CHAPTER I

INTRODUCTION

The interesting aspect in the chemistry of β-diketones is the ability of these compounds to exhibit tautometric equilibrium of keto and enol forms.

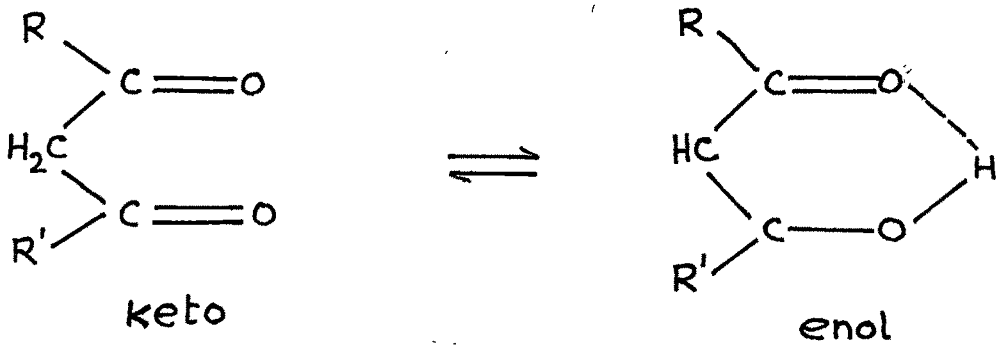
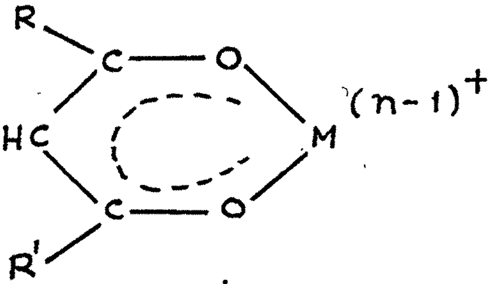


Fig.1

The β-diketones are weak acids and the proton on the third carbon atom can be lost easily to give the enolate anion. The enolate anion has a C_{2v} symmetry. The π molecular orbitals formed by the combination of P_z orbitals, over two oxygens and three non-terminal carbon atoms spread over the whole molecule. The nodal plane of these molecular orbitals lie in the plane of the chelate ring. Besides this the oxygen atoms have non bonding orbitals lying perpendicular to the above π molecular orbital in the plane of the chelate ring. The electrons get filled up in these molecular orbitals in the increasing order of energy.

The enolate ion is bidentate and coordinates with metal ions through two oxygen atoms to form a six membered ring.



complex

Fig.2

Since the enolate ion has one negative charge, the bis β-diketone chelates of bivalent metal ions are neutral inner complex salts. The chelating ability of acetylacetone was first observed by Werner[1] and since then large number of inorganic derivatives of β-diketones have been reported[2]. Morgan[3] in his review in 1914 cited the formation of thirty-nine β-diketone complexes. The interest in β-diketone chemistry continued and the literature on their complexes is now extensive. A number of reviews,[4-13] dealing with various aspects of this chemistry, have appeared in recent years. β-diketone complexes of all the non-metals, metals and even metalloids have been worked out. More than one hundred different types of β-diketones have been synthesised and their metal complexes have been studied.

In bis β-diketone chelates, the two ligands occupy four coordination positions around the metal ions. In cases of bigger metal ions the coordination number is higher and neutral groups like H_2O, NH_3, or pyridine can occupy fifth and sixth positions resulting in the formation of mixed ligand complexes. In such cases attempt to prepare the β-diketone complexes in aqueous solutions leads to the formation of dihydrate $[ML_2(H_2O)_2]$.

The study of the β-diketone complexes has invited the attention of the chemists because of the stability of the metal ligand bond.

In 1945 Calvin and Wilson[14] observed high formation constant values of Cu(II) complexes of β-diketone. This could not be explained only on the basis of the basicity of the ligands. According to them in these complexes a benzenoid resonance effect in the six membered chelate ring, contribute much to the stability of the complex. They suggested following two canonical forms. The chelate ring is supposed to resonate between the two structures -

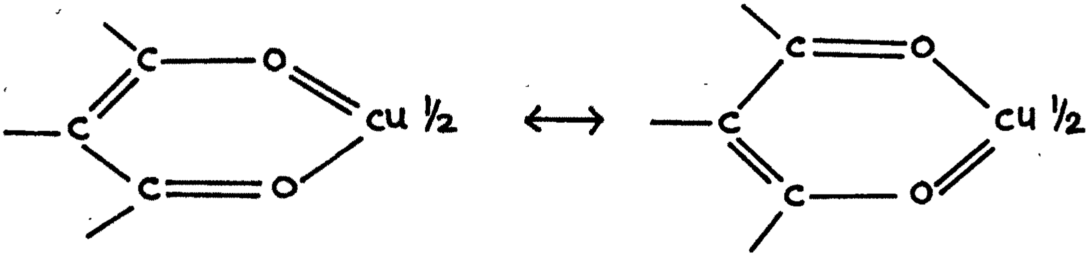


Fig.3

It was also observed that tris acetylacetonato Fe(III) can be distilled without decomposition. Roof[15] studied such chelates in detail and concluded that the individual chelate rings are planar and have C_{2v} symmetry. The pairs of M--O, C--O and C--C distances in each ring were found to be equal. The C--C distances in the rings measured 1.39 A°, thus being intermediate between single and double bond distances. The X-ray study of bis acetylacetonato Cu(II) has also shown that the C--C distance in the ring corresponds to nearly 1,40 Å.

The above studies support the resonating structures suggested by Calvin.[14] This explains the equalisation of the pairs of C--C, C--O and M--O distances. The two resonating six membered chelate ring structures are reminiscent of the two Kekule's forms of benzene structure. In terms of modern quantum mechanical concept it naturally implies that there is delocalisation of π electron clouds over the six membered chelate ring.

π-interaction in the metal ligand bond has been indicated earlier. The higher stability of metal carbonyl and metal cyanide complexes was attributed by Pauling to the back donation of electrons from $d\pi$ orbitals of metal to the vacant ligand $p\pi$ orbitals. The high stability of phosphine and arsine complexes of transition metals was explained by considering $M \longrightarrow L$ $d\pi$-$d\pi$ interaction. A more quantitative calculation has been afforded by the molecular orbital theory. In case of octahedral complexes with O_h symmetry, group theoratical calculations show that the ligand $p\pi$ or $d\pi$ orbitals form ligand group orbitals having T_1g, T_2g, T_1u and T_2u symmetry. They combine with the central metal atom orbitals with same symmetry to form π-bonding and π antibonding molecular orbitals. There are no metal atom orbitals having T_1g or T_2u symmetry. The orbitals with T_1u symmetry are P_x, P_y and P_z and those with T_2g symmetry are d_{xy}, d_{xz} and d_{yz}. Since P_x, P_y and P_z orbitals of the metal ions have been already used up in the formation of σ molecular orbitals, d_{xy}, d_{xz} and d_{yz} orbitals are available for π bonding. Thus the three $d\pi$ orbitals of the metal atom combine with the three ligand group orbitals of T_{2g} symmetry. (made of $p\pi$ or $d\pi$ ligand atom orbitals) to form the bonding and the antibonding molecular orbitals. The filling of electrons in these π bonding molecular orbitals enhances the stability of the complexes.

In case of metal-β-diketonate complexes, the metal $d\pi$ orbitals interact with the π molecular orbitals over the enolate ion; thus forming bonding and antibonding π molecular orbitals. The electrons present in the π bonding molecular orbitals are delocalised over the whole chelate ring. This accounts for the stability of the ring and the shortening and equality of the pair of bonds M--O, C--O and C--C.

Thus, this model of the acetylacetone complexes presumes ring currents in the six membered chelate ring and the delocalisation of metal $d\pi$ electrons on the ligand atom.

Holm and Cotton[16] were correct in stating that, "there is still relatively little concerning the electronic structures of acetylacetone complexes which may be stated with certainity". After making an extensive NMR investigation they concluded that their study does not support the postulate of benzenoid resonance in the chelate ring. The chemical shifts of the chelate ring protons are quite similar to that observed for olefinic protons. No shifts were observed in the region for aromatic or benzene type protons. However, it was pointed out by them that little is known about aromatic heterocycles containing more than one heteroatom.

Further according to Holm and Cotton, if metal to oxygen π bonding is to occur, it should be symbolised as $M \underset{\curvearrowright}{\overset{\curvearrowleft}{-}} O$; due to the fact that there are no vacant orbitals of π symmetry on the acetylacetonate ion. In several metal ions there are vacant $d\pi$ and $p\pi$ orbitals on the metal. Thus $O \longrightarrow M$ π interaction is much likely. In case of metal ions with no vacant $3d\pi$ orbitals $M \longrightarrow O$ π bonding seems impossible unless the $4d\pi$ orbitals of the metal ion is used. Thus, when considered in this light there is really no parallel between the π bonding which might occur in metal acetylacetonates and that believed to occur in cyanides, carbonyls and phosphine complexes in which the ligands have vacant $p\pi$ or $d\pi$ orbitals.

Although extensive $O\ p\pi \longrightarrow M\ p\pi$ (or $d\pi$) bonding does not appear to be likely, some mixing of $O\ p\pi$ and metal $p\pi$ and / or $d\pi$ orbitals will doubtless occur where permitted by symmetry and is likely to have some effect on the electronic structure and spectrum.

Forman, Murell and Orgel[17] have carried out the nuclear magnetic studies of tris acetylacetonato vanadyl(III) complexes. The complexes exhibit a lowering in the chemical shifts of the ring protons. This contact shifts has been attributed to the delocalisation of unpaired π electron density of the metal electrons over the ligand atom. The negative spin density of the electron over the third carbon atom produces a positive spin density over the proton. This brings a shielding effect and shifts the δ value.

Collman and coworkers[12,18-21] have indicated the presence of ring current in the β-diketone chelate ring on the basis of studies on Co(III) and Rh(III) mixed ligand chelates by PMR spectroscopy.

To start with the Rh(III) and Co(III) acetylacetonates were studied. Signals in the ratio of 1:6 were obtained. The first was due to the -CH= of each chelate ring and the other due to the two equivalent methyl groups. When the tris γ-substituted compounds were taken, the first peak (due to the -CH=) disappeared while the other was shifted to lower field. The extent of the shift was found to be dependent on the nature of the metal, the substituent and the solvent employed.[12]

When however, the mixed ligand complex was examined, (with two rings of one type [A] and one ring of a different type [B]) by PMR spectroscopy, the ring [B] exhibits one distinct signal indicating that the two methyl groups are equivalent. However, the [A] type rings show two distinct signals indicative of the fact that the two [A] type rings are in different environments. The different environments due to bonding within the individual rings, has been ruled out due to the fact that, on this basis the four methyl groups, of the two [A] rings are equivalent. According to the authors the molecular model of the complex indicates that the methyl group of one of the [A] rings may be directly above the differently substituted [B] ring thus bringing the [A] ring in a different environment. This shows that the π electrons in one chelate ring produces diamagnetic shielding on the adjacent methyl group on another ring. If the two methyl groups of an [A] type ring are adjacent to two differently substituted rings having π electron clouds of different densities, a different chemical shift is expected for the two methyl groups. Such effects are known in aromatic chemistry. Such effects in the present metal-β-diketonate complexes is an evidence for pseudo-aromatic character in the acetylacetonate ring. The methyl resonances of the compound shown below in CCl_4 are -

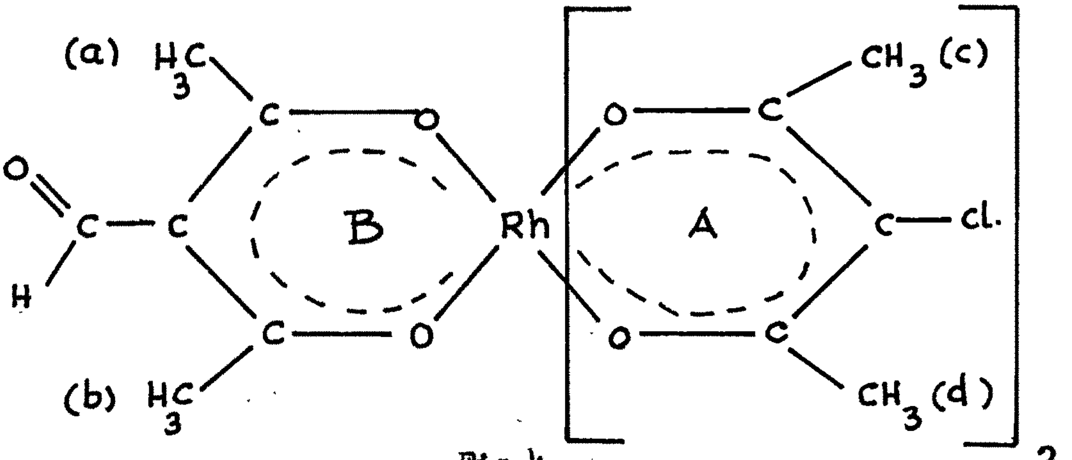


Fig. 4

$CH_3(a) = CH_3(b) = 7.38\,\tau$; $CH_3(c) = 7.59\,\tau$; $CH_3(d) = 7.56\,\tau$.

When all three rings are differently substituted, each of the six methyl groups shows its own signal.

Hester's[22] PMR study of tris acetylacetone silicon chloride is an additional evidence for pseudo aromaticity in acetylacetone. The resonances and assignments made by them are -

CH_3, 7.73 τ; -CH=, 3.74 τ; -2.73 τ (probably due to HCl_2^-) so the compound has been formulated as $[\mathrm{Si(acac)}_3^+]\,\mathrm{HCl}_2^-$. As observed the -CH= peak is at very low field compared to other diamagnetic acetylacetonates (4.46 - 4.75). The value is comparable with that of aromatic protons of order $\sim$2.65 - $\sim$2.85 τ. This is an indication of increased π delocalisation and thus an increase in its aromatic character. According to Hester such a situation arises due to the donation of the lone pair on the oxygens to empty t_{2g} orbitals on silicon. This partial double bond gives some aromatic character to the ring. Due to this there is a desheilding effect not only on the γ protons but also on the methyl groups.

However, as in other metal complexes, the extent of π interaction, in the M--L bond in β-diketone complexes has been questioned. Smith and Wilkins[23] extended an alternative explanation for the lower field shift of -CH= resonance in molecules such as $[\mathrm{Sn(acac)_2Cl_2}]$, $[\mathrm{B(acac)_2F_2}]$ and $[\mathrm{Si(acac)_3}][\mathrm{HCl_2}]$. According to the observation made by Fay and Serpone[24] it is not necessary to consider benzenoid resonance and π interaction between metal and β-diketone, to explain the contact shift in these cases. The shift in the τ values of the C--H protons can be satisfactorily explained by considering the first order (within the complex ion) and second order (between the cation and anion) electrical effects. Both will cause a shift to the low field. This explanation in the case of complexes of non-transition metal ions need not ruled out the possibility of contact shift in transition metal β-diketone due to the π delocalisation. Fay and Serpone[25] have themselves presented evidence of dπ-pπ interaction in case of Group IV transition metal acetylacetonato complexes.

The chemical evidences also support pseudo aromaticity in the metal β-diketonate complexes; by the reactions which these chelates undergo. Collman and coworkers[26,27] and Singh and Sahai[28-33] have carried out extensive investigations of the chemistry of acetylacetonate anion when complexed to a metal. They have found that the ring behaves similarly to aromatic compounds. The γ-proton on the chelate ring is very labile and can be replaced by several groups under electrophilic substitution reaction conditions - - Halogenation, thiocyanation, arylsulfenylation, chlorosulfenylation, nitration, Friedel Crafts acylation, formylation, chloromethylation and dimethylaminomethylation have been carried out. These studies unambiguously show that chemically speaking the chelate ring is aromatic.

The π interaction is, however, still an open question, as the extent of π interaction is not known. The position regarding this problem has been rightly summed up in the observation of Link and Sievers.[34] They have pointed out that the chemically aromatic behaviour of the β-diketonate chelate ring and its structural properties show that there may be significant amount of dπ-pπ interaction. However, due to the difference in nature of the atoms involved in the ring, the ring current may be reduced.

In order to confirm the extent of π interaction in metal β-diketones we have worked out the stability constants of metal-β-diketone complexes and in ternary complex where the primary ligand is dipyridyl, o-phenanthroline or other charged ions and secondary ligand are diketones. Mixed ligand complexes have also been isolated in the solid state in order to confirm the solution studies.

Nucleophilic and electrophilic substitution reactions have been attempted over the mixed ligand complexes, in order to study pseudoaromaticity of β-diketonates in the complexes.

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