● CHAPTER-I ●

CHAPTER I

RESUME OF THE CHEMISTRY OF COORDINATED AROMATIC LIGANDS

1. Introduction

The formation of a metal complex involves the mutual polarization of the highest occupied and the lowest unoccupied group orbitals on the ligand and valence orbitals on metal. It is therefore obvious that the chemical reactivity of ligands is modified on complexation. The steric factors of a chemical reaction are also expected to be modified on complexation. In addition, when the reactant participates in coordination with a metal ion there is an increase in the local concentration of reactant, thus favouring the chemical reaction between the coordinated ligand and the reactant. An increasing interest in the field of chemistry of coordinated ligands especially during the last twenty years has helped to solve the mechanistic aspects of quite a few homogeneous catalytic reactions[1], and has created an impetus in the problems related to bioinorganic chemistry.[2,3] When an aromatic ring is one of the groups attached to the metalloheterocyclic ring, there is a general impression that the polarization of an aromatic ring by the metal ion has no spectacular effect on the chemical reactivity of the

aromatic ring except that there is some influence on the rate of reaction[4-6]. It is, however, necessary to compile the literature which will help to analyse the present status of our knowledge about the extent of the influence of metal ion on the reactivity of such aromatic ring. This chapter appropriately gives a brief summary of this problem.

The metalloheterocyclic ring in $M(ptdn)_n$ is supposed to be pseudoaromatic. These complexes are acid labile. The new agents used in the electrophilic substitution reactions of $M(ptdn)_n$ may be of use in the corresponding reactions of other coordinated aromatic ligands. The detailed analysis of reactivity of coordinated ligand in $M(ptdn)_n$ will be of guidance in analysing other systems.

The reactions of metal complexes in which the metalloheterocyclic ring retains its integrity can be classified into three categories : (a) addition to the central metal ion, (b) reaction at the functional groups and reactive sites pendent to the chelate ring, and (c) substitution of hydrogen or other groups attached to the coordinated ligand. The chemical reactions pertaining to the third category are considered in this chapter.

2. Halogenation reaction

Liquid Br_2 is found to be the best brominating agent

for brominating organic compounds with aromatic character[7].
In analogy, the metal complexes with the characteristic
aromaticity would also be successfully brominated by liquid
Br_2.

Bromination of $Cr(An)_3Cl_3$ using liquid Br_2 in glacial
acetic acid[8] has indicated that the electrophilic substitution
position on the coordinated ligand towards the electrophilic
agents is similar with that on the parent ligand. Similar
observation has been reported for the chlorination reaction
which has been carried by bubbling Cl_2gas through the solution
of $Cr(py)_3Cl_3$ in chloroform or nitrobenzene. The retention
of the electrophilic substitution position on the ligands
upon coordination is explained qualitatively on the basis of
Pauling's principle of electroneutrality[9]. Similar reactions[10]
are extended to $M(oxine)_n$ [M $= Cr(III)$, $Fe(III)$, $Co(III)$,
$Cu(II)$, Al^{3+}] yielding $M(5,7\text{-dihalo, oxine})_n$, Fig. 1.

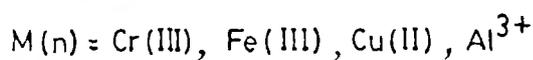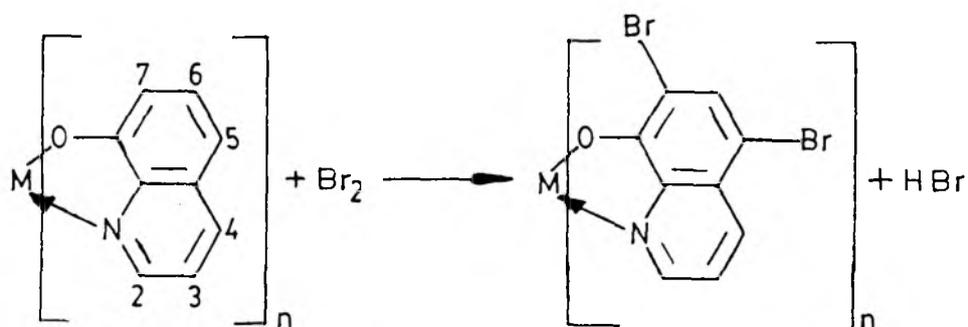$M(n) = Cr(III)$, $Fe(III)$, $Cu(II)$, Al^{3+}

Fig. 1

In the parent ligand[11], the 5- and the 7-positions are susceptible to the electrophilic substitution reactions with the 5-position being somewhat more reactive than the 7-position. Upon coordination, the approach of the incoming electrophilic substituents is retained indicating that the presence of metal ion does not affect the reactive sites. There are reports[12] on the effect of metal ion on the percentage yield of the halogenation products of $M(oxine)_n$. However, these results are to be analysed with caution as the two sets of reactions have been carried out in different solvents.

Liquid Br_2 has been used to brominate $M(ptdn)_3$ [$M(III) = Cr(III)$, $Co(III)$] yielding $M(3\text{-Br}, ptdn)_3$[13]. With a very large excess of liquid Br_2 the participation of the Me group in bromination has been reported[14]. In dioxane the liquid Br_2 has been reported[15] to brominate $Cu(N\text{-n-Butsalim})_2$ yielding $Cu(3,5\text{-Br}_2, N\text{-n-Butsalim})_2$. Thus for the complexes which are stable under the acidic conditions, liquid Br_2 is found to be the best brominating agent. However, it decomposes the acid-labile complexes such as $Cr(Ph,btdn)_3$ and $Cr(Ph_2, prdn)_3$[13]. The more basic brominating agents such as dioxane-Br_2 and py-perbromide also decompose these complexes due to the released HBr.

NBS in chloroform is found to be a suitable brominating agent for the acid labile complexes[16-19]. The

chlorination and iodination of $M(ptdn)_n$ are affected by
using NCS and NIS (or ICI) respectively. The rate of
halogenation by these halogenating agents decreases in the
following order :

$$NBS > NCS > NIS$$

Trisubstituted haloderivative of $M(ptdn)_3$ is formed when an
excess of halogeno succinimide is used; otherwise a mixture
of mono, di and trisubstituted complexes is formed, Fig. 2.
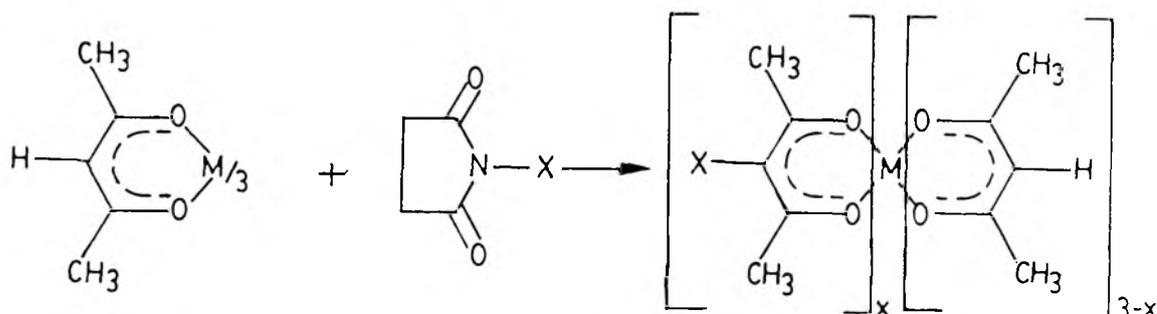
X = Cl , Br or I

x = 3 when excess NXS is used

x = 1 or 2 when less NXS is used

Fig. 2

Similar halogenation reactions of various β-dicarbonyl metal
complexes have been reported[20-31].

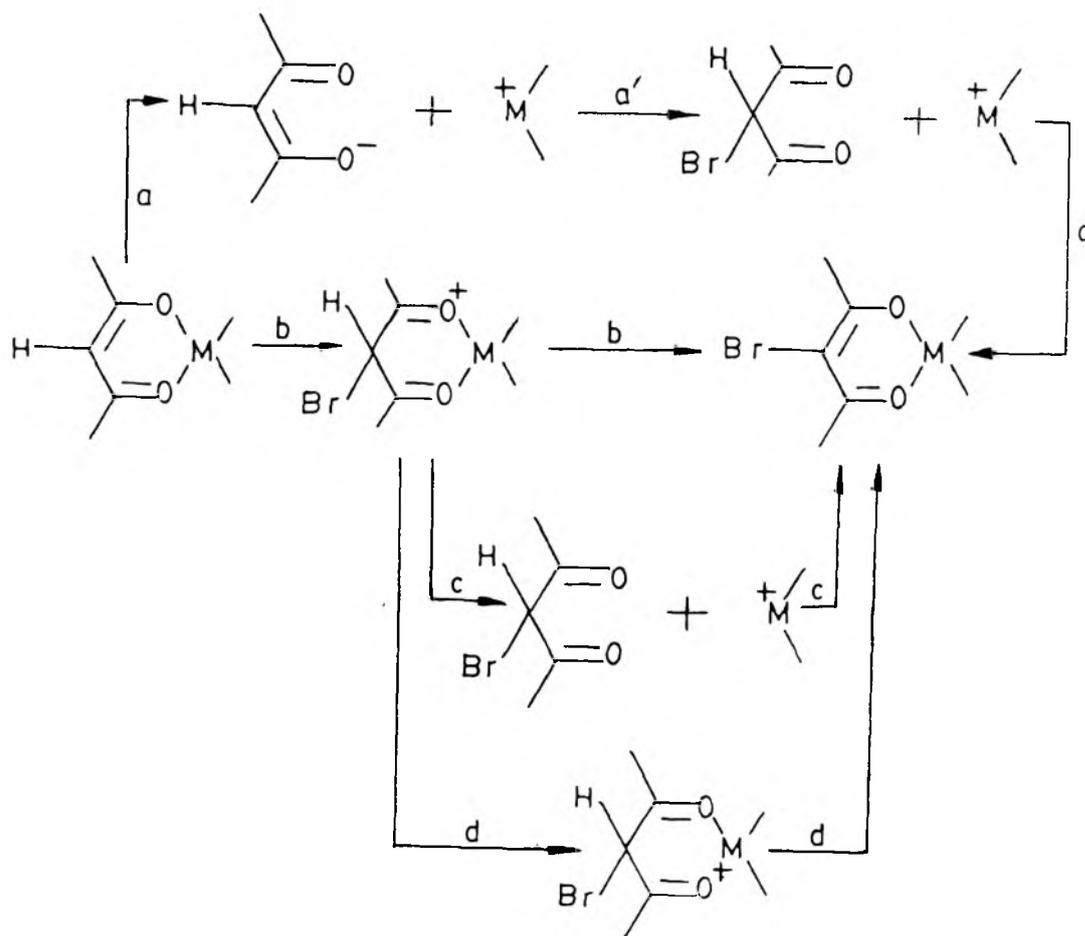Several possible routes have been suggested[32] for the reaction of $M(ptdn)_n$ with NBS, Fig. 3. The equivalent

Fig. 3

amounts of ^{14}C labelled ptdn and $Cr(ptdn)_3$ have been treated with a sufficient amount of NBS to monobrominate both the compounds. The extent of ^{14}C exchange is found to be equal to the exchange that would have occurred in the absence of the brominating agent. This observation suggests that the

bromination of $Cr(ptdn)_3$ takes place without ring cleavage.

The study[33] dealing with the use of various brominating agents and solvents to emphasise their effect on the percentage yield of $M(3\text{-Br, ptdn})_n$ indicates that methanol is the most ideal solvent for such electrophilic substitution reactions. The high dielectric constant of the medium readily produces the electrophile. However, a change of the halogenating agent such as NBS/Br_2 or NCS/Cl_2 does not show any appreciable effect on the yield of halogeno derivative of an acid-stable-complex.

The effect of steric hinderance on the chemical reactions has been demonstrated[34] by a halogenation reaction of $M(Ph, btdn)_n$ and $M(Ph_2, prdn)_n$. The reactive site in these complexes is the same as that in $M(ptdn)_n$. A lowering in yield of the halogenated product and an increase in the reaction time have been observed. These observations are contradictory to the prediction based on the mesomeric effect of the Ph group[35]. Possibly the steric factors experienced by the reaction centre due to the Ph group which tends to be coplanar with the chelate ring may be responsible for the experimental observations. This view has been supported by the observation that the reaction rate of the substitution by the larger iodonium ion is much slower as compared to that by the bromonium or chloronium ion. The Ph group in these ligand

systems is deactivated towards the electrophilic reactions
due to its predominantly electron releasing resonance effect
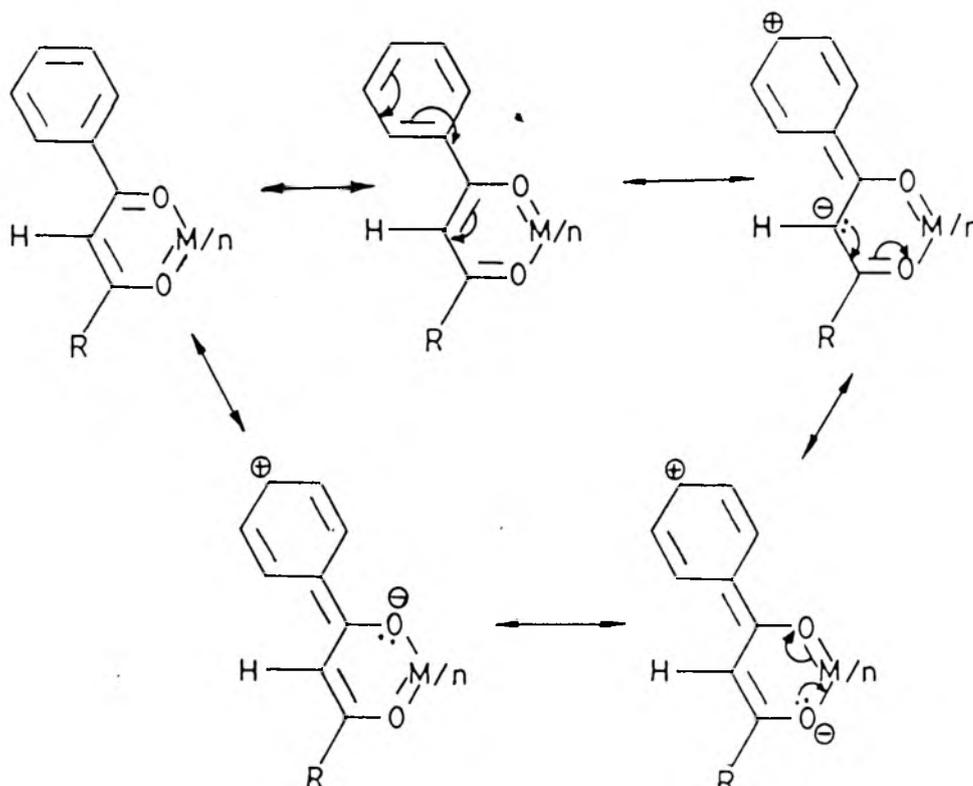in this system, Fig. 4.

Fig. 4

Halogenation reactions have been tried on other acid
labile complexes in order to analyse the role of metal ion
in these reactions. The bromination reaction of $M(sal)_2$,
Fig. 5 [M(II) = Co(II), Ni(II), Cu(II)]   in chloroform

using NBS yields a mixture of $M(5-Br,sal)_2$ and $M(3,5-Br_2,sal)_2$[36].
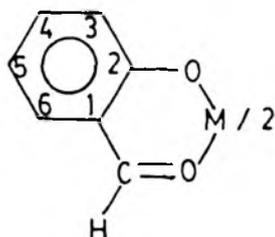

Fig. 5

The acid hydrolysis of the product obtained from the bromina-
tion on reaction of $Cu(sal)_2$ affords a mixture of 5-Br, sal
(60 %) and 3,5-Br, sal (40 %). The corresponding reaction
product of $M(sal)_2$ [M(II) = Co(II), Ni(II)] gives mainly
$3,5-Br_2$, sal upon acid hydrolysis. A change of the reaction
medium from chloroform to DMF gives the quantitative yield
of $M(3,5-Br_2,$ sal$)_2$[37] [M(II) = Co(II), Ni(II), Cu(II)].
The iodination reaction of $M(sal)_2$ [M(II) = Co(II),Cu(II)]
with ICl in DMF results in the degradation of the complex
yielding $3,5-I_2$, sal. The chlorination reaction of
$M(sal)_2$ [M(II) = Co(II), Cu(II)] using NCS in DMF gives a
product which could not be characterised. The bromination
and iodination reactions of $Cu(3-OCH_3,$ sal$)_2$ using NBS and NIS
give $Cu(3-OCH_3, 5-X,$ sal$)_2$[38] (5-X = Br, I respectively).

The first successful bromination reaction[32] of
N-Rsalim metal complexes has been carried out by treating
Ni(N-n-Butsalim)$_2$ with NBS in chloroform. The possibility
of bromination at the azomethine carbon has been suggested[39]
without giving any experimental evidence. However, the
current information[40] indicates that when the metal complex
and the ligand are taken in the mole ratio ca. 1:2,
Ni(5-Br,N-n-Butsalim)$_2$ is formed. The position of the
electrophilic attack on the coordinated ligand is in agreement
with the reactivity of sal[41-43]. When the mole ratio is 1:4,
Ni(3,5-Br$_2$, N-n-Butsalim)$_2$ is formed. These reactions have
been extended to the bromination of the kinetically inert
complex, Co(N-Mesalim)$_3$; in these reactions either
Co(5-Br, N-Mesalim)$_3$ or Co(3,5-Br$_2$, N-Mesalim)$_3$, is formed
depending on the mole ratio of the reactants. Cu(N-n-Butsalim)$_2$
has been brominated using different brominating agents[15].
NBS gives 45 % yield of Cu(5-Br, N-n-Butsalim)$_2$. Thus, in
these complexes with a characteristic aromaticity, it has
been shown that the reactive site for the incoming substituent
is unchanged upon coordination, substantiating the results
obtained on other complexes.

The halogenation reaction of mixed complex, Co(bean)
(ptdn) has indicated that the ring protons of the imine
complex are more reactive than the 3-carbon of ptdn[44].

The use of metal halide such as $CuBr_2$ for the halogenation reaction of ketones and reactive aromatics has encouraged its use in the halogenation reaction of metal complexes such as $Cu(oxine)_2$, $M(ptdn)_n$ and $Cu(sal)_2$[45]. The halogenated $Cu(oxine)_2$ upon acid hydrolysis yields $5,7-Br_2$, oxine and some monobrominated material. The bromination reaction of $M(ptdn)_n$ [M = Cr(III), Co(III) Cu(II)] yields $M(3-Br,ptdn)_n$, and that of $Cu(sal)_2$ yields 5-Br, sal upon acid hydrolysis.

CNBr has been reported[46] to brominate $Cr(ptdn)_3$ in chloroform. The completion of the reaction requires 24 h, and the product is 1:1 chloroform adduct with $Cr(3-Br,ptdn)_3$. This reaction is enhanced by an addition of a catalyst; with $BF_3 \cdot OEt_2$ the reaction completes within 45 min.

3. Nitration reaction

Invariably all organic compounds are nitrated successfully by the nitration mixture $(H_2SO_4 + HNO_3)$[7] and it is expected that the complexes with aromatic character could be analogously nitrated. However, the systems such as $Cr(py)_3Cl_3$ decomposes with the nitration mixture presumably due to its labile nature towards H_2SO_4[8]. The nitration reaction using the mixture of $HNO_3 + BF_3$ gives the nitrated products. Analysis of the nitrated products indicates that

the reactive site on the ligand upon coordination remains unchanged. The nitration of $Cu(oxine)_2^{12}$ using nitric acid yields $5,7-(NO_2)_2$, oxine confirming the unchanged reactive site on the ligand upon coordination. The complex being acid labile, the ligand has been separated.

N_2O_4 has been used for nitrating the acid labile complexes[47,48]. The reaction of $M(ptdn)_2$ [M(II) = Ni(II), Cu(II), Pd(II), Pt(II)] with N_2O_4 in benzene gives a good yield of $M(3-NO_2,ptdn)_2$; $Pd(3-NO_2, ptdn)_2$ could not be separated due to the side reaction products. However, a similar reaction of $Cr(ptdn)_3$ gives a poor yield of nitrogen containing compound which could not be characterised[49].

A mixture of $Cu(NO_3)_2 \cdot 3H_2O$ and acetic anhydride proves to be a successful nitrating agent for organic compounds[50]. In analogy, it has been used to nitrate the acid labile complexes[16,27,51,52]. The simultaneous metal transfer and nitration reactions have also been observed[53] when ptdn metal complexes of beryllium (II), oxovanadium (IV), manganese (III), iron (III), cobalt (II), palladium (II), zirconium (IV), thorium (IV),zinc (II), aluminium (III) have been treated with $Cu(NO_3)_2 \cdot 3H_2O$ in acetic anhydride yielding a common product $Cu(3-NO_2, ptdn)_2$. The suggested mechanism of this reaction is summarised in Fig. 6.

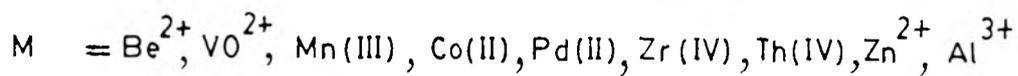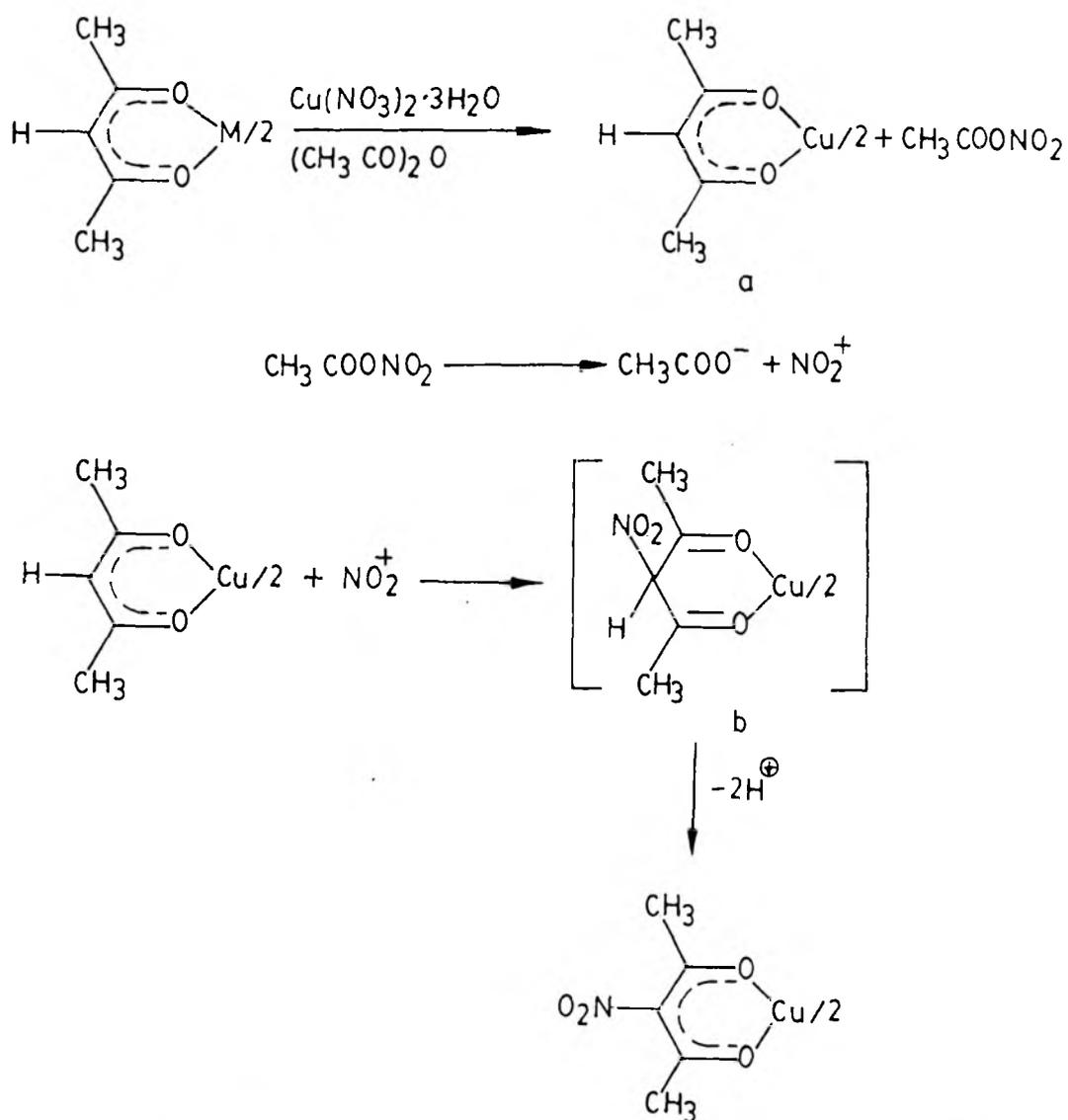M $= Be^{2+}, VO^{2+}$, Mn(III), Co(II), Pd(II), Zr(IV), Th(IV), Zn^{2+}, Al^{3+}

Fig. 6

The reaction of $Co(NO_3)_2 \cdot 6H_2O$ with ptdn in acetic anhydride gives $Co(3-NO_2 \cdot ptdn)_3$. Thus, both the nitration of the ligand and oxidation of the metal ion are involved in this reaction. The latter observation supports the earlier

report[54] that NO_3^- ion is capable of oxidising cobalt (II) to cobalt (III). Similarly, $Ni(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Be(NO_3)_2 \cdot 3H_2O$ have been-used[53-55] as nitrating agents yielding $Ni(3-NO_2, ptdn)_2$, $Fe(3-NO_2, Ptdn)_3$ and $Be(3-NO_2 \cdot ptdn)_2$ respectively upon their reaction with ptdn in acetic anhydride. It is interesting to note that anhydrous $Cu(NO_3)_2$ failed as a nitrating agent[56]. In unhydrous copper (II) nitrate the metal-nitrate bond is predominantly covalent. Anhydrous copper (II) nitrate is therefore unable to produce nitronium ions required for a nitration reaction.

Another nitrating agent, which has gained its importance because of its wide applicablity for nitrating $M(ptdn)_n$ [$M = Be^{2+}$, Cr(III), Cu(II), Al^{3+}] is $Al(NO_3)_3 \cdot 9H_2O$[53-55]. However, a simultaneous metal transfer and nitration reaction has been observed for $M = Mn(III)$, Fe(III), Co(II) yielding a common product $Al(3-NO_2, ptdn)_3$. Among the other nitrating agents $NaNO_3$, $Mg(NO_3)_2 \cdot 2H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$ are found to be unsuccessful. A decrease in yield and an increase in the reaction time of the nitration reaction of $M(Ph, btdn)_n$ and $M(Ph_2, prdn)_n$[56,57] suggests the important role of steric factors.

Apart from the usual methods of nitration that gained importance with the years, an interesting pathway such as the displacement of groups other than hydrogen under the

apparently electrophilic conditions, has been used[16] for

the introduction of $-NO_2$ group into the ptdn ring, Fig. 7.

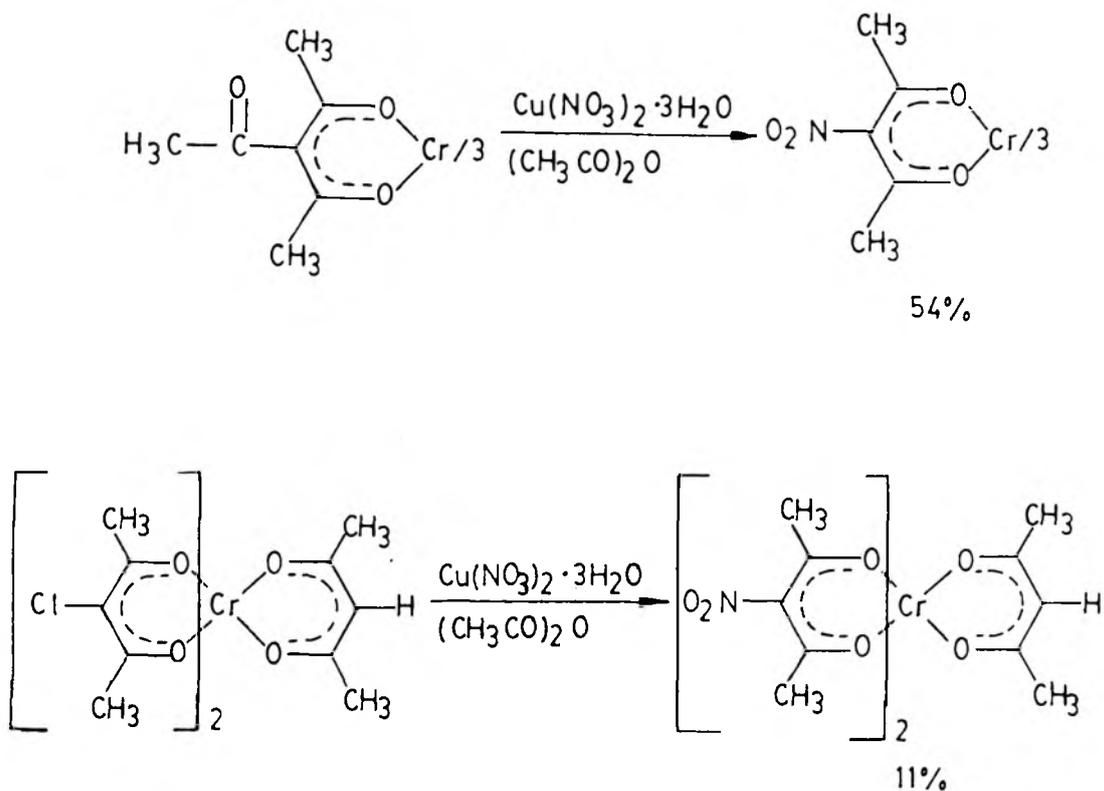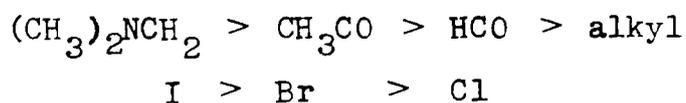Fig. 7

The selectivity of the substituents as leaving groups seems

to be parallel with their stability as carbonium or halonium

ions :

$$(CH_3)_2NCH_2 \; > \; CH_3CO \; > \; HCO \; > \; alkyl$$
$$I \; > \; Br \; > \; Cl$$

M(3-NO$_2$, ptdn)$_n$ could only be obtained by the above mentioned indirect routes since the parent ligand, 3-NO$_2$,ptdn is not yet known. A separation of 3-NO$_2$, ptdn from M(3-NO$_2$, ptdn)$_n$ leads to intractable oil.

M(sal)$_2$ has been nitrated using Cu(NO$_3$)$_2$·3H$_2$O in acetic anhydride as a nitrating agent[36]. The ligand isolation from the complex obtained in this reaction affords a mixture of 3-NO$_2$, sal (40 %) and 5-NO$_2$, sal (60 %). The formation of 3,5,3',5'-(NO$_2$)$_4$ substituted complex has also been reported[37]. Nitration of M(3-OCH$_3$, sal)$_2$[32] [M(II) = Co(II), Ni(II),Cu(II)] with their respective nitrates yields M(3-OCH$_3$, 5-NO$_2$,sal)$_2$·xH$_2$O [M(II) = Co(II), x = 1; Ni(II), x = 2, Cu(II), x = 1)] .

A mechanism similar to that suggested for the apparently electrophilic substitution reaction (such as halogenation reaction) of M(ptdn)$_n$ involving a resonance stabilised 6-complex intermediate has been put forth. The nitration reaction has also suggested that a reactive site on the ligand for the electrophilic substitution remains unchanged upon coordination. Thus, the coordinated metal ion exhibits no effect on the approach of the incoming substituent.

The nitration of M N,N'en(salim)$_2$, Fig. 8, [M(II) = Ni(II), Cu(II)] using nitric oxide as a nitrating agent in the presence of air yields M [N,N'-en(5-NO$_2$,salim)$_2$][58].

Under the identical experimental conditions the parent ligand
fails to give an substituted aromatic product, but instead
results in a nitric acid-adduct of the ligand. Thus, here is
an unique example of the changed reactivity of the parent
ligand upon coordination. The coordination of the parent ligand
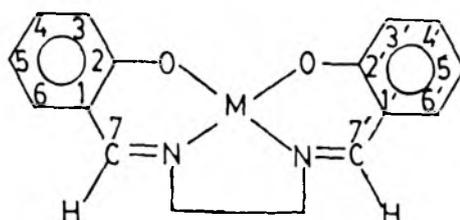
Fig. 8

with the metal ion has made the aromatic ring susceptible to
the incoming substituent under the nitration conditions.
Co-NO[N,N'en (salim)$_2$] fails to react with nitric oxide under
the identical experimental conditions. This behaviour has
been explained on the basis of the relative stability constants
of the metal complexes. The complexes Cu(hapim)$_2$ and
Cu [N,N'en(salim)$_2$] have been nitrated[59] by CH$_3$COONO$_2$
formed in situ by the reaction of Cu(NO$_3$)$_2$°3H$_2$O with acetic
anhydride.

4. Thiocyanation reaction

The reaction of $Cu(oxine)_2$ with $(SCN)_2$ in carbon tetrachloride affords a sticky mass[12]. An acid hydrolysis of this product with HCl (ca~ 10 N) followed by a treatment with H_2S yields a mixture of 5-SCN, oxine (70 %) and 5,7-$(SCN)_2$, oxine (30 %). This reaction gives an additional evidence to the observations made for other electrophilic substitution reactions that the orientation of the electrophilic substituent on the parent ligand remains unchanged upon coordination.

Thiocyanation reaction has been thoroughly investigated for the ptdn metal complexes[46,60,61]. Two alternate methods for the introduction of -SCN group in $M(ptdn)_3$ [M(III) = Mn(III), Cr(III), Co(III), Rh(III), Al^{3+}] are put forth : (a) a reaction with a mixture of KSCN and liquid Br_2(1:1 v/v). This method is similar to the method used for the thiocyanation reaction of indole[62]. The thiocyanation reaction of $Be(ptdn)_2$, however, yields metal-free 3-SCN,ptdn probably due to the acid degradation of the complex (b) a reaction of Cr(3-SCl, ptdn) (3-Cl, ptdn)$_2$ with KCN. This reaction yields Cr(3-SCN, ptdn)(3-Cl, ptdn)$_2$. For acid labile complexes, such as $Cu(ptdn)_2$, the reaction mixture is treated with an excess of solid $NaHCO_3$ to avoid a cleavage of the ligand in the presence of the liberated acid.

A cleavage of the substituents other than hydrogen at 3-C on the ptdn rings by -SCN group has also been used[16] for synthesising the thiocyanato derivatives, Fig. 9.
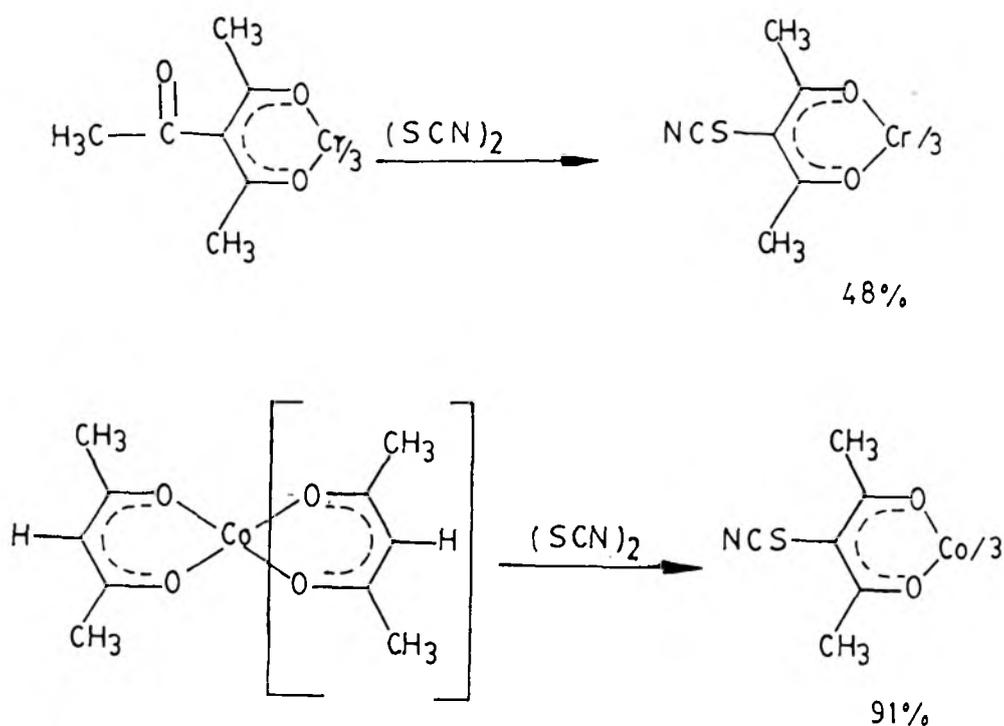
Fig. 9

However, the thiocyanation reaction of Co(3-Cl, ptdn)(ptdn)$_2$ yields Co(3-Cl, ptdn)(3-SCN, ptdn)$_2$ and not Co(3-SCN, ptdn)$_3$.

The reaction path of the thiocyanation reaction is similar to that of the halogenation reaction of aromatic compounds affected by molecular halogens[6], Fig. 10.
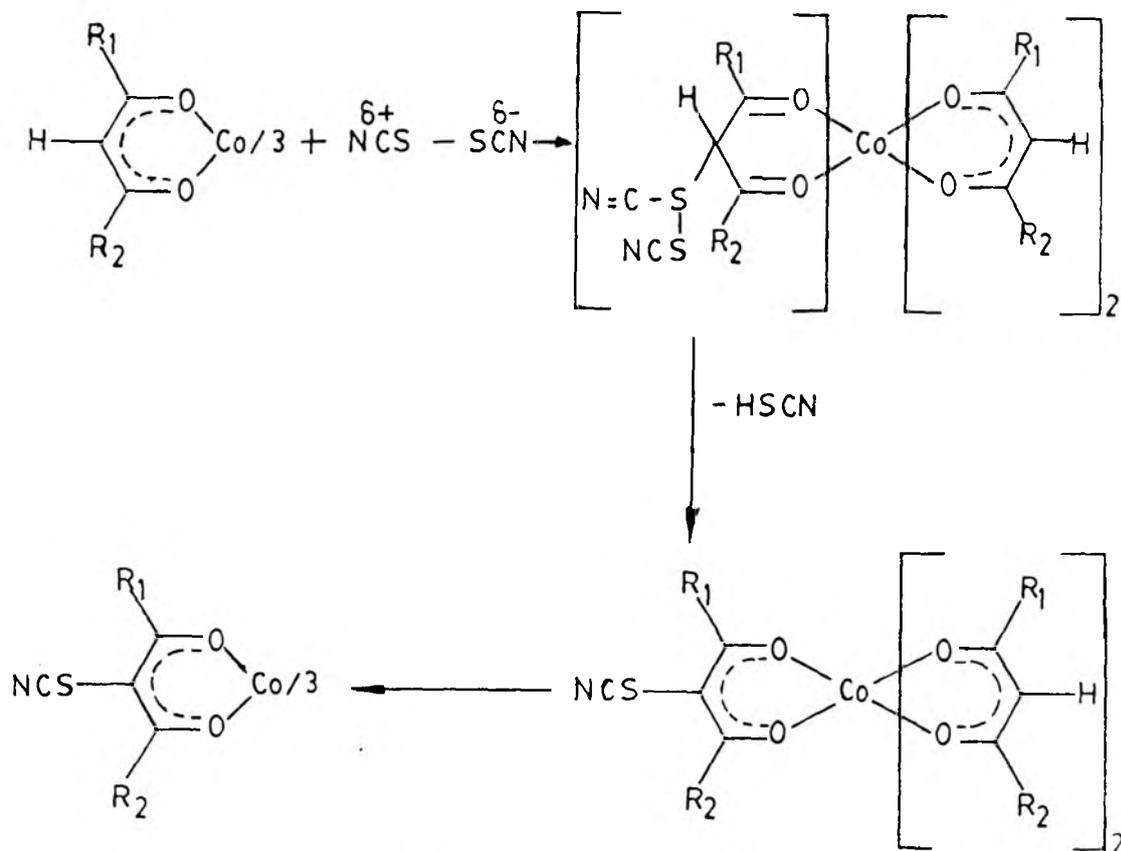
Fig. 10

It has been suggested[63] that the use of polar solvents or Friedel-Crafts catalysis may enhance this substitution reaction similar to other halogenation reactions. The effect of the replacement of Me group by Ph group of the ptdn ring on the thiocyanation reaction is similar to that observed for the bromination and the nitration reactions.

There is no positive report on the thiocyanation reaction of $M(sal)_n$ or its corresponding parent ligand and $M(N-Rsalim)_n$ or its corresponding parent ligand.

5. Acylation reaction

It has been reported that the reaction of Cu(oxine)$_2$[12] with AlCl$_3$+ CH$_3$COCl at 0° - 5° in dry nitrobenzene followed by a treatment with HCl and H$_2$S separates the parent ligand. Thus, the acylation reaction fails under these conditions.

Cr(ptdn)$_3$ and Co(ptdn)$_3$ are fairly stable in the presence of AlCl$_3$[49,60,64]. However, the reaction of these complexes with a mixture of AlCl$_3$+ CH$_3$COCl leads to an extensive decomposition due to acid catalysed degradation of the complex. The comparatively weak acids such as SnCl$_4$ and ZnCl$_2$ are not effective in catalysing the acylation reaction. A mixture of py + CH$_3$COCl or py + (CH$_3$CO)$_2$O has also failed to react. A success in the acylation reaction has been achieved by using (CH$_3$CO)$_2$O + BF$_3$·OEt$_2$ in methylene chloride, Fig. 11. The treatment of these complexes with other acylating
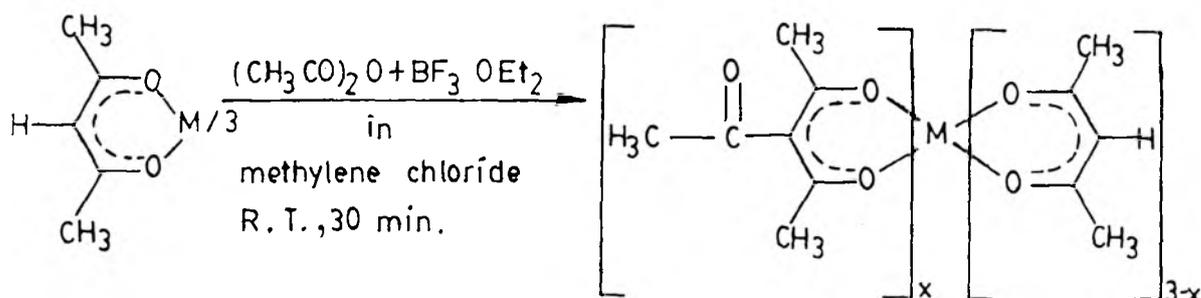
M(III) = Cr(III), x = 1, trace amounts; x = 2, trace amounts; x = 3, 52%

M(III) = Co(III), x = 1, 0·57%; x = 2, 0·68g; x = 3, 0·08g.

Fig. 11

agents such as CH_3CH_2COCl, $(CH_3CH_2CO)_2O$, $CH_3CH_2CH_2COCl$, $(CH_3CH_2CH_2CO)_2O$, C_6H_5COCl or $4\text{-}NO_2\text{-}C_6H_4COCl$ in the presence of $AlCl_3$ or $BF_3 \cdot OEt_2$ results in an extensive degradation of the complex. It has been suggested that the increased bulk of the -COR group sterically inhibits the Friedel-Crafts reaction, so that the competing ring degradation reaction dominates. However, C_6H_5COCl and $CH_3CH_2CH_2COCl$ are used successfully for the acylation reaction of $Rh(ptdn)_3$. It has also been reported that a mixture of $AlCl_3 + CH_3COCl$ gives a success in acylating $Rh(ptdn)_3$.

In $M(ptdn)_n$ the replacement of Me group by Ph group results in a lower yield of the acylated derivative, this observation being similar to that for other electrophilic substitution reactions. The successive introduction of -COCH$_3$ group at 3-C on the subsequent ptdn rings of the same complex molecule becomes increasingly difficult.

Among the other metal complexes, the acylation reaction of $M(hax)_n$ has been reported[65]. There is no definite report on the acylation reaction of $M(sal)_n$ and Schiff base metal complexes. There is also no report on the acetoxylation reaction of metal complexes.

6. Mercuration reaction

This reaction has attracted comparatively little attention. Cu(oxine)$_2$ has been mercurated[12] using Hg(CH$_3$COO)$_2$ in glacial acetic acid. The chemical analysis of the product has suggested that 3 moles of -HgCOOCH$_3$ are present in every mole of the metal complex; presumably one of the chelate rings possesses a single -HgCOOCH$_3$ group, and the other ring has two -HgCOOCH$_3$ groups at 5- and 7-positions.

Mercuration of metal complexes containing β-di-carbonyl groups such as ptdn, tfptdn, Etacac, Aacetn, Cl-Aacetn has been carried out using Hg(CH$_3$COO)$_2$[66]. These metal complexes disintegrate during the reaction yielding di-HgCOOCH$_3$ derivatives of the parent ligand.

The mercuration of Cu(sal)$_2$[36] results in the separation of the monomercurated ligand. The mercuration reaction of the parent ligand yields 3,5-di-HgCOOCH$_3$, sal. Thus, in this metal complex, the presence of the metal ion alters the reaction product.

There is no definite report on the mercuration reaction of Schiff base metal complexes.

7. Kinetic study of the electrophilic substitution reactions of metal complexes

The kinetic study of the reaction of

M(ptdn)$_3$ [M(III) = Cr(III), Co(III)] with NBS in chloroform has been investigated spectrophotometrically[67]. A second order rate law has been observed. The stopped flow pulse Fourier transform ^{1}H nmr technique has been utilized to study the rate of chlorination of Co(ptdn)$_3$ with NCS[68,69]. Similar to the bromination reaction, second order rate law has been observed. However, in both these cases the speculation about the effect of the metal ion on the reaction rates are lacking. It seems this type of study needs further exploration.

The kinetics of the mercuration reaction of Cu(oxine)$_2$ with Hg(CH$_3$COO)$_2$ have been studied[12]; the second order rate law has been observed. A comparison of the reaction rates of the parent ligand and the coordinated ligand indicates an enhancement of the reaction rates on coordination. There is also a report[70] on the higher rates of the bromination reaction of M(oxine)$_n$ [M = Cr(III), Fe(III), Co(III)] as compared to that of the parent ligand. Rates of iodination of 5-SO$_3$H, oxine and its complexes with chromium (III), iron (III), palladium (II) and rhodium (II) have been investigated[71]. The rates of iodination of the parent 8-quinolinolate anion are enhanced on coordination. This difference in behaviour has been explained on an electronic basis.

There is no definite report on the kinetic study of

the electrophilic substitution reactions of $M(sal)_n$ and Schiff base metal complexes.

8. Summary

This chapter gives a brief literature survey of
(a) the nature of the electrophilic substitution reactions of coordinated aromatic / pseudoaromatic ligands, and
(b) the kinetic study of the electrophilic substitution reactions of the metal complexes.

Liquid bromine as a brominating agent has been found to be successful in brominating the acid-stable-complexes such as $Cr(An)_3Cl_3$, $M(oxine)_n$ [M = Cr(III), Fe(III), Co(III), Cu(II), Al^{3+}] and $M(ptdn)_3$ [M = Cr(III), Co(III)].

For acid labile complexes NBS in chloroform has been selected as the ideal brominating agent. The successful bromination reactions of $M(ptdn)_n$, $M(sal)_2$ and $M(N\text{-}Rsalin)_2$ by NBS have been reported.

Chlorine gas has been used to chlorinate $Cr(py)_3$ Cl_3 and $M(oxine)_n$ [M = Cr(III), Fe(III), Co(III), Cu(II), Al^{3+}] . $M(ptdn)_n$ has been effectively chlorinated and iodinated by NCS/Cl_2 and NIS/ICl respectively. However, the chlorination and iodination reactions of $M(sal)_2$ [M(II) = Co(II), Cu(II)] could not be achieved by NCS and NIS respectively. $CuBr_2$ has

been used for the bromination of metal complexes such as
$Cu(oxine)_2$, $M(ptdn)_n$ [M = Cr(III), Co(III), Cu(II)] and
$Cu(sal)_2$. CNBr has been used to brominate $Cr(ptdn)_3$.

In all these halogenation reactions of metal
complexes, the position of the incoming electrophilie
remains unchanged upon coordination. The steric factors
are pronounced in the halogenation reactions of metal
complexes. However, it should be noted here that in the
bromination reaction of $Ni(N-n-Butsalim)_2$, there are
contraversial reports.

The usual nitration mixture (HNO_3 + H_2SO_4) used for
nitrating organic compound is found to be unsuitable for
nitrating coordinated ligands. N_2O_4 in benzene has been
successfully used for nitrating $M(ptdn)_2$ [M = Ni(II), Cu(II),
Pd(II), Pt(II)] . CH_3COONO_2 generated by the reaction of
metal nitrate and $(CH_3CO)_2O$ gained considerable importance
as a nitrating agent for the complexes $M(ptdn)_n$, $M(sal)_n$,
M [N,N'en(salim)$_2$] , $M(N-Rhapim)_2$. An alternate route for
nitrating $M(ptdn)_n$, such as replacement of groups other than
hydrogen under the apparently electrophilic conditions has
been reported. There is no report on the changed reactive
site upon coordination for nitration reaction of metal
complexes. However, there are examples of free ligands which
could not be nitrated under the conditions used for the

successful nitration of coordinated ligands. Similar to the halogenation reaction, the substitution of Me group by Ph group in $M(Ptdn)_n$ affects the nitration reaction time and the yields of the reaction product.

The thiocyanation of $M(ptdn)_n$ using $(SCN)_2$ is found to be successful. The use of polar solvents and Friedel-Craft catalysis enhances this substitution reaction. However, the thiocyanation of other complexes such as $M(sal)_n$, $M(N-Rsalim)_n$ and the corresponding ligands has not been reported.

The usual acylation mixture $AlCl_3$ + CH_3COCl is found to be successful only for $Rh(ptdn)_3$. A mixture of $(CH_3CO)_2O$ + $BF_3 \cdot OEt_2$ in methylene chloride successfully acylates $Cu(oxine)_2$, $M(ptdn)_3$ [M = Cr(II), Co(III)] yielding a mixture of mono-, di-, and tri- acylated derivatives. It is interesting to note that metal ion has a definite effect on acylation of $M(ptdn)_n$; the successive introduction of $-COCH_3$ group at 3-C on subsequent ptdn rings of the same complex molecule become increasingly difficult. Other acylating agents such as CH_3CH_2COCl, $(CH_3,CH_2CO)_2O$, $CH_3CH_2CH_2COCl$, $(CH_3CH_2CH_2CO)_2O$, C_6H_5COCl, or $4-NO_2-C_6H_4COCl$ in the presence of $AlCl_3$ or BF_3OEt_2 lead to an extensive degradation. C_6H_5COCl and $CH_3CH_2CH_2COCl$ are used successfully for the acylation of $Rh(ptdn)_3$. No change

in the orientation of the incoming electrophile has been reported upon coordination. Similar to other electrophilic substitution reactions, the replacement of Me group by Ph group in $M(ptdn)_n$ reduces the yield of the acylated product. There is no definite reports on the acylation reaction of $M(sal)_2$ and Schiff base metal complexes.

$Hg(CH_3COO)_2$ in glacial acetic acid has been reported to a suitable mercuration agent for $Cu(oxine)_2$ and $Cu(sal)_2$. In the latter case there is evidence for a changed reactivity as compared to the parent ligand. For $M(sal)_2$, the 5 position on the benzene ring is attacked, while the reaction of the parent ligand the attack is both at 3- and 5- positions. There is no definite report on the mercuration reaction of the Schiff base metal complexes.

The kinetic study of the electrophilic substitution reactions of metal complexes has not been extensively studied. The bromination and chlorination reactions of $M(ptdn)_2$ [M=Cr(II), Co(II)] using NBS and NCS respectively establish a second order law. The mercuration reaction of $Cu(oxine)_2$ using $Hg(CH_3COO)_2$ exhibits a second order law. In this reaction a definite effect of the metal ion on the reaction rate has been observed. Similarly the kinetic study of bromination of $M(oxine)_n$ indicates the higher reaction rates for the coordinated ligand as compared to the reaction of the

parent ligand. There is no definite report on the kinetic study of the electrophilic substitution reaction of the $M(sal)_n$ and Schiff base metal complexes.

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