

● CHAPTER-III ●

CHAPTER IIIELECTROPHILIC SUBSTITUTION REACTIONS OF  
METAL COMPLEXES - PART I  
(Nitration Reactions)1. Introduction :

Based on the available data of the electrophilic substitution reactions of coordinated aromatic ligands, there is an overall impression<sup>1-3</sup> that (i) the position of incoming electrophiles remain unchanged; and (ii) the central metal ion in a complex has a definite effect on the kinetic aspects of a reaction. The halogenation reactions of metal complexes are well studied. It has been reported<sup>4</sup> that the bromination of bis-(N-n-butylsalim) nickel (II) using N-bromosuccinamide in chloroform affords 5,5'-dibromo-derivative when the ratio of the complex to N-bromosuccinimide was 1:2, and affords 3,3',5,5'-tetrabromoderivative when this ratio was 1:4. Our preliminary results of these reactions<sup>5</sup> afford always a mixture of 5,5'-dibromo and 3,3',5,5'-tetrabromoderivatives even when the ratio of metal to N-bromosuccinimide is greater than 1:8. The results on the nitration reaction<sup>6-12</sup> of metal complexes are comparatively scanty. The direct nitration of salicylaldehyde<sup>13</sup> using nitric acid - acetic acid (1:7 v/v) mixture affords a mixture of 3-nitro-

salicylaldehyde and 5-nitrosalicylaldehyde in the molar ratio 1:4. For the synthesis of 3,5-dinitrosalicylaldehyde this mixture of compounds is further nitrated using sulphuric acid-nitric acid (2:1 v/v). It will be profitable to study the nitration reactions of metal complexes for analysing the effect of central metal atom on the yields of the various nitration products. The present chapter reports the results of the nitration reaction of the complexes with salicylaldehyde, 2-hydroxyacetophenone, 2'-hydroxychalcone and imines of salicylaldehyde and 2-hydroxyacetophenone. Since the metal-ligand bond is generally acid-labile, dinitrogen tetroxide is used as a nitrating agent instead of the usual nitrating mixture. The feasibility of using other nitrating agents is also analysed.

## 2. Experimental

### (A) Materials

- |        |  |          |
|--------|--|----------|
| (i)    | bis(salicylaldehydato)nickel (II)          | <u>A</u> |
| (ii)   | bis(salicylaldehydato)copper (II)          | <u>C</u> |
| (iii)  | bis(2-hydroxyacetophenonato)nickel (II)    | <u>E</u> |
| (iv)   | bis(2-hydroxyacetophenonato)copper (II)    | <u>F</u> |
| (v)    | bis(2'-hydroxychalconato)nickel (II)       | <u>G</u> |
| (vi)   | bis(2'-hydroxychalconato)copper (II)       | <u>H</u> |
| (vii)  | bis(N-n-butylsalicylaldiminato)nickel (II) | <u>J</u> |
| (viii) | bis(N-n-butylsalicylaldiminato)copper (II) | <u>K</u> |

- (ix) bis(2-hydroxyacetophenone-N-n-butylaminato)nickel (II) L  
 (x) bis(2-hydroxyacetophenone-N-n-butylaminato)copper (II) Q

These complexes were synthesised by using the procedures similar to those given in the literature<sup>14,15</sup>.

The solvents used in the present work were purified by the literature method<sup>16</sup>.

(B) Role of nitrating agent in the nitration reaction of N-n-butسالim

(a) Nitration mixture HNO<sub>3</sub> : H<sub>2</sub>SO<sub>4</sub> (3:1 v/v) :

Nitration mixture (4 ml) was added to a stirred solution of N-n-butسالim (0.18 g, 0.001 M) in methanol (15 ml). A mixture of a and b was obtained which was separated by using a procedure similar to that given in (e,i) yielding a (0.06, 36 %) and b (0.05 g, 30 %).

(b) Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O + (CH<sub>3</sub>CO)<sub>2</sub>O :

N-n-Butسالim (0.18 g, 0.001 M) and (CH<sub>3</sub>CO)<sub>2</sub>O (10 ml) were taken in a conical flask fitted with a CaCl<sub>2</sub> drying tube. To this stirred mixture in an ice bath was added powdered Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O (0.96 g, 0.004 M) in small portions over a period of 30 min. The ice bath was removed after 4 h and the stirring was continued for additional 4 h at room temperature

(30 °). The resulting green mixture was poured into 150 ml of ice cold water containing  $\text{CH}_3\text{COONa}\cdot 3\text{H}_2\text{O}$  (1.00 g) and the mixture was further stirred for 2 h. The chloroform extract of this mixture yielded pale yellow low melting compound (0.30 g, 83 %) which was identified as 3-acetoxysalicylaldehyde (m.p. 138.0 - 139.0°) found: C, 60.4; H, 4.0;  $\text{C}_9\text{H}_8\text{O}_4$  requires C, 60.0; H, 4.4 %;  $\nu_{\text{max}}$  : 3400 (bm), 3150 (bm), 1760 (s), 1740 (s), 1700 (s), 1670 (w), 1650 (m), 1600 (w), 1580 (w), 1490 (w), 1450 (w), 1400 (w), 1370 (m), 1340 (w), 1250 (s), 1215 (s), 1195 (s), 1160 (m), 1119 (m), 1071 (m), 1040 (w), 1010 (s), 995 (s), 950 (s), 922 (m), 902 (m), 860 (m), 808 (w), 769 (s), 740 (w), 725 (w), 680 (w), 661 (w), 602 (m), 594 (w), 564 (m), 551 (m) 521 (w), 500 (m)  $\text{cm}^{-1}$ .

(c)  $\text{KNO}_2$  :

5-I, N-n-Butsalim (0.31 g, 0.001 M) was treated with  $\text{KNO}_2$  (0.17 g, 0.002 M) in water : 1,4-dioxane ( 1:1 v/v) was refluxed at 70° for 2 h. The isolated product was shown to be the starting material.

(d)  $\text{N}_2\text{O}_4$  :

Nitration of N-n-Butsalim (0.18 g, 0.001 M) by  $\text{N}_2\text{O}_4$  using the experimental conditions similar to those given in (e, i) gave <sup>an</sup> intractable oil.

(e) Nitration with N<sub>2</sub>O<sub>4</sub> :

(i) A mixture of N<sub>2</sub>O<sub>4</sub> and NO<sub>2</sub> was generated by heating Pb(NO<sub>3</sub>)<sub>2</sub>. This mixture of gases was passed through a thermostated trap kept at 20° to attain an equilibrium (85 %, N<sub>2</sub>O<sub>4</sub>, 15 % NO<sub>2</sub>). N<sub>2</sub>O<sub>4</sub> thus generated was bubbled through a stirred solution of A (0.60 g, 0.002 M) in ethyl acetate (30 ml) for 2 hours. The temperature of reaction medium was maintained at 20°. The reaction mixture was reduced to a small volume in vacuo. The residue was extracted with chloroform. The chloroform extract was reduced to small volume in vacuo. The isolated product (0.450 g) was loaded on a silica gel (100 - 200 mesh) packed column using petroleum ether (60 - 80°).

The fraction eluted with petroleum ether-benzene (1:1 v/v) afforded a pale yellow crystalline compound a (0.125 g, 18 %). The fraction eluted with benzene afforded a lemon yellow crystalline compound b (0.25 g, 37 %).

The chloroform insoluble residue was a yellowish green crystalline solid, B (0.15 g, 19 %).

Product a. m.p. 125.0 - 125.5°. Found : C, 50.1; H, 3.2; N, 8.2 %. C<sub>7</sub>H<sub>5</sub>NO<sub>4</sub> requires C, 50.29; H, 2.99; N, 8.38 %

$\nu_{\max}$  : 3350 (bm), 3100 (s), 1675 (s), 1650 (m), 1600 (m), 1585 (s), 1525 (m), 1380 (s), 1360 (s), 1235 (m), 1200 (w), 1190 (m), 1100 (m), 1020 (w), 940 (m), 920 (w), 845 (m), 780 (m), 755 (m), 725 (m), 648 (m)  $\text{cm}^{-1}$ . The  $^1\text{H}$  n.m.r. spectrum ( $\text{CDCl}_3$ ) showed the resonance at 7.12 (1 H, d), 8.40 (1H, dd), 8.55 (1H, d), 9.94 (1H, s) and 11.51 (1H, s) ppm with the coupling constants  $J_{3,4}$ , 9.8 Hz and  $J_{4,6}$ , 3.2 Hz.

Product b. m.p. 106.0 - 107.0°. Found : C, 50.1; H, 3.2; N, 8.2 %.  $\text{C}_7\text{H}_5\text{NO}_4$  requires C, 50.29; H, 2.99, N, 8.38 %

$\nu_{\max}$  3370 (bm), 3080 (w), 1660 (s), 1620 (m), 1600(m), 1575(m), 1520 (s), 1450 (s), 1400(m), 1350 (s), 1315 (m), 1290 (s), 1270 (m), 1185 (w), 1085(w), 950 (s), 865 (m), 825 (m), 810 (w), 795 (w), 760(m), 720 (w), 679 (s), 640 (w), 612 (m), 560 (w)  $\text{cm}^{-1}$ . The  $^1\text{H}$  n.m.r. spectrum ( $\text{CDCl}_3$ ) showed the resonance at 7.05 (1H, t), 7.97 (1H, dd), 8.20 (1H, dd), 10.40 (1H, s), and 11.47 (1H, s), ppm., with the coupling constants  $J_{4,5}$ , 8.4 Hz;  $J_{4,6}$ , 1.8 Hz and  $J_{5,6}$ , 7.8 Hz.

Product B. m.p. 310 - 312° d.c. Found : C, 42.5; H, 2.4; N, 7.5 %.  $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_8\text{Ni}$  requires C, 43.0; H, 2.0; N, 7.2 %.

$\nu_{\max}$  3080 (w), 1657 (s), 1640 (s), 1602 (m), 1544 (m), 1523 (s), 1503 (w), 1420 (w), 1381 (w), 1355 (s), 1215 (s), 1175 (s), 1135 (w), 1197 (s), 1087 (w), 1005 (w), 960 (s), 935 (s), 910 (w), 840 (s), 780 (bm), 720 (s), 665 (w), 520 (bw)  $\text{cm}^{-1}$ .

Ligand separation from product B by HCl (1 M) :

Reaction of Product B (0.150 g, 0.0005 M) with hydrochloric acid (1 M) in an aqueous medium (15 ml) yielded a yellow solid (0.10 g) from benzene extract. It was purified on <sup>a</sup> silica gel packed column using benzene-petroleum ether (60-80°) (2:1 v/v) as an eluent affording a dark yellow crystalline compound c.

Product c. m.p. 58.5°. Found: C, 39.8; H, 2.1; N, 13.3 %.  $C_7H_4N_2O_6$  requires C, 39.6; H, 1.9; N, 13.2 %  $\nu_{max}$  : 3200 (bs), 3090 (s), 1692 (s), 1612 (s), 1580 (m), 1540 (s), 1442 (s), 1370 (w), 1350 (s), 1310 (w), 1270 (s), 1225 (m), 1210 (w), 1175 (w), 1155 (m), 1100 (s), 1085 (m), 955 (w), 945 (m), 925 (s), 825 (w), 770 (s), 737 (s), 715 (s), 580 (s), 515 (bm)  $cm^{-1}$ . The <sup>1</sup>H n.m.r. spectrum (CDCl<sub>3</sub>) showed the resonances at 8.92 (1H, d), 9.19 (1H, d), 10.78 (1H, d) and 12.25 (1H, d) ppm with the coupling constant  $J_{4,6}$ , 2.8 Hz.

(ii) Nitration of C with N<sub>2</sub>O<sub>4</sub> :

The nitration reaction of C (0.61 g, 0.002 M) was carried out using a procedure similar to that used for the nitration reaction of A using N<sub>2</sub>O<sub>4</sub> (Section e, i). The isolated product (0.46 g) from the chloroform extract was loaded on silica gel packed column using petroleum ether. The fraction eluted with petroleum ether (60-80°)-benzene

(1:1 v/v) afforded a lemon yellow crystalline compound (d) (0.38 g, 58 %) and that eluted with benzene afforded a dark yellow crystalline compound (e) (0.18 g, 28 %). The chloroform insoluble residue was yellowish green needle shaped crystalline solid, D (0.10 g, 12 %).

Product d. The elemental analysis, m.p. infrared spectrum, and  $^1\text{H}$  n.m.r. spectrum of (d) were similar to that of (b).

Product e. The elemental analysis, m.p., infrared spectrum and  $^1\text{H}$  n.m.r. spectrum of (e) were similar to that of (c).

Product D. m.p. 180-190<sup>o</sup> d.c. Found : C, 42.9; H, 2.2; N, 6.8; Cu, 16.2;  $\text{C}_{14}\text{H}_8\text{N}_2\text{O}_8\text{Cu}$  requires C, 42.5; H, 2.0; N, 7.1; Cu, 16.05 %  $\nu_{\text{max}}$ : 3100 (w), 1675 (s), 1650 (w), 1600 (m), 1570 (m), 1525 (m), 1360 (s), 1300(s), 1325 (m), 1200 (w), 1190 (m), 1100 (m), 1020 (w), 940 (m), 920 (w), 845 (m), 780 (m), 755 (m), 725 (m)  $\text{cm}^{-1}$ .

#### Ligand separation from Product D

A procedure similar to that used for the ligand separation from product B (Section e, i) afforded a dark yellow crystalline solid (f). The elemental analysis, m.p., infrared spectrum and  $^1\text{H}$  n.m.r. spectrum of (f) were similar to that of (c).

(e,iii) The nitration reaction of E (0.66 g, 0.002 M) was carried out using a procedure similar to that used for the nitration reaction of A using  $N_2O_4$  (Section e, i). The isolated product (0.52 g) from the chloroform extract was loaded on silica gel packed column using petroleum ether (60-80°). The fraction eluted with petroleum ether-benzene (1:1 v/v) afforded a yellow compound (g) (0.22 g, 30 %) and that eluted with benzene afforded a dark yellow crystalline compound (h) (0.36 g, 40 %). The chloroform insoluble residue could not give reproducible analytical data and could not be characterised.

Product g. Yellow crystalline solid, m.p. 98.5°-99.0°.  
 Found: C, 53.3; H, 4.1; N, 8.2 %;  $C_8H_7NO_4$  requires C, 53.03; H, 3.86; N, 7.73 %.  $\nu_{max}$  3350 (bm), 2841 (w), 2140(w), 1720(s), 1700 (m), 1675 (s), 1660 (w), 1585 (s), 1530 (w), 1430 (w), 1380 (s), 1350 (m), 1210 (w), 1140 (w), 1090 (m), 1040 (w), 970 (w), 840 (w), 815 (m), 780 (m), 735 (m), 648 (m), 630(w), 575 (w),  $cm^{-1}$ . The  $^1H$  n.m.r. spectrum ( $CDCl_3$ ) showed the resonances at 7.11 (1H, d), 8.35 (1H, dd), 8.71 (1H, d) and 13.22 (1H, s) with the coupling constants  $J_{3,4}$ , 9.6 Hz and  $J_{4,6}$ , 3.0 Hz. The high field signal was obtained at 2.82 ppm (3H, s).

Product h. Dark yellow needles, m.p. 124.0° - 125.0°.

Found, C, 43.2; H, 2.85; N, 13.1 %.  $C_8H_6N_2O_6$  requires C, 42.47; H, 2.65; N, 12.38 %.  $\nu_{\max}$  3200 (bm), 3085 (w), 2920 (m), 2141(m), 1740 (m), 1715 (s), 1660 (w), 1575 (m), 1560 (m), 1530 (w), 1430 (w), 1380 (m), 1350 (s), 1210 (w), 1140 (m), 1085(m), 1035 (w), 960 (w), 930 (m), 840 (w), 815 (m), 780 (m), 750 (w), 735 (s), 705 (w), 640 (m), 630 (w), 575 (w),  $cm^{-1}$ . The  $^1H$  n.m.r. spectrum ( $CDCl_3$ ) showed the resonances at 8.98 (1H,d), 9.22 (1H, d) and 13.92 (1H, d) ppm with the coupling constant  $J_{4,6}, 1.6$  Hz. The high field signal was observed at 2.68 ppm (3H, s).

(e, iv) The nitration reaction of F (0.67 g, 0.002 M) was carried out using a procedure similar to that used for the nitration reaction of A, using  $N_2O_4$  (Section e, i). The isolated product (0.53 g) from the chloroform extract was loaded on silica gel-packed column using petroleum ether ( $60^\circ-80^\circ$ ). The fraction eluted with petroleum ether-benzene (1:1 v/v) afforded a yellow compound i (0.23 g) and that eluted with benzene afforded a dark yellow compound j (0.37 g). The chloroform insoluble residue could not give the reproducible analytical data and could not be characterized. The elemental analysis, m.p., infrared spectrum and  $^1H$  n.m.r. spectrum of (i) and (j) were similar to that of products (g) and (h) respectively.

(e, v) Nitration reaction of G (0.50 g, 0.001 M) was carried out using a procedure similar to that used for the nitration reaction of A using  $N_2O_4$  (Section e, i). The isolated product (0.16 g) from the chloroform extract was loaded on silica gel-packed column using petroleum ether ( $60^\circ-80^\circ$ ). The fraction eluted with benzene afforded a yellow compound (k) (0.14 g, 50 %). The chloroform insoluble residue could not give reproducible analytical data and was therefore not characterised.

Product k. Found: C, 57.8; H, 3.6; N, 9.1 %.  $C_{15}H_{10}N_2O_6$  requires C, 57.3; H, 3.2; N, 8.9 %.  $\nu_{max}$ : 3200 (bm), 3096 (w), 1680 (s), 1655 (s), 1630 (w), 1616 (s), 1580 (s), 1540 (bs), 1381 (w), 1340 (s), 1260 (bm), 1225 (w), 1210 (w), 1175 (m), 1155 (w), 1085 (s), 1010 (w), 995 (s), 980 (w), 967 (w), 925 (s), 865 (w), 827 (s), 770 (m), 750 (s), 735 (m), 705 (m), 685 (s), 660 (w), 650 (w), 630 (w), 610 (w), 585 (bm), 510 (bm)  $cm^{-1}$ . The  $^1H$  n.m.r. spectrum ( $CDCl_3$ ) showed the resonances at 8.48 (1H, d) and 8.92 (1H, d) with a coupling constant  $J_{4,6}$  4.0 Hz. A complex multiplet (7H) was observed between 7.23 and 7.95 ppm.  $\delta_{OH} = 12.2 - 13.4$  ppm.

(e, vi). The nitration reaction of H (0.51 g, 0.001 M) was carried out using a procedure similar to that used for the nitration reaction of A using  $N_2O_4$  (section e, i). The

isolated product l (0.170 g) from the chloroform extract was loaded on silica gel packed column using petroleum ether ( $60^{\circ}$ - $80^{\circ}$ ). The fraction eluted with benzene afforded a yellow compound (0.14 g, 50 %) and a compound eluted with chloroform afforded a pale green compound I (0.07 g, 25 %). The analytical data of l were similar to that of product k.

Product I. m.p.  $120 - 121.0^{\circ}$  (colour changes at  $105^{\circ}$  from pale green to dark green). Found: C, 45.24; H, 4.1; N, 8.1; Cu, 16.25 %,  $C_{15}H_{12}N_2O_7Cu$  requires C, 45.51; H, 3.03; N, 7.07; Cu, 16.00 %  $\nu_{max}$  3450 (b), 1689 (s), 1660 (w), 1620 (s), 1610 (s), 1585 (s), 1553 (s), 1510 (w), 1353 (s), 1265 (bs), 1230 (w), 1210 (w), 1175 (s), 1155 (w), 1085 (bs), 1030 (w), 1015 (m), 966 (m), 930 (m), 753 (s), 708 (m), 686 (s)  $cm^{-1}$ .

(e, vii). The nitration reaction of J (0.41 g, 0.001 M) using a procedure similar to that used for the nitration reaction of A using  $N_2O_4$  (section, e, i). The isolated product from the chloroform extract was loaded on silica gel packed column using petroleum ether ( $60^{\circ}$ - $80^{\circ}$ ). The fraction eluted with petroleum ether-benzene (1:1 v/v) afforded a pale yellow coloured compound (m) (0.116 g) and that eluted with benzene afforded a lemon yellow compound n (0.08 g). The chloroform insoluble residue could not give consistent analytical data.

The analytical data of m was similar to that of a and the analytical data of n was similar to b.

(e, viii). The nitration reaction of K (0.42 g, 0.001 M) was carried out using a procedure similar to that used for A using  $N_2O_4$  (Section e,i). The isolated product (0.29 g) from the chloroform extract was loaded on silica gel packed column using petroleum ether ( $60^{\circ}$ - $80^{\circ}$ ). The fraction eluted with petroleum ether - benzene (1:1 v/v) afforded a yellow compound o (0.11 g) and that eluted with benzene afforded a dark yellow crystalline compound p (0.23 g). The chloroform insoluble residue could not give the reproducible analytical data.

The analytical data of o were similar to those of a and the analytical data of p were similar to those of c.

(e, ix). The nitration reaction of L (0.87 g, 0.002 M) was carried out using a procedure similar to that used for A using  $N_2O_4$  (section e, i). The product obtained from benzene extract (0.61 g) was loaded on silica gel packed column using petroleum ether ( $60^{\circ}$ - $80^{\circ}$ ). The fraction eluted with benzene afforded a yellow crystalline compound q (0.11 g) and that eluted with benzene-chloroform (1:1 v/v) afforded dark yellow crystalline compound r (0.16 g). The residue remained after the benzene extract was extracted with chloroform affording yellowish green product M (0.06 g). The residue remained after

the benzene extract was extracted with chloroform affording yellowish green product M (0.06 g). The residue remained after the chloroform extract was extracted with methanol affording a pale green crystalline compound, N (0.10 g).

The elemental analysis, infrared spectrum and  $^1\text{H}$  n.m.r. spectrum of product q were comparable with that of g and the analytical data of r was similar to h.

Product M. m.p.  $104^\circ$ . Found: C, 54.1; H, 5.2; N, 10.6 %  
 $\text{C}_{24}\text{H}_{30}\text{N}_4\text{O}_6\text{Ni}$  requires C, 54.5; H, 5.7; N, 10.6 %.  $\nu_{\text{max}}$  3092 (m)  
 1692 (w), 1620 (s), 1570 (m), 1553 (m), 1453 (s), 1442 (m),  
 1380 (m), 1350 (s), 1260 (m), 1230 (w), 1175 (m), 1150 (w),  
 1090 (s), 1030 (w), 1010 (w), 995 (m), 930 (s), 825 (m),  
 770 (m), 745 (w), 735 (m), 705 (s), 680 (s), 540 (m),  $\text{cm}^{-1}$ .

Ligand separation from M with HCl (1 M).

The complex M was treated with HCl (1 M) and was extracted with benzene. The product obtained from benzene extract was loaded on silica gel packed column using petroleum-ether. The column was thoroughly washed with benzene and then eluted with benzene-chloroform (1:1 v/v) affording product s.

The elemental analysis, melting point, infrared spectrum and  $^1\text{H}$  n.m.r. spectrum of product s was similar to those of h.

Product N : m.p. above 350<sup>o</sup>. Found: C, 32.47; H, 4.37; N, 17.84 %; C<sub>12</sub>H<sub>15</sub>N<sub>5</sub>O<sub>9</sub> requires, C, 33.35; H, 3.47; N, 16.24 %.  $\nu_{\max}$  3375 (bm), 1669 (m), 1620 (s), 1530 (m), 1560 (m), 1380 (m), 1340 (m), 1280 (w), 1235 (w), 1210 (w), 1165 (m), 1085 (m), 1060 (w), 1015 (w), 995 (w), 955 (w), 935 (m), 885 (w), 832 (s), 807 (s), 785 (m), 750 (w), 715 (s), 540 (m) cm<sup>-1</sup>.

(e, x) The nitration reaction of Q (0.88 g, 0.002 M) was carried out using a procedure similar to that used for A using N<sub>2</sub>O<sub>4</sub> (section e,i). The product obtained from the benzene extract (0.62 g) was loaded on silica gel-packed column using petroleum ether (60<sup>o</sup>-80<sup>o</sup>). The fraction eluted with benzene afforded a yellow crystalline compound t (0.12 g, 17 %) and that eluted with benzene-chloroform (1:1, v/v) afforded a dark yellow crystalline compound u (0.17 g, 20 %). The residue remained after the benzene extract could not give consistent analytical data. The elemental analysis, infrared spectrum and <sup>1</sup>H n.m.r. spectrum of product t was comparable with that of g and the analytical data of u was similar to h.

### 3. Results

Nitration reaction of A with N<sub>2</sub>O<sub>4</sub> afforded three products a, b and B.

The elemental analysis of a fitted well with that

expected for the mononitro derivative of salicylaldehyde. Infrared spectrum of a displayed a broad band at  $3350\text{ cm}^{-1}$  due to the -OH stretching mode of vibration. A strong intensity band observed at  $1675\text{ cm}^{-1}$  was associated with  $\nu_{\text{C=O}}$ . Two strong intensity bands observed at  $1585\text{ cm}^{-1}$ ,  $1380\text{ cm}^{-1}$  and a medium intensity band observed at  $648\text{ cm}^{-1}$  were associated with the aromatic -NO<sub>2</sub> group. A comparison of the elemental analysis, m.p. and infrared spectra of the authentic sample of 5-nitrosalicylaldehyde with that of a suggested that a was 5-nitrosalicylaldehyde (lit. m.p.  $126^{\circ}$ ). The <sup>1</sup>H n.m.r. spectrum of a in the aromatic region exhibited a pattern typical of ABC spin system. It displayed a doublet at 7.12 ppm ( $J_{3,4} = 9.8\text{ Hz}$ ) due to 3-CH<sub>2</sub>, a doublet of doublet at 8.40 ppm ( $J_{4,6} = 3.2\text{ Hz}$ ) due to 4-CH and a doublet at 8.55 ppm due to 6-CH. The downfield signals observed at 9.94 ppm and 11.51 ppm were associated with the -CH<sub>2</sub>O and -OH protons respectively.

The elemental analysis of b was comparable with that expected for the mononitroderivative of salicylaldehyde. Infrared spectrum of b showed a broad band at  $3370\text{ cm}^{-1}$  due to the -OH stretching mode of vibration. A strong band observed at  $1660\text{ cm}^{-1}$  suggested the presence of -C=O group. A medium intensity band observed at  $1575\text{ cm}^{-1}$ , a strong intensity band at  $1350\text{ cm}^{-1}$ , a weak band at  $640\text{ cm}^{-1}$  were due

to the aromatic  $\text{-NO}_2$  group. A comparison of the elemental analysis, m.p. and infrared spectrum of the authentic sample of 3-nitrosalicylaldehyde (lit. m.p.  $109-110^\circ$ ) with that of b indicated that b was 3-nitrosalicylaldehyde. The  $^1\text{H}$  n.m.r. spectrum ( $\text{CDCl}_3$ ) of b in the aromatic region exhibited a pattern typical of AA'B spin system. It displayed a triplet (or overlapped double doublet) at 7.05 ppm due to 5-CH, a doublet of doublet at 7.97 ppm due to 6-CH and another doublet of doublet at 8.20 ppm due to 4-CH. The coupling constants  $J_{4,5}$  (8.4 Hz) and  $J_{5,6}$  (7.8 Hz) were quite close. The down-field signals observed at 10.40 ppm and 11.47 ppm were associated with the  $\text{-CHO}$  and  $\text{-OH}$  protons respectively.

Elemental analysis of B suggested that two nitro groups were substituted in the coordinated-salicylaldehyde. These two nitro groups would be on the same coordinated ligand affording dinitrosalicylaldehyde or would be on two different salicylaldehyde nuclei affording mononitro salicylaldehyde. Infrared spectrum of B displayed a strong intensity band at  $1657\text{ cm}^{-1}$  due to the  $\text{-C=O}$  group. The strong intensity bands at  $1523\text{ cm}^{-1}$  and  $1355\text{ cm}^{-1}$  were due to the aromatic  $\text{-NO}_2$  group. The absence of a strong band at  $3400\text{ cm}^{-1}$  suggested the absence of free  $\text{-OH}$  group. Due to the solubility limitations, the  $^1\text{H}$  n.m.r. spectrum of B could not be taken. The complex B was therefore treated with hydrochloric acid (1 M) and the

mixture was extracted with benzene. The  $^1\text{H}$  n.m.r. spectrum of the crude organic compound suggested that it was a mixture of two compounds in the molar ratio 1:1. The elemental analysis of a dark yellow compound c obtained from purification on silica gel-packed column suggested that it was dinitrosalicylaldehyde. Its infra red spectrum displayed a strong and broad band at  $3200\text{ cm}^{-1}$  due to  $\nu_{\text{O-H}}$  and a strong band at  $1692\text{ cm}^{-1}$  was due to  $\nu_{\text{C=O}}$ . A medium intensity band at  $1580\text{ cm}^{-1}$  and a strong band at  $1350\text{ cm}^{-1}$  were associated with  $-\text{NO}_2$  groups. Its  $^1\text{n.m.r.}$  spectrum ( $\text{CDCl}_3$ ) displayed a doublet at 8.92 ppm due to 6- $\text{CH}$  and another doublet at 9.19 ppm due to 4- $\text{CH}$ ; the coupling constant  $J_{4,6}$  had a small value (2.8 Hz) indicating meta coupling. The downfield signals observed at 10.78 ppm and 12.25 ppm were associated with  $-\text{CHO}$  and  $-\text{OH}$  protons respectively. (As compared to  $\delta_{\text{OH}}$  observed for compounds b and a. The one observed for compound c was broad). These observations suggested that the compound c was 3,5-dinitrosalicylaldehyde (lit. m.p.  $58-60^\circ$ ). On the basis of the characterisation of the separated ligands, the complex B was therefore shown to be (3,5-dinitrosalicylaldehydato)(salicylaldehydato) nickel (II).

The nitration reaction of c with  $\text{N}_2\text{O}_4$  afforded three products d, e and D. The analytical data of d and e indicated that these compounds were b and c respectively. The product D was characterised as (3,5-dinitrosalicylaldehydato)(salicyl-

aldehydato) copper (II); its reaction with hydrochloric acid (1 M) afforded the organic compound f which was characterised as 3,5-dinitrosalicylaldehyde.

The nitration reaction of E and F with  $N_2O_4$  afforded two organic products, g and h. The elemental analysis of g fitted well with that expected for the mononitro derivative of 2-hydroxyacetophenone, infrared spectrum of g displayed a broad band at  $3350\text{ cm}^{-1}$  due to the -OH stretching mode of vibration. A strong intensity band observed at  $1720\text{ cm}^{-1}$  was associated with  $\nu_{C=O}$ . The strong intensity bands observed at  $1585\text{ cm}^{-1}$ ,  $1380\text{ cm}^{-1}$  and a medium intensity band observed at  $648\text{ cm}^{-1}$  were associated with the aromatic  $-NO_2$  group. A comparison of the elemental analysis, m.p. and infrared spectra of the authentic sample of 5-nitro-2-hydroxyacetophenone. The  $^1H$  n.m.r. spectrum of g in the aromatic region exhibited a pattern typical of ABC spin system. It displayed a doublet at 7.11 ppm ( $J_{3,4} = 9.6\text{ Hz}$ ) due to 3-CH<sub>2</sub> a doublet of doublet at 8.35 ppm ( $J_{4,6} = 3.0\text{ Hz}$ ) due to 4-CH<sub>2</sub> and a doublet at 8.71 ppm due to 6-CH<sub>2</sub>. The signals observed at 2.82 ppm and 12.64 ppm were associated with the  $-CH_3$  and  $-OH$  protons respectively.

The elemental analysis of the product h suggested that it was dinitro-2-hydroxyacetophenone. Its infrared spectrum displayed a strong and broad band at  $3200\text{ cm}^{-1}$  due

to  $\nu_{\text{O-H}}$  and a strong band at  $1715 \text{ cm}^{-1}$  was due to  $\nu_{\text{C=O}}$ . A medium intensity band at  $1575 \text{ cm}^{-1}$  and a strong band at  $1350 \text{ cm}^{-1}$  were associated with  $-\text{NO}_2$  groups. Its  $^1\text{H}$  n.m.r. spectrum ( $\text{CDCl}_3$ ) displayed a doublet at 8.98 ppm due to 6- $\text{CH}$  and another doublet at 9.22 ppm due to 4- $\text{CH}$ ; the coupling constant  $J_{4,6}$  had a small value (1.6 Hz) indicating meta-coupling. The signals observed at 2.68 ppm and 13.5 ppm were associated with  $-\text{CH}_3$  and  $-\text{OH}$  protons respectively. These observations suggested that the compound h was 3,5-dinitro-2-hydroxyacetophenone.

From the nitration reaction of G, the Compound k gave the reproducible analytical data. The elemental analysis of k fitted well with that expected for dinitroderivative of 2'-hydroxychalcone. The infrared spectrum of k displayed a broad band at  $3200 \text{ cm}^{-1}$  due to  $-\text{OH}$  stretching mode of vibration, and the strong intensity bands were observed at  $1680 \text{ cm}^{-1}$  and  $1655 \text{ cm}^{-1}$  due to  $\nu_{\text{C=O}}$  and  $\nu_{\text{C=C}}$  respectively. Two strong intensity bands were observed at  $1580 \text{ cm}^{-1}$  and  $1340 \text{ cm}^{-1}$  due to nitro-groups containing hydroxy group. The  $^1\text{H}$  n.m.r. spectrum ( $\text{CDCl}_3$ ) of k was compared with that of 2'-hydroxychalcone. The pattern displayed by compound k 8.45 - 9.00 ppm was typical of AB system; 2'-hydroxychalcone did not show any signal in this region. This observation suggested that both the nitro groups were on the same aromatic

nucleus, and was further substantiated from the  $^1\text{H}$  n.m.r. spectrum observation in the region 7.2 to 8.0 ppm. It was a complex multiplet corresponding to 7 H associated with 5H on the aromatic nucleus and 2H of the HC=CH group in substituted chalcone (k). Thus the elemental analysis, infrared spectrum and  $^1\text{H}$  n.m.r. spectrum of compound k indicated that it was 2'-hydroxy-3',5'-dinitrochalcone (l).

From the nitration reaction of H, an organic compound l was separated. The elemental analysis, melting point, infrared spectrum and  $^1\text{H}$  n.m.r. spectrum of compound l was similar to that of k indicating that l was 2'-hydroxy-3,5'-dinitrochalcone. The complex I was separated from this reaction. The elemental analysis indicated that each molecule of the complex contained metal and ligand in the molar ratio 1:1, and it also contained two nitro groups. The ligand separated from complex I was characterised as 2'-hydroxy-5'-nitrochalcone. The infrared spectrum of complex I displayed a broad band at  $3450\text{ cm}^{-1}$  which was associated with the coordinated water molecule. A colour change observed at  $105^\circ$  during the determination of melting point was probably due to the thermal removal of water molecule from the coordinated sphere.

The nitration reaction of the imine complex J afforded two organic compounds m and n which were characterised

respectively as a and b from the elemental analysis, melting point, infrared spectrum and  $^1\text{H}$  n.m.r. spectrum. Similarly the organic compounds o and p obtained from the nitration reaction of imine complex K were characterised respectively as a and c from the analytical data. The compounds containing metal atoms from these reactions could not give reproducible analytical data, and could not be therefore characterised.

The organic compounds q and r obtained from the nitration reaction of L were characterised respectively as 2-hydroxy-5-nitroacetophenone (g) and 2-hydroxy-3,5-dinitroacetophenone (h). From this reaction two complexes M and N were separated. The elemental analysis of these complexes suggested that these were nitro imine complexes. The infrared spectrum of complex M displayed a strong band at  $1620\text{ cm}^{-1}$  due to  $\nu_{\text{C=N}}$ . The medium intensity bands observed at  $1570\text{ cm}^{-1}$  and  $1380\text{ cm}^{-1}$  were associated with aromatic  $\text{NO}_2$  group. The treatment of complex M with  $\text{HCl}$  afforded 2-hydroxy-3,5-dinitroacetophenone (s). Thus the elemental analysis and infrared spectrum of the complex M and the characterisation of the organic compound s( $\equiv$  h) separated from the  $\text{HCl}$  treatment of the complex M suggested that the complex M was the mixed ligand complex containing 2-hydroxy-3,5-dinitroacetophenone-*n*-butylimine and 2-hydroxyacetophenone-*n*-butylimine. The elemental analysis of complex N suggested that there were four

nitro groups present in one molecule of the complex and there was only one coordinated imine group. These observations suggested that the coordinated ligand was dinitroimine, and two nitro groups were directly coordinated to nickel.

Infrared spectrum of complex N displayed a strong band at  $3375\text{ cm}^{-1}$  due to  $\nu_{\text{OH}}$ , a strong band at  $1620\text{ cm}^{-1}$  due to C=N, and bands at  $1380\text{ cm}^{-1}$  and  $1560\text{ cm}^{-1}$  due to the aromatic  $\text{NO}_2$  group; a strong band was observed at  $1340\text{ cm}^{-1}$  and a weak band was observed at  $1280\text{ cm}^{-1}$  were tentatively assigned to M- $\text{NO}_2$  groups. The infrared spectra of complexes M and N displayed an additional band at  $540\text{ cm}^{-1}$ ; it was tentatively assigned to  $\nu_{\text{M-N}}$ .

A decomposition of complex N with HCl (1 M) afforded the organic compound s. The elemental analysis, infrared spectrum and  $^1\text{H}$  n.m.r. spectrum of compound s were similar to that of h. These observations suggested that the complex N was (3,5-dinitroacetophenone N-n-butylaminato) (dinitro) nickel (II).

The organic compounds t and u obtained from the nitration reaction of Q were characterised respectively as g and h. The residue remained after the benzene extract could not give consistent analytical data and was not characterised.

#### 4. Discussion :

The usual nitration mixture ( $\text{HNO}_3 + \text{H}_2\text{SO}_4$ ) used for the organic compounds could not be used for the nitration of most of the metal complexes due to their acid lability.  $\text{CH}_3\text{COONO}_2$  (generated by the reaction of cupric nitrate with acetic anhydride) was used as a nitrating agent for  $\text{M}(\text{ptdn})_2^{17}$ ,  $\text{M}(\text{sal})_2^{18,19}$ ,  $\text{M}(\text{N-R-hapim})_2^{20}$  and  $\text{M}(\text{N,N'en}(\text{salim})_2)^{20}$ . The use of  $\text{CH}_3\text{COONO}_2$  as an acetoxyating agent was also recognised. For example, the reaction of xylene and olefins with  $\text{CH}_3\text{COONO}_2$  resulted in the formation of the corresponding acetoxy derivatives.<sup>21-23</sup> It was therefore necessary to develop another nitrating agent to avoid the acetoxylation.

There was a report of the use of  $\text{N}_2\text{O}_4$  as a nitrating agent for  $\text{M}(\text{ptdn})_2^{17}$ . This chapter analyses the use of  $\text{N}_2\text{O}_4$  as a nitrating agent for complexes containing the related ligands such as salicylaldehyde, 2-hydroxyacetophenone, 2'-hydroxy-chalcone and imines of salicylaldehyde and 2-hydroxyacetophenone. In literature benzene was used as a solvent for nitration of  $\text{M}(\text{ptdn})_2$  with  $\text{N}_2\text{O}_4$ .<sup>24</sup> For the complexes we selected, the nitration reaction was negligible in benzene; instead the reaction was smooth in ethyl acetate.

The reaction of bis(salicylaldehydato)nickel (II), (A), with  $\text{N}_2\text{O}_4$  afforded the benzene soluble product which was

characterised as a mixture of 3-nitrosalicylaldehyde b and 5-nitrosalicylaldehyde a in the mole ratio 2:1. The chloroform insoluble product obtained from this reaction was with the chemical composition  $C_{14}H_8N_2O_8Ni$  (B). Because of its little solubility in the usual organic solvents, its  $^1H$  n.m.r. spectrum could not be obtained. The coordinated ligand from this complex was therefore separated by treating the complex with HCl and the organic compound was extracted in benzene. The  $^1H$  n.m.r. spectrum of the crude organic product suggested that it was a mixture of 3,5-dinitrosalicylaldehyde c and unsubstituted salicylaldehyde in the mole ratio 1:1. These two compounds were separated from the mixture on the silica-packed column using petroleum ether ( $60^\circ-80^\circ$ ): benzene mixture (1:1 v/v) as an eluent for c and using methanol as an eluent for salicylaldehyde. The analytical data of the organic compound thus separated were comparable with those of the corresponding authentic compounds. These observations suggested that the complex (B) was a mixed-ligand complex; one of the coordinated ligand was c and the other was salicylaldehyde.

The direct reaction of salicylaldehyde with  $N_2O_4$  did give an intractable oily mass, while the reaction of the metal complex was smooth, yielding compounds with definite composition.  $N_2O_4$  can be dissociated homolytically into two  $NO_2$  radicals; this process is favoured by heat. The heterolytic

dissociation of  $N_2O_4$  into  $NO_2^+$  and  $NO_2^-$  ions can be made possible by a reagent capable of combining readily with either  $NO_2^+$  or  $NO_2^-$  ions. For example  $N_2O_4$  readily forms a complex with  $BF_3$  with the formula  $(F_3B \leftarrow NO_2)^- (NO_2)^+$  and it has been successfully used as a nitrating reagent for aromatic compounds and olefins such as benzene, naphthalene, cyclohexene and methylacrylate. Thus during the reaction of  $N_2O_4$  with a metal complex the metal ion has probably played a key role in these reactions.

During the reaction of a metal complex with the dipolar molecule  $N_2O_4$ , the negative end of the dipole presumably formed a bond with the metal ion. The consequence of such a bond formation was the close proximity of the positive end of  $N_2O_4$  with the nucleophilic site on the aromatic ring. The molecular model of the intermediate dipolar complex suggested that both these positions were sterically favoured. (While making the model it was assumed that the chelate ring including the aromatic ring was planar). The stereoelectronic interactions initiated the rupture of the N-N bond in  $N_2O_4$ , which held the two dipoles. In this process one mole of nitrous acid was produced. When the metal-ligand bond was acid labile, the ligand would be separated from the coordination sphere (Fig. 1).

Since free salicylaldehyde was not detected in the

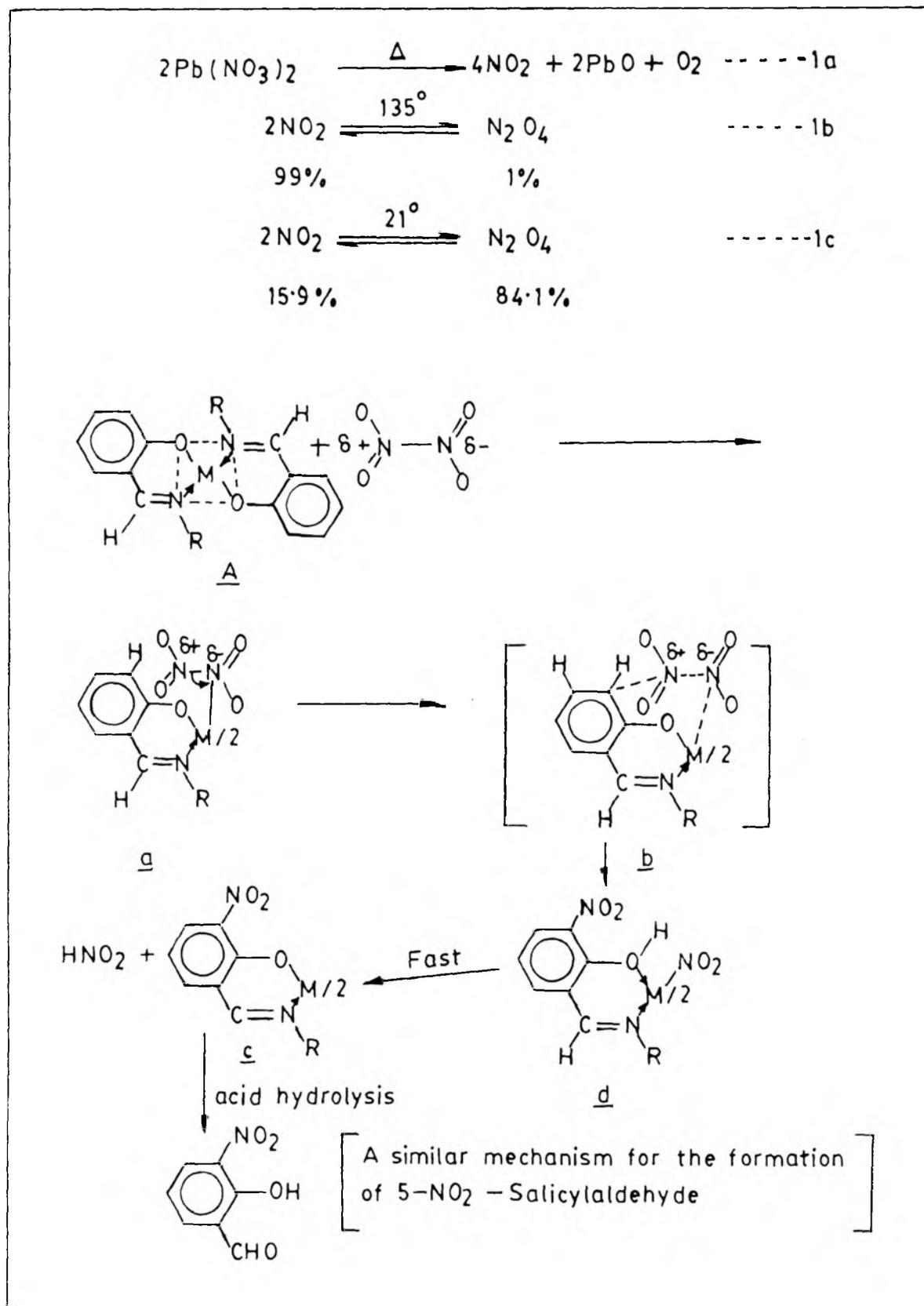


Fig. 1 :Mechanism of nitration reaction of salicylaldehyde metal complex by dinitrogen tetroxide.

final reaction product, the product obtained in the first stage of nitration reaction would react with a second mole of  $N_2O_4$  before acid hydrolysis. The reaction of the second mole of  $N_2O_4$  might involve a ligand not containing  $NO_2$  group or a ligand in which  $NO_2$  was substituted at 3 or 5 position. The first reaction would afford mono-substituted ligands, while the second reaction would afford 3,5-dinitrosubstituted ligand.

We separated a complex containing 3,5-dinitro-salicylaldehyde (B), and a complex containing 3-nitrosalicylaldehyde and 5-nitrosalicylaldehyde could not be obtained. This observation suggested that the metal-ligand bond in a complex containing mononitrosalicylaldehyde was more acid labile than that in a complex containing 3,5-dinitrosalicylaldehyde.

The nitration reaction of bis(salicylaldehydato) copper (II) (C) with  $N_2O_4$  using the experimental conditions similar to those used for nitration of complex A, afforded 3-nitrosalicylaldehyde and 3,5-dinitrosalicylaldehyde in the molar ratio 2:1 from benzene extract. It should be noted here that a nitration reaction of complex A, afforded 3-nitrosalicylaldehyde and 5-nitrosalicylaldehyde in the molar ratio 2:1, and 3,5-dinitrosalicylaldehyde was obtained as a nickel (II) complex. The copper (II) complex obtained from

the nitration reaction was found to have the formula (D) similar to that for nickel (II) complex (B). In this reaction 5-nitrosalicylaldehyde was not obtained.

The effective quantitative aspects of these nitration reactions were as follows :

- (i) With complex A, 3-nitrosalicylaldehyde, 45 %; 5-nitrosalicylaldehyde, 25 %; 3,5-dinitrosalicylaldehyde, 15 %.
- (ii) With complex C, 3-nitrosalicylaldehyde, 58 %; 3,5-dinitrosalicylaldehyde, 28 %; (5-NO<sub>2</sub> salicylaldehyde was not obtained).
- (iii) The nitration of salicylaldehydato complex using N<sub>2</sub>O<sub>4</sub> afforded the formation of 3,5-dinitrosalicylaldehyde.

These observations suggested that during the nitration of complex A using N<sub>2</sub>O<sub>4</sub>, the substitution of NO<sub>2</sub> group could take place independently at 3 or 5 position; the nitration of complex C, using similar experimental conditions the substitution first took place at position 3 followed by the substitution at position 5. If the geometries of complex A and C were very similar, the polarizing effects of metal ion on ligand would be of similar nature, and there would be no appreciable variations in the reaction products. The observed results suggested that the expected difference in

the geometries of nickel (II) and copper (II) complexes played an important role in controlling the relative yields of nitro-salicylaldehydes.

These interesting results regarding the role of metal ion in the electrophilic substitution reaction of coordinated aromatic ligand prompted us to carry out the nitration reaction using other related coordinated aromatic ligands.

The nitration of bis(2-hydroxyacetophenonato) metal (II) [metal (II) = Ni(II), Cu(II)] yielded 2-hydroxy-5-nitroacetophenone; and 2-hydroxy-3,5-dinitroacetophenone; 2-hydroxy-3-nitroacetophenone was not obtained. The mole ratio of the nitro derivatives with the change of metal ion was as follows :

Metal complex	2-hydroxy-5-nitroacetophenone	2-hydroxy-3,5-dinitroacetophenone
Ni(II)	1.5	1.0
Cu(II)	1.0	1.5

Thus the direct formation of 2-hydroxy-3,5-dinitroacetophenone was possible using a metal complex for nitration and the yield of 2-hydroxy-3,5-dinitroacetophenone was higher using Cu(II) complex. This observation was similar to that obtained with bis-salicylaldehydato metal (II) complexes.

The metal containing compound separated from these reactions was found to be a mixture of different complexes from the elemental analysis. The  $^1\text{H}$  n.m.r. spectrum was determined of the organic compound separated from the complex mixture by treating with HCl. It indicated that the organic compound was a mixture of 2-hydroxy-5-nitroacetophenone, 2-hydroxy-3,5-dinitroacetophenone and unsubstituted 2-hydroxyacetophenone.

Since 2-hydroxy-3-nitroacetophenone was not obtained as a coordinated ligand or as a free organic compound the nitration of the coordinated ligand took place first at 5-position and then at 3-position.

To analyse further the role of the coordinating site on a nitration reaction of the neighbouring aromatic ring, a ligand containing an aromatic ring away from the coordinating site, 2'-hydroxy chalcone, was used. The experimental observations were as follows : (i) The organic ligand separated from these reactions was characterised as 2'-hydroxy-3',5'-dinitrochalcone. (ii) The nitration took place in an aromatic ring close to the coordinating centres; the other aromatic ring remained unsubstituted. (iii) The complex (I) separated from the nitration reactions of complex H contained one molecule of coordinated 2'-hydroxy-3',5'-dinitrochalcone and one coordinated  $\text{NO}_2$  group.

These observations clearly showed that the coordinated metal ion decided the site of the  $\text{NO}_2$  substitution.

The complexes used in the above experiments contained metal ions coordinated through oxygen of the ligand. The nucleophilicity of the coordinated ligand could be modified by changing the coordinated centres. The change in the nature of coordinating centre would have a direct influence on the polarisation of aromatic ring; the polarisation through metal atom would have also a different contribution when the nature of the coordination site was changed. The coordination site might be changed from oxygen to nitrogen by using the imines of salicylaldehyde and 2-hydroxy-acetophenone.

In a nitration reaction of bis(N-n-butylsalim)metal (II) [ metal (II) = Ni(II), Cu(II) ] using  $\text{N}_2\text{O}_4$  a complex containing substituted imine could not be separated indicating the acid labile nature of the imine complexes. Here we assumed that the mechanism of nitration reaction was similar to that of the salicylaldehydato complexes given in Fig. 1 according to which  $\text{HNO}_2$  was a side product during the reaction. It was also observed that the organic compound separated from the nitration reaction was the substituted salicylaldehyde and not the substituted imine. These observations suggested that the acid formed in the reaction hydrolysed the imine  $>\text{C}=\text{N}$ -bond. With the complex J [ M(II) = Ni(II) ] the organic product was shown

to be a mixture of 3-nitrosalicylaldehyde and 5-nitrosalicylaldehyde in the mole ratio 1:1.5, while with the complex K [ M(II) = Cu(II) ], the organic product was shown to be a mixture of 5-nitrosalicylaldehyde and 3,5-dinitrosalicylaldehyde in the mole ratio 1:2. The yields were practically quantitative. The comparison of these results with those obtained from the nitration of the salicylaldehyde complexes gave the following observations : (i) The nickel (II) complex A the yield of 3-nitrosalicylaldehyde was higher than that of 5-nitrosalicylaldehyde. With complex J, the yield of 5-nitrosalicylaldehyde was higher than that of 3-nitrosalicylaldehyde. (ii) With the copper (II) complex C, 5-nitrosalicylaldehyde was not obtained. With complex K, 3-nitrosalicylaldehyde was not obtained. With complex C, the yield of 3-nitrosalicylaldehyde was higher than that of 3,5-dinitrosalicylaldehyde; with complex K, the yield of 3,5-dinitrosalicylaldehyde was higher than that of 5-nitrosalicylaldehyde. (iii) The observation (ii) suggested that with complex C, the nitro group first entered at 3- and then at 5-position, while with complex K the nitro group entered first at 5-position and then at 3-position, (iv) For the synthesis of 3,5-dinitrosalicylaldehyde in good yield complex K was a suitable starting material; for the synthesis of 5-nitrosalicylaldehyde, the complex J was a suitable starting material; and for the

synthesis of 3-nitro-salicylaldehyde in good yield, the complex A, was a suitable starting material.

A nitration reaction of the complexes of bis(2-hydroxy-acetophenone N-n-butyliminato with nickel (II), L, gave different results. From the benzene washings of reaction mixture, 2-hydroxy-5-nitroacetophenone g and 2-hydroxy-3,5-dinitroacetophenone (h) were separated. The chloroform soluble product was characterised as the complex M. Both the chelated ligands contained  $\text{NO}_2$  group at position 3 and 5. The decomposition of complex M with HCl afforded 2-hydroxy-3,5-dinitroacetophenone. The chloroform insoluble product was characterised as complex N. Its infrared spectrum displayed a strong and broad band at  $3375 \text{ cm}^{-1}$  associated with  $\nu_{\text{OH}}$ ; the bands due to  $\nu_{\text{NO}_2}$  associated with  $\text{M-NO}_2$  were observed at  $1280 \text{ cm}^{-1}$  and  $1340 \text{ cm}^{-1}$ . The  $^1\text{H}$  n.m.r. spectrum of the organic compound separated from the complex N on treatment with HCl, indicated that the coordinated ligand in the complex N was 2-hydroxy-3,5-dinitroacetophenone imine. Thus the elemental analysis and infrared spectrum of the complex and  $^1\text{H}$  n.m.r. spectrum of the separated ligand suggested that it was the nickel-nitrite adduct with the imine of 2-hydroxy-3,5-dinitroacetophenone. The separation of complex N suggested that the intermediate of the type b, shown in Fig. 1, rearranged to d, instead of the complex of the type C.

From a similar nitration reaction of copper (II) complex 0, only organic compound was separated; no metal complex could be separated in pure form. The organic product was characterised as 2-hydroxy-5-nitroacetophenone and 2-hydroxy-3,5-dinitroacetophenone. The organic compound obtained from the treatment of complexes of 2-hydroxyacetophenone and its n-butylamine were the same.

### 5. References :

1. Jones, M.M., Adv. Chem. Ser. 37, 116 (1963).
2. McNutt, R.C. and M.M. Jones, J. Inorg. Nucl. Chem., 29, 1415 (1967).
3. Chawla, N.K. and M.M. Jones, Inorg. Chem., 3, 1549 (1964)
4. Rukhadze, E.G., G.P. Talyzenkova and A.P. Terent'ev, Zh. Coshch. Khim., 39, 401 (1969); J. Gen. Chem., 39 378 (1969).
5. Kawathekar, C.J., 'Chemical Reactions of Metal Complexes', Ph.D. Thesis, Univ. of Poona, India (1980).
6. Djordjević, C., J. Lewis and R.S. Nyholm, Chem. Ind. London, 122 (1959).
7. Djordjević, C., J. Lewis and R.S. Nyholm, J. Chem. Soc., 4778 (1962).
8. Collman, J.P., Angew. Chem. Intern. Ed., 4, 132 (1965).
9. Bhasin, S.K., P. Umapathy and D.N. Sen., J. Indian Chem. Soc., 49, 1113 (1972).
10. Collman, J.P., R.I. Marshall, W.L., Young (III) and S.D. Goldby, Inorg. Chem., 1, 704 (1962).
11. Patil, J.N., and D.N. Sen, Indian J. Chem., 12, 189 (1974).
12. Thankarajan, N. and D.N. Sen, Indian J. Chem., 2, 64 (1964).
13. Clifford C. Hach, Lawrence M. Liggett, and Harvey Diehl. Ibid. C.A. 42, 1240 (1948).
14. Luigi Sacconi, Piero Paoletti and Giuseppe Del Re. J. Amer. Chem. Soc., 79, 4P62 (1957).

15. Biradar, N.S., *Inorg. Chem. acta* 15, 33-38 (1975).
16. Weissberger, A. and E.S. Proskauor, ed., 'Technique of Organic Chemistry, Vol.III - Organic Solvents' (Interscience Publishers, London). (1955).
17. Collman, J.P., *Angew. Chem., Intern. Eds*, 4 132 (1965).
18. Bhasin, S.K., P. Umapathy and D.N.Sen., *Indian J. Chem.*, 8, 645 (1970).
19. Singh, P.P., R. Sahai and I.J. Sharma, *J.Indian. Chem. Soc.*, 49, 211 (1972).
20. Thaker, B.T. and P.K. Bhattacharya, *Bull. Chem. Soc., Japan*, 49, 211 (1972).
21. Bordwell, F.C. and E.W. Garbisch, Jr., *J.Amer.Chem.Soc.*, 82, 3588 (1960).
22. Fischer, A., A.J. Read and J. Vaughan, *J.Chem. Soc.*, 3691 (1964).
23. Bodor, N. and M.J.S. Dewar, *Tetrahedron*, 25, 5777 (1969).
24. Djordjevic, C., J. Lewis and R.S. Nyholm (a) *Chem. Ind. London*, 122 (1959); (b) *J. Chem. Soc.*, 4778 (1962).