proton was observed at 0.76 ppm and a signal due to OH proton was observed at 10.78 ppm. These observations suggested that the compound g was 5-I, salicylaldehyde and the complex H was Ni(II) complex with 5-I, salicylaldehyde.

The reaction of F with  $(\text{SCN})_2$  gave a sticky mass which could not be characterised. The treatment of complex H with KSCN after purification on column gave a crystalline product with benzene. Its elemental analysis suggested that it was Ni(II) complex with a substituted salicylaldehyde containing iodo and thiocyanato group. The infra red spectrum of complex I displayed a strong band at  $1651 \text{ cm}^{-1}$  due to coordinated C=O group and medium intensity band was observed at  $1383 \text{ cm}^{-1}$  indicating the presence of (SCN) thiocyanato-S group. No strong band was observed between  $1500$  to  $1470 \text{ cm}^{-1}$  suggesting that the bonding of the aromatic ring with the thiocyanato group is through sulphur. The comparison of *the* infra red spectrum of the Ni(II) complex of 3-5, I<sub>2</sub>, salicylaldehyde with that of complex I in the region  $650$  to  $750 \text{ cm}^{-1}$ , indicates that the medium intensity band was observed at  $705 \text{ cm}^{-1}$  for the complex I, which may be assigned to C-S. Thus the observation of  $\nu_{\text{C=N}}$ ,  $\nu_{\text{C-S}}$  and the absence of the band associated with C-S, suggested that the thiocyanato group is bonding to aromatic ring through sulphur and not through nitrogen.

The ligand separated from the complex by treatment with HCl. The elemental analysis of h suggested that it was substituted salicylaldehyde containing iodo and thiocyanato group. Its infrared spectrum displayed a  $\nu_{C=O}$  at  $1665\text{ cm}^{-1}$  and the band associated with thiocyanato group were observed at  $2400\text{ cm}^{-1}$  and  $700\text{ cm}^{-1}$ . Its  $^1\text{H}$  NMR spectra was typical of AB system with the substitution in meta position. Two doublets were observed at 7.8 ppm and 8.2 ppm. The coupling constant was 2.0 Hz. The signal observed at 9.68 ppm was due to CHO proton and a singlet observed at 11.67 ppm was due to OH proton.

These observations suggested that h was 3-thiocyanato-5-iodo salicylaldehyde (3-SCN-5-I, sal), and the complex I was the Ni(II) complex with 3-thiocyanato-5-I salicylaldehyde.

A similar treatment of complex H with  $\text{KNO}_2$ , KOAc did not show any reaction. The reaction of complex H with silver acetate,  $\text{AgNO}_3$  and AgCN were carried out but a definite product was obtained with silver acetate.

The elemental analysis of i fitted well with that of the expected mono acetoxy derivative of salicylaldehyde. Infrared spectrum of i displayed two strong and sharp bands at  $1700\text{ cm}^{-1}$  and  $1740\text{ cm}^{-1}$ , which were assigned to C=O group of CHO and  $\text{OCOCH}_3$  respectively. A broad band was observed at

3150  $\text{cm}^{-1}$  due to intramolecularly H-bonded OH group. The medium intensity band was observed at 1450  $\text{cm}^{-1}$  due to C-CH<sub>3</sub> deformation mode. Three strong bands were observed at 1190  $\text{cm}^{-1}$ , 1205  $\text{cm}^{-1}$  and 1210  $\text{cm}^{-1}$ . This region is associated with the CO stretching mode of ester group and phenol group to OH deformation mode. These results suggested that the compound i was 5-acetoxy, salicylaldehyde. The <sup>1</sup>H NMR spectrum of i substantiated the structure given on the basis of elemental analysis and infrared spectrum to i.

Similarly the assignment of two bands observed between 1370  $\text{cm}^{-1}$  and 1375  $\text{cm}^{-1}$  is difficult. It is associated with OH deformation mode, CO stretching mode and C-CH<sub>3</sub> deformation mode.

A signal observed at 2.35 ppm was due to protons present in the acetoxy group. The signal due to OH proton was comparatively broad at 10.95 ppm. The signal due to CHO proton was comparatively high field at 8.4 ppm. The nature of this signal suggested the involvement of CHO group in intramolecular H-bonding. It is noted here, the C=O group frequency of H-bonded carboxylic group is generally observed at 1650  $\text{cm}^{-1}$  to 1670  $\text{cm}^{-1}$  and the chemical shift of COOH proton lies between 10 to 14 ppm. The presence of CHO group in i was substantiated by treating i with n-butylamine yielding the corresponding imine.

#### 4. Discussion :

The use of halogenosuccinimides in the halogenation reactions of acid labile compounds is well recognised. Since the side product is the basic compound succinimide, under such experimental conditions, such systems are supposed to be stable. The imine group is susceptible for hydrolysis in an acid medium and it is obvious that the reaction of liquid bromine with  $\text{Cu} [\text{N-n-butylim}]_2$  would yield 3-5,  $\text{Br}_2$ -sal.<sup>9</sup> Our experiments confirm this prediction and it is contrary to the report of obtaining  $\text{Cu} (3-5, \text{Br-N-n-butylim})_2$  during such a bromination reaction. The bromination of N-Rsalim complexes is effected by using NBS. The reaction of  $\text{Ni} (\text{N-n-butylim})_2$  (A) afforded a mixture of complexes B and C which were characterised as  $\text{Ni} (3-5, \text{N-n-butylim})_2$  and  $\text{Ni} (5\text{-Br}, \text{N-n-butylim})_2$  B and C, from the elemental analysis and infra red spectrum. The position of the bromo group on the aromatic nucleus was confirmed from the <sup>1</sup>H NMR spectra of the ligands separated b and c from these complexes using alkaline reagent such as KCN. The bromination reaction was carried out using different ratios of  $\text{Ni} (\text{N-n-butylim})_2$  and NBS. It was observed that for all these ratios a mixture of dibromo and monobromo derivatives were obtained. For the higher ratio of complex to NBS the proportion of monobromo derivative was high and for the smaller ratios the dibromo

derivative was obtained in larger proportion. It has been reported<sup>3</sup> in the literature that for the mole ratio 1:2 pure Ni (5-Br, N-n-butsalim)<sub>2</sub> was obtained, while for the ratio 1:4 pure Ni (3-5, Br<sub>2</sub>, N-n-butsalim)<sub>2</sub> was obtained.

Our experiments were carried out under identical conditions used in literature and our results are contrary to the reported work. Even the variation of substituent on the imine nitrogen and the change of the coordinated metal ion does not yield pure 5-Br, N-n-butsalim or 3-5, dibromo derivative. Enormous solvent effect was observed in these reactions. The bromination reactions in 1,4-dioxane-ethanol, in excess of NBS yielded dibromo derivative. The bromination reactions of the parent ligand using the experimental conditions similar to that used for metal complexes yields a mixture of 5-Br and 3-5, Br<sub>2</sub> derivative of N-n-butsalim irrespective of the nature of the solvents used. Thus the similar reaction products obtained from bromination reaction of coordinated ligand and the parent ligand indicates that the position of the electrophilic attack on the aromatic nucleus remains unchanged, upon coordination. This observation substantiates the reported observation on the unchanged reactive site upon coordination during the electrophilic substitution reaction of the metal complex with definite aromatic character.<sup>10</sup>

Although the position of the electrophilic attack

remains unchanged upon coordination during the bromination reaction, the present preliminary work suggest that the rate of the reaction was definitely modified upon coordination.<sup>11-12</sup> The bromination reaction was slow with the parent ligand as compared to that of the corresponding metal complexes. Probably the metal ligand ( $M \rightarrow L$ ) charge transfer modifies the extent of polarisation of the coordinated ligand; this affecting the rate of the bromination reactions. It would be interesting to study the rates of bromination reactions of metal complexes containing different metal ions to throw light on the role of metal ligand ( $M \rightarrow L$ ) charge transfer in these substitution reactions.

Our preliminary results of the bromination reactions suggested that the rate of bromination reaction depends on the polarity of the solvent. The reaction rate is faster in ethanol as compared to that in 1-4, dioxane and chloroform. As the polarity of solvent affects the rate of reaction, probably polar intermediates are involved during the reaction pathway. The light and atmospheric oxygen have a definite effect on the rates of these reactions. The bromination reaction takes larger time to go to completion in the absence of light. Similarly in the inert atmosphere the reaction rate is considerably inhibited as compared to that in the normal atmosphere. These observations will be

important while analysing the probable mechanism of the bromination reactions using the kinetics data.

One of the earlier reports on the bromination reaction of Ni (N-n-butylsalim)<sub>2</sub> suggested the substitution at imine H at 7-CH<sup>3</sup>. The systematic study of the bromination reactions in our laboratory did not give any evidence of such a substitution, even as an intermediate from the <sup>1</sup>H NMR spectra studied during the progress of the reactions.

The Schiff bases used in the present work are bidentate and methanol was used in some of the stages during the bromination reactions. We have not observed the addition of methanol at the C=N group as has been reported<sup>13</sup> for the planer tetradentate Schiff base metal complexes. We have also used chloroform in some of the stages of the substitution reactions. There is a report in the literature that the Schiff base<sup>14</sup> complexes catalyse the dehalogenation of chloroform, leading to the formation of mixed complex containing Cl<sup>-</sup> as one of the ligand. At least under our experimental conditions we could not get such an observation.

The reaction carried out using ICl did give a oily product, which could not be characterised. The successful iodination of Ni (N-n-butylsalim)<sub>2</sub> was carried out using NIS. The results obtained for iodination reaction were similar to that with the bromination reactions. A mixture of nickel (II)

complex with 3-5, I<sub>2</sub>, N-n-butylsalim and 5-I, N-n-butylsalim complexes D and E were obtained. These complexes were fully characterised by separating the ligands d and e using KCN. These iodo derivatives are reported for the first time. The effect of the nature of the coordinated metal ion, the dielectric constant of the medium and the catalytic effect of light and atmospheric oxygen on the iodination reaction was similar to that for the bromination reactions.

Since we were successful in iodinating the coordinated Ni (N-Rsalim)<sub>2</sub> complexes using NIS, we carried out similar reactions using the bis(salicylaldehydato) Ni(II) complex (I). In literature there was a negative report for such a reaction. We have obtained the results similar to that for the halogenation reactions of the imine complexes of Ni(II). A mixture of Ni (3-5, I<sub>2</sub>, sal)<sub>2</sub> (G) and Ni(5-I, sal)<sub>2</sub> were obtained. The structures of which were confirmed by characterising the isolated ligands f and g from these complexes using KCN.

The pseudohalogens such as thiocyanate was substituted using (SCN)<sub>2</sub> in the coordinated pseudoaromatic ligand, such as 2,4-pentanedione. The reaction of (SCN)<sub>2</sub> with Ni(sal)<sub>2</sub> gave an oily mass, which could not be identified. It was interesting that the reaction of Ni (5-I, sal)<sub>2</sub> (H) with KSCN yielded a novel complex which was characterised as Ni(3-SCN, 5-I, sal)<sub>2</sub>,

the structure of the complex I was suggested on the basis of elemental analysis and infra red spectrum of complex I and the  $^1\text{H}$  NMR spectrum and other analytical data of the ligand b separated from the complex I. We are not aware of any report of such a compound till date. This reaction prompted us to study the reaction of complex H with other potassium salts such as  $\text{KNO}_2$  and  $\text{KOAc}$ . We could not get a observable reaction with these salts. We therefore carried out the reaction with the silver salts with complex H. The crude product obtained from the reaction of complex H with  $\text{AgCN}$ , displayed a band at  $2145\text{ cm}^{-1}$  due to  $\nu_{\text{C}\equiv\text{N}}$  suggesting the substitution of CN group in the aromatic nucleus. However the complex as well as the ligand separated from the complex could not be fully characterised probably due to the limitation in the separation of pure compound from the reaction mixture.

The product obtained from the reaction of silver acetate with the complex I was fully characterised. The purification of the reaction product on silica packed column yielded a complex J, which was characterised as  $\text{Ni}(\text{5-OCOCH}_3, \text{sal})_2$ . The ligand separated from the complex J was characterised as  $\text{5-OCOCH}_3, \text{sal}$  (i). This reaction suggested that  $\text{Ag}^+$  ion present in the silver salt catalyses the dissociation of iodo group, and the acetoxy group was substituted in the place of iodo group.

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