J. Indian Inst. Sci. 65(B), Nov. 1984, pp. 291-313

Substitution reactions of coordinated β-diketones β-ketoamines and thio β-diketones — A review

G. SHANKAR, K. PAULRAJ, V. BALASUBRAMANIAN[+] AND S.K. RAMALINGAM*
Dept. of Inorganic Chemistry, School of Chemistry, Madurai Kamaraj University, Madurai 625 021, India.

Received on March 9, 1984

Abstract

Electrophilic substitution reactions of metal coordinated β-ketoamines and thio β-diketones are surveyed. Methods of diagnosing substitution at the γ-carbon of the chelate are also reviewed.

Key words: γ-substitution reactions of, reactions of coordinated β-diketones, β-diketones, β-ketoamines and thio β-diketones.

1. Introduction

Studies in coordination chemistry have in general led to a preoccupation with the effect of complex formation and in the past little consideration has been given to the reactivity of the ligands in coordination with the metal. As an instance, the ligand system β-diketones, known to form a complex with every metal ion, has attracted the attention of chemists right from 1887; but not much work has been done prior to 1960 regarding the reactivities of these complexes. A prime motive behind the study of reactivities of coordinated ligands is to explore new synthetic routes for a variety of metal derivatives of such ligands that are not otherwise preparable by routine techniques. It is obvious that a metal ion can strongly influence the reactions of coordinated ligands as compared with the uncoordinated ligand by causing changes in intra-ligand charge distribution both by σ-withdrawal and by π-donation or withdrawal. This may lead to enhancement of a particular reaction of the coordinated ligand, force a given reaction to occur by a different mechanistic pathway or yield a product not attainable without prior metal coordination.

In this review is presented a survey of the reactions of the ligand systems — β-diketones, β-ketoamines and thio β-diketones—coordinated to various metal ions. Metal β-diketones find increasing application in NMR as contact shift reagents, in laser technology, in gas chromatography and in solvent extraction. A review highlighting the reactions of coordi-

---

[+] Dept. of Chemistry, Presidency College, Madras 600 005, India.

* Author for correspondence.

ated ligands in general[1] has appeared as early as 1966. In 1977, Joshi and Pathak[2] have eviewed the overall characteristics of the 1,3-(β)-diketonates with emphasis on fluorinated -diketonates. Mehrotra *et al*[3] have given a comprehensive account of the metal β-iketonates. In all the above reviews dealing with the various properties of β-diketonates, ot much emphasis is laid on the reactivity aspects. Further, little or no mention is made bout the reaction of the coordinated β-ketoamines (Schiff base of β-diketones) and hio β-diketones. This review covers the literature from the early days up to the present and ocusses attention on the reactions of the title compounds and the importance in understanding the quasi-aromaticity of the chelate rings.

Reactions of metal chelates in which the metal containing rings retain their integrity can be laced in three categories: (a) addition to the central metal atom or the chelate molecule as a whole (b) reaction at functional groups and reactive sites dependent on the chelate ring and c) substitution of *H* or other groups attached directly to the ring. Of particular interest are those reactions involving substitution on the ring as they provide information on the lectronic structure of the ring as well as yield new chelate compounds. The reaction studies have helped extensively in the understanding of the mode of metal-ligand interaction, rationalisation of the factors influencing the reactivity of the coordinated ligands like the effect of the size and nature of the metal ion, the nature of the donor atoms of the ligands, steric effects offerred by the substituents on the ligand molecules, ring effect, field effect, conjugate effect, chelate effect and the possible mechanistic pathways in general. The synthetic aspect assumes importance in such readily available materials as the metal β-dicarbonyl chelates (and related compounds) where substitution of reactive functional groups for the *H* atom attached directly to the ring would give rise to polyfunctional chelates. These in addition to any other utility could prove useful in the preparation of chelate polymers.

The substitution reaction which is the most basic of all has been used extensively in organometallic chemistry. Mechanistic aspects have been widely studied. Most of the reactions undergone by the title compounds fall into this category. In all the cases studied, the *H* on the γ-carbon of the chelate ring is substituted by the incoming electrophile (fig. 1).

The influence of the metal ion on the reactivity[4] of the coordinated ligands is conditioned by (a) reorganisation of electrons within the molecule by a variety of electronic effects (b) formation of chemically active centres in the ligands as a result of coordination and (c) introduction of stereo specific chemical geometry in the coordinated ligand. The important factors that govern electrophilic substitution reactions in these compounds are: (a) the electron density at the central carbon of the chelate ring at which the substitution takes place is dependent on both the types of metal ions as well as the nature of the other ligands present in the complex[5]; (b) the choice of the solvent is important in the formation of γ-carbon

FIG. 1. M = Cr(III), Co(III), Rh(III), Be(II), Cu(II), etc. X = Br, Cl, I, NO, NO_2, etc.

substituted derivatives presumably owing to the instability of the metal chelates in some of the solvents[3]; (c) the degree of steric hindrance around the central carbon of the chelate ring; and (d) the overall charge on the complex.

In the study of the reactions of β-diketonates and related compounds the aromatic character of these complexes is an important consideration, X-ray crystallographic studies prove beyond doubt that the double bonds in the chelate rings are not localized. However, the precise nature of bonding in these chelates is not well established. Nevertheless, reactions like halogenation, nitration, nitrosation, thiocyanation, diazotisation, formylation, etc., do indicate the aromatic nature of the chelate rings[6–16]. The reactions are generally carried out under electrophilic substitution reaction conditions without allowing the metal β-diketonate chelate rings to degrade, since they are acid-lable. The most widely studied β-diketonate chelates which undergo electrophilic substitution reactions are those of Cr(III), Co(III) and Rh(III) which are kinetically stable. The β-diketone derivatives of Be(II), Cu(II), Fe(II), Al(III), Pd(II), Mn(II), Ni(II), Zn(II), VO(II), Th(IV) and Zr(IV) however undergo only some of the above electrophilic substitution reaction[3]. Although both polar (*e.g.* methanol chloroform) and non-polar (*e.g.* benzene and carbon tetrachloride) solvents have been employed, the reactions appear to be faster in the former owing to the higher dielectric constant of the media and ease of production of electrophiles.

2. Various electrophilic substitution reactions

a) *Halogenation:* In a study of halogenation reaction of metal β-diketonates with a variety of reagents such as halogens, N-halogenoamides and iodine monochloride in polar or non-polar solvents it has been generally observed that N-halogenoamides are the best halogenating agents, the rate of bromination being much greater than that of iodination or chlorination[3]. The success of the halogenation reaction appears due mainly to the absence of reactive or strongly acidic by-products and the halogenating agent employed. For example, chromium(III) acetylacetonate reacts[7, 17], with bromine in glacial acetic acid solution to form the 3-bromo derivative while the benzoylacetonate and dibenzoylmethanate complexes of Cr(III) give the 3-bromo product with NBS in the presence of chloroform or acetic acid.

Reaction of metal bis β-diketonates with NBS to produce bromo chelates can be visualised as proceeding by several routes as shown in fig. 2. Bromination may proceed through initial ring cleavage and then halogenation and ring formation (a) or halogenation of the ring itself could give rise to an intermediate which stabilises itself by partial or complete ring cleavage (c and d). Finally bromination may take place with the ring remaining intact throughout the transformation (b). In this latter reaction, the metal chelate acts similar to metalloheterocycle. Initial side chain halogenation followed by rearrangement of the halogen to the ring is ruled out by the apparent stability of the known halomethyl chelates.

Compared with metal-acetylacetonates the halogenation of metal-benzoylacetonates and metal-dibenzoylmethanates results in a decreased yield of the halogenated product and an increase in the reaction time. This may be due to the steric hindrance caused by the phenyl rings adjacent to the reaction centre, a fact supported by the difficulty encountered by the larger iodonium ion in substitution as compared with the relatively smaller chloronium and bromonium ions.

An interesting phenomenon is observed during the bromination (with NBS) of lanthanide β-diketonates[18]. In contrast to the tris-chelates of Co(III), Cr(III) and Rh(III) β-

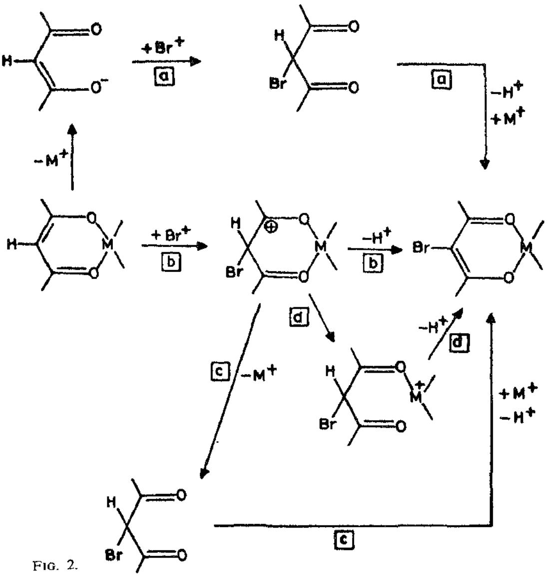


FIG. 2.

diketonates, the tris chelates of lanthanides seem to undergo γ-substitution with ring flipping giving a product containing two five-membered rings, whose bromine is bonded both to the carbon atom and to the central metal ion, and a six-membered ring with normal γ-substitution. A probable mechanism as shown (fig. 3) can be visualised.

The fluoroacetylacetonates of many metals are resistant to halogenation there being only a couple of reports[19a,b] of such reactions. The low reactivity may be attributed to the pronounced inductive effect of the fluoromethyl group in the ligand moiety.

There have been a few isolated investigations on the reactivity of systems in which one of the oxygen atoms in the acetylacetonate ring is replaced by another heteroatom.

A study[20] of the bromination reaction of Ni(baen) and Ni(bapn) and Cu(baen) indicates that the reaction conditions must be carefully controlled. For example, bromination with Br_2 instead of NBS gives the 3-bromo product but in a much lesser yield than with NBS due to acid degradation and formation of considerable amount of side product. It is also interesting to note that Br_2 in acetonitrile gives the γ-bromo product with Ni(baen) (fig. 4(a)) whereas with the macrocyclic ligand derived from acetylacetone, oxidative dehydrogenation is observed to give a new product with increased conjugation (fig. 4(b)).

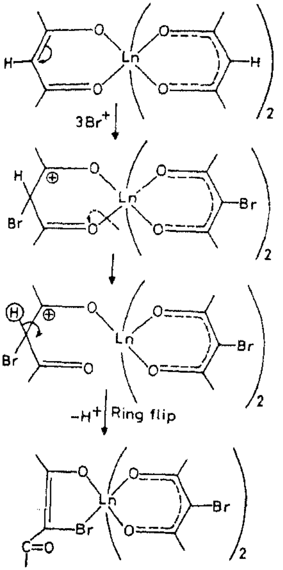


FIG. 3.

The charge on the complex seems to play a part in these substitution reactions. Thus naturally a positively charged complex would be more difficult to be substituted by electrophilic reagents than a neutral or -vely charged complex. This is amply brought out by the reactivity[21] of the mixed ligand complexes (I) NH_4 [Cr (acac) (ata) (H_2O)]; (II) [Cr (acac) (edda)]. 2 H_2O and (III) [Cr (acac) (edma) (H_2O)] Cl. $2H_2O$ towards NBS, NCS and NIS. Although halogenation occurred at the γ-position of the chelate ring in all the three cases, III is relatively difficult to be halogenated as compared to I or II. This indicates that the electron density at the γ-position of the actylacetone ring in the +vely charged complex is somewhat more deficient than that of −vely charged or neutral complex and impedes electrophilic substitution.

However, it is not the charge alone that plays a vital role in these reactions according to Kuroda *et al*[22,23]. These authors have carried out halogenation and nitration reactions on fac-(N)−[Co(acac) (i−dtma)] ClO_4 and mer-(N)−[Co(acac) (i−dtma)] ClO_4 as also on the mixed ligand complex containing acac and en, α-trien and β-trien. These substitution reactions being ionic rather than radical processes a +vely charged complex should be more difficult to be γ-substituted than a neutral or negatively charged species. However, this is not

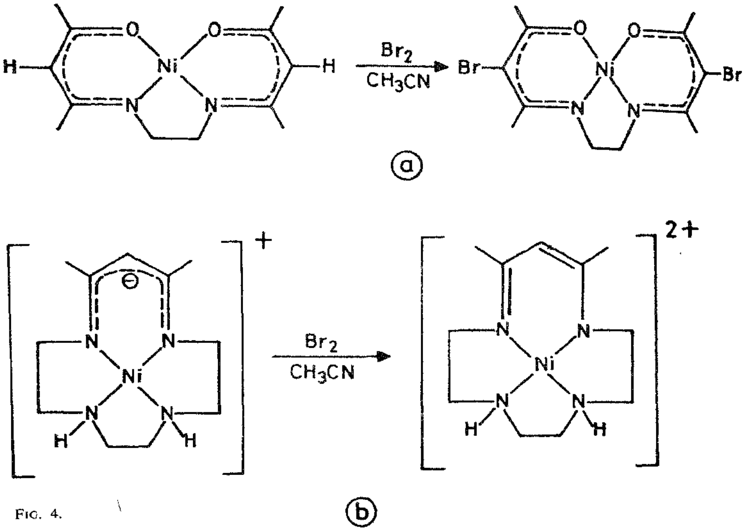


FIG. 4.

the case since a quantitative camparison of chlorination indicates that it is the degree of distortion from the regular octahedral structure which appears to be more influential since the dipositive β-trien complex is the most reactive. According to Pauling's electroneutrality principle the net charge of a complex ion is distributed among the atoms which exist on the surface of the ion. Thus the methine H must be more +ve as the net charge of the complex ion increases. This means that the methine carbon in the more +ve ion is possibly the more −ve and is the more reactive with the electrophilic reagents. Kinetic measurements[23] on the chlorination of $[Co(acac)(en)_2]$[24] support the above view and indicate that the reaction proceeds with a direct attack of the NCS molecule on to the substrate, for which no bond rupture between the metal and ligands is involved as an activation process. This could be a possible explanation for the minor effect of net charge of the complex on the reactions.

Fujii *et al*[24] have made some interesting observations on the halogenation of $Ni(tfac_2en)$. In the presence of an alcoholic solvent, a stable intermediate containing the electrophile bonded to γ-carbon and the alkoxide ion bonded to the carbon carrying the trifluoromethyl group has been isolated.

Not much work has been reported on the reactivities of the coordinated thio β-diketonates, owing probably to the unstable nature of many of the thio β-diketones and the difficulty in synthesizing stable chelates in sufficient yields and purity[3].

Halogenation of $M(Lss)_2$ type compounds[25] where M=Ni(II) or Co(II) gives $M(Lss)_2Cl_4$ and $M(Lss)_2Br_6$. The structure of the Ni(II) and Co(II) complexes are as follows. Four chlorine atoms are directly bonded to the central metal atom and the dithiolium ions to the metal as monodentate. Their IR spectra are very similar to those of $M(Lss)_2X_4$ type complexes. The bromo complexes contain six bromine atoms per metal atom. The hexabromo complexes decompose slowly at room temperature and rapidly at 100° C.

$$Co(Lss)_2Br_6 \xrightarrow{100^\circ C} Co(Lss)_2Br_4 + Br_2$$

$$Ni(Lss)_2Br_6 \xrightarrow{100^\circ C} Br_2 + \text{black product}$$

It is reasonable to assume that these compounds are adducts of Br_2 to $M(Lss)_2Br_2$ although Knauer *et al*[26] propose that the excess bromine atoms may bond to either a γ-carbon or β-carbon atom of the chelate.

Halogenation has been carried out on many other similar systems[27–30]

b) *Nitration:* A wide variety of reagents can be employed for nitration. Some of the important characteristics of these reagents are as follows:

(1) The usual nitrating agents (nitric and sulphuric acids) are not good reagents for nitration of acid-labile metal β-diketonates[17].

(2) Metal nitrates are better nitrating agents than dinitrogen tetroxide; but, sometimes the ring metal atom may be replaced by the metal atom of the nitrating agent[31].

(3) Hydrated copper nitrate is a good nitrating agent for metal β-diketonates but anhydrous copper nitrate which is insoluble in acetic anhydride is useless because of the covalent nature of the dehydrated form.

(4) Mixture of nitrogen dioxide and benzene[32,33], nitrogen dioxide and boron trifluoride[34], aluminium nitrate and nitric acid[31] and copper nitrate and acetic anhydride[31] have been found to be the most useful reagents for nitrating many metal β-diketonates.

(5) Alternatively, the identical 3-nitro substituted metal β-diketonate chelates can be obtained in a direct single step process involving metal nitrates, acetic anhydride and β-diketone ligands.

The nitration of acetylacetonates of Cr(III), Co(III) and Rh(III) can be achieved by the use of a mixture of copper nitrate and acetic anhydride, the reactivity of the mixture being suspected to be the deep blue solution of the acetyl nitrate of copper(II). Nitration of acetylacetonates of Be(II), Al(III), VO(II), Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Zr(IV) and Th(IV) with copper nitrate yields nitro-acetylacetonate of Cu(II). The benzoylacetonates and dibenzoylmethanates of Al(III), Cr(III) and Pd(II) can be nitrated by hydrated copper nitrate and acetic anhydride. These nitro chelates are stable towards further chemical reaction[14,35].

A mechanism similar to halogenation can be proposed for nitration (fig. 5).

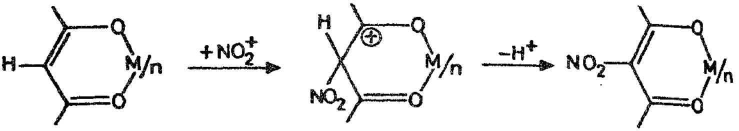


FIG. 5.

Nitration reaction has been carried out on the Schiff base of acetylacetone to give 3-nitro substituted products[36]. Reaction of the Schiff base complex (fig. 6) with nitrogen electrophiles has been found to convert the complexes, Ia, IIa, IIIa and IVa in fig. 6 to the corresponding dinitro species Ib, IIb, IIIb and IVb. The reaction can be contrasted with electrochemical oxidation[37]. The electron density affected site appears to be different in the two reactions. In the former case, electrophilic attack occurs at the central carbon atom of the charge delocalized six-membered chelate rings while in the latter case, the central metal ion is oxidized. The isolation of the dinitro products thus provides evidence for the nucleophilic behaviour of these substituted γ-carbon atoms.

Nitration reaction has also been carried on a number of similar systems[19, 38–44]

c) *Nitrosation:* Organic compounds containing vinylic group ($\supset\!>$C-H) react with a variety of nitrosating agents (nitric oxide, acidified solution of sodium nitrite, nitroso sulphuric acid, nitrosyl halides, organic nitrites, etc.) giving isonitroso derivatives[45]. Since coordinated β-diketones also possess vinylic functionality, they too can be expected to undergo nitrosation reactions. However, the presence of a metal ion may modify the rate and the pathway of these reactions. There can be three possibilities of the nitrosation reactions as indicated below.

i) $M^{n+1}\,L \xrightarrow{NO} M^{n+1}\,L.NO$ (oxidative addition yielding simple additive chelate derivatives).

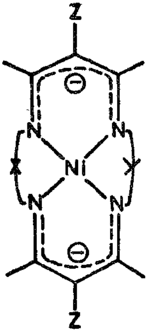
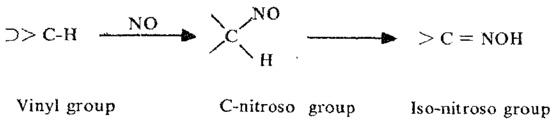


FIG. 6.

I: $X = C_2H_4$, $Y = C_3H_6$ a: $Z = CH_3CO$ b: $Z = NO_2$
II: $X = (CH_3)_2\,CCH_2$, $Y = C_3H_6$ a: $Z = CH_3CO$ b: $Z = NO_2$
III: $X = C_2H_4$, $Y = C_3H_6$ a: $Z = COOCH_2CH_3$ b: $Z = NO_2$
IV: $X = (CH_3)\,CCH_2$, $Y = C_2H_4$ a: $Z = CH_3CO$ b: $Z = NO_2$

ii) Nitroso substituted compounds (the analogues of C-nitroso compounds)[46].

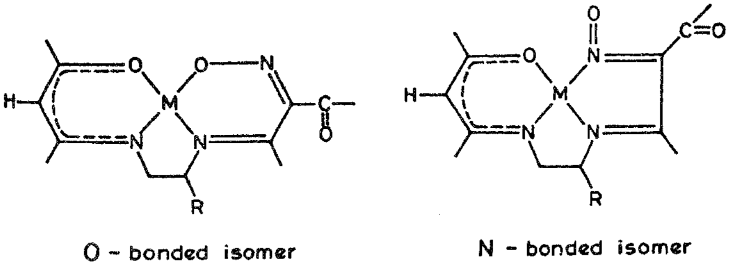
iii) The unstable secondary nitroso derivative produced may ultimately tautomerise to a isonitroso product.



A number of nitrosation reactions have been studied[47-54]. Nitrosation reactions of coordinated β-diketones and their nitrogen analogues assume a special importance in the realm of reactions of coordinated ligands. In these reactions the γ C-H group is generally converted into an isonitroso group. This can coordinate to the central metal atom through either nitrogen or oxygen giving rise to chelate linkage isomers. In other words, the isonitroso group can function as ambidentate moiety. A large number of linkage isomers have, in fact, been prepared by the reactions of coordinated ligands. Several mononitrosated Ni(II), Cu(II) and Pd(II) complexes of tetradentate Schiff bases of β-diketones have been prepared by the nitrosation of the chelates[55]. This type of ligand reactions includes molecules containing multidonor atoms but employ two donor sites at a time for coordination with a metal ion. The linkage isometric complexes of this type of ligands are relatively rare.

The hydroximino group (-NOH) introduced at the ring γ-carbon dislodges the coordinated carbonyl group and coordinates to metal ion either through N or O giving rise to chelate linkage isomers. In other words, the ambidenate coordination of the isonitroso group is manifested in one and the same molecule of the complex. This phenomenon is termed as 'intra molecular chelate linkage isomerism'. The preferential mode of coordination of the hydroximino group essentially depends on the nature of the metal ion, the electronic charge distribution in the rings and steric factor[56] (fig. 7).

Some interesting results[57] are obtained when studying the chelate linkage isomerism of Cu(II), Ni(II) and Pd(II) complexes of the tetradentate Schiff base (fig. 8). The hydroxi-



O - bonded isomer

N - bonded isomer

G. 7.

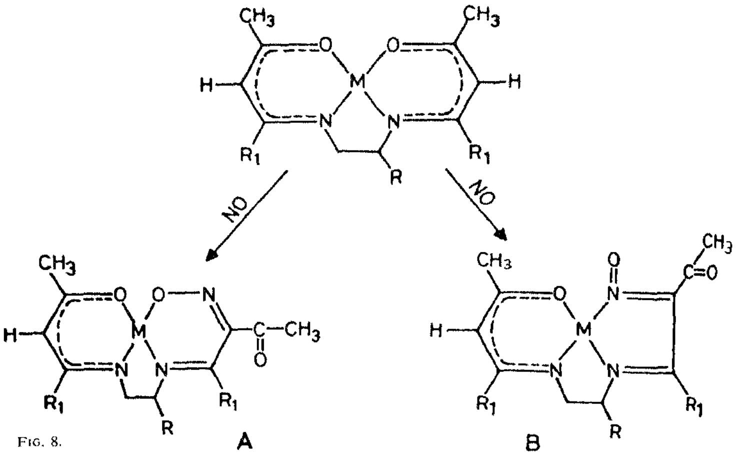


FIG. 8.

$$\left.\begin{array}{l} R = H:\ R = CH_3:\ R = CH_3 \\ R_1 = CH_3:\ R_1 = CH_3:\ R_1 = C_6H_5 \end{array}\right\} \quad M = Ni\ (Ia - Ic)$$

$$\left.\begin{array}{l} R = CH_3:\ R = H:\ R = CH_3 \\ R_1 = CH_3:\ R_1 = C_6H_5:\ R_1 = C_7H_5 \end{array}\right\} \quad M = Cu\ (id - If)$$

$$\left.\begin{array}{l} R = H:\ R = CH_3 \\ R_1 = CH_3:\ R_1 = CH_3 \end{array}\right\} \quad M = Pd\ (ig - Ih)$$

mino group introduced coordinates through either N or O atom to metal by dislodging the carbonyl group already coordinated. This gives rise to two linkage isomers, one with N-bonded and the other with O-bonded hydroximino group in the case of Ni(II) and Pd(II) and a single isomer with O-bonded hydroximino group in Cu(II) complexes.

In the solid state, isomer A of IB (fig. 8) is hydroximino O-bonded while isomer B is hydroximino N-bonded. In chloroform at 40° C, each of these isomers give an equilibrium mixture of A and B isomers. The transformation is irreversible.

$$\text{Ni complex of Ib} \xrightarrow[40^\circ C]{CHCl_3} \text{Isomers } (A+B)$$

isomer A or B

Similarly, isomer A and Ic also isomerizes in $CHCl_3$

$$\text{Ni complex of Ic} \xrightarrow[50^\circ C]{CHCl_3} \text{Isomers } (A+B)$$

isomer A

The isomerization is not favoured in Id (Hydroximino O-bonded) Pd(II) and Cu(II) complexes under similar conditions. Probably the high activation energies associated with these complexes appear to be responsible for their failure to isomerize.

A probable mechanism for the nitrosation reaction can be postulated as delineated in fig. 9.

Nitrosation reaction has been carried out on the dithioacetylacetonate of Co(II)[58] giving monomeric, non-electrolytic complexes of Co(NO) $(C_5H_7S_2)_2$ and $Co(NO)_2$ $(C_5H_7S_2)$. These are considered to be simple five-and four-coordinated complexes with pseudo-square pyramidal and tetrahedral stereochemistries, respectively. The mononitrosyl Co(NO) $(C_5H_7S_2)_2$ disproportionates in solution to $Co(NO)_2$ $(C_5H_7S_2)$. The stoichiometry of the disproportion reaction is confirmed by IR and NMR study to be

$$2Co(NO)(Lss)_2 \longrightarrow Co(NO)_2(Lss) + Co\ (Lss)_3.$$

However, the mechanism of the reaction requires detailed kinetic study for its elucidation. The overall stoichiometry raises the interesting possibility that association to a bimolecular transition state involving octahedrally coordinated cobalt might be involved (fig. 10). However, reasonable dissociative mechanisms can also be formulated.

Similar reactions have been carried out on various Schiff bases of β-diketones[59–62]

d) Thiocyanation and introduction of other sulphur electrophiles: One of the facile electrophilic reactions undergone by the acetylacetonates and benzoylacetonates of Co(III), Cr(III), Rh(III), Fe(III) and Pd(II) is thiocyanation reaction[63] (fig. 11). The reactivity of thiocyanogen in electrophilic substitution is enhanced by the presence of Friedel Crafts catalysts[64]. In view of this, Singh and Sahai[63] suggested a mechanism involving polarization of S-S bond most probably aided by the associated polar molecules of the solvent (or Friedel-Crafts catalysts) in the transition state (fig. 12).

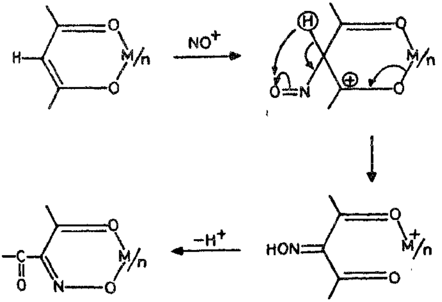


FIG. 9.

• However, the literature version of the reaction scheme shows the electrophilic nitrosonium ion attacking the metal centre which is highly improbable.

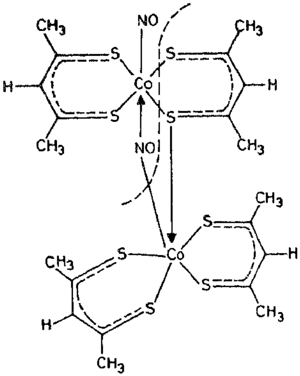


FIG 10.

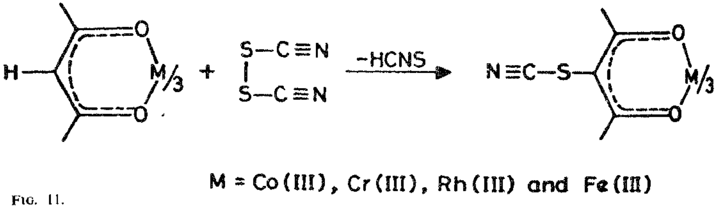


FIG. 11.

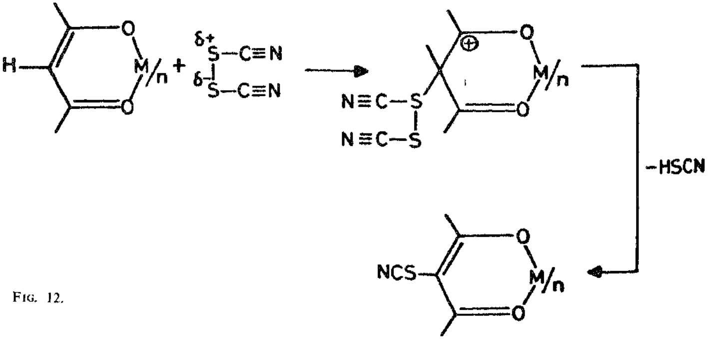


FIG. 12.

The chelate halides are found to be inert towards further reactions in which the chelate rings remain intact[11]. On the other hand, chelate sulfenyl chlorides are capable of further conversion[15]. Addition of SCl_2 to olefins has proved relatively unsuccessful[65,66] while reaction of SCl_2 with an enolic compound such as acetylacetone[67] yields a sulphide. The isolation of sulfenyl chlorides in the present case is due to favourable stoichiometric solubility and also steric shielding of the 3-position by the adjacent methyl groups (fig. 13). The ability of Al(III) and Be(II) chelates to survive the reaction conditions without apparent ring cleavage may be explained by the relative inertness of these chelates due to large charge to radius ratios of the metal atoms and the absence of any low energy level orbitals.

Chromium tris (3-bromo acetylacetone) is found to be unreactive towards SCl_2. This emphasizes the importance of an unsubstituted 3-position and supports the direct substitution of the 3-position rather than an initial radical attack on a side chain methyl group followed by an allylic migration to the ring.

Thiocyanation reaction has also been carried out on the Ni(II) and Cu(II) Schiff base acetylacetone ethylenediimine complexes[68]. These chelate sulfenyl chlorides react with diverse reagents such as amines, phenols, thiocyanates and olefins to form anticipated derivatives[69]

e] *Friedel-Crafts reaction:* A wide variety of reagents have been used for the acylation of β-diketonates, and some of the characteristic features may be summarized as follows.

(1) Mixtures of aluminium chloride with acetyl chloride are not suitable for acylation of metal β-diketonates since these decompose the chelate ring.

(2) Attempts of acylate β-diketonate chelate rings with pyridine-acetic anhydride and pyridine-acetyl chloride are also unsuccessful.

(3) Weak acids like stannic chloride or zinc chloride are also ineffective for catalysing the acylation reaction.

(4) A mixture of acetic anhydride and boron trifluoride etherate in methylenechloride medium could acylate both Co(III) and Cr(III) β-diketonates but not Rh(III) β-diketonates[13,16,17] (fig. 14). Rh (III) acetylacetonate can be acetylated using acid chloride and aluminium chloride[13] (fig. 15).

(5) Treatment of Cr(III) and Co(III) acetylacetonates with other agents such as propionyl chloride, propionic anhydride, butyryl chloride, butyric anhydride, benzoyl chloride and *p*-nitro benzoyl chloride in the presence of aluminium chloride or boron trifluoride etherate results in extensive chelate degradation.

It seems likely that increased bulk in the acylating agent sterically inhibits the Friedel-Crafts reaction so that competing ring degradation dominates.

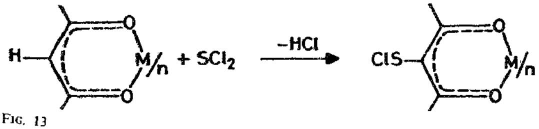


FIG. 13

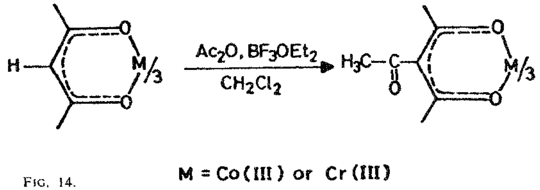


FIG. 14.

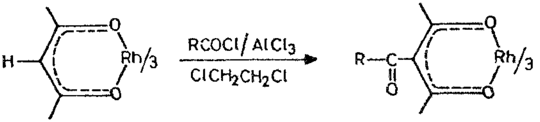


FIG. 15.

f) Dimethylaminomethylation and chloromethylation: Metal tris (acetylacetonates) undergo a modified Mannich type reaction in which an uncoordinated amino function is introduced into the chelate rings to produce a product with drastically altered properties[70] Mannich product (A) undergoes further reactions (fig. 16).

Treatment of Cl-substituted Rh(III) acetylacetonate with monochloromethyl ether and boron trifluoride diethyl etherate yields an amorphous yellow polymeric solid L (fig. 17) which was not isolated but allowed to react further with nucleophiles as absolute ethanol or methanol. The ether (M) and (N) were isolated from such treatment. The isolation of these products indicates that the reaction to yield a polymeric product most probably proceeds through an ionization mechanism, whereas with the Cr chelates, Mannich products are obtained.

g) Diazotization: Direct amination of the chelate rings of metal acetylacetonates, the logical precursors of chelate diazonium salts, are unsuccessful[35]. Reduction of nitro groups on Co(III) or Rh(III) to the desired amine also failed [14]. Chemical or catalytic reduction of the nitro chromium chelate (A) (fig. 18) either affords unchanged starting material or results in intractable mixtures of unidentified products. Treatment of (A) with Zn dust in pyridine at 60°C affords (B). However, treatment of this nitro compound (A) with hydrogen over $Pd(OH)_2$ affords the mono amine (C) which is dissolved in fluroboric acid at 0°C and this is treated with a cold solution of $NaNO_2$ to yield the purple coloured chelate diazonium fluoroborate (D) which undergoes further reactions (fig. 19).

h) Formylation: Collman *et al*[1,14] reported that acetylacetonates of Co(III), Cr(III) and Rh(III) would undergo formylation by a mixture of dimethyl formamide and phosphorus oxychloride. Formylation of one chelate ring of metal β-diketonates deactivates the remaining unsubstituted rings and hence these reactions are slower than the other electrophilic substitution reactions such as halogenation, nitration, etc. For example, only monoformylated Cr(III) and Rh(III) β-diketonates have been isolated under rigorous conditions.

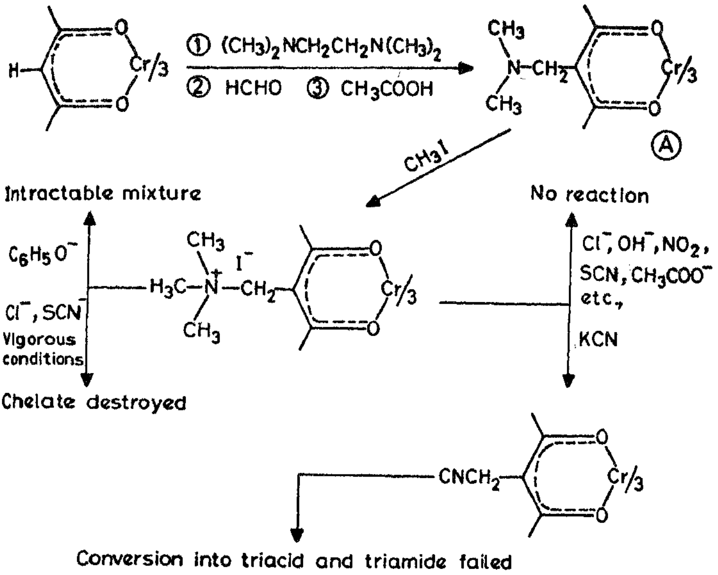


FIG. 16.

Compared with a mixture of phosphorus oxychloride and dimethyl formamide, a mixture of N-methylformanilide and phosphorus oxychloride has been found to be ineffective for formylation of $Cr(acac)_3$. It appears that in the initial stage dimethyl formamide and phosphorus oxychloride form a strong polar dichlorophosphoric acid complex I (fig. 20) which adds to the double bond of the chelate ring that is to be formylated to give an intermediate (II) which on elimination of chlorophosphoric acid followed by hydrolysis gives the formylated derivative[14]

3. Deduction of substitution at γ (3)-position

In all the above substitution reactions, mention has been made that substitution occurs at γ-position of the chelate ring. Although this is the position most favoured by the incoming electrophile, it is the usual routine of the chemist to confirm without doubt the exact nature of substitution (at γ-position). The most frequently used technique is IR spectroscopy followed by UV, NMR and elemental analyses techniques.

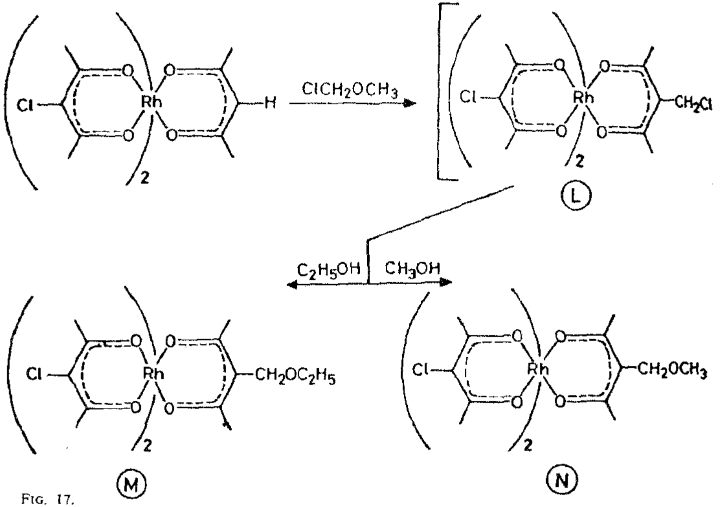


FIG. 17.

i) Infrared spectroscopy: The main point to look at from IR spectroscopy is: (1) bands in the parent unsubstituted complex that are most likely to be affected on substitution, and (2) the presence of new bands due to the incoming electrophile.

In the parent metal β-diketonates, the three main bands that are likely to be affected are ($\nu_{C-H} + \nu_{C=O}$) at 1520 cm^{-1}; the weak in-plane bending mode of γ_{C-H} (δ_{C-H}) at 1195 cm^{-1} and weak out-of plane bending mode of of γ_{C-H} (π_{C-H}) at 795 cm^{-1} [71,72]

Spectra of the substituted complexes are interpreted in terms of Dryden's rule[73] according to which the substitution at the γ-position of the β-diketonate ring should cause the disappearance of the band at 1520 cm^{-1} ($\nu_{C-H} + \nu_{C=O}$) and the appearance of a new band at 1560^{-1}.

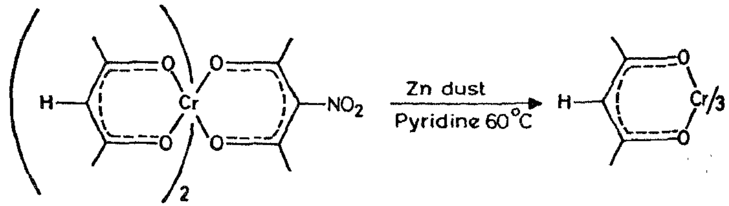


FIG. 18.

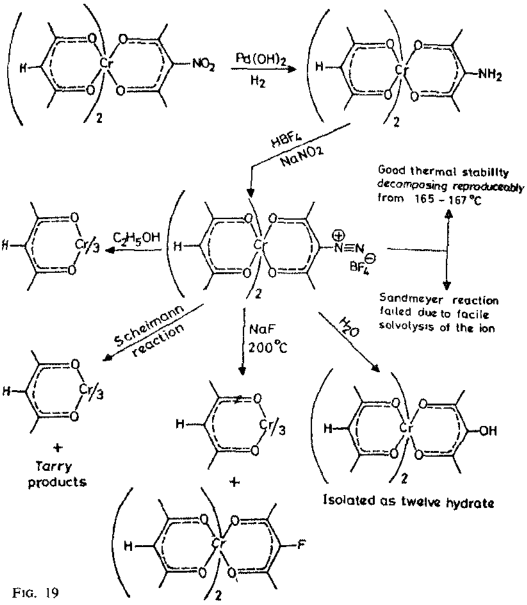


FIG. 19

However, later studies of Djordjevic *et al*[34], Winston[73] and Nakamoto *et al*[74] have proved that Dryden's rule is not applicable to all the cases. A more conclusive proof would be the disappearance of δ_{C-H} and π_{C-H} bands on substitution. The above points can be illustrated by the following examples.

a) Halogenation: In the halo chelates, bands at 1520 cm^{-1} 1195 cm^{-1} and 795 cm^{-1} are absent while the presence of a band at 1550 cm^{-1} indicates γ-substitution. Moreover, there is a new band due to C-X.

b) Nitrosation: As already mentioned, nitrosation can give rise to either N-bonded or O-bonded isomer. In the nitrosated products, the disappearance of π_{C-H} and δ_{C-H} bands confirms γ-substitution. ν_{NO} frequency occurs around 1140-1150 cm^{-1} and IR spectroscopy further distinguishes between N-bonded and O-bonded isomers. In the case of N-coordinated isomer, $\nu_{C=O}$ occurs at 1650 cm^{-1} and for O-coordinated isomer at 1670-1690 cm^{-1} [75-78].

c) Diazotization: In addition to the disappearance of the above mentioned three bands, the presence of a band at 2200 cm^{-1} confirms the presence of the diazonium ion at the γ-position.

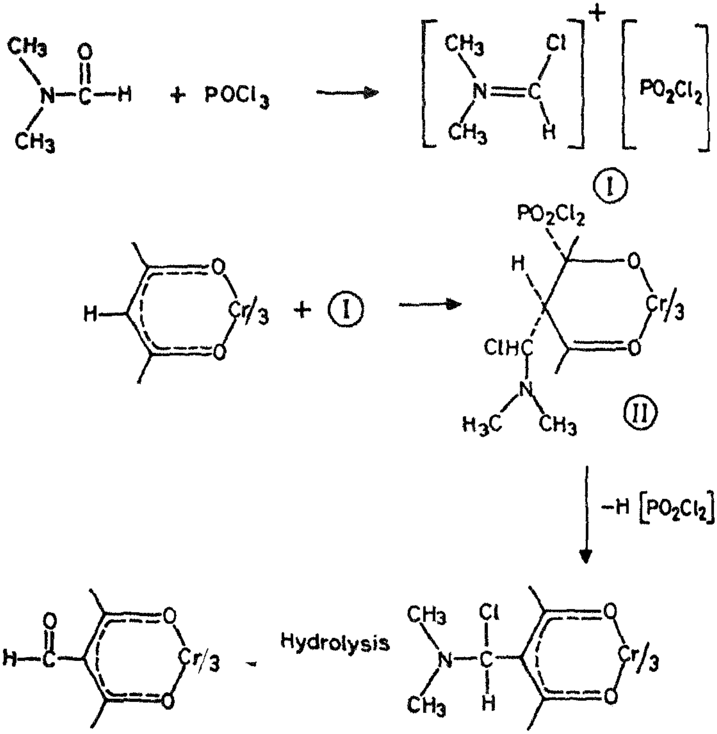


FIG. 20.

ii) Ultra-violet spectroscopy: Sometimes UV spectra might be used for deduction of γ-substitution. As a point in case the halogenated chelates exhibit an extension of conjugation (seen from their spectra) not found in the unsubstituted chelate. Only introduction of halogen at the central carbon of the chelate ring would produce this spectral shift to longer wavelengths.

iii) Nuclear magnetic resonance spectroscopy: Clear cut evidence for γ-substitution is possible from ^{1}H NMR. The unsubstituted chelate should show a $\gamma_{C\text{-}H}$ signal while in the substituted chelate this should be absent. ^{13}C NMR spectrum also is useful as a diagnostic tool since carbon resonance of the carbon bonded to the electronegative groups would show considerable deshielding.

4. Conclusion

Carrying out reactions characteristic of aromatic systems on metal acetylacetonates systematically, apart from other information, may provide (i) further evidence regarding the question of aromaticity of metal acetylacetonates, (ii) a large number of new chelates useful for further studies on the bonding and stability, etc., of metal acetylacetonates, (iii) simpler methods for preparing important organic reaction intermediates (substituted ligands) in good yields, and (iv) a better understanding of the role of metal ion catalysis in certain organic reactions.

Acknowledgements

GS is grateful to UGC, New Delhi, for the JRF and KP to CSIR, New Delhi, for the SRF.

Abbreviations

acac — Acetylacetone
bzac — Benzoylacetone
dbzm — Dibenzoylmethane
tfacac — Trifluoroacetylacetone
hfacac — Hexafluoroacetylacetone
NCS — N-Chlorosuccinimide
NBS — N-Bromosuccinimide
NIS — N-Iodosuccinimide
baen — Bis-(acetylacetone-ethylenediamine)
bapn — Bis-(acetylacetone-propylenediamine)
ata — Ammonium triacetate anion
edda — Ethylenediamine diacetate anion
edma — Ethylenediamine monoacetate anion
tmen — Triethylene tetramine
i-dtma — Bis-[(2-aminoethyl) amino acetate ion]
[4-diethylene triamine monoacetate ion]
tfac$_2$en — Ethylene bid-(5.5'trifluoromethyl-4-oxo 2-pentaniminato)
Lss — Dithioacetylacetone

References

1. COLLMAN, J.P. In *Transition metal chemistry* edited by R.L. Carlin, Marcel Dekker, Inc., New York, 1966, **2.**

2. JOSHI, K.C. AND PATHAK, V.N. *Coord. Chem. Rev.*, 1977, **22**, 37.

3. MEHROTRA, R.C., BOHRA, R., AND GAUR, D.P. In *Metal β-diketonates and allied derivatives*, Academic Press, 1978.

4. BASOLO, F. AND PEARSON, R.G. In *Mechanism of inorganic reactions — A study of complexes in solution*, Wiley, New York, 1958.

5. Collman, J.P. In *Advances in chemistry*, Series No. 37, ACS, Washington DC, 1963, p. 78.

6. Kluiber, R.W. *J. Am. Chem. Soc.* 1960, **82**, 4839.

7. Calvin, M. and Wilson, K.W. *J. Am. Chem. Soc.*, 1945, **67**, 2003.

8. Burdett, J.L. and Rogers, M.T. *J. Am. Chem. Soc.*, 1964, **86**, 2105.

9. Roof, R.B. *Acta Cryst.*, 1956, **9**, 7B.

10. Lingafeter, E.C. and Braun, R.L. *J. Am. Chem. Soc.*, 1966, **88**, 2951.

11. Collman, J.P., Moss, R.A., Maltz, H. and Heindel, C.C. *J. Am. Chem. Soc.*, 1961, **83**, 531.

12. Collman, J.P., Marshall, R.L. Young, W.L. III and Sears, C.T. Jr. *J. Org. Chem.* 1963, **28**, 1449.

13. Collman, J.P. *Angew. Chem.*, 1965, **4**, 132.

14. Collman, J.P. Marshall, R.L. Young, W.L. (III) and Goldby, S.D. *Inorg. Chem.* 1962, **1**, 704.

15. Kluiber, R.W. *J. Am. Chem. Soc.*, 1961, **83**, 3030.

16. Singh, P.R. and Sahai, R. *Indian J. Chem.*, 1970, **8**, 178.

17. Collman, J.P., Moss, R.A., Goldby, S.D. and Trhanovosky, W.S. *Chem. Ind. (Lond.)*, 1960, 1213.

18. Shankar, G. and Ramalingam, S.K. *Transition Met. Chem.*, 1984, **9**, 449.

19a. Joshi, K.C. and Pathak, V.N. *J. Chem. Soc. (Perkin Trans.)*., 1973, 57.

b. Joshi, K.C., Pathak, V.N. and Grover, V. *J. Fluorine Chem.*, 1980, **15**, 527.

20. Lindoy, L.F., Lip, H.C. and Moody, W.E. *J. Chem. Soc. (Dalton Trans.)*, 1974, 44.

21. Fujii, Y., Kyuno, E. and Tsuchiya, R. *Bull. Chem. Soc. (Jap.)* 1969, **42**, 1301.

22. Kuroda, K. and Kamiiba, Y. *Chem. Lett.*, 1975, 1027.

23. Kuroda, K. Yashitani, K. Kunigita, K. Kamibia, Y. and Watanabe, W. *Bull. Chem. Soc.* (Jap.), 1976, **49**, 2445.

24. Fujii, Y. Ito, M. and Akiyama, K. *Bull. Chem. Soc. (Jap.)*, 1981, **54**, 2527.

25. Furuhashi, A., Watanuki, K. and Ouchi, A. *Bull. Chem. Soc. (Jap.)*, 1969, **42**, 260.

26. Knauer, K. Hemmerich, P. and Van Voorst, J.D.W. *Angew. Chem. Int. Edn. Engng.*, 1967, **6**, 262.

27. Moran, M. and Fernandez, V. *Ann. Quin.*, 1979, **75**, 196.

28. Collman, J.P. and Kittleman, E.T. *Inorg. Chem.* 1962, **1**, 499.

29. Balasubramanian, V. The reactions of coordinated ligands, Ph.D. Thesis, Indian Institute of Science, Bangalore, India, 1980.

30. Balasubramanian, V. Dixit, N.S. and Patel, C.C. *J. Inorg. Nucl. Chem.*, 1979, **41**, 122.

31. Singh, P.R. and Sahai, R. *Aust. J. Chem.*, 1967, **20**, 649.

32. Thankarajan, N. and Sen, D.N. *Indian J. Chem.*, 1964, **2**, 65.

33. Sen, D.N. and Thankarajan, N. *Indian J. Chem.*, 1965, **3**, 215.

34. Djordjevic, C., Lewis, J. and Nyholm, R.S. *Chem. Ind. (Lond.)*, 1959, 122.

35. Collman, J.P. and Yamada, M. *J. Org. Chem.*, 1963, **28**, 3017.

36. Hipp, C.J. and Busch, D.H. *Inorg. Chem.*, 1973, **12**, 894.

37. Gore, E.S. Lovecchii, F.V. and Busch, D.H. (Unpublished results).

38. Kuroda, K. Yamaguchi, K. and Yamoka, N. *Bull. Chem. Soc. (Jap.)*, 1977, **50**, 535.

39. Singh, P.R. and Sahai, R. *Inorg. Nucl. Chem. Lett.*, 1968, **4**, 513.

40. Patil, J.N. and Sen, D.N. *Indian J. Chem.*, 1974, **12**, 189.

41. Djordjevic, C. Lewis, L. and Nyholm, R.S. *J. Chem. Soc.*, 1962, 4778.

42. Dey, K. and De, R.L. *J. Inorg. Nucl. Chem.*, 1984, **36**, 1182.

43. Hipp, C.J. and Busch, D.H. *J. Chem. Soc. Chem. Comm.*, 1972, 737.

44. Kasahara, A. and Izumi, T. *Bull. Chem. Soc. (Jap.)*, 1968, **41**, 2185.

45. Touster, O. In *Organic reactions* edited by R. Adams *et al*, John Wiley & Sons, Inc., New York, *Vol. VII*, 1953, 327.

46. Gavenlock, B.G. and Lattke, W. *Q. Rev.*, 1958, **12**, 321.

47. Lacey, M.J., Macdonald, C.G. Shannon, J.S. and Collin, P.J. *Aust. J. Chem.*, 1970, **23**, 2279.

48. Dixit, N.S., Bose, K.S., and Patel, C.C. *Indian J. Chem.*, 1976, **14A**, 507.

49. Iyengar, R.R., Bose, K.S, and Patel, C.C. *Inorg. Chim. Acta.*, 1973, **7**, 3.

50. Sharma, B.C., Bose, K.S. and Patel, C.C. *Inorg. Nucl. Chem. Lett.*, 1972, **8**, 805.

51. Bose, K.S., Sharma, B.C. and Patel, C.C. *Inorg. Chem.*, 1973, **12**, 120.

52. Iyengar, R.R. and Patel, C.C. *Indian J. Chem.*, 1978, **16A**, 846.

53. Sudha, B.P., Dixit, N.S. and Patel, C.C. *Proc. Indian Acad. Sci.*, 1977, **86A**, 471.

54. Dixit, N.S., Sudha, B.P. and Patel, C.C. *Indian J. Chem.*, 1978, **16A**, 851.

55. Sudha, B.P. and Patel, C.C. *Proc. Indian. Acad. Sci.*, 1978, **87A**, 363.

56. Iyengar, R.R. and Patel, C.C. *J. Coord. Chem.*, 1978, **8**, 135.

57. Dixit, N.S., Sudha, B.P. and Patel, C.C. *Bull. Chem. Soc. (Jap.)* 1978, **51**, 2160.

58. Hendrickson, A.R. Ho, R.K.V. and Martin, R.L. *Inorg. Chem.* 1974, **13**, 1279.

59. Masuda, I., Tamaki, M. and Shira, K. *Bull. Chem. Soc. (Jap.)*, 1969, **42**, 157.

60. Dixit, N.S. and Patel, C.C. *Synth. React. Inorg. Metal Org. Chem.*, 1976, **6**, 265.

61. Balasubramanian, V., Iyengar, R.R. and Patel, C.C. *Indian. J. Chem.*, 1981, **20A**, 677.

62. Balasubramanian, V. Iyengar, R.R. and Patel, C.C. *Proc. Indian. Acad. Sci. (Ser). Chem. Sci.*, 1981, **90**, 433.

63. Singh, P.R. and Sahai, R. *Inorg. Chim. Acta.*, 1968, **2**, 102.

64. Soderback, E. *Acta. Chem. Scand.*, 1954, **8**, 1851.

65. Conant, J.B., Harshorn, E.B. and Richardson, G.O. *J. Am. Chem. Soc.*, 1920, **42**, 585.

66. Fuson, R.C., Price, C.C. Bauman, R.A.., Bullitt, O.H. Hatchard, W.R. and Maynert, E.W. *J. Org. Chem.*, 1946, **11**, 469.

67. Angeli, A. and Magnani. *Gazz. Chim. Ital.*, Part I, 1894, **24**, 342.

68. Bogdanowiz, S.K., Jamrosik, M. and Sledzcewska, E. *Bull. Acad. Pol. Sci. Ser. Sci. Chem.*, 1979, **27**, 257.

69. Kharasch, N. Potempa, S.J. and Wehrmeister, H.L. *Chem. Rev.*, 1946, **38**, 269.

70. Barker, R.H., Collman, J.P. and Marshall, R.L. *J. Org. Chem.*, 1964, **29**, 3216.

71 Howells, P.N., Kenney, J.W., Nelson, J.H. and Henry, R.A. *Inorg. Chem.*, 1976, **15**, 124.

72. Eckberg, R.P., Nelson, J.R., Kenney, J.W., and Henry, R.A. *Inorg. Chem.*, 1977, **16**, 3128.

73. Dryden, R.P. and Winston, A. *J. Phy. Chem.*, 1958, **62**, 635.

74. Nakamoato, K., McCarthy, P.J. and Martell, A.E. *J. Am. Chem. Soc.*, 1961, **83**, 1272.

75. Bose, K.S. Studies on copper(II) and nickel(II) complex of nitrogen donor ligands, Ph.D. Thesis, Indian Institute of Science, Bangalore, India, 1970.

76. Iyengar, R.R. Isonitroso-β-ketoimino nickel(II) complexes. A study in ambidentate coordination, Ph.D. Thesis, Indian Institute of Science, Bangalore, India, 1975.

77. Dixit, N.S. Reactions and structure of coordinated Schiff base complexes of nickel(II), copper(II) and palladium(II). A study in the linkage isomerism of the oximino group, Ph.D. Thesis, Indian Institute of Science, Bangalore, India, 1976.

78. Sudha, B.P. Synthesis, structure and reactions of palladium(II), nickel(II) and copper(II) complexes with some flexidentate ligands, Ph.D. Thesis, Indian Institute of Science, Bangalore, India, 1977.