Awarded Ph.D

STUDIES ON METAL CHELATES
OF
β-DICARBONYL COMPOUNDS

A THESIS SUBMITTED TO
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BY
N. THANKARAJAN M. Sc.
NATIONAL CHEMICAL LABORATORY, POONA.

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C O N T E N T S

PART I

GENERAL INTRODUCTION

GENERAL INTRODUCTION

Coordination compounds of acetylacetone were first reported by Werner[1] in 1901 and since then, the study of metal acetylacetonates has been vigorously pursued. Acetylacetonates of practically all metals (of and outside the transition series) and non-metals have been prepared[2,3] and have been largely instrumental in the development of coordination theory. In view of Werner's own writings[4] and other excellent reviews[5,6], no attempt is made here to trace the history of this development.

Esters, amides and anilides of β-ketoacids are capable of forming the same type of metal derivatives as the β-diketones; the term, β-dicarbonyl compounds embraces all. β-Dicarbonyl compounds exist in tautomeric equilibrium between a diketo-form and an enol-form[7], the latter having a resonating conjugated chelate structure[8,9] (Fig.1.1). Metal chelates[10] result when the chelated hydrogen of the enol is replaced by metal ions. If the coordination number of the metal atom is twice that of its oxidation state, the inner complex formed is a non-electrolyte[11] (Fig.1.2).

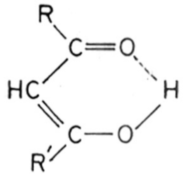


Fig. 1·1

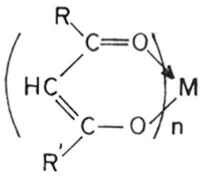


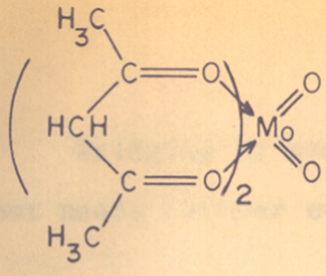
Fig. 1·2

n	M
1	Li, Na, etc
2	Be, Cu ,,
3	Al, La ,,
4	Zr, Th ,,

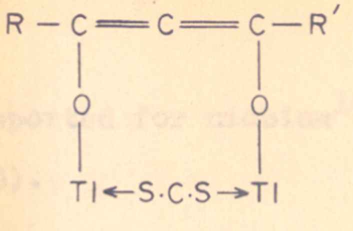
In the foregoing instances, the metal derivative is formed from the monoenolate anion of the ligand. Though this is the most important and the normal type, this is by no means the only way a β-dicarbonyl compound might attach itself to a metal atom. The following variety, in addition to the normal type, is observed.

Instance of a β-dicarbonyl compound acting as neutral ligand is reported[12] for molybdenyl (Fig.2.1). In part II of this thesis, two uranyl chelates of the normal type containing an excess molecule of the neutral ligand are reported.

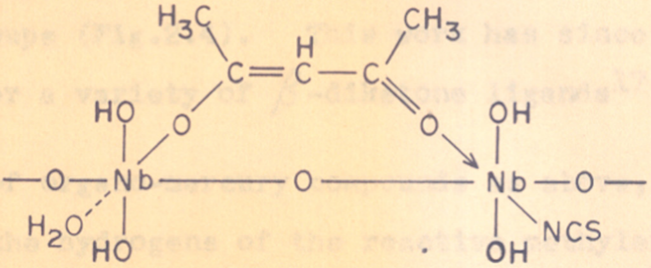
In the presence of carbon disulphide, β-dicarbonyl compounds attach to thallium as bridging dienolate anions[13] (Fig.2.2).



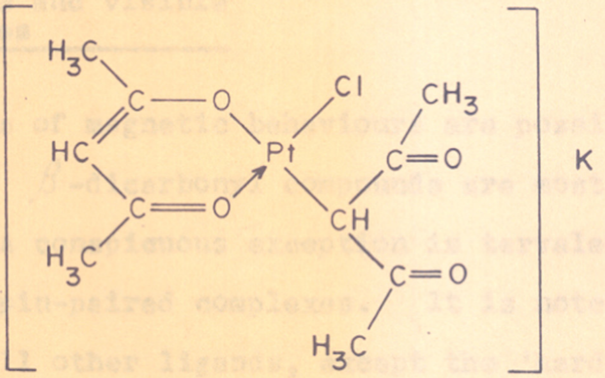
(Fig. 2·1)



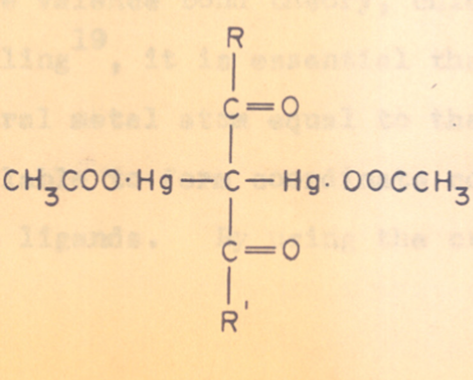
(Fig. 2·2)



(Fig. 2·3)



(Fig. 2·4)



(Fig. 2·5)

Bridging by mono-enolate ion is reported for niobium[14], but needs further confirmation (Fig.2.3).

Bivalent platinum forms an acetylacetone derivative[15,16] in which the metal is bonded to the carbon atom in between the carbonyl groups (Fig.2.4). This work has since been extended to cover a variety of β-diketone ligands[17,18].

Formation of organo-mercury compounds as above, but replacing both the hydrogens of the reactive methylene group of the ligands is reported in Part II of this thesis (Fig.2.5).

Magnetic properties and visible spectra of complexes

When two types of magnetic behaviours are possible, the metal complexes of β-dicarbonyl compounds are mostly of the high-spin type. A conspicuous exception is tervalent cobalt which forms only spin-paired complexes. It is noteworthy that practically all other ligands, except the 'hardest' base, fluoride ion, cause spin pairing of cobalt(III).

According to the valence bond theory, chiefly developed for complexes by Pauling[19], it is essential that a number of orbitals on the central metal atom equal to the number of ligands be made available to form coordinate covalent bonds with orbitals on the ligands. By using the criterion that maximum angular overlap of two orbitals forms the strongest covalent bond, it is shown that the original atomic orbital should be hybridized to form a new set of equivalent bond orbitals with definite directional properties.

Each hybrid orbital accepts a pair of electrons. However, a difference arises as to whether the d orbitals used for hybridization are of the same quantum number as the s and p or of the next lower principal quantum number. In the latter case, the d electrons of the metal are crowded into the remaining d orbitals resulting in reduction of spin. The two types have been termed as outer orbital and inner orbital complexes respectively by Taube[20].

The more electronegative atoms such as oxygen and fluorine favour outer orbital type of bonding, since they concentrate the bonding electrons about themselves. The higher d orbitals from the metal, having greater extension in space can still overlap appreciably in such a case. Ligands of low electronegativity such as phosphorus and arsenic will utilize the lower d orbitals more efficiently. Particularly, if -bonding can occur, there will be greater tendency to use the inner d orbitals and achieve a shorter and stronger bond.

Due to the relation between the type of hybridization and the magnetic spin, magnetic effects offer as a valuable guide to steric arrangements. Magnetic susceptibility measurements, however, fail to serve as a criterion for distinguishing between bond characters in the compounds of

the non-transition metals. Interpretation of the visible spectra of transition metal complexes is beyond the scope of this theory. For d^7 low-spin octahedral complexes and d^9 square planar complexes certain ad hoc reasoning becomes inevitable. For the former type, in order that there be only one unpaired electron, as required by the experimental magnetic moment, there must be spin pairing in three of the d orbitals. If the other two d orbitals are used in bonding, the seventh d electron must be promoted to a higher energy atomic orbital such as one of the 4d orbitals. This seems reasonable and is often cited as a reason that covalent cobalt(II) complexes are powerful reducing agents. However, this interpretation must be used again for copper(II) square planar complexes, which are not good reducing agents.
A difference arises, however, in that in copper(II) planar complexes (dsp^2 hybridization[19]), the np_z orbital is available for the promoted electron (nin~~e~~th d electron) to occupy.

According to the crystal field theory (Bethe[21], Schlapp and Penney[22], Van Vleck[23]), the five d orbitals which are degenerate and equal in energy in the gaseous metal ion, become differentiated in the presence of the electrostatic field due to ligands (the crystal field). Though originally applied to crystalline solids, it is equally applicable to any orderly arrangement of electrically interacting particles such as a single complex.

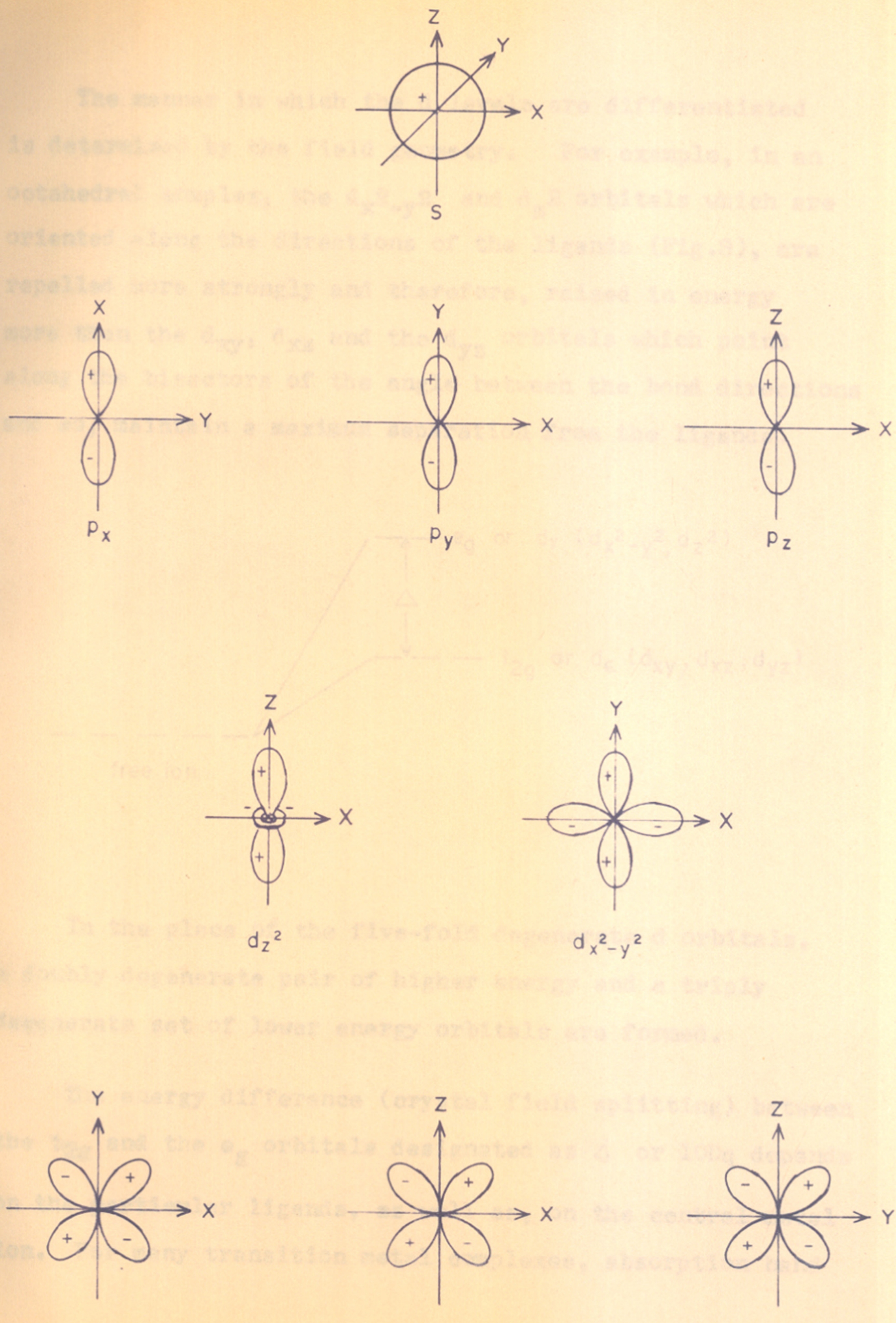
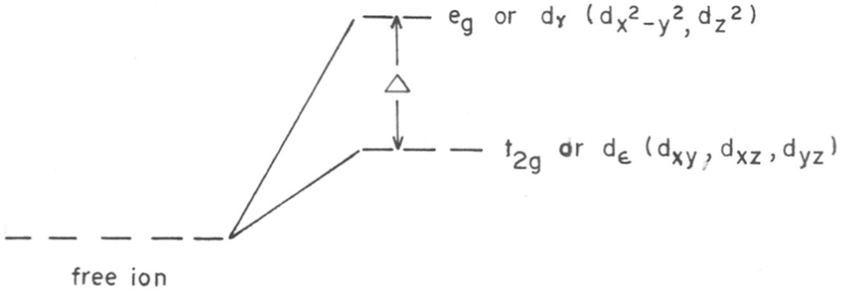


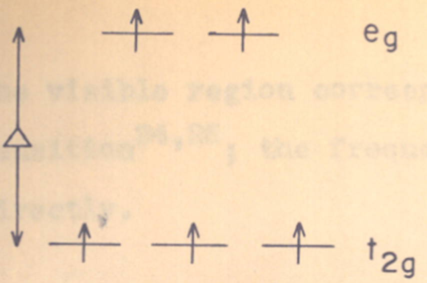
FIG. 3. s, p and d ORBITALS

The manner in which the d levels are differentiated is determined by the field geometry. For example, in an octahedral complex, the $d_{x^2-y^2}$ and d_{z^2} orbitals which are oriented along the directions of the ligands (Fig.3), are repelled more strongly and therefore, raised in energy more than the d_{xy}, d_{xz} and the d_{yz} orbitals which point along the bisectors of the angle between the bond directions and so, maintain a maximum separation from the ligands.



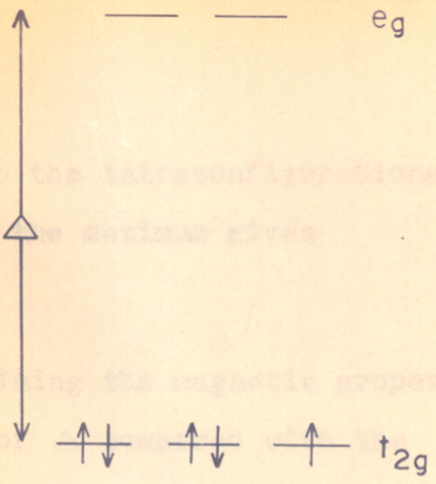
In the place of the five-fold degenerate d orbitals, a doubly degenerate pair of higher energy and a triply degenerate set of lower energy orbitals are formed.

The energy difference (crystal field splitting) between the t_{2g} and the e_g orbitals designated as Δ or 10Dq depends on the particular ligands, as well as, on the central metal ion. For many transition metal complexes, absorption band



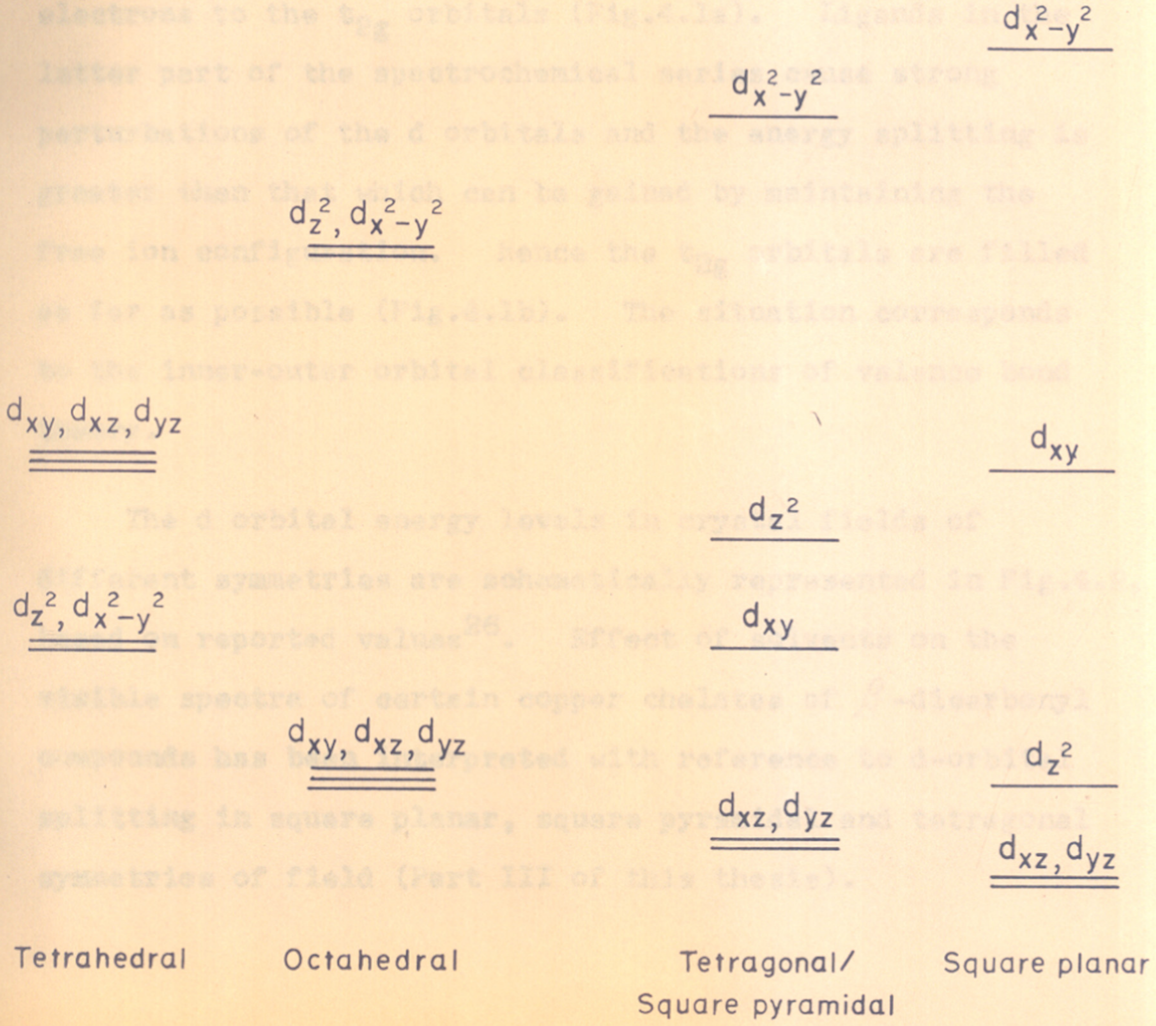
(Ferric acetylacetonate)

Fig·4·1a



(Ferricyanide)

Fig·4·1b



Fig·4·2

in the visible region corresponds to the intraconfigurational d transition[24,25]; the frequency at the maximum gives Δ directly.

The important factor in determining the magnetic properties of complexes is the magnitude of Δ compared with the energy required to pair the d electrons. Ligands in the beginning of the spectrochemical series give rise only to a weak field; the splitting is, therefore, small and the energy difference insufficient to restrict all of the d electrons to the t_{2g} orbitals (Fig.4.1a). Ligands in the latter part of the spectrochemical series cause strong perturbations of the d orbitals and the energy splitting is greater than that which can be gained by maintaining the free ion configuration. Hence the t_{2g} orbitals are filled as far as possible (Fig.4.1b). The situation corresponds to the inner-outer orbital classifications of valence bond theory.

The d orbital energy levels in crystal fields of different symmetries are schematically represented in Fig.4.2, based on reported values[26]. Effect of solvents on the visible spectra of certain copper chelates of β-dicarbonyl compounds has been interpreted with reference to d-orbital splitting in square planar, square pyramidal and tetragonal symmetries of field (Part III of this thesis).

According to the ligand field* and molecular orbital[28] theories the atomic orbitals of the ligands can be combined together in various ways, so as to give orbitals for the whole ligand array of various symmetries. Thus, in the regular octahedral complexes, where the ligands define a cartesian coordinate system, the six ligand orbitals may be combined together to form symmetry orbitals, of which one is totally symmetric and interacts with the 4s orbital of the metal, three have a single nodal plane and interact with the three 4p metal orbitals and two interact with the $3dz^2$ and $3d_{x^2-y^2}$ orbitals respectively. Each interaction between a symmetry orbital of the ligands and an atomic orbital of the metal gives rise to a bonding orbital more stable than either, concentrated primarily on the ligand and an antibonding orbital, less stable than either and concentrated mainly on the metal. The $3d_{xy}$, $3d_{yz}$ and $3d_{xz}$ orbitals, usually, have no counterparts on the ligands and contribute nothing to the bonding (non-bonding orbitals). The resulting energy bands are schematically represented in Fig.5.1.

To complete the picture, electrons must be placed in these orbitals in the order of increasing energy, in accordance with Hund's rule for degenerate orbitals. The twelve electrons from the ligands are paired in the six

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* Ligand field theory is a hybrid approach to Bethe's crystal field theory and Mulliken's molecular orbital theory[27].

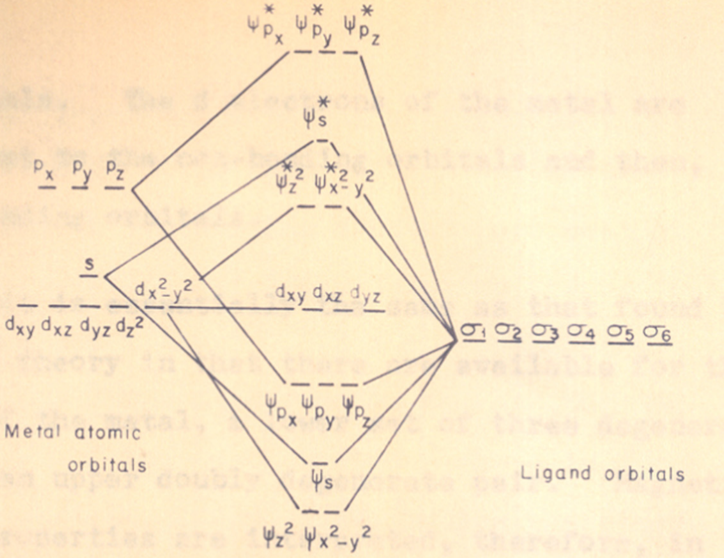


Fig. 5·1 Molecular Orbitals of an Octahedral complex

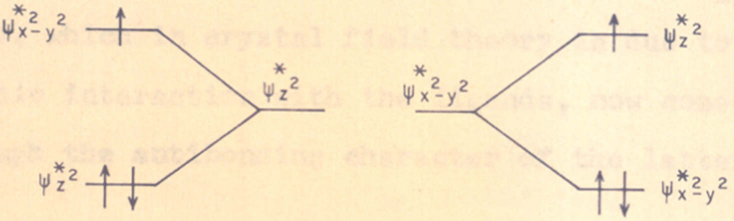


Fig.5·2a

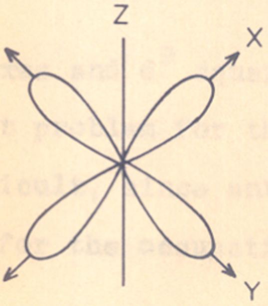


Fig.5·2b

Jahn-Teller Distortion

bonding orbitals. The d electrons of the metal are relegated first to the non-bonding orbitals and then, to the antibonding orbitals.

The result is essentially the same as that found by crystal field theory in that there are available for the d electrons of the metal, a lower set of three degenerate orbitals and an upper doubly degenerate pair. Magnetic and optical properties are interpreted, therefore, in exactly the same way as with crystal field theory, except that now, the optical transition is from an atomic d orbital to an antibonding molecular orbital rather than to another atomic orbital. The splitting of the t_{2g} and e_g orbitals, which in crystal field theory is due to the electrostatic interaction with the ligands, now comes about through the antibonding character of the latter orbital.

Similar conclusions can be reached about square planar and tetrahedral complexes.

The d^7 low spin octahedral complexes and d^9 square planar complexes which pose a difficult problem for the valence bond theory are no longer difficult, since antibonding orbitals are always available for the occupation of the promoted electron.

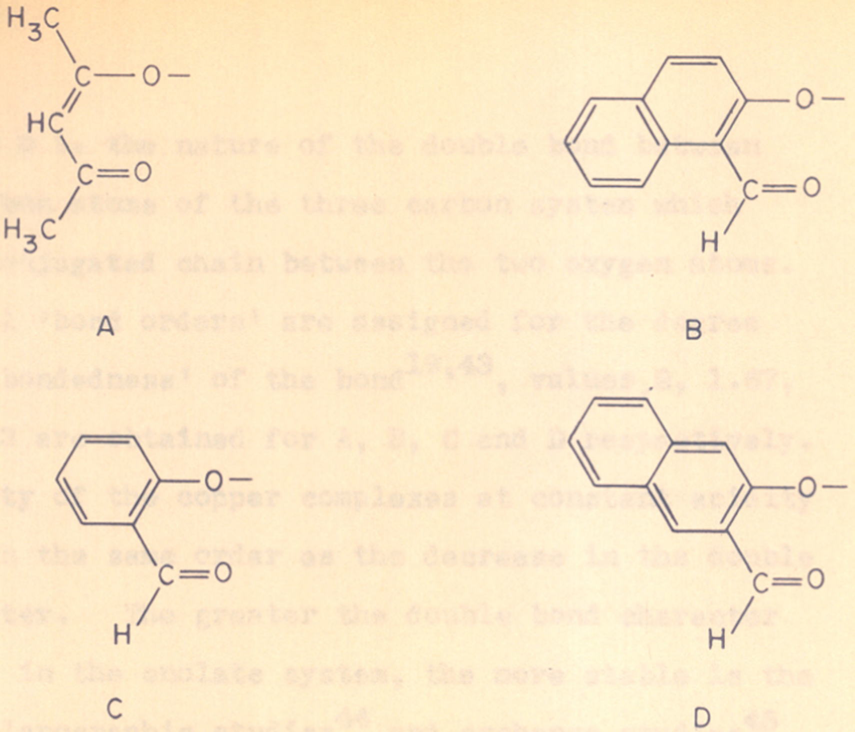
Octahedral complexes with the configuration d^9, d^7 (low spin) and d^4 (high spin) having an odd number of electrons in the antibonding orbitals are subject to a further complication, first predicted on theoretical grounds by Jahn and Teller[29]. For a d^9 octahedral complex which has three electrons in the antibonding orbitals, either of the configurations shown in Fig.5.2a and 5.2b are possible. The first implies that there is more antibonding in the z direction than in the x and y directions, while the second implies the reverse. Since more antibonding character in a particular bond corresponds to a weaker and, therefore, longer bond, it follows that the first configuration would lead to a distortion of the octahedral shape by extension in the z direction, while for the second, a similar distortion would result in the x and y directions. Experimental data favour the former[30]. For 1:2 adducts formed by certain β-dicarbonyl chelates of copper, with pyridine, a distorted octahedral structure (tetragonal) is therefore invoked for explaining the visible spectra (Part III).

Stability

Thermal stability of certain metal derivatives of β-dicarbonyl compounds is exceptionally high; many of the acetylacetonate derivatives can be distilled without decomposition at temperatures, over even 300°C, which led Morgan[10] to remark that acetylacetone has given wings to the metals. Various attempts made till 1953 to interpret the stability of complexes in general, have been summarized by Irwing and Williams[31]. Attempts to draw broad generalizations regarding solvolytic and thermal stability of metal acetylacetonates were not very rewarding[32-34].

General consideration of stability of metal chelates[5,31,35,36] will not be attempted, nor the theory and measurement of stability constants[37-39] will be described. Instead, certain observations which have direct bearing on metal derivatives of β-dicarbonyl compounds will be made.

Stable chelate rings involving two double bonds are usually six-membered structures[40], as are formed by β-dicarbonyl compounds. Calvin and Wilson[41], using the method of Bjerrum[42], found a straight line relationship between the basic strength of enolate β-diketones and the stability of copper(II) complexes. Their work, also, indicated the necessity for subdividing the ligands into similar groups, in order to establish a correlation (Fig.6.1). The most important difference in the structures



A B C D

Fig. 6·1

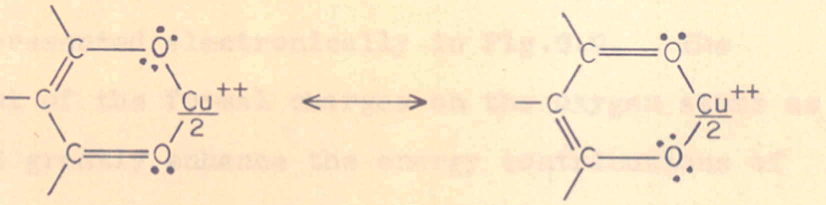


Fig. 6·2

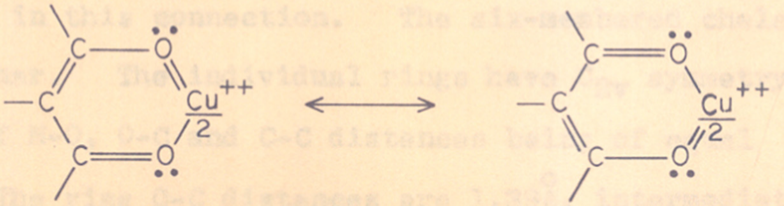


Fig. 6·3

A, B, C and D is the nature of the double bond between the two carbon atoms of the three carbon system which forms the conjugated chain between the two oxygen atoms. If numerical 'bond orders' are assigned for the degree of 'double bondedness' of the bond[19,43], values, 2, 1.67, 1.5 and 1.33 are obtained for A, B, C and D respectively. The stability of the copper complexes at constant acidity decreases in the same order as the decrease in the double bond character. The greater the double bond character of the bond in the enolate system, the more stable is the complex; polarographic studies[44] and exchange studies[45] lend support to this conclusion.

Accepting resonance as a major factor in the stability of chelates, Calvin suggested two possible structures. The first is represented electronically in Fig.6.2. The rearrangement of the formal charges on the oxygen atoms as shown, would greatly enhance the energy contributions of the enolate resonance.

Roof[46] established the interatomic distances of ferric acetylacetonate and made the following conclusions which are of interest in this connection. The six-membered chelate ring is planar. The individual rings have C_{2v} symmetry, the pairs of M-O, O-C and C-C distances being of equal lengths. The ring C-C distances are 1.39Å, intermediate between single and double bond distances (and also equal to the C-C distance in benzene) and the C-O distances are 1.28Å, also intermediate between single and double bond distances. These structural data should force one to conclude on the existence of resonance in the chelate rings. Several other investigations also led to the same conclusions[47-52]. Resonance equalization of bond orders in the acetylacetonate skeleton of metal chelates has been, therefore, the subject of several infrared spectral studies[53-57].

In the second structure (Fig.6.3), Calvin represented the chelate ring as a fully conjugated six-membered ring analogous to benzene, pyridine and pyrilium salts. McGarvey from his studies on paramagnetic resonance[58] and electron spin resonance[59] in copper acetylacetonate, arrived at the conclusion that π-bonding is involved. Barnum[60] and Basu and Chatterjee[61] on the basis of electronic spectra of certain metal β-dicarbonyl chelates also arrived at the same conclusion. Findings of proton magnetic resonance studies of Holm and Cotton[62] are compatible with either of the representations. Collman *et.al.*[63], however, support the fully conjugated structure from their similar studies on unsymmetrically substituted metal acetylacetonates. From studies of infrared spectra of acetylacetonates of bivalent metals, Nakamoto et.al.[56] suggested that in strong chelates, π -electrons as well as d electrons of the metal might tend to be more or less delocalized in the whole chelate ring. Grittes and Patmore[64], who studied some free radical reactions in metal acetylacetonates, found the back-donation of electrons from the metal to the organic ligand very important in determining the relative reactivities.

Concept of a fully conjugated structure, however, is against the electrical neutrality principle. An electron balance shows[5] that the electron pair used to form the metal oxygen double bond came from the oxygen rather than from the metal ion. Such a double bond[62] would aggravate the formal negative charge already on the metal atom. Another consequence of this electron shift towards the metal would be a decrease in electron charge on the remainder of the ring and a reduced tendency towards electrophilic substitution. However, this is not what is observed[65] (electrophilic substitutions are referred to in a later section).

To assume that the copper(II) ion behaves in a normal fashion and uses d electrons to form a double bond with the oxygen is equally distasteful, since oxygen has no low level orbital which would permit it to serve as an acceptor without destroying the conjugated double bond system in other parts of the ring[66].

The precise nature of the bonding in these chelates continues to be the subject of considerable controversy. Although extensive $O_{p\pi} \rightarrow M_{p\pi}$ (or $d\pi$) bonding does not appear to be likely, some mixing of the O_p and metal $p\pi$ and/or $d\pi$ orbitals will occur when permitted by symmetry. The two structures given by Calvin are, therefore, considered as representing the two extremes for the structure of metal chelates of β-dicarbonyl compounds.

Any interference with the chelate resonance is detrimental to the chelate stability. The poor stability of copper chelates of ethylacetoacetate and benzoylacetone was interpreted by Calvin as due to cross conjugation of the ester group resonance in the first and phenyl resonance in the other. Stabilities of copper chelates of β-ketoamide and β-ketoanilides were, therefore, determined to examine the effect of interference by amide resonance (Part III of this thesis).

Factors, other than chelate resonance, which should be of importance in the stability of metal β-dicarbonyl chelates are the basic strength of oxygen donor atom and steric considerations[41]. There will be occasion to refer to these effects in the section that follows.

Reactivity of metal chelates of β-dicarbonyl compounds

Metal complex formation is generally attended with changes - sometimes drastic and dramatic - both on the central atom and on the organic moiety.

A well known effect, which is of considerable practical significance, is the stabilization of certain unusual oxidation states of the metal atom in the proximity of suitable ligands[67]. The most important factor involved in these stabilizations is the formation of π-type molecular orbitals between the metal and ligand atoms[68]. When the ligand orbitals happen to be of low energy and vacant, the bonding π-type molecular orbitals can contain the electrons from the d orbitals of the metal and those which are added during the reduction of the complex. This leads to stabilization of low valent states of the metal atom. On the other hand, if the ligand orbitals are filled, they provide enough electron to fill the π-type molecular orbitals, and the metal electrons are forced into higher energy antibonding orbitals from where the same may be readily removed by oxidation. Higher valent states are stabilized in this way.

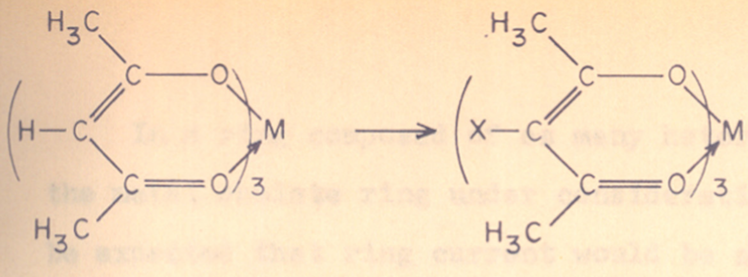
One of the best characterized non-electrolytic compounds of manganese(III) is its acetylacetonate, which affords the most indisputable evidence of tervalent manganese[69]. Manganese(III) acetylacetonate was, therefore, used for the preparation of the corresponding EDTA - chelate by ligand exchange (Part II).

Effect of the metal ion on the reactivity of coordinated ligand[70,71] may be catalytic[72], when it may assist the bond making and/or the bond breaking reaction steps. It may be a metal template reaction[70], wherein neighbouring group effect is exploited; the metal atom may hold reactive groups in juxtaposition so that complicated multi-step reactions may occur in a sterically highly selective manner. In yet other cases, the metal ions might cause the electrons of the organic chelating agent to be redistributed causing at times stabilization of organic molecules which are otherwise unstable; in a conjugated system the mobility of the π-electrons and hence the reactivity at some point in the chelate ring itself, may be altered as in the case of metal chelates of β-dicarbonyl compounds.

Under electrophilic conditions, a number of substitutions which are typical aromatic reactions[73], have been reported to take place in chelated β-dicarbonyl compounds, particularly in the most stable chelates like acetylacetonates of chromium(III), cobalt(III) and rhodium(III) (Fig.7.1). Four comprehensive reviews, which appeared recently[6,70,74,75] on this theme, make any detailed account unnecessary.

Tendency to undergo substitution reactions with a number of reagents that ordinarily simply add across the double bond, is a reflection of extra stability associated with aromatic systems, for, in addition reactions, these systems are destroyed, whereas in substitution reactions, they are preserved. On this basis, "metalloheterocycles" of the type formed by β-dicarbonyl compounds have been termed as aromatic[76].

The recent use as the criterion of aromatic structure, of the presence of a cyclic conjugated π-electron system capable of conducting an induced ring current[77,78] invites examination of the aptness of the term "aromatic" to β-dicarbonyl chelates.



X = I, Br, Cl, SCN, SAr, SCl, NO_2, CH_2Cl, COR, CHO.

M = Co^{III}, Cr^{III} and Rh^{III}

Fig.7.1

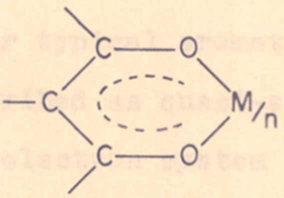


Fig.7.2

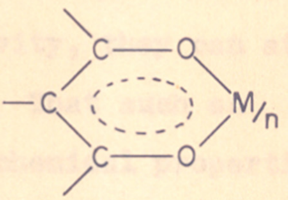


Fig.7.3

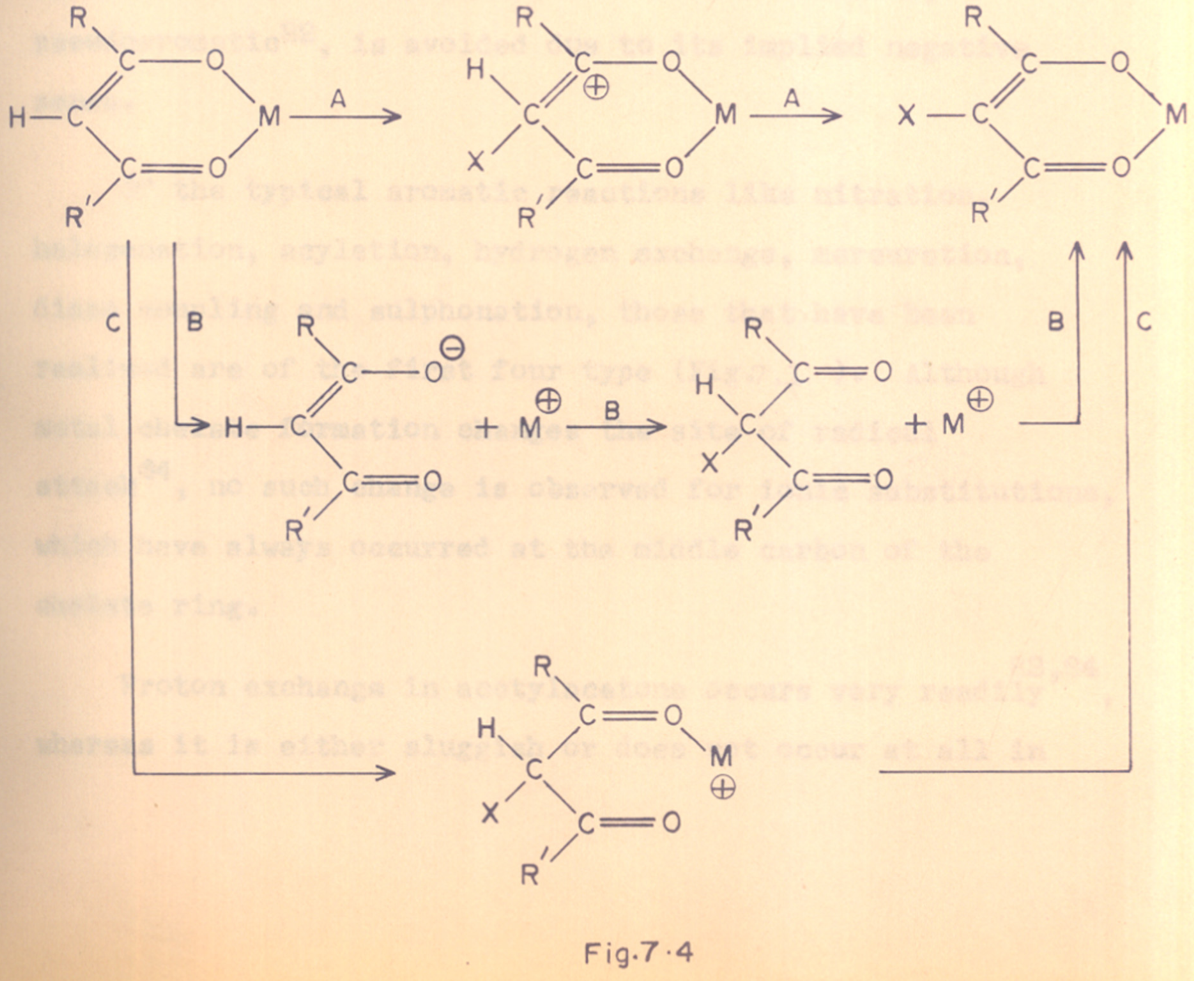


Fig.7.4

In a ring composed of as many heteroatoms as in the metal chelate ring under consideration, it is to be expected that ring current would be small[79]. If the π-electron system is cyclic as in Fig.7.3 these compounds can properly be called "aromatic". If, however, it is acyclic as in Fig.7.2, they are not aromatic and in view of their typical aromatic reactivity, they can at best be described as quasi-aromatic. That such an acyclic π-electron system can have chemical properties similar to those of aromatic compounds is shown independently by the chemistry of the isoelectronic 2,3-dihydro-1,4-diazepine systems[80,81]. The term, pseudoaromatic[82], is avoided due to its implied negative sense.

Of the typical aromatic reactions like nitration, halogenation, acylation, hydrogen exchange, mercuration, diazo coupling and sulphonation, those that have been realized are of the first four type (Fig.7.1). Although metal chelate formation changes the site of radical attack[64], no such change is observed for ionic substitutions, which have always occurred at the middle carbon of the chelate ring.

Proton exchange in acetylacetone occurs very readily[83,84], whereas it is either sluggish or does not occur at all in metal acetylacetonates[85,86]. Ketene does not react with acetylacetonates, although it forms triacetylmethane readily with the ligand[87]. Certain acylation reactions become progressively difficult so that complete substitution is often unattainable. Collman explains this as due to intramolecular interannular electronic deactivation[74] by the substituent group. Kluiber, by means of a competitive bromination of acetylacetone and the chromium chelate, showed that their rates of bromination are comparable[65]. Thus in many cases, substitution in the metal chelate does not offer any greater advantage over effecting substitution in the ligand and then obtaining the substituted metal chelate (aqueous instability of some of the substituted ligands might lead to synthetic difficulties).

Nitration of metal acetylacetonates is, however, most interesting, since 3-nitroacetylacetone does not exist and can be obtained only as the metal stabilized form[88]. Nitro substitution was, therefore, given major attention in this investigation (Part II), though other substitutions were also studied.

As a logical sequel, possibilities of mercuration, sulphonation and diazocoupling in metal β-dicarbonyl compounds have also been examined. Though mercuration occurred the products did not contain the original metal atoms (Part II). Diazo coupling did not occur with any of the metal chelates examined. Attempts to sulphonate resulted in complete damage of the metal chelates.

Difference in the rates of reaction of the ligand and of the metal chelate may in part be due to the difference in the reaction mechanism itself. In the metal chelate, the reaction may occur when the ring is intact, or when it is dissociated from the metal atom or when it is partly open (Fig.7.4 A, B and C respectively).

The bromination of chromium acetylacetonate has been shown to take place without ring cleavage by means of tracer studies with C^{14} labelled acetylacetone[65]. The observation that substitution in acetylacetonates of cobalt(III), chromium(III) and rhodium(III) did not cause total racemization[89], is against the concept of ring opening during substitution. This leads to the inference that the kinetically active species is the closed metal chelate ring itself. However, the formation of copper nitroacetylacetonate when copper nitrate is used for nitrating beryllium and aluminium acetylacetonates, as found in the present investigation (Part II), shows that the above need not always be the case, at least for labile metal chelates.

In all these substitution reactions the leaving group is the proton. A circumstance that favours electrophilic substitution is that the attacking electrophile may form a new bond before the old one breaks and the energy that becomes available when the new bond forms, may be used to bring about the breakage of the old bond.

Electrophilic substitutions do not occur in all metal β-dicarbonyl chelates. For instance, bromination does not occur in chromium chelates of trifluoro- and hexafluoroacetylacetone[74]. This, in part, can be due to the electron withdrawing CF_3 group, depleting electron density at the reaction site. Another aspect that also must be considered, is the effect of pendant groups of the ring on the basicity of the bonding oxygen atoms - more the basicity, stronger the chelate. Electron withdrawing groups will decrease the basicity and, hence, impair the stability of the metal chelate.

The complex, bis-(ethylenediamine)-2,4-pentanedionocobalt(III) cation also cannot be brominated[74]. Here, one of the reasons might be distraction of the course of the electrophilic substituent by the anions of the complex. In the case of chelates formed by β-ketoamides, the pendant nucleophilic group can also interfere likewise, which is probably why substitutions do not occur in these chelates. With metal chelates of ethylacetoacetate, even under very mild conditions, nitration and bromination, were always attended by breakage of the metal oxygen bond and formation of the substituted ligand. This may be expected, since these chelates, which have low stability, should become further weak when electron withdrawing groups, which lower the basicity of the bonding oxygen atoms, are introduced into the ring.

Steric considerations are important. Chelate rings with bulky pendant groups, such as phenyl, are not nitrated, since these shield the reaction site from attack by electrophilic reagents[75]. Another effect is forced structures which deviate from planarity, resulting from steric over-crowding. These deviations will affect resonance and hence stability of the substituted product[41,44,90].

The substituted metal acetylacetonates are surprisingly inert. Attempted reactions of the group have met with only sporadic success. Shielding by the flanking methyl groups might be a major contributing factor towards this inertness. The 3-bromoacetylacetonate of chromium did not react with magnesium or lithium in benzene or tetrahydrofuran, nor did any replacement of the bromine atom in the chelate by azide, acetate, nitrate or iodide occur[91]. The only reaction that has been successfully carried out with halogenated compounds is the catalytic reduction with hydrogen to the metal acetylacetonate.

Many attempts to reduce nitro groups by the use of conventional chemical reducing agents, gave anomalous results[88,92]. However, hydrogenation of 'mononitrochromium acetylacetonate' in ethanol over palladium hydroxide catalyst gave the 3-amino chelate which was subsequently diazotized[92,93]. This has been a much-wanted reaction, since the ability to stabilize a diazo group is one of the classic tests for the aromaticity of a compound.

PART II

REACTIVITY OF METAL CHELATES OF β-DICARBONYL COMPOUNDS

REACTIVITY OF METAL CHELATES
OF
β-DICARBONYL COMPOUNDS

An extensive field is encompassed by the term 'reactivity of metal chelates of β-dicarbonyl compounds'. In the present context, it refers to susceptibility of the metal chelates to electrophilic substitution (Chapters 1, 2, 3 and 4), residual affinity of metal atom in metal chelates (Chapter 5) and replaceability of the ligands (Chapter 6).

CHAPTER 1

NITRATION OF METAL ACETYLACETONATES

NITRATION OF
METAL ACETYLACETONATES

Most of the substitution studies in metal acetylacetonates have been confined to robust chelates. In addition to those of transition metal chelates, acetylacetonates* of beryllium(II) and aluminium(III) have been chosen for study in this investigation since the latter two acetylacetonates have excellent solubility behaviour, apart from moderate stability. Furthermore, these diamagnetic compounds are amenable to proton magnetic resonance spectral analysis.

Nitration of metal acetylacetonates cannot be carried out by the familiar nitric-sulphuric acid mixture, since the complexes are rapidly decomposed in it. The most successful nitrating agent[1-3] reported for metal acetylacetonates is a mixture of copper nitrate trihydrate and acetic anhydride. This nitrating agent has been found to be of general applicability to robust acetylacetonates. In the present investigation, however, the method was found to yield copper nitroacetylacetonate when used for the nitration of labile acetylacetonates of aluminium and

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* 2,4-pentanedionates.

beryllium. This prompted the need to look for other nitrating agents.

Two new nitrating agents, aluminium nitrate in acetic anhydride and concentrated nitric acid in acetic anhydride, have been introduced in the course of this investigation as nitrating agents of general applicability.

Aluminium nitrate and nitric acid as nitrating agents for metal acetylacetonates

A metal nitrate which showed great promise as a nitrating agent for metal acetylacetonates is aluminium nitrate, $Al(NO_3)_3.9H_2O$. Conditions have been standardized for using it as a nitrating agent for robust and labile chelates alike. Metal acetylacetonates nitrated, using this nitrating agent in cold acetic anhydride are of cobalt(III), chromium(III), copper(II) and beryllium(II).

An interesting nitration brought about by this reagent has been in the preparation of the nitroacetylacetonate* of aluminium in a single step. Acetylacetone and aluminium nitrate reacted in acetic anhydride yielding the aluminium

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* 3-nitro-2,4-pentanedionate.

nitroacetylacetonate. This elegant preparation obviates the need to prepare aluminium acetylacetonate as an intermediate in the preparation of aluminium nitroacetylacetonate.

Under carefully controlled conditions, nitric acid in acetic anhydride proved to be even better a nitrating agent than aluminium nitrate in acetic anhydride. All the nitrations achieved with aluminium nitrate - acetic anhydride mixture, were accomplished in greater yield with the nitric acid - acetic anhydride mixture.

The nitration brought about by nitric acid, particularly in the labile acetylacetonates is very encouraging, since it shows that even drastic reagents can be used for carrying out reactions in metal chelates, provided, of course, the right conditions are found and adopted.

The following table is illustrative of the comparative merits of the two nitrating agents. The yields reported are of purified materials. Robust chelates could be purified by chromatography on acid-washed alumina[4]. The labile chelates, particularly the aluminium compound was found to leave a streak on its way down the column, showing partial decomposition. A chromatographic adsorbent found suitable for the purification of the aluminium compound is polycaprolactam powder[5] (commercial nylon-6 beads, treated with hydrochloric acid at room temperature, washed, dried and pulverized to 100-200 mesh. Thin layer chromatography on calcium sulphate was used to examine homogeneity of the products.

Nitroacetyl-acetonate of	Method of preparation	Yield %
Aluminium(III)	$Al(NO_3)_3$ + Ac_2O + acetylacetone	50
	$Al(acac)_3$ + Ac_2O + HNO_3	57
Chromium(III)	$Cr(acac)_3$ + Ac_2O + $Al(NO_3)_3$	25
	$Cr(acac)_3$ + Ac_2O + HNO_3	25
Cobalt(III)	$Co(acac)_3$ + Ac_2O + $Al(NO_3)_3$	43
	$Co(acac)_3$ + Ac_2O + HNO_3	47
Beryllium(II)	$Be(acac)_2$ + Ac_2O + $Al(NO_3)_3$	46
	$Be(acac)_2$ + Ac_2O + HNO_3	65
Copper(II)	$Cu(acac)_2$ + Ac_2O + $Al(NO_3)_3$	50
	$Cu(acac)_2$ + Ac_2O + HNO_3	53
	$Cu(NO_3)_2$ + Ac_2O + $Be(acac)_2$	45
	$Cu(NO_3)_2$ + Ac_2O + $Al(acac)_3$	53

acac = $C_5H_7O_2$, acetylacetonate anion.

Ac_2O = acetic anhydride.

From vapour pressure measurements in the nitric acid-acetic anhydride systems, Vandoni and Viala[6] concluded that for solutions containing low percentage of nitric acid, most of the acid is converted to acetyl nitrate.

$$Ac_2O + HNO_3 \rightleftharpoons AcO.NO_2 + AcOH$$

At higher concentrations of the acid, appreciable amounts of dinitrogen pentoxide are formed

$$Ac_2O + 2HNO_3 \rightleftharpoons N_2O_5 + 2AcOH$$

Considerable evidence from Raman spectra[7], vapour pressure measurements[8] and infrared spectra[9] support the conclusions of Vandoni and Viala.

Under conditions of the chelate nitration, acetyl nitrate

$$CH_3COONO_2 \rightleftharpoons CH_3COO^- + NO_2^+$$

is, therefore, considered responsible for the nitro-substitution. The greater efficiency of nitric acid-acetic anhydride mixture over that of aluminium nitrate-acetic anhydride, is probably due to the greater facility of formation of acetyl nitrate from the acid than from aluminium nitrate.

Infrared spectral evidences have been very useful in characterizing the nitration products. Metal acetylacetonates absorb strongly in the 1500-1600 cm^{-1} region and a doublet is usually observed. A very useful observation[10] has been that in metal acetylacetonates substituted at the third carbon atom, the lower frequency band is conspicuously absent, unless the substituent absorbs in this region. The disappearance of the lower frequency band has been ascribed to mass effect of the substituent[10].

A medium intensity band at 1200 cm^{-1} is observed in the parent acetylacetonates. From deuteration studies this band has been assigned to γ-CH vibration[11]. In the 3-substituted acetylacetonates this band does not occur indicating the entry of the group in this position[11]. Other changes do occur but are of less significance. The above-mentioned changes in the spectra, and the occurrence of bands characteristic of the substituent can be taken as evidence of substitution in metal acetylacetonates.

In all the nitroacetylacetonates, the 1500-1600 cm^{-1} region of the spectra, showed two strong absorptions. The lower 1520 cm^{-1} band is attributable to the assymetric nitro stretching frequency[2]. A characteristic feature of the spectra is the appearance of a strong peak around 825 cm^{-1}, which is presumed to be a nitrogen-oxygen mode[2]. The 1200 cm^{-1} region, as expected, did not show any absorption. Infrared spectra of aluminium acetylacetonate and aluminium nitroacetylacetonate are shown in Figs.8 and 9

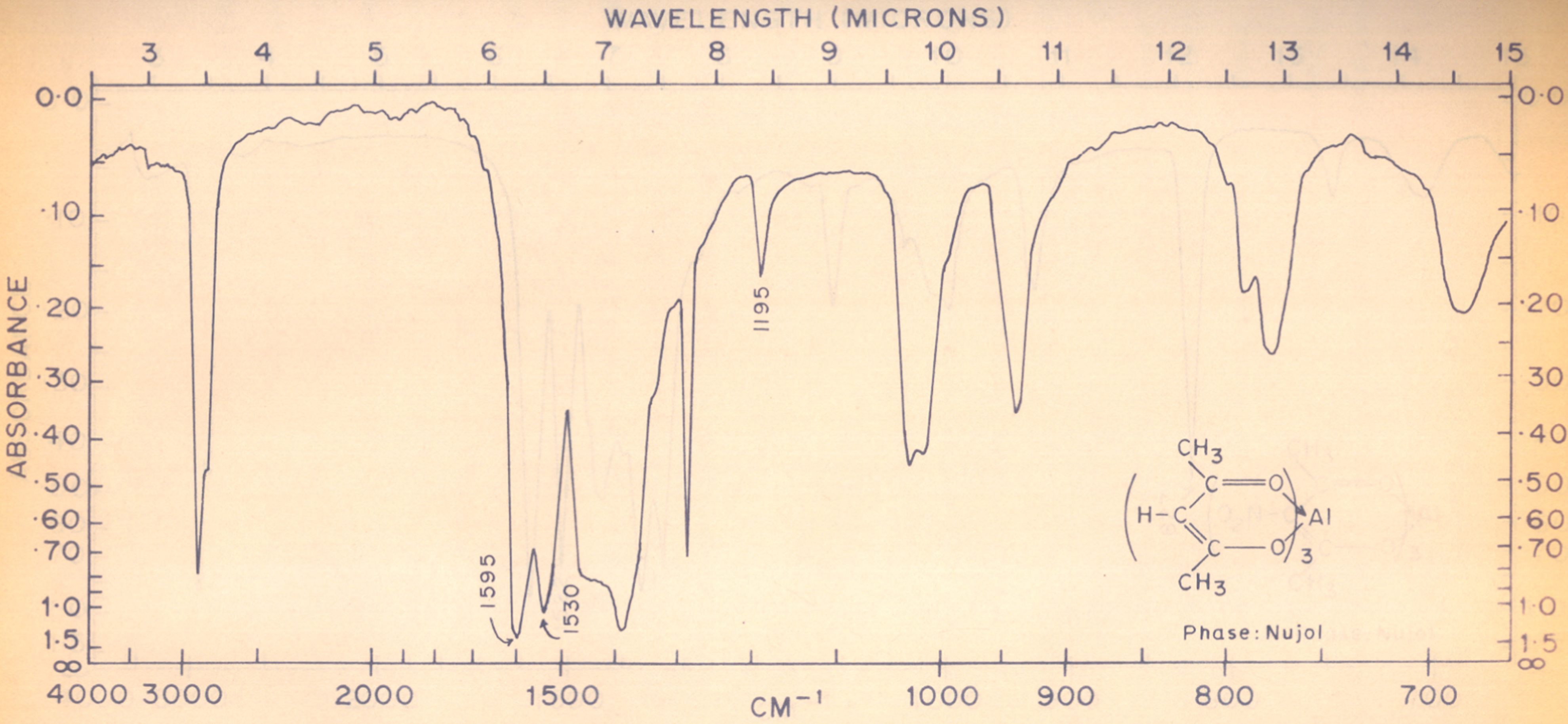

Fig. 8. IR Spectrum

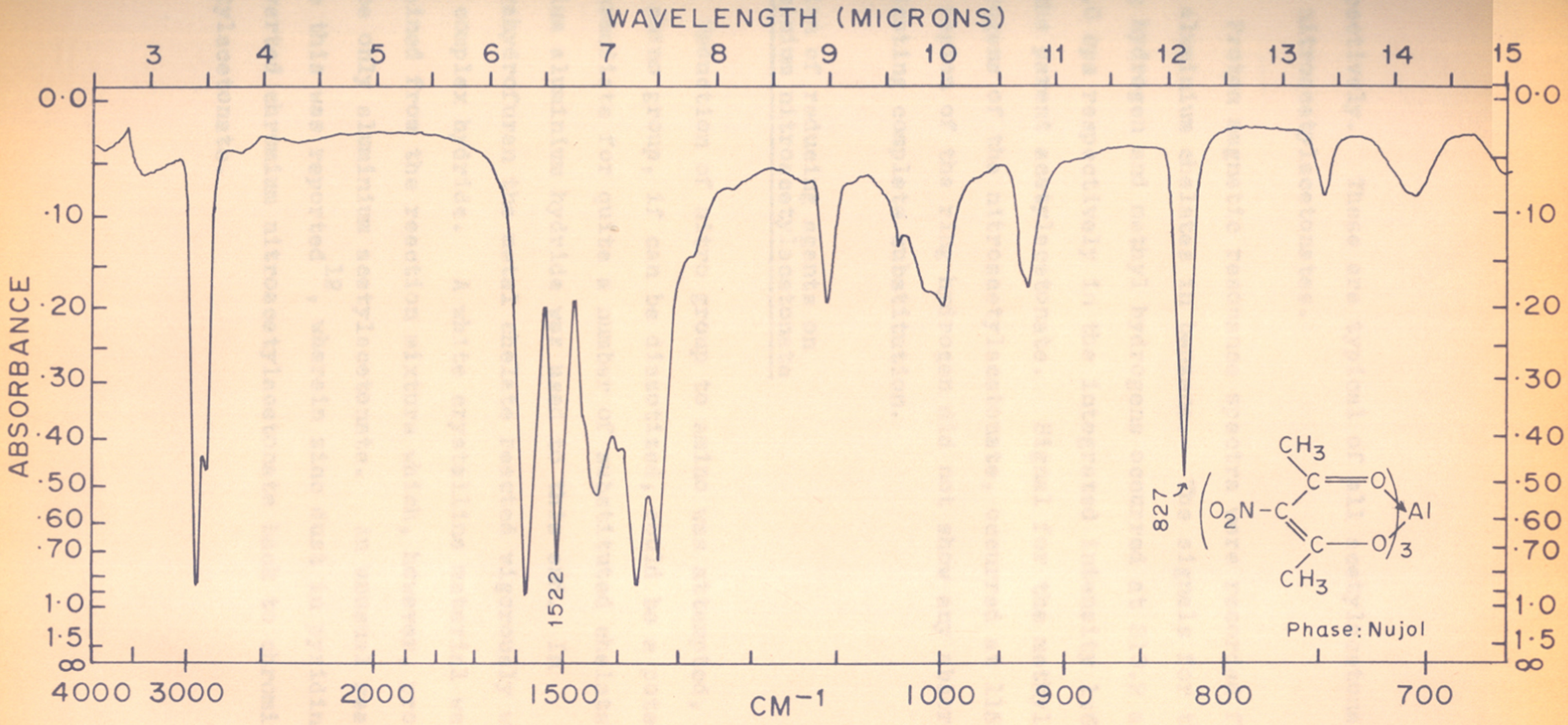

Fig. 9. IR Spectrum

respectively. These are typical of all acetylacetonates and nitroacetylacetonates.

Proton magnetic resonance spectra were recorded for the aluminium chelates in benzene. The signals for the ring hydrogen and methyl hydrogens occurred at 310.2 and 105.0 cps respectively in the integrated intensity 1:6 in the parent acetylacetonate. Signal for the methyl hydrogens of the nitroacetylacetonate, occurred at 115.0 cps. The region of the ring hydrogen did not show any absorption, indicating complete substitution.

Action of reducing agents on aluminium nitroacetylacetonate

Reduction of nitro group to amino was attempted, since the amino group, if can be diazotized, could be a potential intermediate for quite a number of substituted chelates. Sodium aluminium hydride was used to this end. In tetrahydrofuran the metal chelate reacted vigorously with the complex hydride. A white crystalline material was obtained from the reaction mixture which, however, proved to be only aluminium acetylacetonate. An unusual reaction like this was reported[12], wherein zinc dust in pyridine converted chromium nitroacetylacetonate back to chromium acetylacetonate.

Hydrazine hydrate in conjunction with Raney nickel is known to effect specific reduction of nitro groups in delicate systems[13]. It was, therefore, of interest to try this method on aluminium nitroacetylacetonate.

Hydrazine hydrate and Raney nickel reacted with a suspension of aluminium nitroacetylacetonate in alcohol. The brown sticky substance obtained was extracted with ether; from the ether extract a metal-free white crystalline material was obtained which melted sharply at 125°C.

The formation of the metal-free product was thought to be due to the lability of the metal chelate itself. Hence, the same reaction was re-examined using stable chromium nitroacetylacetonate. However, the same metal-free product was obtained. This was subsequently identified as 4-nitro-3,5-dimethylpyrazole[14] from melting point, analysis and infrared spectrum[15]. Under similar conditions aluminium acetylacetonate yielded 3,5-dimethylpyrazole[16,17], which is obtainable also from acetylacetone and hydrazine hydrate[18].

In preference to reduction, it was condensation of the β-diketone with hydrazine, that occurred. The preparation of 4-nitro-3,5-dimethylpyrazole by this method is significant, since aluminium nitroacetylacetonate has been used as intermediate in the place of non-existent 3-nitroacetylacetone.

Attempted preparation of 3-nitroacetylacetone

Since 3-nitroacetylacetone is reported as non-existent[19], an attempt was made to obtain it by indirect means. Copper nitroacetylacetonate was suspended in cold dilute sulphuric acid and was extracted with ether. The ether extract after drying was allowed to evaporate, when a pale yellow thick liquid was obtained. On careful distillation under vacuum, a colourless liquid was obtained which solidified to a pale yellow material on standing. From melting point, analysis and infrared spectrum it was found to be nitroacetone.

Nitroacetylacetone seems to have undergone hydrolytic carbon-carbon cleavage resulting in the formation of acetic acid and nitroacetone. Such a C-C cleavage has been reported for acetylacetone[20], although in alkaline medium.

Experimental

Acetylacetonates of aluminium(III), chromium(III), cobalt(III), copper(II) and beryllium(II) were prepared and purified according to reported methods[21,22,23].

$Al(acac)_3$:- Found: C,55.60; H,6.62%. Calcd.: C,55.55;H,6.48%.
$Cr(acac)_3$:- Found: C,51.61; H,6.23%. Calcd.: C,51.58;H,6.02%.
$Co(acac)_3$:- Found: C,50.71; H,5.85%. Calcd.; C,50.58;H,5.90%.
$Cu(acac)_2$:- Found: C,45.95; H,5.51%. Calcd.: C,45.90;H,5.35%.
$Be(acac)_2$:- Found: C,58.12; H,6.71%. Calcd.: C,57.97;H,6.76%.

Single-step preparation of aluminium nitroacetylacetonate

Acetylacetone (3 ml; 0.03 mole) and acetic anhydride (20 ml.) were taken in a conical flask and the mixture stirred magnetically, in an ice bath. Crystals of aluminium nitrate, $Al(NO_3)_3.9H_2O$, (3.75 g.; 0.01 mole) were pulverized and added in six portions to the stirred solution during 30 min. After stirring for 1 hr. the flask was taken out of the ice bath, but the stirring was continued. The contents of the flask slowly became yellow through an exothermic reaction. Pressure developed inside the flask was released by occasional lifting of the stopper, and undue rise in temperature was promptly checked by dipping the flask in ice-cold water. A yellow deposit was formed after the clear solution had become orange and then turbid. The mixture was stirred for 4 hr. at room temperature and then poured into 200 ml. of ice-cold water containing sodium acetate and stirred for 1 hr. The yellow residue obtained on filtration was washed first with water and then with ethanol. After air drying, the product was crystallized twice from benzene; yield, 2.3 g.

A part of the material (0.3 g.) was further purified by column chromatography on polycaprolactam powder (30 g., 2 cm. dia. column). Benzene was used for both development and elution (total volume 85 ml.), yellow glistening crystals were obtained from the eluate. Yield, 0.21 g.

Calcium sulphate, for thin layer chromatography, was prepared from an aqueous solution of calcium chloride and an equivalent quantity of sulphuric acid according to the method of Matis _et.al_.[24]. The material was washed thoroughly with water until entirely free of acid and dried at 115-120°C. Ground and sieved. The powder which passed through 200 mesh was used.

About 4 g. of the adsorbent was slurried with 12 ml. of water and was used to coat four thoroughly degreased glass plates (3.5 x 15 cm.). Dried at 100-110°C for 2 hr. and cooled in a desiccator over silica gel.

The applicator used for obtaining a uniform layer of 0.5 mm. and the technique adopted have been described in detail recently by Gupta and Sukhdev[25]. When the solvent (benzene) front reached the 10 cm. mark, the spot of the aluminium nitroacetylacetonate had reached 8.4 cm.(Rf = 0.84). The spot did not show any separation. Melting point, 250-251°C. Found: C,39.44; H,4.07; N,9.31; Al,6.03%. $C_{15}H_{18}N_3O_{12}Al$ requires: C,39.22; H,3.92; N,9.15; Al, 5.88%.

Nitration using aluminium nitrate

Beryllium nitroacetylacetonate :- Beryllium acetylacetonate (3.1 g.; 0.015 mole) and acetic anhydride (25 ml.) were taken in a conical flask, cooled and stirred. Powdered aluminium nitrate (3.75 g.; 0.01 mole) was slowly added. The rest of the procedure was the same as in the single-step preparation described earlier. The product was sucked dry on a filter. Extracted with benzene. A yellow material obtained from the extract was crystallized from hot ethanol as lustrous yellow needles, m.p.,186.5°C. Found: C,40.53;

H,4.31; N,9.57; Be, 2.99%. Required for $C_{10}H_{12}N_2O_8$ Be : C,40.40; H,4.04; N,9.43; Be, 3.03%.

Copper, cobalt and chromium acetylacetonates were nitrated similarly.

Copper nitroacetylacetonate :- Green crystals, m.p.,233-234°C (decomp.). Found: C,34.27; H,3.63; N,8.03; Cu,18.17%. $C_{10}H_{12}N_2O_8Cu$ requires: C,34.14; H,3.41; N,7.97; Cu,18.09%.

Chromium nitroacetylacetonate :- Red-violet needles; m.p., 257°C. Found: C,37.41; N,3.98; N,8.91; Cr,10.90%. $C_{15}H_{18}N_3O_{12}Cr$ requires: C,37.19; H,3.72; N,8.68; Cr,10.74%.

Cobalt nitroacetylacetonate :- Green needles, m.p.,194-195°C (decomp.). Found: C,36.91; H,3.93; N,8.51; Co,11.93%. $C_{15}H_{18}N_3O_{12}Co$ requires : C,36.67; H,3.67; N,8.55; Co,12.00%.

Nitration using nitric acid

Aluminium nitroacetylacetonate :- Aluminium acetylacetonate (3.25 g.; 0.01 mole) was suspended in ice-cooled and magnetically stirred acetic anhydride (25 ml.). To this was added, drop by drop, conc. nitric acid (16N; 2.2 ml; 0.035 mole) which was previously cooled to 0°C. A clear yellow solution was obtained when the cooling bath was removed after 1 hr., but when the stirring was continued yellow deposition slowly occurred. After stirring for 4 hr., the reaction mixture was worked up as in the case of nitration with aluminium nitrate. Yield, 2.6 g. Analytical data were similar to those obtained for the product from the single-step process.

Nitration of the other metal acetylacetonates was conducted similarly. Attempted nitration of aluminium and beryllium acetylacetonates, using copper nitrate (whereby copper nitroacetylacetonate was formed) was also conducted similarly.

Nitration products obtained by different methods gave identical IR spectra and similar analytical data.

Attempted reduction of aluminium nitroacetylacetonate with sodium aluminium hydride

Sodium aluminium hydride (0.54 g.; 95% pure) in tetrahydrofuran (25 ml.) was added to a solution of aluminium nitroacetylacetonate (1.15 g.; 0.0025 mole) in the same solvent (80 ml.) drop by drop. The solution became warm and viscous. This was carefully neutralized with dilute hydrochloric acid. The product obtained was removed, sucked dry and crystallized from benzene. Yield: 0.68 g. of aluminium acetylacetonate.

Attempted reduction of nitroacetylacetonates with hydrazine hydrate

Aluminium nitroacetylacetonate (1.15 g.; 0.0025 mole) in alcohol (30 ml.) was treated with hydrazine hydrate (4 ml.; 0.08 mole) and a pinch of Raney nickel. Refluxed over a water bath for 3 hr. The hot solution was filtered and evaporated to dryness. Extracted with ether. Colourless needles; yield, 0.9 g.(82%). Found: C,43.01; H,4.89; N,29.80%. Required for $C_5H_7N_3O_2$: C,42.55; H,4.99; N,29.79%.

Method was essentially the same when chromium nitroacetylacetonate and aluminium acetylacetonate were treated with hydrazine hydrate. The product obtained from aluminium acetylacetonate gave the following analytical data: C,62.32; H,9.86; N,29.31%. Required for $C_5H_8N_2$: C,62.5; H,8.33; N,29.17%.

Attempted preparation of 3-nitroacetylacetone

Copper nitroacetylacetonate (3.5 g.; 0.01 mole) was suspended in dilute sulphuric acid (50 ml., 10%) and shaken with ether (three times successively, using 30 ml. each time). The ether extract (pale yellow) was dried with sodium sulphate, solvent removed and the product distilled carefully in vacuum, when a colourless liquid was obtained which solidified to a pale yellow solid; m.p.,50°C. Moderately soluble in water, the solution being acidic to litmus. Found: C,34.66; H,4.87; N,13.21%. $C_3H_5NO_3$ requires: C,34.95; H,4.85; N,13.59%. Infrared spectrum showed strong adsorption at 1732, 1550, 1305, 1200 and 747 cm^{-1}.

In this chapter and unless otherwise stated, throughout the investigation covering this thesis, carbon, hydrogen and nitrogen were determined by micro analysis. Metal was determined, after decomposing the compound with concentrated sulphuric-nitric acid mixture, by standard quantitative methods. Infrared spectra were recorded in a Perkin Elmer infracord spectrophotometer. Proton magnetic resonance spectra were obtained in a Varian Associates model A-60 spectrometer operating at 60 Mc with tetramethyl silane as an internal standard. Chemical shifts are expressed in cps downfield from TMS.

CHAPTER 2

BROMINATION OF METAL ACETYLACETONATES

BROMINATION OF METAL ACETYLACETONATES

Bromine is reported to bring about destructive bromination of metal β-dicarbonyl chelates[26]. Most of the bromination studies with metal acetylacetonates have been carried out using N-bromosuccinimide[1,3,27]. The success of bromination using this reagent, has been ascribed to the absence of strongly acidic by-products[27]. It was implied that the decomposition of metal chelates, on bromination with bromine, was due to the acidity of the hydrogen bromide liberated during the course of substitution. Bromination of six metal acetylacetonates was re-examined in this investigation using bromine in the presence of excess calcium carbonate, so that the acidity would be kept in check.

Bromination of aluminium(III), beryllium(II) and chromium(III) acetylacetonates was quite successful by this method. Though calcium carbonate was found effective in warding off the adverse effect of hydrogen bromide in bromination of the above three metal acetylacetonates, it was entirely ineffective in the bromination of copper(II), cobalt(III) and manganese(III) acetylacetonates. In the decomposed products obtained in the bromination of the latter three metal acetylacetonates, copper(I), cobalt(II) and manganese(II) species respectively, have been found present.

Acidity of hydrogen bromide cannot be the reason for the decomposition of copper, cobalt and manganese acetylacetonates, since labile aluminium acetylacetonate has undergone non-destructive bromination under the same condition. The facility of reduction of compounds of copper(II), cobalt(III) and manganese(III) to stable lower oxidation states is well known. Reducibility of these metal ions should, therefore, be the cause of destruction of their metal chelates under the experimental conditions.

The results lead to the conclusion that the reducing nature of the hydrogen bromide is far more destructive than its acidity to acetylacetonates of certain transition metals, which have stable lower oxidation states.

The above findings are supported by the work of Nakamura and Kawaguchi[28], whose attempted bromination of copper acetylacetonate with bromine, resulted in the formation of cuprous bromide and γ-bromoacetylacetone. Furthermore, the formation of cupric chloride, cuprous bromide and cuprous iodide from copper(II) ethylacetoacetate[29] on reaction with chlorine, bromine and iodine respectively, is in conformity with the above line of reasoning.

Bromination of beryllium(II), aluminium(III) and chromium(III) acetylacetonates was conducted in both carbon tetrachloride and chloroform. When the latter solvent was used, bromoacetylacetonates* of aluminium and chromium were rendered insoluble by the formation of chloroform clathrates[27]. These clathrates were completely desolvated on extraction with hot benzene and drying the residue obtained from it in *vacuo*.

Analytical data and melting points of the three bromoacetylacetonates agreed with those reported. The infrared spectra of these compounds did not show any absorption in the 1200 cm^{-1} region. The 1500-1600 cm^{-1} region was characterized by a single sharp absorption. Infrared spectra of these compounds were superposable with those of authentic samples. Melting points remained undepressed on admixture with the authentic samples. Infrared spectrum of beryllium bromoacetylacetonate is shown in Fig.10, as a representative type.

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* 3-bromo-2,4-pentanedionates.

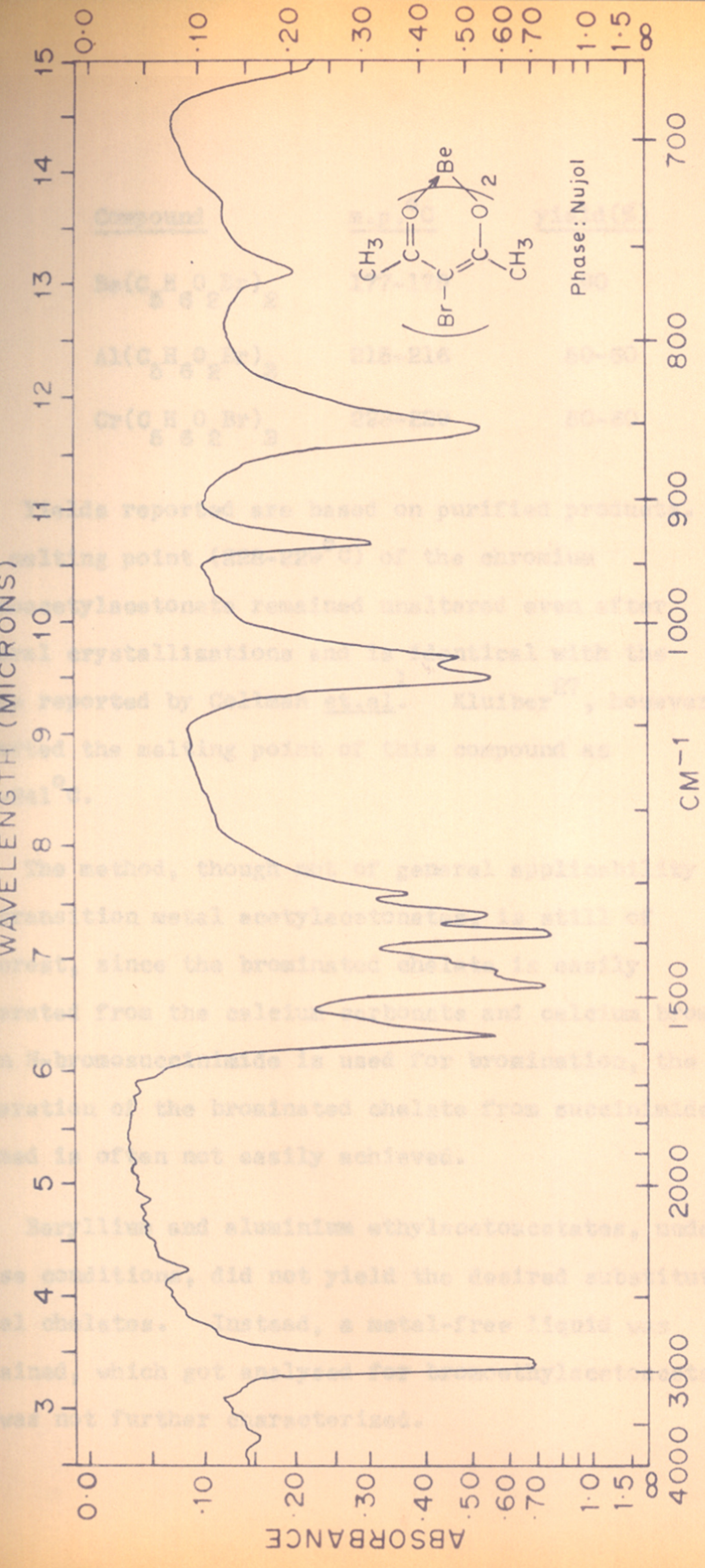

Fig. 10. IR Spectrum

Compound	m.p.°C	yield(%)
$Be(C_5H_6O_2Br)_2$	177-179	90
$Al(C_5H_6O_2Br)_3$	215-216	50-60
$Cr(C_5H_6O_2Br)_3$	228-229	50-60

Yields reported are based on purified products. The melting point (228-229°C) of the chromium bromoacetylacetonate remained unaltered even after several crystallizations and is identical with the value reported by Collman et.al.[1] Kluiber[27], however, reported the melting point of this compound as 240-241°C.

The method, though not of general applicability to transition metal acetylacetonates, is still of interest, since the brominated chelate is easily separated from the calcium carbonate and calcium bromide. When N-bromosuccinimide is used for bromination, the separation of the brominated chelate from succinimide formed is often not easily achieved.

Beryllium and aluminium ethylacetoacetates, under these conditions, did not yield the desired substituted metal chelates. Instead, a metal-free liquid was obtained, which got analysed for bromoethylacetoacetate. It was not further characterized.

Experimental

Manganese(III) acetylacetonate :- Prepared from manganous chloride, potassium permanganate and acetylacetone[30]. Found: C, 51.34; H,6.08%. Calculated: C,51.17; H,5.97%.

Aluminium ethylacetoacetate :- Aluminium isopropoxide (10.2 g.; 0.05 mole), suspended in absolute alcohol (50 ml.), was stirred vigorously with freshly distilled ethylacetoacetate (19.52 g.; 0.15 mole). The mixture was subsequently evaporated to dryness over a water bath. Alcohol (50 ml.) was again added and the evaporation repeated. From the residue, very pure aluminium ethylacetoacetate was obtained by extraction with petroleum ether. Colourless crystals, m.p., 78-79°C. Yield, 19.5 g.(94%). Found: C,52.30; H,6.67; Al,6.63%. Required for $C_{18}H_{27}O_9Al$: C,52.18; H,6.52; Al,6.52%.

Beryllium ethylacetoacetate :- Prepared from beryllium chloride, ethylacetoacetate and aqueous ammonia[31]. Found: C,54.20; H,6.85%. Calcd.: C,53.94; H,6.74%.

Beryllium bromoacetylacetonate :- Beryllium acetylacetonate (2.07 g.; 0.01 mole) was dissolved in dry chloroform (40 ml.), cooled and kept stirred in a conical flask along with finely powdered calcium carbonate (5 g.; 0.05 mole) using a magnetic stirrer. Bromine (3.2 g.; 0.02 mole) in chloroform (15 ml.) was slowly added from a dropping funnel fitted to the flask and provided with pressure equalizing arrangement and a calcium chloride drying tube. After complete addition which took about 1.5 hr., the contents were stirred at room temperature for an additional hour, filtered and the filtrate evaporated to dryness. The residue was extracted with benzene; the product obtained from the benzene extract was crystallized once from benzene-petroleum ether. Yield, 3.28 g. Found: C,33.10; H,3.41; Be,2.63%. $C_{10}H_{12}Br_2O_4Be$ requires: C,32.90; H,3.29; Be,2.47%.

Bromination procedure was essentially the same for all chelates. Aluminium and chromium bromoacetylacetonates were found being precipitated out. Hence, after the reaction the solvent was removed by evaporation and the residue extracted with hot benzene. The material recovered from the benzene extract was heated in vacuum at 80°C. The products were further purified by crystallization from benzene-petroleum ether.

Aluminium bromoacetylacetonate :- Found: C,32.30; H,3.43; Al,4.92%. $C_{15}H_{18}Br_3O_6Al$ requires:- C,32.10; H,3.21; Al,4.82%.

Chromium bromoacetylacetonate :- Found: C,30.97; H,3.31; Cr,8.93%. Required for $C_{15}H_{18}Br_3O_6Cr$: C,30.73; H,3.07; Cr,8.89%.

In the bromination of the acetylacetonates of cobalt(III), manganese(III) and copper(II), the filtrate did not contain any metal chelate, nor was the residue extractable with solvents in which the parent or substituted chelates are soluble. The filtrate, however, contained a metal-free oil presumably 3-bromoacetylacetone. Another metal-free oil was obtained in the attempted bromination of aluminium and beryllium ethylacetoacetates.

Yields obtained from carbon tetrachloride were comparable to those obtained from chloroform for the bromoacetylacetonates, of beryllium, aluminium and chromium.

CHAPTER 3

THIOCYANATION OF METAL ACETYLACETONATES

THIOCYANATION OF METAL ACETYLACETONATES

The direct replacement of a hydrogen atom by a thiocyano, (SCN), group through the use of thiocyanogen, $(SCN)_2$, is commonly termed thiocyanation. The non-destructive thiocyanation reported for certain robust metal acetylacetonates[32] is significant, since this substitution reaction is limited mostly to aromatic amines and phenols, although a few particularly reactive aromatic hydrocarbons are also thiocyanated[33]. It was, therefore, of interest to examine the possibility of thiocyanation of labile acetylacetonates of aluminium(III) and beryllium(II). Manganese(III) acetylacetonate was also included for study.

Thiocyanogen, which is a pseudo-halogen, is used in synthesis in essentially the same way as the halogens, with the exception that certain precautions must be observed owing to the instability of thiocyanogen[33]. At room temperature, it polymerizes rapidly to pseudo- or para- thiocyanogen. Although stable in inert dry solvents, thiocyanogen may polymerize on standing, under the catalytic influence of heat, light, moisture or oxygen. It is also readily hydrolysed. For these reasons, when thiocyanogen is employed in chemical reactions, it is prepared in solution or more commonly produced in <u>situ</u>. In this investigation, a fresh solution of it in ethylenedichloride was obtained from lead thiocyanate and bromine and was used immediately, after filtering under nitrogen.

Although aluminium(III) and beryllium(II) acetylacetonates yielded the fully substituted chelates, the product from manganese(III) acetylacetonate was metal-free. Aluminium and beryllium thiocyanatoacetylacetonates* were characterized through their analytical data and infrared and proton magnetic resonance spectra. A sharp peak at 2175 cm^{-1} due to C$\equiv$N stretching and another around 740 cm^{-1} due to C-S stretching vibrations, characteristic of thiocyanato group, were observed in the infrared spectra of both the compounds (Figs. 11 and 12). The medium intensity peak at 1200 cm^{-1} of the parent chelates was absent in these substituted chelates. The 1500-1600 cm^{-1} region showed a single strong absorption. The proton

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* 3-thiocyanato-2,4-pentanedionates

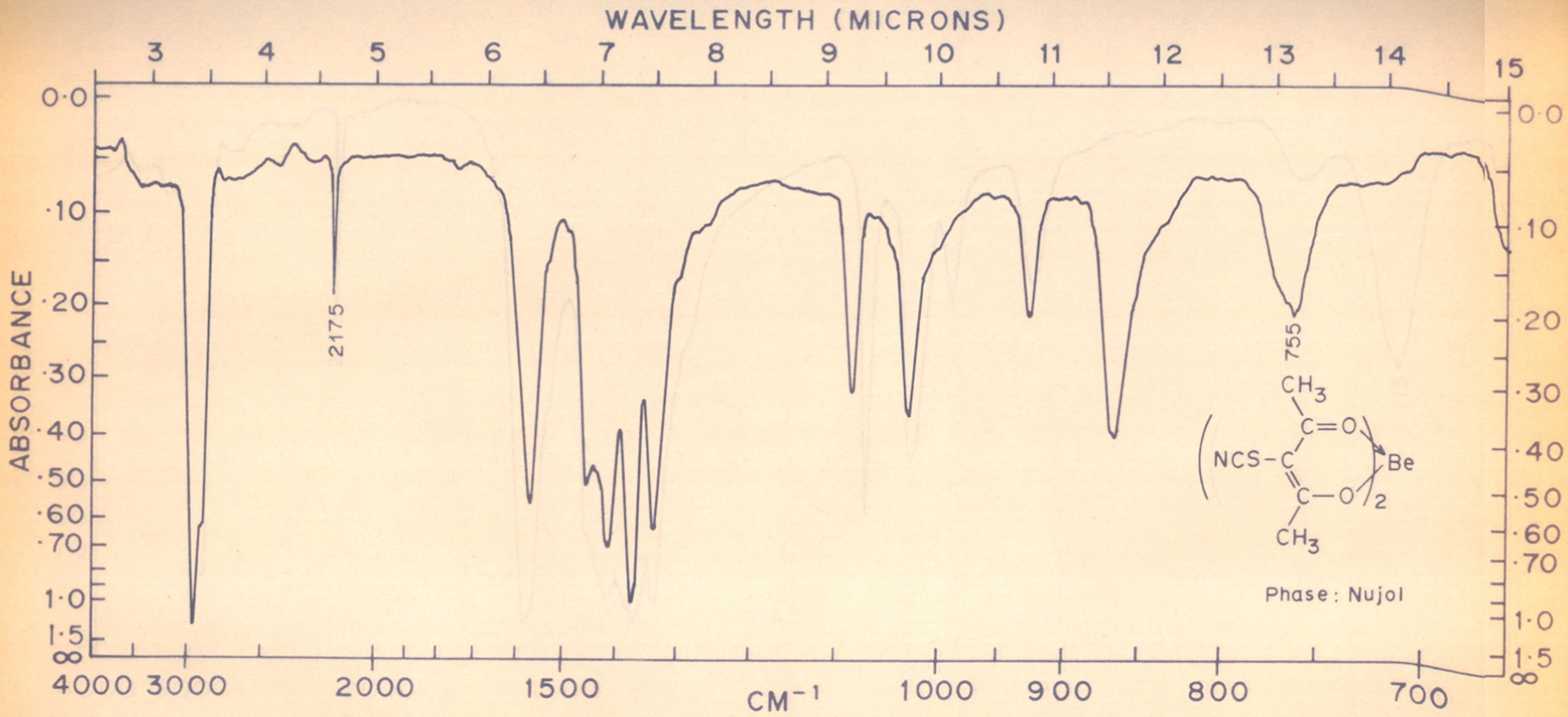


Fig. 11· IR Spectrum

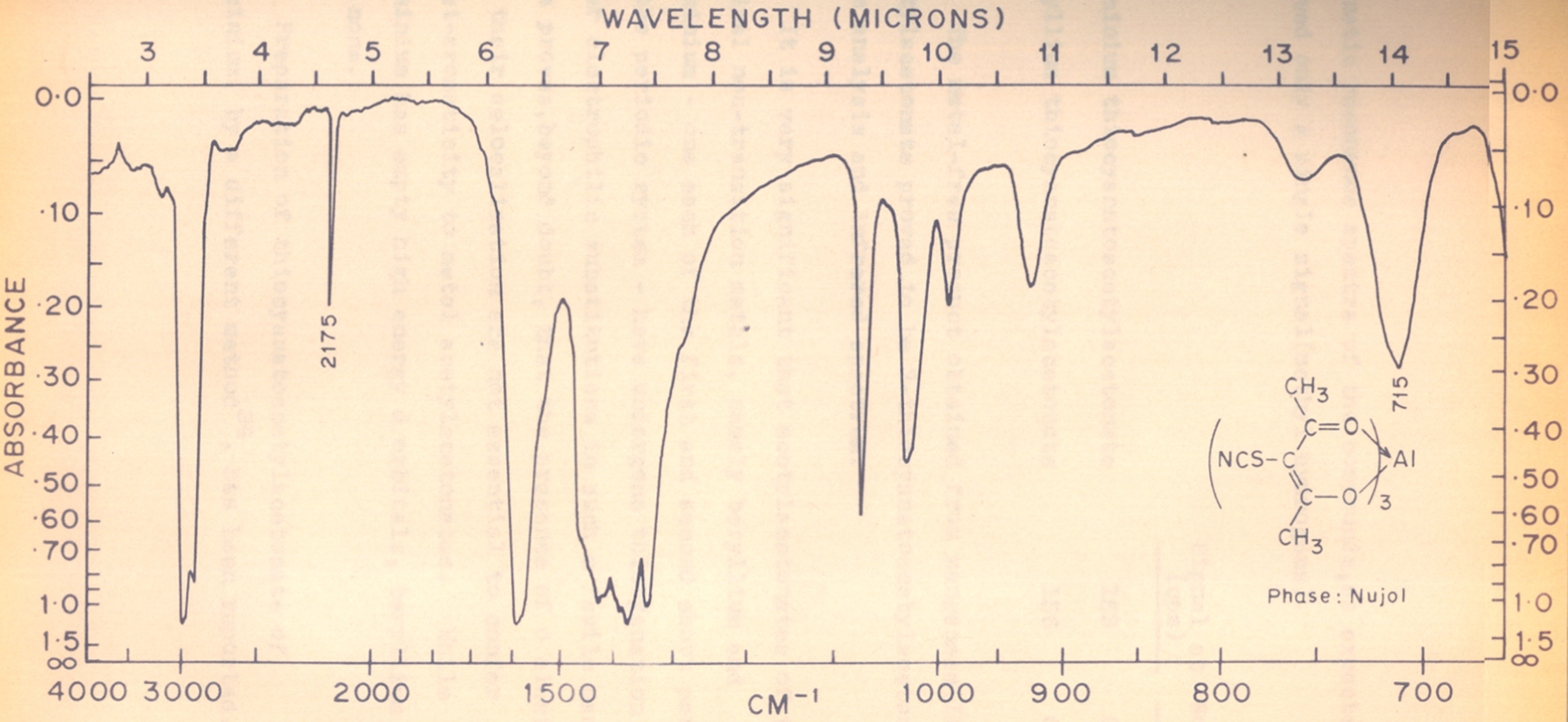


Fig 12. IR Spectrum

magnetic resonance spectra of the compounds,as expected, showed only a single signal(methyl hydrogens).

	Signal at (cps)	Solvent
Aluminium thiocyanatoacetylacetonate	153	$CHCl_3$
Beryllium thiocyanatoacetylacetonate	156	CCl_4

The metal-free product obtained from manganese(III) acetylacetonate proved to be 3-thiocyanatoacetylacetone from analysis and infrared spectrum.

It is very significant that acetylacetonates of two typical non-transition metals, namely beryllium and aluminium - one each of the first and second short periods of the periodic system - have undergone thiocyanation and other electrophilic substitutions in such a facile manner. This proves,beyond doubt, that the presence of d electrons and their delocalization are not essential to confer quasi-aromaticity to metal acetylacetonates. While aluminium has empty high energy d orbitals, beryllium has none.

Preparation of thiocyanatoacetylacetonate of aluminium, by a different method[34], has been reported.

Experimental

Aluminium thiocyanatoacetylacetonate :- Bromine (10.6 g.; 3.37 ml.; 0.066 mole) in 1,2-dichloroethane (20 ml.) was added slowly to a vigorously stirred suspension of anhydrous lead thiocyanate (21.4 g.;0.066 mole) in the same solvent (80 ml.), kept cooled in a freezing-mixture. The red bromine colour was allowed to disappear before each successive addition~~s~~ of bromine. The mixture of thiocyanogen and lead bromide produced was stirred for 5 min. after the bromine addition was complete.

The solid lead bromide formed was allowed to settle and the colourless thiocyanogen solution was filtered with a filter-stick under nitrogen pressure, directly into the solution of aluminium acetylacetonate (6.6 g.; 0.02 mole) in 1,2-dichloroethane (50 ml.) kept cooled in a freezing-mixture. The mixed solutions were stirred and cooled for 2 hr. after which the contents were allowed to come to room temperature and react for an additional hour. At this stage an yellowish suspension was noticed, which was sent back into solution by adding 50 ml. more of the solvent.

The solution was extracted twice with water (150 ml. each time) after which the organic phase was dried with calcium chloride, filtered and evaporated to dryness in vacuum. The residue obtained was recrystallized from methylene chloride - chloroform mixture. Grey material; yield, 7.5 g.(70-80%); m.p., 183-4°C. Found: C,43.91; H,4.00; N,8.70; Al,5.39%. $C_{18}H_{18}N_{3}O_{6}S_{3}Al$ requires : C,43.64; H,3.64; N,8.48; Al,5.45%.

The same method was used for the thiocyanation of beryllium and manganese acetylacetonates; care being exercised to mix equivalent quantities of the reactants.

Beryllium thiocyanatoacetylacetonate :- Crystallized twice from benzene-petroleum ether. Yellowish-brown material; yield, 65%; m.p., 147-8°C. Found: C,44.87; H,3.92; Be,2.91%. $C_{12}H_{12}N_{2}O_{4}S_{2}Be$ requires: C,44.86; H,3.74; Be,2,80%.

The metal-free residue obtained from manganese acetylacetonate, was recrystallized from ethylene dichloride-petroleum ether mixture. Brown residue; yield, 50%; m.p., 79-80°C. Found: C,45.87; H,4.97%; $C_{6}H_{7}NO_{2}S$ requires: C,45.90; H,4.46%. IR spectrum showed strong absorptions at 2174, 1724 and 1585 cm^{-1}.

CHAPTER 4

MERCURATION

Action of mercuric acetate on metal chelates of β-dicarbonyl compounds

MERCURATION

Action of mercuric acetate on metal chelates of β-dicarbonyl compounds

Mercuration is a typical aromatic reaction. Though the quasi-aromatic nature of metal chelates of β-dicarbonyl compounds has~~e~~ often been indicated and discussed, no attempt seems to have been made to mercurate the metal chelates. It was, therefore, thought desirable and timely to examine the possibility of this reaction on metal chelates of β-dicarbonyl compounds.

Mercuration of aromatic nuclei is accomplished by heating with such mercuric salts as the chloride, nitrate or acetate[35].

$$\mathrm{ArH} + \mathrm{HgX_2} \rightarrow \mathrm{Ar{-}Hg{-}X} + \mathrm{HX}$$

The product is an organo-metallic compound (involving direct metal-carbon bond).

In the present investigation, mercuric acetate was used, since the chloride and nitrate, if employed, would lead to the formation of strong mineral acids.

Mercuration reactions with mercuric acetate are best conducted in glacial acetic acid[36]. Copper acetylacetonate is soluble and stable in this medium. By reacting copper acetylacetonate with mercuric acetate in glacial acetic acid the desired product was not obtained. However, copper acetylacetonate was found to react slowly with warm aqueous mercuric acetate solution. White residue obtained was found to contain mercury and no parent metal. The blue filtrate contained copper quantitatively.

Other labile acetylacetonates like those of beryllium and nickel also reacted likewise. Analysis and infrared spectra showed that the products obtained from the various acetylacetonates were all identical.

Copper chelates of trifluoroacetylacetone, ethylacetoacetate, acetoacetanilide and acetoacet-orthochloroanilide, all yielded white residues under similar conditions.

From analytical data it was apparent that the materials obtained were the diacetoxymercuri derivatives of the ligands concerned.

In all these compounds, the mercury retains its salt-forming character and mercuric ions are split off with relative ease. For example, boiling the salts with sodium or ammonium sulphide solution, or passing hydrogen sulphide through aqueous suspension, results in the deposition of mercuric sulphide, while alkaline stannous chloride solution immediately gives a dark grey precipitate of mercury. The latter test is in fact a very convenient one for identifying mercury compounds of the so-called 'half-complex' class in which one valence of mercury retains its salt-forming inorganic character, as distinguished from the 'full-complex' class in which the mercury is fully bound between two carbon atoms[37].

Substances containing mercury in the place of hydrogen atoms in reactive methylene group are unusually reactive towards hydrogen sulphide[38]. The fast and facile precipitation of mercuric sulphide from these compounds by hydrogen sulphide (as has been mentioned earlier) is suggestive of the site of attachment of mercury to the organic moiety.

All the above organo-mercury compounds disintegrate in dilute hydrochloric acid, liberating the original ligand. Mercury bonded to a carbon atom in the α-position to a carbonyl group is known to be cleaved easily and such compounds have been shown to behave in like fashion to dilute acids[39]. Decomposition of these materials in the presence of dilute hydrochloric acid was made use of in estimating mercury in them.

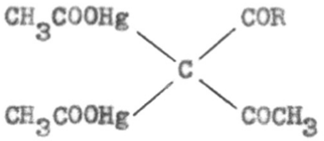
Aqueous potassium iodide brought about a complete splitting of the mercury-carbon linkage in these compounds, with the liberation of alkali. This is to be expected from compounds containing mercury, substituted for the hydrogen atoms in the grouping $-CO-CH_2-CO-$[40]. Formation of one equivalent of alkali for each carbon-mercury linkage can be envisaged through the following reaction

$$RHgX + KI + H_2O \longrightarrow RH + HgXI + KOH$$

The amount of alkali liberated in each case was found to be in agreement with that calculated for diacetoxymercuri derivatives of the various β-dicarbonyl compounds. Determination of the rate of this reaction should give a comparative account of the stability of carbon-mercury bond in these compounds. This was attempted, but the extreme fastness of the reaction precluded such a possibility.

The instantaneous liberation of black mercury from these compounds by hydrazine hydrate or phenyl hydrazine shows further the weakness of the carbon-mercury bond in these compounds.

From the foregoing evidences and as supported by analytical data the compounds are represented as:



No.	R	Compound	Decomp. point °C
1	CH_3	Diacetoxymercuri acetylacetone	215
2	CF_3	Diacetoxymercuri trifluoroacetylacetone	230
3	OC_2H_5	Diacetoxymercuri ethylacetoacetate	245
4	$NH.C_6H_5$	Diacetoxymercuri acetoacetanilide	205
5	$NH.C_6H_4Cl$	Diacetoxymercuri acetoacet.orthochloroanilide	208

All these compounds share the common property of being insoluble in all common organic solvents. They have poor thermal stability above 200°C.

Robust cobalt and chromium compounds did not react with mercuric acetate even on prolonged contact. This suggests the possibility that in the labile chelates, mercuration occurs in the ligand anions formed through dissociation of the metal chelates under the conditions of preparation.

Attempts to prepare monoacetoxymercuri derivatives using restricted quantities of mercuric acetate were not successful; in all cases only diacetoxymercuri derivatives were formed, almost quantitatively. This is another indication that dissociation might be a prior step to mercuration. The ligand anions formed by the slow dissociation of the metal chelate, will have all the mercuric acetate to react with. Consequently, only the diacetoxymercuri derivatives are formed.

Mercuration of the aromatic nucleus(compounds 4 and 5) did not occur under the experimental conditions. From analytical data and decomposition points, compounds 3 and 4 are found to be the same as prepared by Patel and Mankad[41] and by Naik and Patel[42], from the respective ligands.

Experimental

Copper trifluoroacetylacetonate, copper ethylacetoacetate and copper acetoacetanilide were prepared by reported methods[43,44].

Copper trifluoroacetylacetonate :- Found: Cu,17.25%. Calcd.: Cu,17.19%.

Copper ethylacetoacetate :- Found: C,45.01; H,5.75%. Calcd.: C,44.79; H,5.60%.

Copper acetoacetanilide :- Found: C,57.50; H,5.01%. Calcd.: C,57.77; H,4.81%.

Copper acetoacet.orthochloroanilide was prepared by the same method as used for copper acetoacetanilide[44]. Recrystallized from chloroform; m.p., 200°C(decomp.). Found: C,50.01; H,4.04; N,5.82; Cu,13.01%. $C_{20}H_{18}Cl_2N_2O_4Cu$ requires: C,49.55; H,3.72; N,5.78; Cu,13.11%.

Diacetoxymercuri acetylacetone

In the initial attempts of mercuration copper acetylacetonate and mercuric acetate were mixed in the 1:2 mole ratio. About 50% of the copper chelate remained unaffected in such cases. Hence the ratio used in all cases was 1:4.

Mercuric acetate (12.75 g.; 0.04 mole) was dissolved in water (100 ml.) containing a drop of acetic acid, for clarity. Powdered copper acetylacetonate (2.62 g.; 0.01 mole) was added and the mixture stirred while being warmed over a hot plate. The reaction was complete in an hour. Filtered and the white residue was washed repeatedly with water. Sucked dry. The dry product was washed repeatedly with warm chloroform in order to remove any trace of the copper chelate that might be present. The solvent was removed from the product in vacuum. Yield, 11.5 g.(93%). Found: Hg,64.10; C-methyl, 9.32%. Required for $C_9H_{12}O_6Hg_2$: Hg,64.98; C-methyl, 9.72%.

The method was the same in all preparations; almost theoretical yield was obtained in all cases.

Diacetoxymercuri trifluoroacetylacetone :- Found: Hg, 58.92%. Required for $C_9H_9F_3O_6Hg_2$: Hg, 59.77%.

Diacetoxymercuri ethylacetoacetate :- Found: Hg, 61.01; C-methyl, 9.30%. Required for $C_{10}H_{14}O_7Hg_2$: Hg, 61.97; C-methyl, 9.27%.

Diacetoxymercuri acetoacetanilide :- Found: Hg, 57.50; C-methyl, 6.51%. Required for $C_{14}H_{15}NO_6Hg_2$: Hg, 57.79; C-methyl, 6.48%.

Diacetoxymercuri acetoacet.orthochloroanilide :- Found: Hg, 54.94; C-methyl, 7.32%. Required for $C_{14}H_{14}ClNO_6Hg_2$: Hg, 55.05; C-methyl, 7.29%.

Metal was determined in these organometallic compounds as mercuric sulphide. A known weight of the substance was suspended in dilute hydrochloric acid and stirred vigorously. Decomposition was facilitated by warming. The solid ligands deposited during decomposition were filtered off.

A slow stream of hydrogen sulphide was then passed until the colour of the precipitate turned completely black, and the precipitate settled down. Filtered through a tared sintered glass crucible, washed successively with water, alcohol and carbon disulphide and dried at 105-110°C.

Alkali liberated on treatment with potassium iodide was determined using standard hydrochloric acid. The acid was standardized against 'AnalaR' mercuric oxide[45]. Methyl orange was used as indicator. The presence of the ligands was found not to affect the end point. Alkali liberated from one mole of each organo-metallic compound was found to be 2 moles ± 0.01 mole.

The microanalytical section of this laboratory does not undertake carbon and hydrogen micro analysis of organomercury compounds. Hence the C-methyl estimations.

CHAPTER 5

ADDUCT FORMATION

Uranyl complexes of acetoacetanilide and acetoacet.orthochloroanilide

ADDUCT FORMATION

Uranyl complexes of acetoacetanilide and acetoacet.orthochloroanilide

The factors which lead to a high coordination number for a given metal atom has not been well established for molecular species. It was once assumed that the first-row elements could not surpass a coordination number of four, but there are now many examples of five and six coordination, especially for boron[46,47]. Eight coordination for third-row elements has been reported, for instance, in the diarsine chelate of titanium(IV)[48,49]. Bivalent metals, particularly those of the first transition series, are found in their normal chelates to increase the coordination sphere by forming adducts of the Lewis acid-base type with oxygen, nitrogen, sulphur and phosphorus donors[50-53]. Recently, it has been demonstrated that tropolone[54] forms compounds with many metals in which the metal atoms exhibit high coordination numbers. These reports call for a reappraisal of the characteristic coordination numbers of elements.

Uranyl ion (UO_2^{++}) is one of the most prolific in complex formation; in the complexes formed, uranium shows variability of coordination number. Well-defined crystalline compounds which are formed with it and β-dicarbonyl compounds[55] conform to the general formula UO_2A_2, where A stands for the anion of the dicarbonyl compound HA. In these hexacovalent compounds, however, uranium is coordinatively unsaturated and shows proclivity to increase the coordination number further. This tendency manifests itself in solvation or adduct formation. Indeed, the best solvents for these chelates are oxygen-donors like alcohol, acetone and ether, from which they crystallize with a molecule or more of the solvent[55]. When formed from aqueous medium, these chelates contain from 1 to 2.8 moles of water, which are eliminated only with difficulty. Stable 1:1 adducts are formed by the chelates with ammonia, amines and heterocyclic bases[55].

Occasionally the urge for increased coordination number finds expression in polymerisation as is the case of the eight-coordinate, uranyl benzoylnicotinoylmethane polymer[55]. In a few other cases, an extra molecule of the ligand itself is held with the chelates. This occurs when the acetylacetonate chelate of uranyl is crystallized from acetylacetone[56] or when uranyl is extracted with a solution of dibenzoylmethane[57]. A similar case has also been detected in solution with thenoyltrifluoroacetone[58]. Perhaps, the most well-defined of such cases is the 8-hydroxyquinolinate of uranyl. When prepared, it invariably contains an excess molecule of the ligand held tenaciously[59]. This reaction which forms the basis for the quantitative determination of uranyl[45,60] has been extensively studied[61,62].

Acetoacetanilide and acetoacet.orthochloroanilide complexes of uranyl which are reported here furnish two other instances where an extra molecule of the ligand is strongly associated with the chelate.

Aqueous solution of uranyl nitrate hexahydrate on treatment with an alcoholic solution of acetoacetanilide or acetoacet.orthochloroanilide, does not yield any solid product even after brief warming and subsequent cooling. However, well-defined crystals are obtained if the above mixed solution is carefully neutralized with alcoholic potash. The products, after recrystallization from alcohol or acetone and drying at 80°C in vacuum, got analysed for complexes containing three moles of the ligand per uranyl.

The same products are obtained without the neutralization step and in a much purer state when an aqueous solution of uranyl acetate dihydrate is treated with an alcoholic solution of acetoacetanilide or acetoacet.orthochloroanilide and stirred for a short while.

It was found subsequently that the two compounds are best prepared when an aqueous solution of the uranyl acetate and alcoholic solution of the ligand are mixed in the 1:3 ratio; in the earlier attempts, the ratio used was 1:2.

Even after several crystallizations the compounds did not undergo any change in composition. A thermogravimetric analysis was, therefore, attempted. The acetoacetanilide complex of uranyl lost one mole of the ligand quickly in a single sharp step between 180° and 230°C. The decomposition continued thereafter at a much slower rate. The acetoacet.orthochloroanilide complex of uranyl behaved very similarly. In this case, the removal of one mole of the ligand occurred between 220° and 265°C. Same results were obtained when the thermogravimetric analyses were repeated. In Fig.13, the thermogravimetric data have been presented on an absolute weight loss basis, in keeping with the widespread practice of reporting the results of thermogravimetric analysis of inorganic and coordination compounds[63].

Evidence for the structure of the compounds comes from their infrared spectra, which have been compared with those of the ligands and copper and chromium chelates of the ligands.

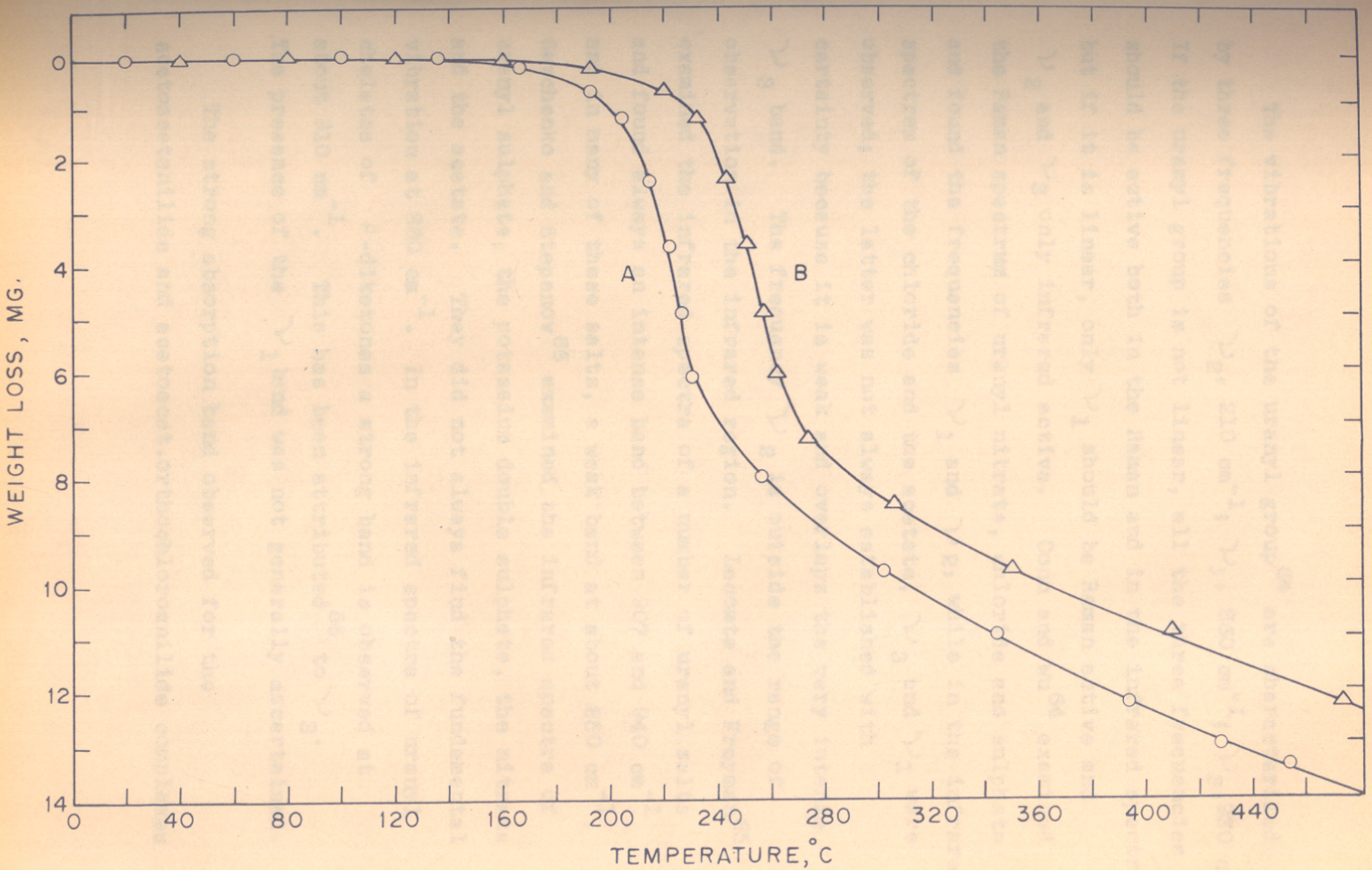


Fig.13. Thermograms of Uranyl acetoacetanilide complex (A), and Uranyl acetoacet-orthochloroanilide complex (B) in nitrogen. Wt. taken A = 28·7 mg.; B = 26·3 mg.

The vibrations of the uranyl group[64] are characterized by three frequencies ν_2, 210 cm^{-1}; ν_1, 860 cm^{-1}; ν_3, 930 cm^{-1}. If the uranyl group is not linear, all the three frequencies should be active both in the Raman and in the infrared spectra, but if it is linear, only ν_1 should be Raman active and ν_2 and ν_3 only infrared active. Conn and Wu[64] examined the Raman spectra~~m~~ of uranyl nitrate, chloride and sulphate and found the frequencies ν_1 and ν_2, while in the infrared spectra~~m~~ of the chloride and the acetate, ν_3 and ν_1 were observed; the latter was not always established with certainty because it is weak and overlaps the very intense ν_3 band. The frequency ν_2 is outside the range of observation in the infrared region. Lecomte and Freyman[65] examined the infrared spectra of a number of uranyl salts and found always an intense band between 907 and 940 cm^{-1} and in many of these salts, a weak band at about 850 cm^{-1}. Sevchenko and Stepanov[66] examined the infrared spectra of uranyl sulphate, the potassium double sulphate, the nitrate and the acetate. They did not always find the fundamental vibration at 860 cm^{-1}. In the infrared spectra of uranyl chelates of β-diketones a strong band is observed at about 910 cm^{-1}. This has been attributed[55] to ν_3. The presence of the ν_1 band was not generally ascertained.

The strong absorption band observed for the acetoacetanilide and acetoacet.orthochloroanilide complexes of uranyl in the region 895-912 cm^{-1}, is undoubtedly due to the asymmetric stretching of the uranyl. Even when this band is excluded, the 850-1600 cm^{-1} region of the spectra of these uranyl compounds show more complex a band pattern than the corresponding chromium and copper compounds. This should be expected in view of the presence in the uranium compounds of a molecule of the ligand, bonded somewhat differently from the remaining two molecules as has been brought out by their thermograms.

In the spectra of acetoacetanilide and acetoacet. orthochloroanilide (ligands), there are two strong bands in the 1650-1730 cm^{-1} region, which can be assigned to the acetyl and anilide carbonyls[67]. There is no absorption in this region in the copper and chromium chelates, since the perturbed carbonyl frequency (through chelation to the metal) is shifted to longer wave-lengths. In the uranyl complexes, however, a medium intensity band is observed at about 1700 cm^{-1}. From its position it is attributable to the free acetyl carbonyl of the third molecule of the ligand. Since the free anilide carbonyl band is not observed, its entry into bonding with uranium is inferred. The N-H stretching frequency is observed at the same region in the copper and

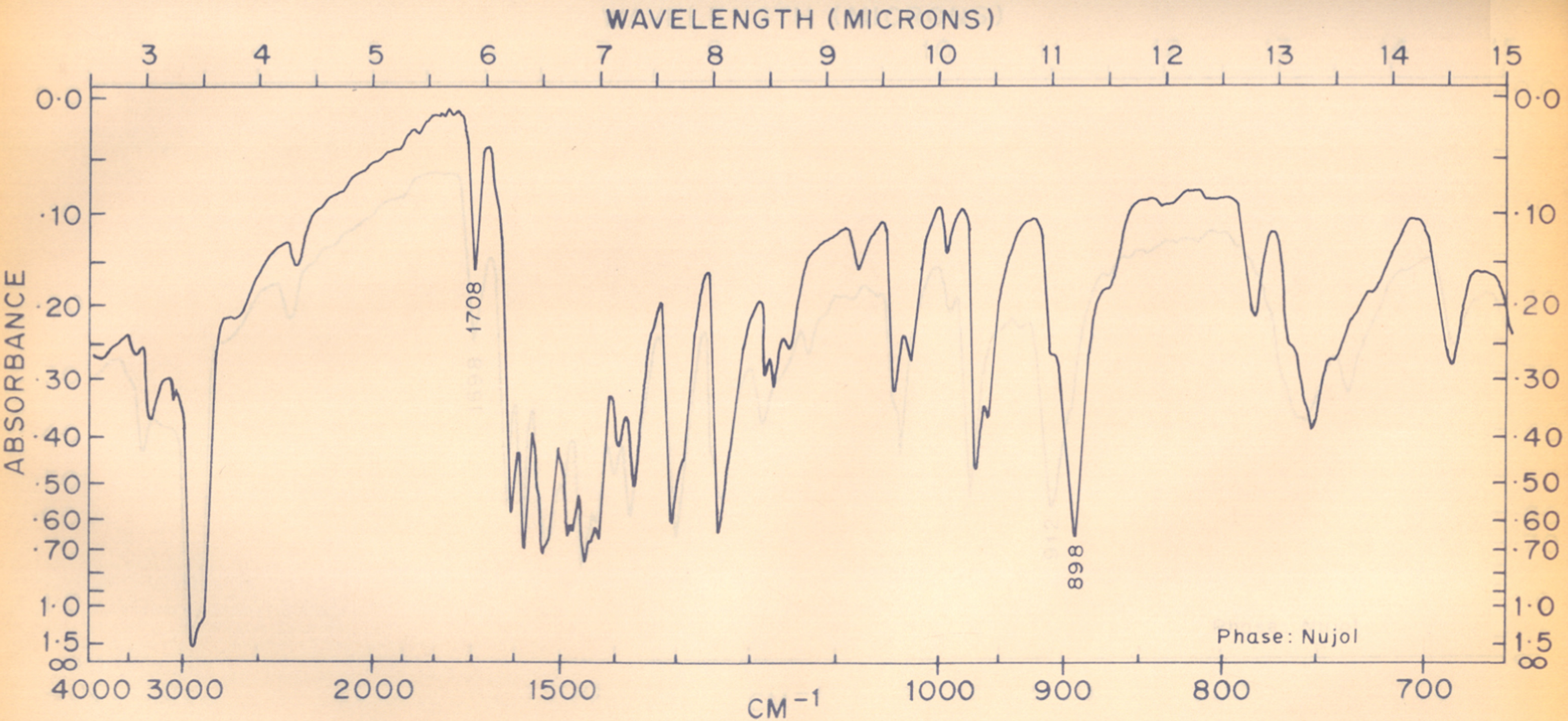


Fig. 14. IR Spectrum of acetoacetanilide complex of uranyl

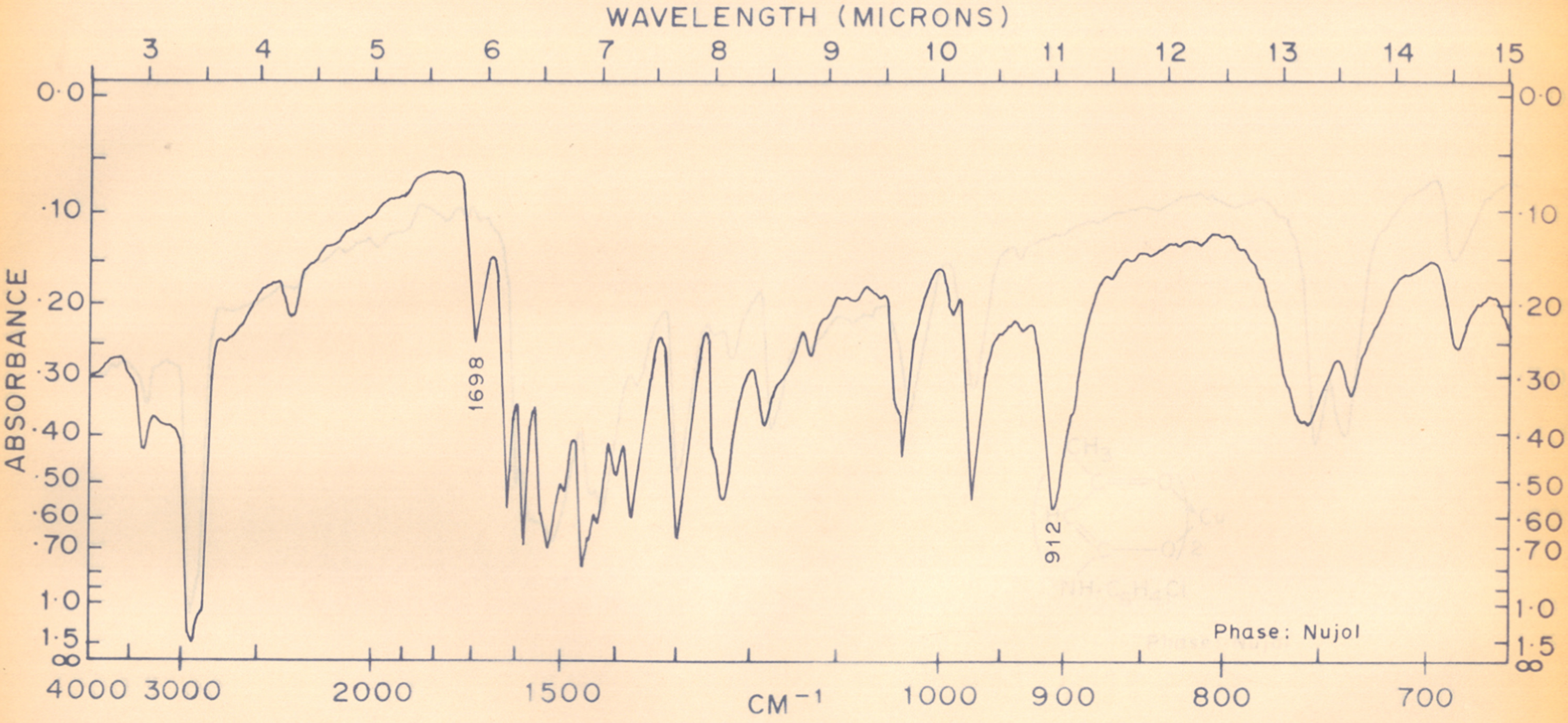


Fig. 15. IR Spectrum of acetoacet. orthochloroanilide complex of uranyl

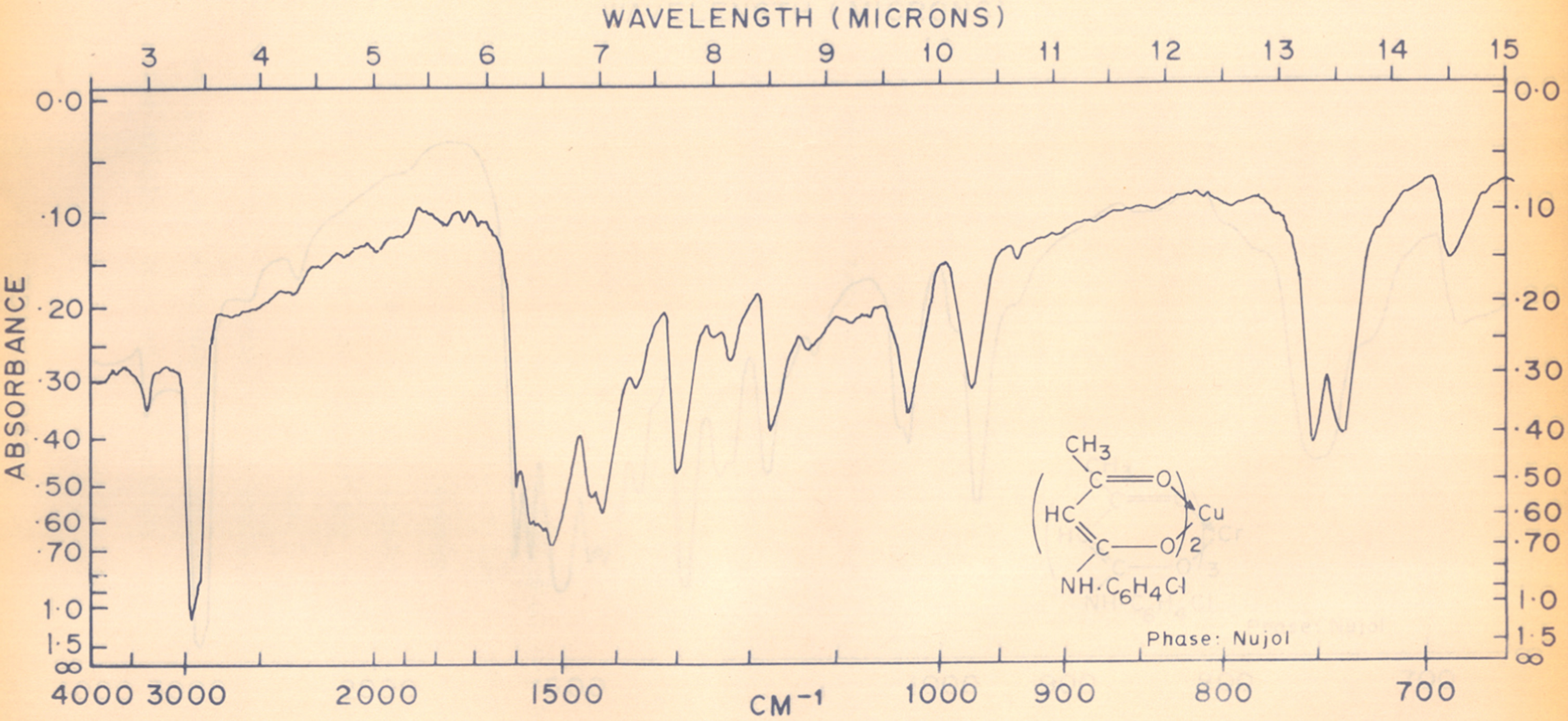


Fig. 16· IR Spectrum

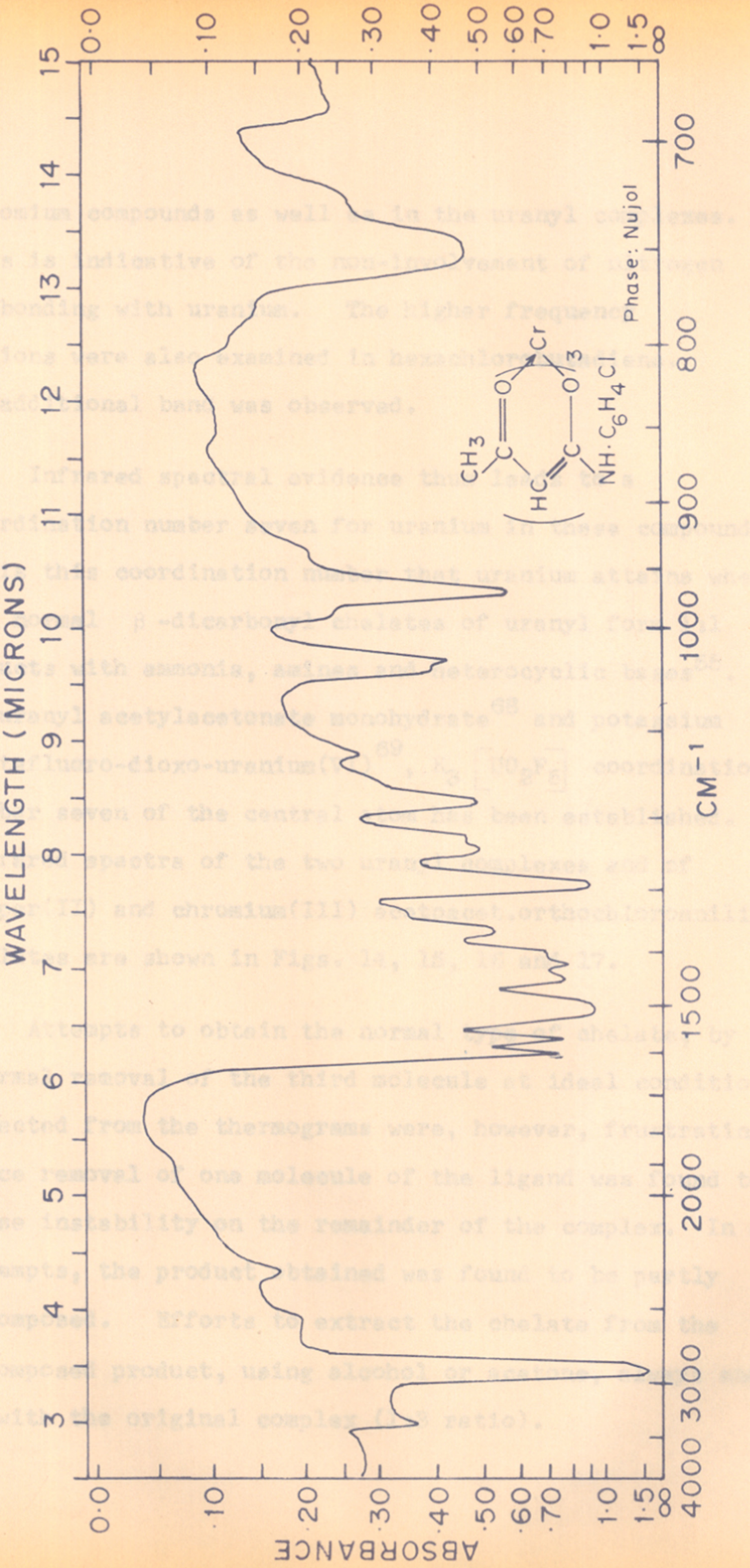


Fig. 17. IR Spectrum

chromium compounds as well as in the uranyl complexes. This is indicative of the non-involvement of nitrogen in bonding with uranium. The higher frequency regions were also examined in hexachlorobutadiene. No additional band was observed.

Infrared spectral evidence thus leads to a coordination number seven for uranium in these compounds. It is this coordination number that uranium attains when the normal β-dicarbonyl chelates of uranyl form 1:1 adducts with ammonia, amines and heterocyclic bases[55]. In uranyl acetylacetonate monohydrate[68] and potassium pentafluoro-dioxo-uranium(VI)[69], $K_3[UO_2F_5]$ coordination number seven of the central atom has been established. Infrared spectra of the two uranyl complexes and of copper(II) and chromium(III) acetoacet.orthochloroanilide chelates are shown in Figs. 14, 15, 16 and 17.

Attempts to obtain the normal type of chelate, by thermal removal of the third molecule at ideal conditions selected from the thermograms were, however, frustrating since removal of one molecule of the ligand was found to cause instability on the remainder of the complex. In all attempts, the product obtained was found to be partly decomposed. Efforts to extract the chelate from the decomposed product, using alcohol or acetone, always ended up with the original complex (1:3 ratio).

Experimental

Uranyl acetoacetanilide complex :- Acetoacetanilide (5.31 g.; 0.03 mole) was dissolved in absolute alcohol (70 ml.) and then added slowly with stirring to an aqueous solution (55 ml.) of uranyl acetate dihydrate (4.24 g.; 0.01 mole). The deep red, clear solution obtained was stirred for 3 hr. The reddish brown crystalline precipitate formed was filtered, washed with water and sucked dry. Crystallized twice from alcohol. The solvent was removed from the crystals at 80°C in vacuum. Yield : 3.9 g.(50%); m.p., 164°C. Found: C,44.95; H,4.01; N,5.41; U,29.63%. Required for $C_{30}H_{31}N_3O_8U$: C,45.06; H,3.88; N,5.26; U,29.80%.

Uranyl acetoacet.orthochloroanilide complex :- Prepared similarly. Orange red crystals; yield, 45%; m.p.,210°C. Found: C,39.71; H,3.25; N,4.53; U,26.50%. $C_{30}H_{28}Cl_3N_3O_8U$ requires: C,39.90; H,3.10; N,4.65; U,26.37%.

Chromium chelate of acetoacetanilide :- Prepared from chromic chloride, acetoacetanilide and urea as in the preparation of chromium acetylacetonate. Found: C,62.05; H,5.29; N,7.35; Cr,9.02%. Required for $C_{30}H_{30}N_3O_6Cr$: C,62.05; H,5.17; N,7.24; Cr,8.96%.

Chromium chelate of acetoacet.orthochloroanilide :- Prepared as in the above preparation. Recrystallized from chloroform. Found: C,52.91; H,4.08; N,6.32; Cr,7.71%. Required for $C_{30}H_{27}Cl_3N_3O_6Cr$: C,52.67; H,3.95; N,6.14; Cr,7.61%.

The thermal behaviour of the uranyl complexes in a stream of nitrogen was determined in a thermogravimetric balance using a McBain-Bakr type quartz spring[70]. This had a sensitivity of 2.5 mg./mm. extension and required only about 25 mg. of the sample for investigation. The temperature of the furnace was raised at a constant rate of about 2°C/min. by means of a programming system[71]. The extension of the spring was measured with a travelling microscope every 2 minutes.

Uranium in the uranyl complexes was~~e~~ estimated by ignition at 900°C to U_3O_8.

CHAPTER 6

LIGAND REPLACEMENT IN METAL ACETYLACETONATES BY ETHYLENEDIAMINETETRAACETIC ACID

LIGAND REPLACEMENT IN METAL ACETYLACETONATES BY ETHYLENEDIAMINETETRAACETIC ACID

During the past several years Schwarzenbach and his associates have published a series of papers dealing with complexing agents of extraordinary potency. To these aminocarboxylic acids they gave the name 'complexones'. The most familiar of these and possibly the most useful is ethylenediaminetetracetic acid*, EDTA.

EDTA was first made available by the I.G.Farbenindustrie[72] in 1936 and has since found ever increasing use as a complexing agent for metal ions. Its sodium salts are referred to in the literature by several trade names; Versene, Sequestrene, Trilon B and Complexone II, III or IV.

The acid itself is sparingly soluble in water and, therefore, has been of limited interest. The sodium salts have been generally used for studies involving EDTA. The chemistry of EDTA is characterized by the large number of metals for which it possesses an affinity rather than the quality of specificity.

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* (ethylenedinitrilo)tetraacetic acid.

The peculiar ability of EDTA to form very stable complexes results from the availability of four carboxyl and two tertiary amine groups to enter into strainless, five-membered rings, each ring including the metal ion. This system of rings is further stabilized by the ethylenic linkage between the two nitrogen atoms. The formation of more than four such rings is, however, difficult due to steric effects, leaving in the coordination sphere at least one molecule of water[73], which is replaceable by such groups as OH^-, NH_3, SCN^-, etc.[74].

Though question has been raised[75] as to the ability of an EDTA anion to occupy six coordination positions in the coordination sphere, a number of types of evidences for its hexadentate nature have been cited[76-78].

Solid EDTA chelates of metals have been prepared in many instances using simple metal salts and alkali or ammonium salts of EDTA[79-83]. Possibilities of anion penetration[74,84] leaves in doubt the exact composition of the products obtained. It was, therefore, of interest to synthesize metal-EDTA chelates by ligand replacement.

Several metal acetylacetonates were found in this investigation to react with EDTA in aqueous suspension.

From the resulting solution well-defined crystals of metal-EDTA chelates have been obtained.

When equivalent quantities are used the reaction proceeds to completion. The solution so obtained does not contain any other crystallizable substance, nor anions which can penetrate, so that almost theoretical yield of the pure substance is possible.

The EDTA chelates prepared by ligand replacement are of copper(II), nickel(II), cerium(III), lanthanum(III), neodynium(III), zirconium(IV) and thorium(IV). These compounds are represented as:

$CuH_2Y.H_2O$

$NiH_2Y.H_2O$

$CeHY.H_2O$

$LaHY.H_2O$

$NdHY.H_2O$

$ThY.2H_2O$

$ZrY.2H_2O$

where Y stands for the ethylenediaminetetraacetate anion.

The best use of this method, however, has been in the preparation of manganese(III) chelate of EDTA. A very well defined and stable non-ionic compound showing the unusual oxidation state of three for manganese is its acetylacetonate[30]. This has been used for the preparation of the EDTA chelate. However, the corresponding acid

($MnHY.nH_2O$) was found to decompose on standing in solution. Hence the stable potassium salt($KMnY.2H_2O$) was prepared using the acetylacetonate, EDTA and potassium hydroxide in the right proportion.

EDTA chelate of titanium(IV) was also prepared. However, in this preparation the starting material used was dichloro-bis(acetylacetonato)titanium(IV) and hence the disodium salt of EDTA was employed in place of EDTA. Due to the presence of sodium chloride in solution, only a small first crop was obtained pure ($TiY.H_2O$).

Infrared spectra of the compounds have been found to be similar to those reported[79,81,82,84,85]. A comparison of the spectra of these compounds is instructive.

All the EDTA chelates show a medium intensity band at about 1110 cm^{-1}. The occurrence of this band in anhydrous and hydrated metal EDTA chelates has been cited as an evidence of the nitrogen atoms being bonded to the metal in either type[79]. It is necessary that the nitrogens be coordinated to the metal, as otherwise, the ring structures formed will be unusually large.

The copper EDTA chelate showed two absorption bands of almost equal intensity at 1720 and 1605 cm^{-1}. The spectrum of the nickel compound is similar, but for the broadening of the 1605 cm^{-1} band. In the rare-earth metal chelates, a medium intensity band at 1670 cm^{-1} and a strong band at 1600 cm^{-1} were observed. The absorption at the higher frequency is due to the carboxylate group(s) of the ligand protected from coordination to the metal by being bonded to proton(s); the lower frequency band being due to the carboxylate groups bonded to the metal[76,79,83].

The relative intensities of the two bands are in agreement with the number of coordinated and uncoordinated carboxylate groups present. The EDTA residue, therefore, occupies four coordination positions of copper and nickel, and five coordination positions of the rare-earth metals.

For the cobalt(III) EDTA chelate, which is considered to be covalently bonded, the band due to the metal-bonded carboxylate groups occurs[86] at 1650 cm^{-1}. An increase in this frequency corresponds to an increase in the covalent character[83]. The occurrence of the band in these compounds near 1600 cm^{-1} shows the ionic nature of the carboxylate-metal bonds.

In the EDTA chelates of manganese(III), titanium(IV), thorium(IV) and zirconium(IV), the two bands were found to merge in the 1600-1700 cm^{-1} region, forming a single broad band. In thorium and manganese compounds, the broad band also showed fine structure. From the merging of the two bands, it is inferred that in these compounds all the four carboxylate groups are bonded to the metal. The broadness and fine structure might be due to small differences in the strengths of the metal-carboxylate bonds. Strain resulting from six-coordination of the ligand might lead to difference in bond lengths.

Experimental

Acetylacetonates of nickel(II), cerium(II), lanthanum(III), neodymium(III), zirconium(IV), thorium(IV) and titanium(IV) were prepared and purified by reported methods[21,30,87-89].

$Ni(acac)_2$:- Found:C,47.10; H,5.62%. Calcd.:C,46.76; H,5.45%.

$Ce(acac)_3$:- Found:C,41.32; H,4.95%. Calcd.:C,41.18; H,4.80%.

$La(acac)_3$:- Found:C,41.63; H,4.97%. Calcd.:C,41.30; H,4.82%.

$Nd(acac)_3$:- Found:C,41.10; H,4.71%. Calcd.:C,40.80; H,4.76%.

$Zr(acac)_4$:- Found:C,49.47; H,5.93%. Calcd.:C,49.26; H,5.75%.

$Th(acac)_4$:- Found:C,38.51; H,4.64%. Calcd.:C,38.21; H,4.46%.

$TiCl_2(acac)_2$:Found:C,37.49; H,4.61%. Calcd.:C,37.87; H,4.42%.

$CuH_2Y.H_2O$:- Powdered copper acetylacetonate(3.9 g.; 0.015 mole) was added to a suspension of AnalaR EDTA

(4.5 g.; 0.015 mole) in water (50 ml.) and stirred briskly. Warmed over a hot plate. The deep blue solution obtained was filtered and concentrated over a water bath. When crystals started appearing, it was allowed to cool slowly. When cold, it was further cooled in ice water, filtered, washed with ice-cold water and sucked dry. Another crop was obtained similarly. The bluish-green glistening crystals were powdered and further dried in a dessicator over concentrated sulphuric acid for a week. Yield: 4.1 g.(75%). Found: C,32.62; H,4.05; N,7.70, Cu,17.23%. Required for $C_{10}H_{16}N_2O_9Cu$: 32.29; H,4.30; N,7.54; Cu,17.09%.

Other EDTA chelates except those of manganese and titanium were prepared similarly. Shining crystals were obtained in all cases. Yield: 75-85%.

<u>$NiH_2Y.H_2O$</u> :- Found: C,32.37; H,4.73; N,7.66; Ni,16.23%. Required for $C_{10}H_{16}N_2O_9Ni$: C,32.73; H,4.36; N,7.64; Ni,16.01%.

<u>$CeHY.H_2O$</u> : - Found: C,27.01; H,3.85; N,6.42; Ce,31.12%. $C_{10}H_{15}N_2O_9Ce$ requires: C,26.84; H,3.35; N,6.26; Ce,31.31%.

LaHY.H_2O :- Found: C,26.58; H,3.22; N,6.13; La,31.41%.

$C_{10}H_{15}N_2O_9La$ required: C,26.91; H,3.36; N,6.28; La,31.16%.

NdHY.H_2O :- Found: C,26.93; H,3.56; N,6.04; Nd,32.23%.

$C_{10}H_{15}N_2O_9Nd$ requires: C,26.59; H,3.32; N,6.20; Nd,31.98%.

ZrY.$2H_2O$:- Found: C,28.87; H,4.01; N,6.51; Zr,22.13%.

$C_{10}H_{16}N_2O_{10}Zr$ requires: C,28.91; H,3.85; N,6.75; Zr,21.98%.

ThY.$2H_2O$:- Found: C,21.70; H,2.71; N,5.31; Th,42.11%.

$C_{10}H_{16}N_2O_{10}Th$ requires: C,21.58; H,2.87; N,5.04; Th,41.73%.

KMnY.$2H_2O$:- Powdered manganese(III) acetylacetonate (3.52 g.; 0.01 mole) was added to a thoroughly stirred mixture of potassium hydroxide (0.56 g.; 0.01 mole) and EDTA (3.73 g.; 0.01 mole) in cold water (15 ml.). A deep red solution was obtained, which was filtered. Cold alcohol (20 ml.) was added and the mixture kept in a refrigerator for 2 days. Well-defined deep red crystals were obtained. Another crop was obtained by adding more alcohol (10 ml.) and cooling again. Washed with alcohol and sucked dry. Yield: 2.5 g.(60%). Found: C,28.93; H,3.61; N,6.75; Mn,13.26%. $C_{10}H_{16}N_2O_{10}KMn$ requires: C,28.71; H,3.83; N,6.70; Mn, 13.14%.

TiY.H_2O :- Powdered dichloro-bis(acetylacetonato)titanium(IV) complex[89] (3.17 g.; 0.01 mole) was added to a solution of disodium salt of EDTA (3.72 g.; 0.01 mole) in water (100 ml.). After stirring briskly, it was filtered. To the clear filtrate alcohol was added with stirring until turbidity appeared. At this stage it was allowed to crystallize slowly. Uniform white crystals. Washed with alcohol and sucked dry. Yield: 1.2 g.(35%). Another crop obtained was found to be contaminated. Found: C,33.98; H,4.21; N,8.05; Ti,13.81%. Required for $C_{10}H_{14}N_2O_9Ti$: C, 33.90; H,3.96; N,7.91; Ti,13.53%.

Copper and manganese were estimated iodometrically. Other metals were determined by direct ignition to oxide. Nitrogen was estimated by Kjeldahl's method.

PART III

SPECTROSCOPIC STUDIES OF β-DICARBONYL COMPOUNDS AND THEIR METAL CHELATES

SPECTROSCOPIC STUDIES OF
β-DICARBONYL COMPOUNDS
AND THEIR METAL CHELATES

Ultraviolet and visible spectral studies (Chapter 1), proton magnetic resonance spectral studies (Chapter 2), and mass spectral studies (Chapter 3), are included in this part.

CHAPTER 1

ELECTRONIC ABSORPTION SPECTRA OF COPPER CHELATES OF β-DICARBONYL COMPOUNDS

ELECTRONIC ABSORPTION SPECTRA OF COPPER CHELATES OF β-DICARBONYL COMPOUNDS

Although the electronic absorption spectra of a few β-diketones and their metal chelates were reported repeatedly[1-8], and at times, attempts made[9-11] to gain structural information from these incomplete spectra, proper assignments of the ultraviolet bands were made only recently by Fackler, Cotton and Barnum[12]. These investigators studied the spectra of a broad span of α- and γ-substituted β-diketone complexes of copper. However, studies on the visible spectral region have been meagre.

In the present investigation, ultraviolet and visible absorption spectra of copper chelates of ethylacetoacetate, acetoacet.diethylamide, acetoacetanilide and acetoacet-orthochloroanilide have been studied in various solvents. Acetylacetonate, 1,1,1-trifluoroacetylacetonate and 3-nitroacetylacetonate of copper were also included in the study for comparison. Ultraviolet spectra of the respective ligands (except that of nitroacetylacetone, which could not be obtained) were recorded in methanol and in aqueous sodium hydroxide.

A separate review of the earlier work will not be attempted. Relevant references will be cited and discussed at appropriate places. The characteristic ultraviolet spectra of a few β-diketones and visible spectra of their metal chelates have been utilized for analytical purposes[13-17].

In methanol and in dilute aqueous sodium hydroxide, the ligand molecules studied in this investigation gave only a single band (in the ultraviolet region), due to transitions in the conjugated enol and in the conjugated enolate anion respectively (Table 1).

Table 1

Enol and enolate bands

Compound	Enol band		Enolate band	
	λ max. (mμ)	ε max.	λ max. (m μ)	ε max.
1. Acetylacetone	270	9250	285	17750
2. 1,1,1-trifluoro-acetylacetone	285	9833	286	10340
3. Ethylacetoacetate	239	2000	267	10570
4. Acetoacet.diethylamide	250	2862	270	10000
5. Acetoacetanilide	239	14470	290	22000
6. Acetoacet.orthochloro-anilide	238	14000	288	20660

In addition to large increase in intensity (enolization and ionization can be considered more or less complete in the alkaline medium[26]) the absorption bands are shifted to longer wave-lengths in aqueous sodium hydroxide. The shift to lower energy can be due to better equalization of the bond orders in the anion than in the hydrogen bonded enol[8].

The ultraviolet absorption spectrum of acetylacetone anion was studied theoretically by Hashimoto, Tanaka and Nagakura[27] who concluded that the band is caused by intramolecular charge transfer from the central carbon atom to the two carbonyl groups.

Unlike those of the ligands, the spectra of the metal chelates are characterized by three high intensity absorption bands in the ultraviolet (around 205 mμ, 235 mμ and 280 mμ), a shoulder of medium intensity in the near ultraviolet (at about 380 mμ) and a broad band in the visible (500-800 mμ) regions (Fig.18). These bands will henceforth be referred to as A, B, C, D and E respectively as in Fig.18.

Structure of the chelates vis-a-vis their spectra

There can be no doubt regarding the bonding atoms in β-diketone chelates. However, in chelates of β-ketoester, β-ketoamide and β-ketoanilide, two different structures are

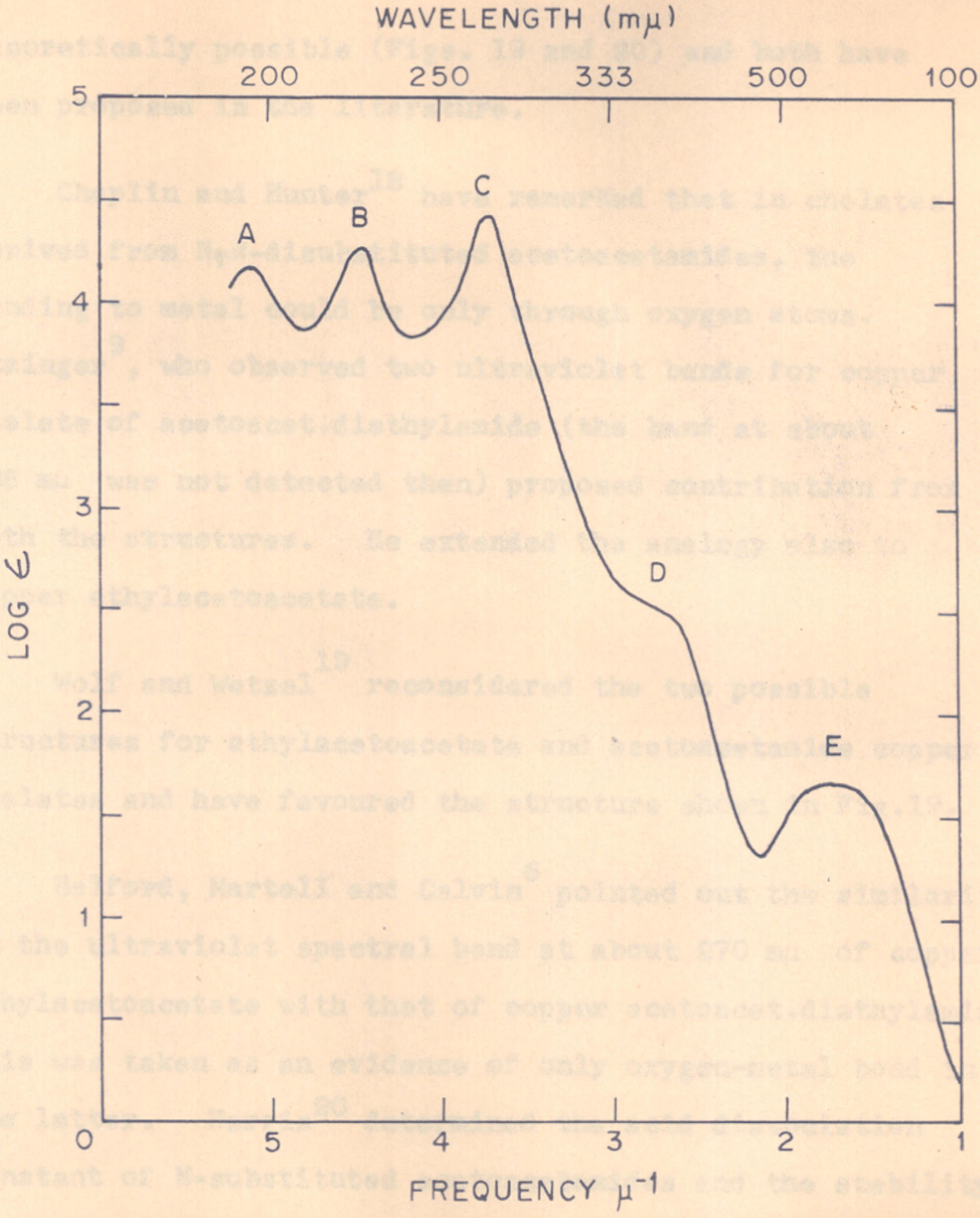


FIG. 18. ELECTRONIC ABSORPTION SPECTRUM OF COPPER CHELATES OF β-DICARBONYL COMPOUNDS.

theoretically possible (Figs. 19 and 20) and both have been proposed in the literature.

Chaplin and Hunter[18] have remarked that in chelates derived from N,N-disubstituted acetoacetamides, the bonding to metal could be only through oxygen atoms. Utzinger[9], who observed two ultraviolet bands for copper chelate of acetoacet.diethylamide (the band at about 205 mμ was not detected then) proposed contribution from both the structures. He extended the analogy also to copper ethylacetoacetate.

Wolf and Wetzel[19] reconsidered the two possible structures for ethylacetoacetate and acetoacetamide copper chelates and have favoured the structure shown in Fig.19.

Belford, Martell and Calvin[6] pointed out the similarity in the ultraviolet spectral band at about 270 mμ of copper ethylacetoacetate with that of copper acetoacet.diethylamide; this was taken as an evidence of only oxygen-metal bond in the latter. Harris[20] determined the acid dissociation constant of N-substituted acetoacetamides and the stability constant of their beryllium chelates. The complexes formed were considered to be chelates involving oxygen donor atoms by reason of their analogy with other diketo compounds and by virtue of the uniform relationship between complex formation and acid dissociation; the latter relation is not

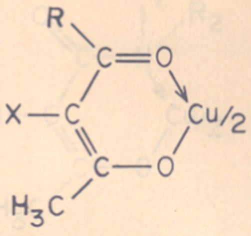
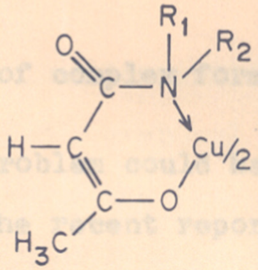
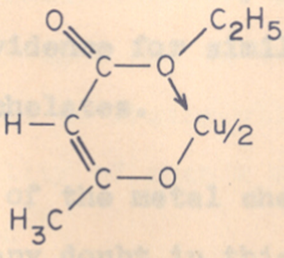


Fig. 19

	X	R	Chelate
1	H	CH_3	Copper acetylacetonate
2	H	CF_3	Copper trifluoroacetylacetonate
3	H	OC_2H_5	Copper ethylacetoacetate
4	H	$N(C_2H_5)_2$	Copper acetoacet·diethylamide
5	H	$NH \cdot C_6H_5$	Copper acetoacetanilide
6	H	$NH \cdot C_6H_4Cl$	Copper acetoacet·orthochloroanilide·
7	NO_2	CH_3	Copper nitroacetylacetonate



R_1	R_2	Chelate
C_6H_5	H	Copper acetoacetanilide
$C_6H_4 \cdot Cl$	H	Copper acetoacet·orthochloroanilide
C_2H_5	C_2H_5	Copper acetoacet·diethylamide



Chelate

Copper ethylacetoacetate

Fig 20

expected if the mode of complex formation differs.

The structural problem could have been considered as settled, but for the recent report[21] of the mass spectrum of copper acetoacetanilide, which has reopened the question of bonding atoms in these chelates. In addition to the molecular ion and the various degradation products, peaks were obtained in the 331 region which correspond to $(CuL + NHC_6H_5)^+$. This apparently gives the impression that nitrogen is bonded to the metal in the chelate. Assuming the chelate to be all-oxygen coordinated, the authors accounted for m/e 331 by postulating molecular rearrangement.

Electronic spectra of these compounds should give valuable information in this regard since a change in the bonding atom with the attended differences in the nature of conjugation should lead to striking spectral changes. The excellent agreement observed in number, position and intensity of the absorption bands can be regarded as a clear evidence for similar structure (Fig.19) for all the chelates.

Infrared spectra of the metal chelates should be sufficient to dispel any doubt in this regard. No absorption is observed in any of these chelates (spectrum of copper acetoacet.orthochloroanilide is shown in Part II, Chapter 5) in the carbonyl region above 1620 cm^{-1}, where one normally expects the free carbonyl group of the alternate structure (Fig.20) to absorb.

The alternate structure can be dismissed also from stability considerations. Bond angle requirements restrict the most favourable structure for chelates to a five-membered singly bonded ring or a six-membered ring with two double bonds. In the six-membered chelate ring of structure II, there is only one double bond.

Band C

This band is considered first since in many of the earlier studies with β-diketone chelates, only this band has been reported. Yamasaki and Sone[22,23] examined the position of this band in a number of bivalent metal acetylacetonates, with respect to the enol band of acetylacetone. They found that the shift was more in stabler chelates and brought out on this basis a stability order which ran parallel to Irving-William stability order[24]. The possibility of such a correlation was subsequently questioned[25].

Whereas Yamasaki and Sone kept the ligand the same and varied the metals, in this investigation the metal was kept the same but the ligands were varied. The position and intensity of band C of the metal chelate in methanol and shift in wave-length from the corresponding enol band are tabulated below (Table 2).

Table 2

Band C of copper chelates(in methanol)

Copper chelates of	Band C λ max. (mμ)	Band C ϵ max.	Shift from the enol band position(m μ)
1. Acetylacetone	289	23160	19
2. 1,1,1-trifluoroacetylacetone	289	24670	4
3. Ethylacetoacetate	269	19250	30
4. Acetoacet.diethylamide	272	19500	22
5. Acetoacetanilide	290	37340	51
6. Acetoacet.orthochloroanilide	288	35555	50
7. 3-nitroacetylacetone	284	28430	-

The data prove convincingly that the hypothesis of Yamasaki and Sone does not hold good for different ligands and same metal. From the shift it would appear that copper ethylacetoactate is stabler than copper acetylacetonate, though the much higher stability of the latter is certain[28]. Copper trifluoroacetylacetonate, which is comparable in stability to copper ethylacetoacetate[28-30], appears much less stable. In this investigation copper acetoacet.diethylamide has been found to be more stable than the two acetoacetanilide chelates. Here also, data in the chart show the opposite order.

Band B

Though the occurrence of this band has been mentioned in most of the earlier reports, only recently was its origin explained[12]. A band in this region was observed for metal chelates containing aromatic pendant groups and consequently this band was related to the conjugation of the aromatic ring with the unsaturated chelate ring system[31]. In the compounds studied, even where aromatic side group is present, it is not directly attached to the chelate ring. The origin should, therefore, be different.

Barnum suggested[32] that this band also could be due to $\pi - \pi^*$ transition as is band C. A more likely assignment proposed later is as a charge transfer band involving the jump of a σ bonding or oxygen n electron to a metal orbital[12].

Unlike band C which did not show any clear trend, band B, though rather broad, showed a small but definite blue shift (hypsochromic shift) with increase in the polarity of the solvent (Table 3).

Table 3

Position of band B in cyclohexane and methanol(blue shift)

Copper chelate of	Cyclohexane	Methanol	
	λmax.(mμ)	λmax. (mμ)	ϵ max.
1. Acetylacetone	242	236	15790
2. 1,1,1-trifluoro-acetylacetone	237	232	14000
3. Ethylacetoacetate	235	225	10500
4. Acetoacet.diethylamide	232	229	17500
5. Acetoacetanilide	Insoluble	240	27280
6. Acetoacet.orthochloro-anilide	244	238	31110
7. 3-nitroacetylacetone	Insoluble	230	14670

This is diagnostic of electronic transitions of the n-π^* type[33,34] for organic compounds. Since metal-caused perturbations are already there in these compounds, this conclusion may have to be taken with caution. Also, n-π^* transition in conjugated ketones occurs in the near ultraviolet region[35,36] where a shoulder is observed in the spectra of these compounds. The earlier assignment as due to the jump of an oxygen n electron to a metal orbital seems reasonable, in which case the transition is of the reduction type, i.e. the electron goes from the ligand to the metal. Beryllium chelates of acetylacetone, ethylacetoacetate and acetoacet.diethylamide did not show this band.

Band A

The occurrence of band A in metal chelates of diketones was detected only very recently[12]; it has been ascribed to π-π^* transition. The position of this band which is very close to the transparency limit of the solvent used for recording it, could not be judged precisely in all cases. The chart shows such positions which were ascertained. (Table 4).

Table 4

Position and intensity of Band A in cyclohexane

Compound	$\lambda_{max.}$(mμ)	$\epsilon_{max.}$
1. Copper acetoacet.diethylamide	205	16600
2. Copper acetoacetanilide	207	27300
3. Copper acetoacet.orthochloroanilide	208	30000

Band D

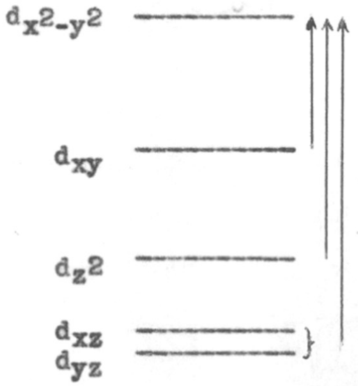
This band appears only as a shoulder. In the trifluoroacetylacetonate and nitroacetylacetonate chelates the shoulder is hardly distinguishable. But the band becomes conspicuous with greater inductive effect of the substituent and also appears to occur at lower energy (Fig.21). These evidences support the assignment as due to n-π^* transition. The band, being an unresolved shoulder, occurrence of blue shift could not be detected.

Band E

The low intensity of the broad band is typical of forbidden transitions and is attributable to 3-d orbital transitions. From the asymmetric contour of the band, its composite nature was never in doubt. The band was found quite sensitive to the solvent used.

The broadness and the solvent susceptibility of the bands are in striking contrast to the crystal field spectra of lanthanide complexes[37]. The latter spectra consist of very sharp lines, since the transitions which are observed arise and terminate upon levels which have very little bonding or antibonding character, arising as they do from the purely $4f^n$ configuration. Since the inner f electrons are almost unaffected by ligands or solvents, the transitions are not affected appreciably by outside perturbations.

Crystal field theory and ligand field theory have produced a standard picture of bonding in divalent copper chelates. In this picture one thinks of the four ligand atoms around the cupric ion as forming an approximate square. The electrostatic field created by the presence of the ligands, removes the degeneracy of the five d-orbitals.



In a centric molecule, all levels can be classified as gerade (g) and ungerade(u); g ⟶ g and u ⟶ u transitions are forbidden. All the 3d orbitals and their descendants in the centric molecule are g. Hence d-d transitions are forbidden purely on symmetry grounds. These Laporte forbidden transitions, neverthelelss, occur at low intensity, due to vibrational removal of the centre of symmetry of the molecule. The transitions are said to be 'vibronically' allowed.

Of the five d orbitals the xz and the yz are still degenerate, and as shown in the diagram, a maximum of three transitions are possible. The crystal field theory does not preclude the existence of ordinary covalent bonds, but merely asserts their irrelevance, except, as a source of potential for the particular transitions under consideration. The theory is only applicable to the weak transitions among the d orbital levels and cannot account for the much stronger absorptions considered earlier.

For copper acetylacetonate and copper 3-ethylacetylacetonate the visible band has been resolved into three gaussian components[38], to account for the three transitions. Basu and Basu[39] also resolved the visible bands of copper ethylenediamine-bis(acetylacetone), copper salicylaldehyde, copper salicylethylenediamine and copper salicylaldoxime into three components. However, the simple picture is at variance with the findings of the crystal spectral studies of copper acetylacetonate[40]. Many attempts made[41-45] to interpret the polarized spectra correctly and to connect with the solution spectra did not meet with complete success, owing to molecular stacking in the crystal[41].

Graddon[46] assigning the near ultraviolet shoulder (Band D) also to crystal field transition, resolved the visible band into two gaussian components and accounted for the three transitions in copper ethylacetoacetate. But, since then the shoulder has been assigned differently[12]. The existing evidence suggests strongly that all the possible transitions lie in the visible region only[41].

Solvent susceptibility

Solvents used in this study can be divided into three groups, according to their effect on the visible spectrum.

(1) Non-reacting solvents (cyclohexane, benzene and chloroform).

(2) Oxygen-donor solvents (methanol, acetone and tetrahydrofuran) in which the effect was moderate, and

(3) Nitrogen-donor solvents (dimethyl formamide and pyridine) in which the effect was considerably large.

Increasing coordinating power of the solvent was found to bring about increasing red shift (bathochromic shift) indicating the possibility of solvents coordinating to the metal in the z axis. Such an attachment raises the energy of the d_{z^2} orbital. The d_{xz} and d_{yz} orbitals are also accordingly raised in energy. Any secondary effect[49] would be to lower the energy of the $d_{x^2-y^2}$ and the d_{xy} orbitals. Consequently, the transitions

$$\left.\begin{matrix} d_{xz} \\ d_{yz} \end{matrix}\right| \rightarrow d_{x^2-y^2} \qquad \text{and}$$

$$d_{z^2} \rightarrow d_{x^2-y^2}$$

occur at lower energy; hence the red shift of the band.

The most dramatic solvent effect, however, has been the very large increase in intensity of the visible band of copper acetoacetanilide and copper acetoacet.orthochloroanilide, with increasing coordinating power of the solvent, especially with pyridine. Earlier reports[38,46] of such enormous increase in intensity (hyperchromic effect) of the visible band of copper acetylacetonate and copper ethylacetoacetate in pyridine were also confirmed in this investigation. The visible band of copper trifluoroacetylacetonate, copper nitroacetylacetonate and copper acetoacet.diethylamide, however, registered comparatively much less increase. This difference is attributed to

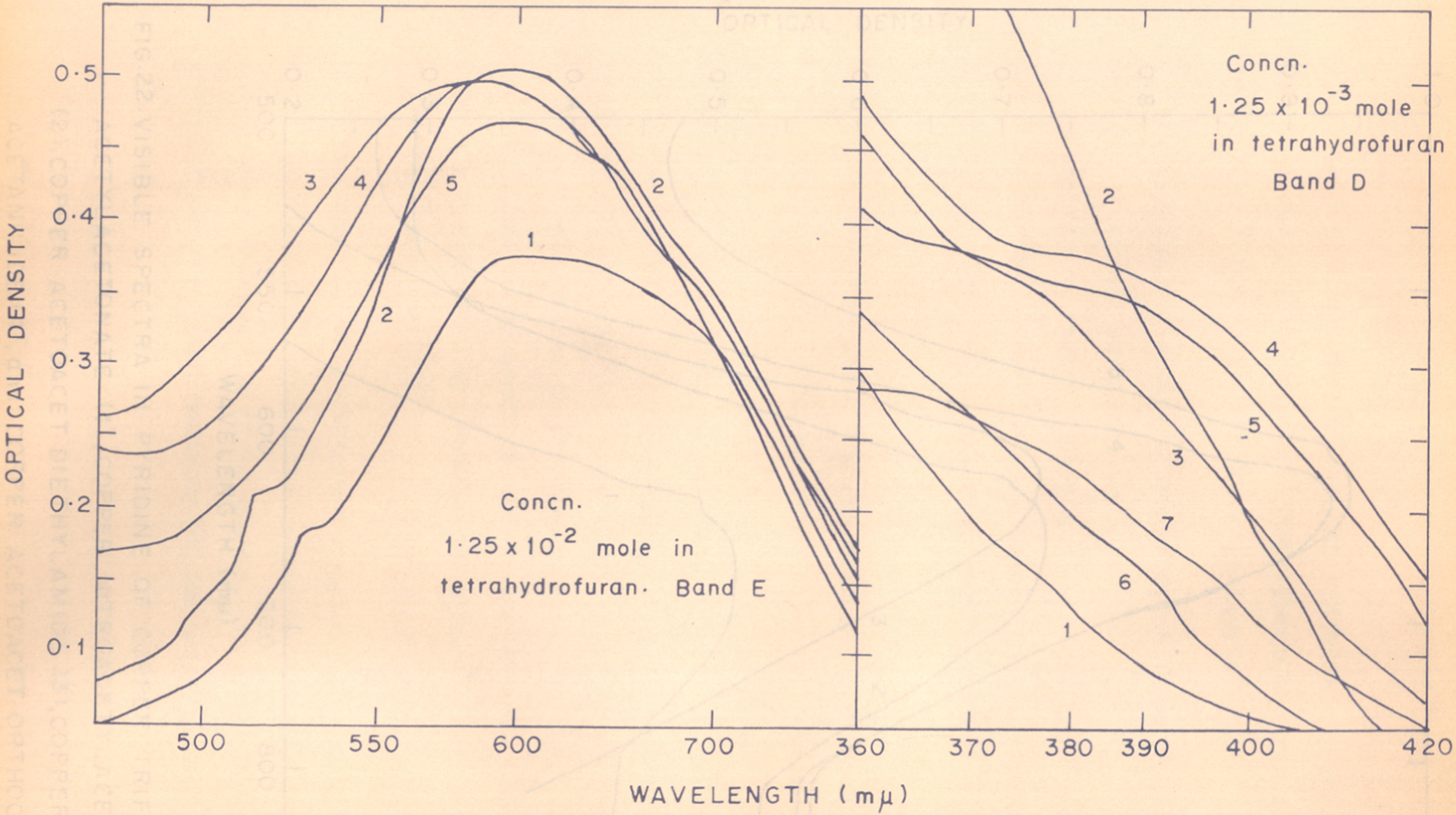


Fig. 21. Copper trifluoroacetylacetonate (1), Copper nitroacetylacetonate (2), Copper acetoacet·diethylamide (3), Copper acetoacetanilide (4), Copper Acetoacet· orthochloroanilide (5), Copper acetylacetonate (6), and Copper ethylacetoacetate (7).

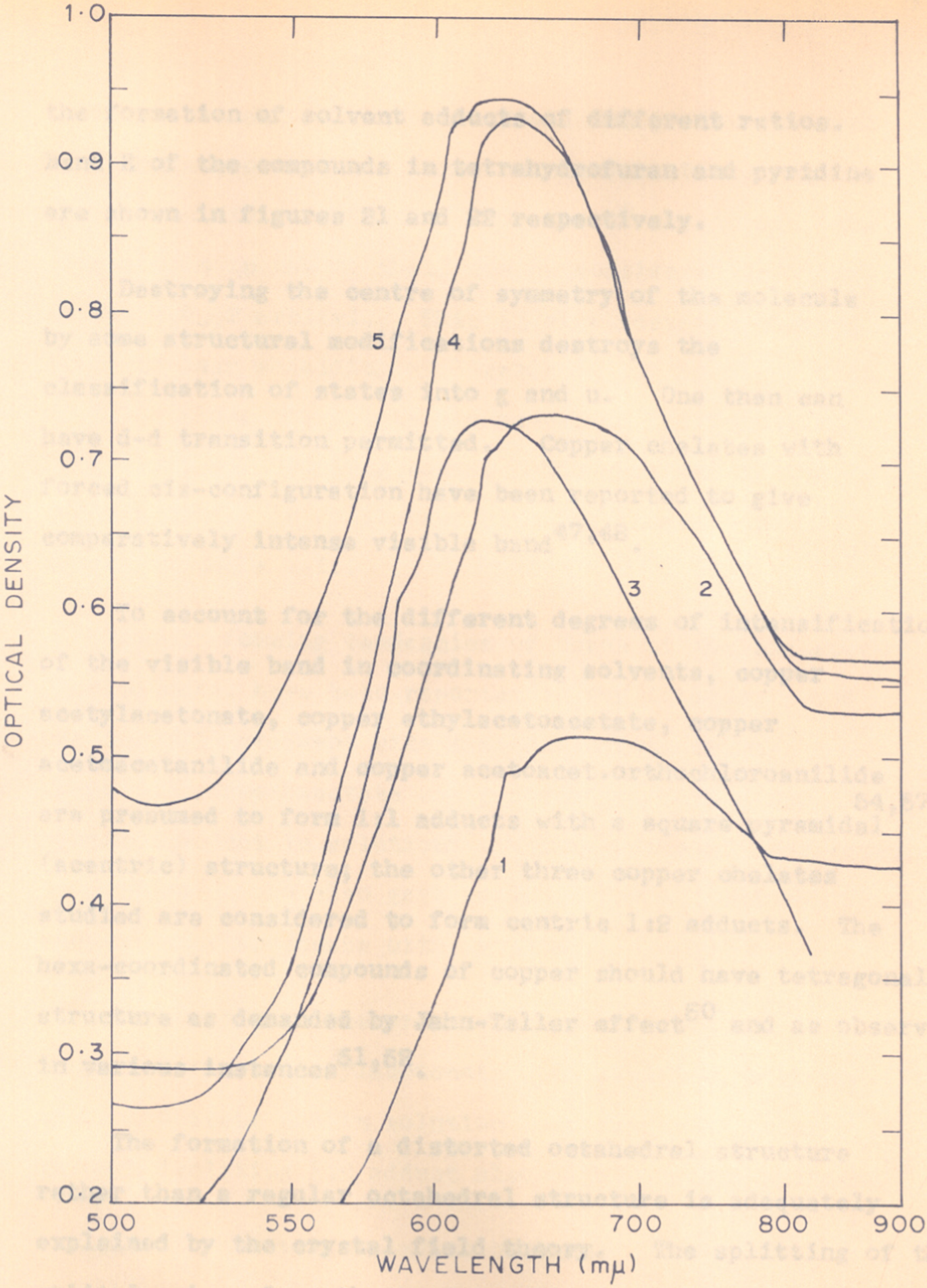


FIG. 22. VISIBLE SPECTRA IN PYRIDINE OF COPPER TRIFLUOROACETYLACETONATE (1), COPPER NITROACETYLACETONATE (2), COPPER ACETOACET DIETHYLAMIDE (3), COPPER ACETOACETANILIDE (4), and COPPER ACETOACET ORTHOCHLOROANILIDE (5).

the formation of solvent adducts of different ratios. Band E of the compounds in tetrahydrofuran and pyridine are shown in figures 21 and 22 respectively.

Destroying the centre of symmetry of the molecule by some structural modifications destroys the classification of states into g and u. One then can have d-d transition permitted. Copper chelates with forced cis-configuration have been reported to give comparatively intense visible band[47,48].

To account for the different degrees of intensification of the visible band in coordinating solvents, copper acetylacetonate, copper ethylacetoacetate, copper acetoacetanilide and copper acetoacet.orthochloroanilide are presumed to form 1:1 adducts with a square pyramidal[54,57,58] (acentric) structure; the other three copper chelates studied are considered to form centric 1:2 adducts. The hexa-coordinated compounds of copper should have tetragonal structure as demanded by Jahn-Teller effect[50] and as observed in various instances[51,52].

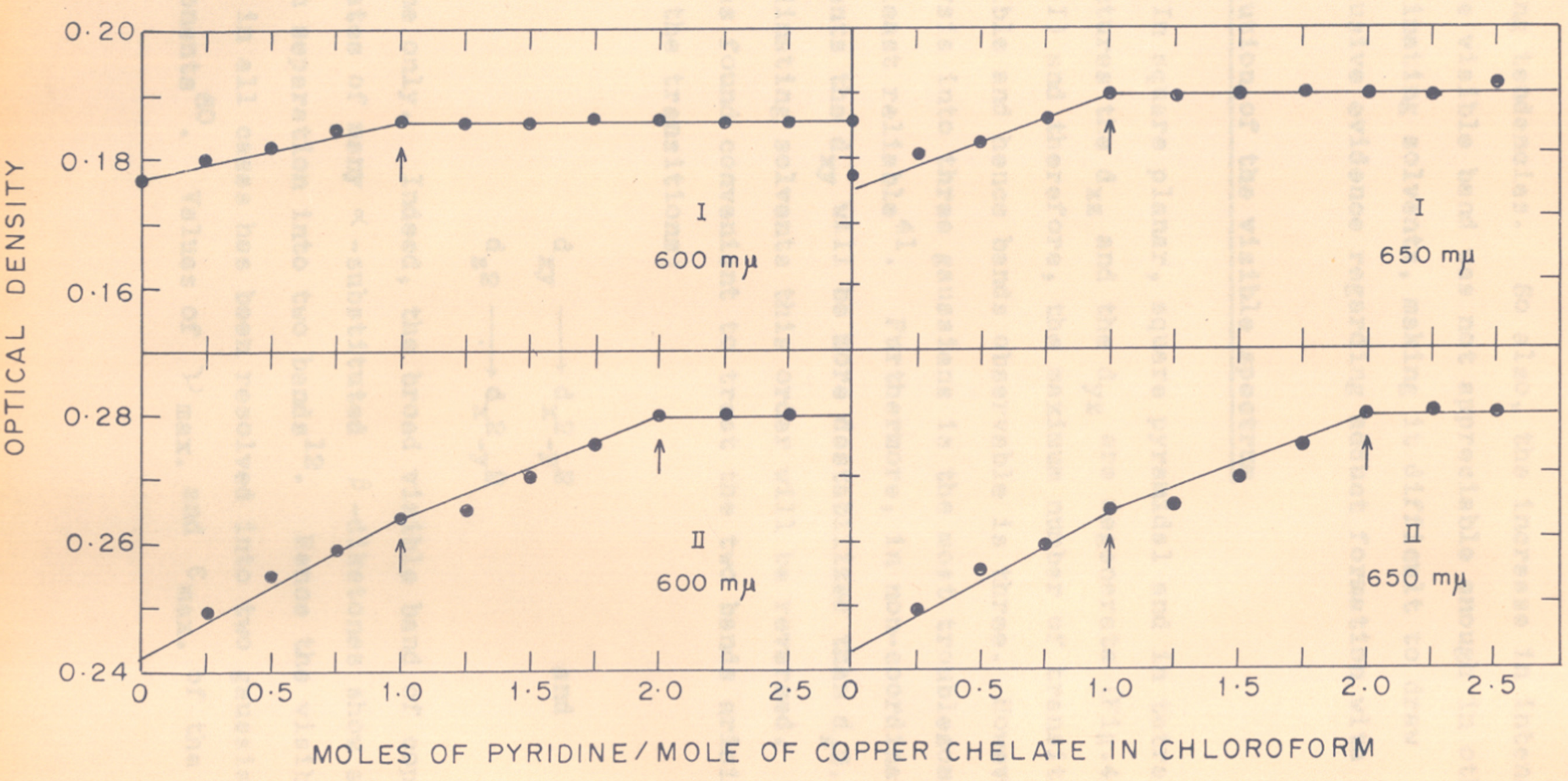
The formation of a distorted octahedral structure rather than a regular octahedral structure is adequately explained by the crystal field theory. The splitting of the orbitals arises from the tendency of the metal electrons to avoid those regions where the field due to the attached ligands is greatest and hence to concentrate in regions where this field is least. For the d^9 cupric ion, the single hole in the 3d shell can be considered to occur in the $d_{x^2-y^2}$ orbital. This in electrostatic theory, leads to less shielding of ligands in the xy plane than of those along the z axis and hence, to the formation of four short and two long bonds. The weakness of the 'adduct bonds' is consistent with the longer bond length in the z axis.

Adduct forming tendencies of three of the chelates studied here, have been reported in the literature and are in full agreement with the conclusions drawn. Copper ethylacetoacetate was reported to form a 1:1 pyridine adduct in solution[53]. This was confirmed later by Graddon[54], who also gave evidence for 1:1 adduct of copper acetylacetonate with pyridine.

The report on the preparation of 1:2 adduct[55] of copper trifluoroacetylacetonate with pyridine, both in the solid state and in solution, was supported later through isolating 1:2 adduct also with 4-methyl pyridine[56].

It is, however, relevant to think whether some of the above reports wherein the adduct formation with pyridine was examined in non-coordinating solvents like chloroform, cyclohexane etc. can be applicable also to solution entirely of pyridine. It is noteworthy in this regard that addition of liberal excess of pyridine did not show any increased ratio in the above studies[54]. So also, copper tetrammine species, which in aqueous solution formed 1:1 adduct with another molecule of ammonia, did not show any other ratio even in liquid ammonia[59].

Attempts to prepare solid pyridine adduct of the remaining four chelates studied in this investigation, did not meet with success. In each case the original chelate was finally obtained unchanged, presumably due to the instability of the adducts. However, evidence for copper acetoacet.orthochloroanilide forming a 1:1 adduct with pyridine was obtained in chloroform solution by the mole ratio method (spectrophotometry, Fig.23). No other adduct was formed. Under similar conditions copper acetoacet.diethylamide gave evidence of forming 1:1 and 1:2 adducts (Fig.23). It is reasonable to regard that in solution entirely of pyridine, only the higher ratio adduct is formed. For copper nitroacetylacetonate and copper acetoacetanilide, due to their insufficient solubility in non-reacting solvents, it was not possible to check the adduct



FIG· 23· COMPOSITION OF PYRIDINE ADDUCTS OF COPPER ACETOACET·ORTHOCHLORO-ANILIDE I, and COPPER ACETOACET·DIETHYLAMIDE II·

forming tendencies. So also, the increase in intensity of the visible band was not appreciable enough in other coordinating solvents, making it difficult to draw conclusive evidence regarding adduct formation with them.

Resolution of the visible spectrum

In square planar, square pyramidal and in tetragonal structures the d_{xz} and the d_{yz} are degenerate (Fig.4.2, Part I) and therefore, the maximum number of transitions possible and hence bands observable is three. However, analysis into three gaussians is the most troublesome and the least reliable[41]. Furthermore, in non-coordinating solvents the d_{xy} will be more destabilized than d_{z^2}. In coordinating solvents this order will be reversed. Hence, it was found convenient to treat the two bands arising from the transitions

$$d_{xy} \longrightarrow d_{x^2-y^2} \qquad \text{and}$$

$$d_{z^2} \longrightarrow d_{x^2-y^2}$$

as one only. Indeed, the broad visible band of copper chelates of many α-substituted β-diketones show a rough separation into two bands[12]. Hence the visible band in all cases has been resolved into two gaussian components[60]. Values of $\nu_{max.}$ and $\epsilon_{max.}$ of the resolved curves are given in Tables 5-8, along with apparent $\nu_{max.}$ of the experimental curve, which is indicative of the red shift:

Band at lower frequency (resolved Band I)	$$\left.\begin{array}{l} d_{xy} \longrightarrow d_{x^2-y^2} \\ d_{z^2} \longrightarrow d_{x^2-y^2} \end{array}\right\}$$
Band at higher frequency (resolved band II)	$$\left.\begin{array}{l} d_{xz} \\ d_{yz} \end{array}\right\vert \longrightarrow d_{x^2-y^2}$$

Diffuse reflectance spectra were also recorded. The bands remained unresolved, although the outline had a wavy appearance particularly when transferred to the more symmetric wave-number scale. Reflectance spectra of copper acetoacet.diethylamide is shown in Fig.24 as a representative type.

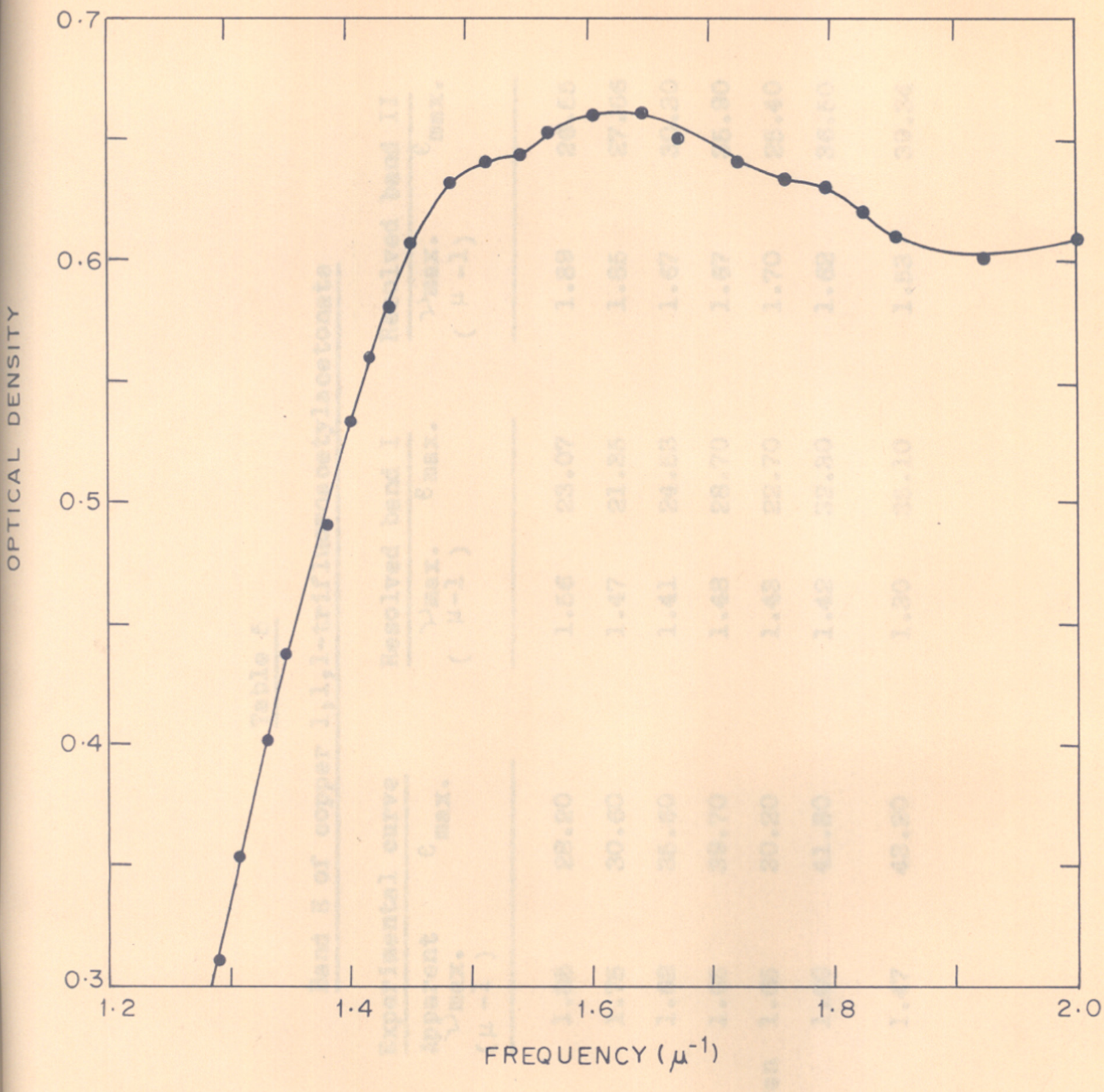


Fig. 24. Reflectance spectrum of copper acetoacet.diethylamide

Table 5

Band E of copper 1,1,1-trifluoroacetylacetonate

Solvent	Experimental curve		Resolved band I		Resolved band II	
	Apparent $\nu_{max.}$ (μ^{-1})	$\epsilon_{max.}$	$\nu_{max.}$ (μ^{-1})	$\epsilon_{max.}$	$\nu_{max.}$ (μ^{-1})	$\epsilon_{max.}$
Benzene	1.85	28.20	1.56	23.07	1.89	26.55
Chloroform	1.75	30.60	1.47	21.35	1.85	27.66
Methanol	1.62	35.60	1.41	24.53	1.67	30.30
Acetone	1.65	39.70	1.48	28.70	1.67	35.90
Tetrahydrofuran	1.65	30.20	1.43	22.70	1.70	25.40
Dimethylformamide	1.60	41.80	1.42	32.30	1.62	36.50
Pyridine	1.47	43.20	1.30	35.10	1.53	39.34

Table 6

Band E of copper acetoacet.diethylamide

Solvent	Experimental curve		Resolved band I		Resolved band II	
	Apparent ν max. (μ^{-1})	ϵ max.	ν max. (μ^{-1})	ϵ max.	ν max. (μ^{-1})	ϵ max.
Benzene	1.80	36.00	1.59	29.43	1.88	33.45
Carbon-tetrachloride	1.80	35.60	1.57	29.09	1.91	32.24
Chloroform	1.85	34.90	1.65	28.30	1.92	31.38
Methanol	1.72	35.80	1.59	26.97	1.79	30.80
Acetone	1.75	37.00	1.54	27.47	1.88	31.34
Tetra-hydrofuran	1.75	40.00	1.53	26.63	1.80	34.53
Dimethyl-formamide	1.70	41.50	1.56	30.30	1.79	37.08
Pyridine	1.60	58.00	1.36	36.10	1.62	48.90

Table 7

Band E of copper acetoacetanilide(I)
and
copper 3-nitroacetylacetonate(II)

Compound	Solvent	Experimental curve		Resolved band I		Resolved band II	
		Apparent νmax. (μ^{-1})	ϵ max.	νmax. (μ^{-1})	ϵ max.	νmax. (μ^{-1})	ϵ max.
I	Acetone	1.77	42.40	1.58	33.05	1.87	38.20
I	Tetrahydrofuran	1.72	40.00	1.55	29.70	1.77	35.40
I	Dimethylformamide	1.69	51.60	1.54	40.16	1.73	47.04
I	Pyridine	1.57	74.20	1.37	49.90	1.60	63.90
II	Acetone	1.67	51.60	1.50	37.75	1.71	45.97
II	Tetrahydrofuran	1.69	41.00	1.51	29.17	1.72	37.00
II	Pyridine	1.55	58.40	1.32	46.85	1.57	52.30

Table 8

Band E of copper acetoacet.orthochloroanilide(I), copper acetylacetonate(II), and copper ethylacetoacetate(III)

Compound	Solvent	Experimental curve		Resolved band I		Resolved band II	
		Apparent ν max. (μ^{-1})	ϵ max.	ν max. (μ^{-1})	ϵ max.	ν max. (μ^{-1})	ϵ max.
I	Chloroform	1.85	36.10	1.59	28.40	1.94	31.00
I	Tetrahydrofuran	1.67	37.80	1.51	29.40	1.73	32.93
I	Dimethylformamide	1.67	49.60	1.54	40.76	1.72	45.00
I	Pyridine	1.59	75.60	1.37	50.40	1.62	64.40
II	Dimethylformamide	1.72	51.90	1.53	35.43	1.76	44.03
III	Dimethylformamide	1.61	57.40	1.44	45.42	1.65	52.93

Polarographic stability comparison of copper chelates

Polarographic behaviour of coordination compounds and important applications of polarography in coordination chemistry have been recently reviewed[61]. Evaluation of stability constants of complexes on the basis of polarographic data was the subject matter of a recent treatise by Biernat[62].

Polarographic method has been used by several investigators for stability comparison among copper chelates of β-diketones[28,30,63,64]. However, such studies were not extended to copper chelates of β-ketoamides and β-ketoanilides. It was thought desirable to obtain an idea of the stability orders of copper chelates of acetoacet.diethylamide, acetoacetanilide and acetoacet.orthochloroanilide,in order to check the hypothesis of Yamasaki and Sone.

Due to poor solubility behaviour, selection of a suitable polarographic solvent, common for all the three chelates, posed a difficult problem. Aqueous pyridine (50% V/V) was found to satisfy the conditions. This solvent system introduces possibilities of solvation, but it does not preclude a qualitative comparison of the stability orders. Potassium nitrate was used as supporting electrolyte. As has been observed by Calvin and Bailes[28] in this system the cupric ion was reduced in two one electron stages (Fig.25).

For the copper chelates, the second wave ($Cu^{+} \rightarrow Cu^{o}$) is identical with that obtained with cupric acetate. However, the first wave($Cu^{2+} \rightarrow Cu^{+}$) occurs at more negative potentials in the chelates than in copper acetate. The difference $\Delta E_{1/2}$ between the first half wave potential for the chelate and that for the unchelated cupric ion should be a measure of the stability of the Cu(II) chelates.

The relative stabilities in the series are obtained directly from the relative $E_{1/2}$ values of the compounds[28]; the more negative the potential, the greater the stability of the chelate.

Chelate	First half-wave potential $E_{1/2}$
Copper acetoacet.diethylamide	-0.112
Copper acetoacetanilide	-0.075
Copper acetoacet.orthochloroanilide	-0.070

Copper acetoacet.diethylamide emerges as the most stable; it is considerably more stable than the acetoacetanilide chelates.

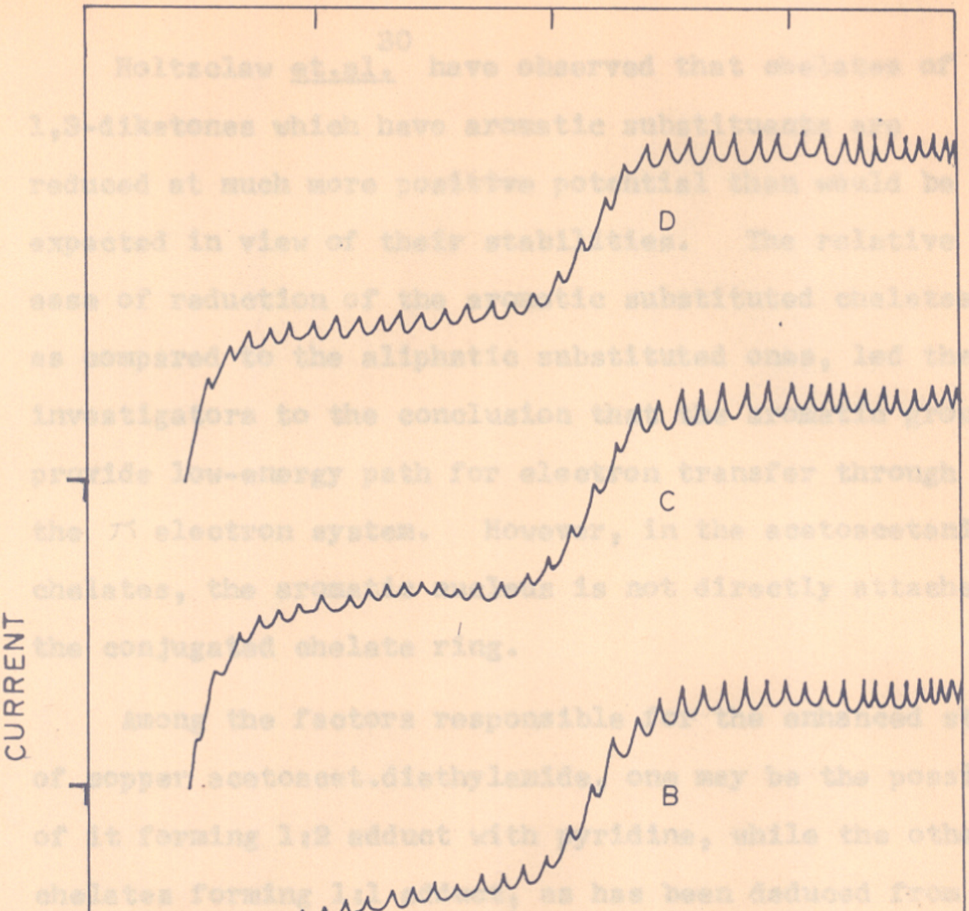


Fig.25. Polarograms of Copper acetate (A), Copper acetoacet. diethylamide(B), Copper acetoacetanilide (C), and Copper acetoacet.orthochloroanilide(D) in 1:1 pyridine-water mixture (concn. 0·001 mole)

Holtzclaw et.al.[30] have observed that chelates of 1,3-diketones which have aromatic substituents are reduced at much more positive potential than would be expected in view of their stabilities. The relative ease of reduction of the aromatic substituted chelates as compared to the aliphatic substituted ones, led these investigators to the conclusion that the aromatic groups provide low-energy path for electron transfer through the π electron system. However, in the acetoacetanilide chelates, the aromatic nucleus is not directly attached to the conjugated chelate ring.

Among the factors responsible for the enhanced stability of copper acetoacet.diethylamide, one may be the possibility of it forming 1:2 adduct with pyridine, while the other two chelates forming 1:1 adduct, as has been deduced from the solvent susceptibility of their visible spectral bands. The effect of change in coordination number on stability has, hitherto, been to a large extent overlooked.

Since the copper chelates and copper acetate give similar second wave ($E_{1/2}$, -0.545), it is considered that the same species is reduced at this stage in all cases. Decomposition of metal chelates on reduction to Cu(I) and formation of pyridine solvates in all the instances can be envisaged.

Materials, Methods and Procedures

Copper acetoacet.diethylamide was prepared by reported method[9]. Found: C,51.31; H,7.61%. Calcd.: C,51.12; H,7.46%.

Beryllium acetoacet.diethylamide :- Prepared as follows: Basic beryllium carbonate~~s~~, $BeCO_3.Be(OH)_2$, (1.12 g., 0.01 mole) was dissolved in minimum quantity of hot dilute hydrochloric acid and filtered. Acetoacet.diethylamide (6.3 g.; 0.04 mole) was dissolved in water (45 ml.) by adding ammonium hydroxide drop by drop. The latter solution was then added to the former solution slowly, with vigorous stirring. White crystals were formed immediately. Filtered, washed with water and sucked dry. Recrystallized from benzene-petroleum ether. Yield: 5.5 g.(86%); m.p.; 109.5°C. Found: C,60.01; H,8.93; N,8.65; Be,2.79%. $C_{16}H_{28}N_2O_4Be$ requires: C,59.81; H,8.72; N,8.72; Be,2.80%.

Preparation of all other compounds has been described in Part II.

Spectroscopic grade solvents were used for recording the spectra. These were stored full in amber coloured bottles.

The following concentrations were used for recording the enol spectra in methanol:

Acetylacetone	8×10^{-5} mole
1,1,1-trifluoroacetylacetone	6×10^{-5} "
Ethylacetoacetate	3×10^{-4} "
Acetoacet.diethylamide	2.9×10^{-4} "
Acetoacet.orthochloroanilide	5×10^{-5} "
Acetoacetanilide	5×10^{-5} "

For recording the spectra of the enolate anions, known quantity of the β-dicarbonyl compound was dissolved in 0.1N sodium hydroxide and then diluted to volume. After preparation of the solutions spectra were recorded as quickly as possible in order to minimize possible base hydrolysis. Concentrations used were as follows:

Acetylacetone	4×10^{-5} mole
1,1,1-trifluoroacetylacetone	3×10^{-5} "
Acetoacet.diethylamide	2×10^{-5} "
Ethylacetoacetate	3.5×10^{-5} "
Acetoacet.orthochloroanilide	1.5×10^{-5} "
Acetoacetanilide	1.5×10^{-5} "

For recording bands A, B and C of the metal chelates, concentration used was 2.5×10^{-5} mole, except for the acetoacetanilide chelates for which the concentration employed was 1.25×10^{-5} mole. Bands D and E were recorded at concentrations 1.25×10^{-3} mole and 1.25×10^{-2} mole respectively. For bands A and B only methanol and cyclohexane could be used. For the other bands chloroform, benzene, tetrahydrofuran, acetone, dimethylformamide and pyridine were used in addition to the above two solvents, wherever solubility permitted. Tetrahydrofuran, in which the chelates are quite soluble, afforded an ideal solvent for recording bands C to E. All bands were recorded in a Beckman Model DK-2 Spectrophotometer using 1 cm. calibrated quartz cell.

Gaussian curves

When the separation of two or more similar bands is only of the order of their half-widths, considerable overlapping should occur and the individual band must be found by resolution of the experimental curve into its gaussian components (after transferring to the symmetric wave-number scale).

Gaussian curve can be represented as :

$$\varepsilon_1 = \varepsilon_0 \, 2^{-\left(\frac{\nu_1 - \nu_0}{\delta}\right)^2} \qquad \ldots(A)$$

where ε_0 is the extinction coefficient in the maximum; ν_0, the frequency corresponding to ε_0 and δ, the half-width.

When a given experimental curve is to be resolved into two gaussian curves, it is good approximation to consider the outer edges unaffected by the overlapping in the middle. The two edges of the given curve will, therefore, be represented by two different gaussian curves having different δ, ϵ_o and ν_o values. By taking three sets of values for ϵ_1 and ν_1 from each edge of the curve, one can arrive from equation A at the following expression for δ, ν_o and ϵ_o.

$$\log \frac{\epsilon_i}{\epsilon_o} = -\left(\frac{\nu_i - \nu_o}{\delta}\right)^2 \log 2 \qquad \ldots(B)$$

$(i = 1, 2, 3)$.

By solving the three equations expressed in (B), one obtains the following expressions for the parameters ν_o, ϵ_o and δ.

$$\nu_o = \frac{-\beta \pm \sqrt{\beta^2 - 4\alpha\gamma}}{2\alpha}$$

where $\alpha = 2 \log \epsilon_2$

$$\beta = -2\left\{\nu_3 \log \frac{\epsilon_1}{\epsilon_2} + \nu_2 \log \frac{\epsilon_3}{\epsilon_1} + \nu_1 \log \frac{\epsilon_2}{\epsilon_3}\right\}$$

$$\gamma = \log \frac{\epsilon_1}{\epsilon_2}\nu_3^2 + \log \frac{\epsilon_3}{\epsilon_1}\nu_2^2 + \log \frac{\epsilon_2}{\epsilon_3}\nu_1^2$$

$$\log \epsilon_o = \frac{(\nu_2 - \nu_o)^2 \log \epsilon_1 - (\nu_1 - \nu_o)^2 \log \epsilon_2}{(\nu_2 + \nu_1 - 2\nu_o)(\nu_2 - \nu_1)}$$

$$\delta^2 = -(\nu_1 - \nu_o)^2 \log 2 \left[\frac{1}{\log \epsilon_1 - \log \epsilon_o}\right]$$

ν_o, ϵ_o and δ can completely describe the component curves.

Spectrophotometric determination of the composition of pyridine adducts

A solution of copper acetoacet.orthochloroanilide (1.25×10^{-2} mole) in chloroform was prepared. Two millilitres of this stock solution was diluted to 5 ml. after adding calculated quantities of pyridine in chloroform; intensity of the spectrum in these solutions was observed at 600 and 650 mμ using 1 cm. cell in a Unicam SP 500 spectrophotometer.

Due to better solubility of copper acetoacet. diethylamide a stock solution of 2×10^{-2} mole concentration could be prepared. The rest of the procedure was similar.

Powder spectra

Diffuse reflectance spectra were measured on a Unicam SP 500 spectrophotometer equipped with diffuse reflectance attachment. Magnesium carbonate was employed as standard.

The chelates were ground under identical conditions in an agate mortar for the same length of time (15 min.).

Polarography

Sargent XXI Pen-recording polarograph was used with the damping switch in position 2. An H-type cell carrying a saturated calomel electrode as reference electrode was employed. An agar bridge (4% agar saturated with potassium chloride) reinforced by a coarse porosity sintered glass pyrex disc was used in the cross member. The cell resistance measured by Wheatstone bridge was found to be less than 500 ohms.

The capillary had an 'm' value of 2.1 mg./sec. and the mean drop time was 3.5 seconds per drop at a potential of -1.0V and corrected mercury pressure (h) of 34.5 cm. The polarograms were obtained at 30 ± 0.2°C.

A stream of oxygen-free nitrogen was bubbled through the solution to be polarographed for 15 min. before recording the polarogram. To prevent any loss of solvent, the nitrogen gas was first passed through a 1:1 mixture of pyridine and water, before its entry into the 'H' cell containing the sample solution.

The solutions employed were 0.001M with respect to copper compound and 0.1M with respect to potassium nitrate.

CHAPTER 2

PMR SPECTROSCOPIC STUDIES ON ACETOACET.DIETHYLAMIDE AND ITS BERYLLIUM CHELATE

PMR SPECTROSCOPIC STUDIES ON ACETOACET.DIETHYLAMIDE AND ITS BERYLLIUM CHELATE

Ultraviolet spectral studies (Chapter I), which were restricted to very dilute solutions in methanol, showed the presence of varying quantities of enol in the β-dicarbonyl compounds used. Acetoacet.diethylamide was examined further in the present investigation, since no definite study has been reported on its enol-content, whereas such data are available for the other compounds studied[6,65-67].

Infrared spectrum of acetoacet.diethylamide was examined in carbon tetrachloride (0.12M, 0.5 mm.cell). Apart from a sharp peak at 2945 cm^{-1} and a weak shoulder at 2850 cm^{-1} (both due to C-H stretching), a broad band extending from 2450 - 2800 cm^{-1} was observed. This is indicative of the occurrence of hydrogen-bonded enol[68], since no other peak is observed in the higher frequency regions.

The bromine-titration technique of Kurt Meyer[69], for determining the equilibrium ratio of keto-enols, has the disadvantage of possible chemical perturbation of the equilibrium positions. In ultraviolet, Raman and infrared spectroscopy, though possibilities of such perturbations are eliminated, extinction coefficients and departures from Beer's Law must be investigated, if absolute equilibrium constants are required.

The advantages of proton magnetic resonance technique in studies of tautomeric phenomena and hydrogen bonding have been amply demonstrated in recent years[65,66,70-79]. This method gives directly the absolute value of the equilibrium constant, because the intensities of the signals are related to the number of protons involved by a common factor.

PMR technique has been used in the present investigation for evaluating enol-content of acetoacet.diethylamide. Spectrum of its beryllium chelate was also recorded for comparison.

The PMR spectrum of beryllium acetoacet.diethylamide is shown in Fig.26. There are four magnetically non-equivalent kinds of protons in this compound; these are marked in the diagram as A, B, C and D. Signal for the ring hydrogen (A) is obtained as a singlet at 289 cps*. The N-CH_2-protons(B) which are coupled with the methyl hydrogens

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* chemical shifts are expressed in cps downfield from TMS (at 60 Mc.).

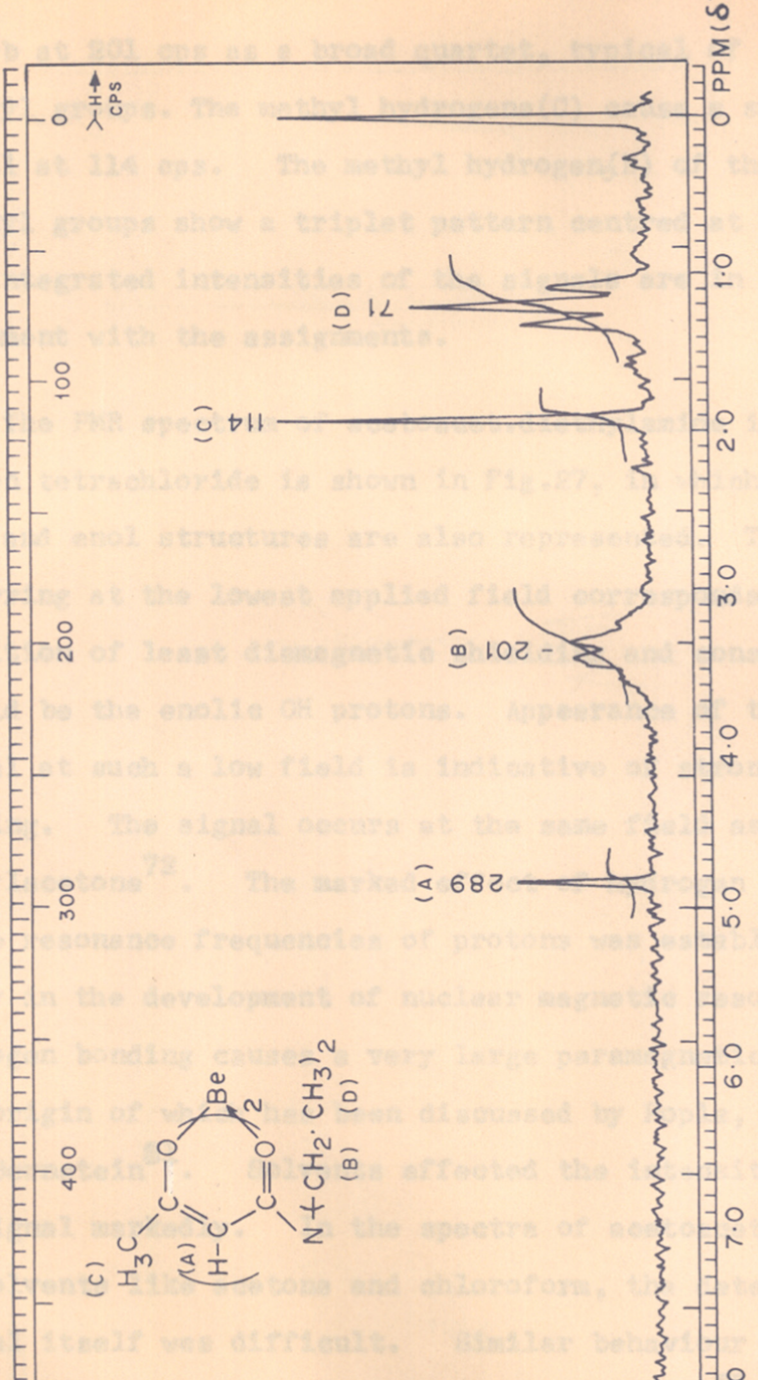


Fig. 26. PMR Spectrum in CCl_4

absorb at 201 cps as a broad quartet, typical of N-ethyl groups. The methyl hydrogens(C) cause a single signal at 114 cps. The methyl hydrogens(D) of the N-ethyl groups show a triplet pattern centred at 71 cps. The integrated intensities of the signals are in full agreement with the assignments.

The PMR spectrum of acetoacet.diethylamide in carbon tetrachloride is shown in Fig.27, in which the keto and enol structures are also represented. The signal occurring at the lowest applied field corresponds to the condition of least diamagnetic shielding and consequently should be the enolic OH protons. Appearance of this signal at such a low field is indicative of strong hydrogen bonding. The signal occurs at the same field as with acetylacetone[72]. The marked effect of hydrogen bonding on the resonance frequencies of protons was established very early in the development of nuclear magnetic resonance[80]. Hydrogen bonding causes a very large paramagnetic shift, the origin of which has been discussed by Pople, Schneider and Bernstein[81]. Solvents affected the intensity of the OH signal markedly. In the spectra of acetoacet.diethylamide in solvents like acetone and chloroform, the detection of the signal itself was difficult. Similar behaviour of the OH signal of acetylacetone enol has been reported[65].

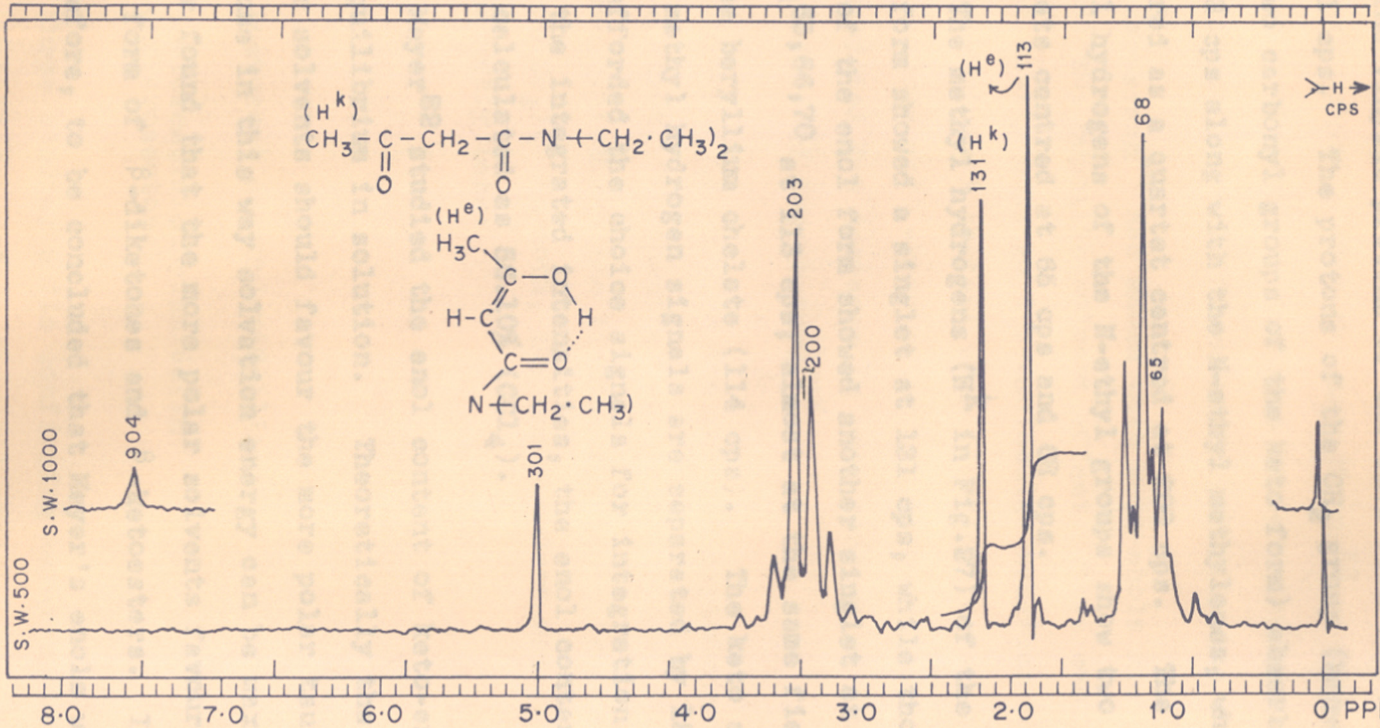


Fig. 27· PMR Spectrum in CCl_4

The vinylic protons of the enol form absorb at 301 cps. The protons of the CH_2 group (between the two carbonyl groups of the keto form) absorb at 203 cps along with the N-ethyl methylenes, which appeared as a quartet centred at 200 cps. The methyl hydrogens of the N-ethyl groups show two triplets centred at 65 cps and 68 cps.

The methyl hydrogens (H^k in Fig.27) of the keto form showed a singlet at 131 cps, while those (H^e) of the enol form showed another singlet at higher field[65,66,70] at 113 cps; almost at the same field as in the beryllium chelate (114 cps). The keto and enol methyl hydrogen signals are separated by 18 cps and afforded the choice signals for integration. From the integrated intensities, the enol content has been calculated as 56.10% (CCl_4).

Meyer[82] studied the enol content of keto-enols in equilibrium in solution. Theoretically the more polar solvents should favour the more polar tautomer, because in this way solvation energy can be maximized. Meyer found that the more polar solvents favoured the keto form of β-diketones and β-ketoesters. It is, therefore, to be concluded that Meyer's enols were less polar than the keto forms. As far as is known, such enols are more volatile than the keto forms[83]. Both effects support an internally hydrogen bonded structure for enols, whereby considerable decrease in polarity can occur.

Wasserman[84] has shown that keto-enols are likely to exhibit the opposite solvent effect, where enolic forms cannot easily undergo intramolecular hydrogen bonding. Increase of enol content with dilution for a number of β-diketones and β-ketoesters has been reported[66]. Reeves[65] demonstrated the decrease in enol content of acetylacetone with increased temperature.

In order to examine the solvent dependence of the enol-content, PMR spectra were recorded also of acetoacet.diethylamide liquid, and of it in deuteroacetone ($CD_3.CO.CD_3$). In both, the enol-content was found to be considerably less:

	Enol content
Acetoacet.diethylamide(liquid)	40.00%
Acetoacet.diethylamide(in deuteroacetone)	24.50%

These studies while confirming Meyer's observations, also enabled to confirm the enol resonance peaks.

Experimental

Solutions (1.15 M) of acetoacet.diethylamide containing a small amount of tetramethylsilane as internal standard, were allowed to equilibrate for a week[77], before the spectra were recorded on a Varian A-60 NMR spectrometer at 60 Mc; calibration of the chart was made using TMS in deuterated chloroform (436 cps). Ratio of intensities of H^e and H^k signals, calculated graphically, agreed well with the integrated intensity.

CHAPTER 3

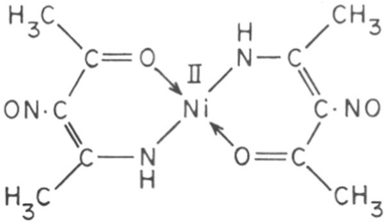
MASS SPECTROSCOPIC STUDIES OF A REACTION PRODUCT OF NICKEL ACETYLACETONATE

MASS SPECTROSCOPIC STUDIES OF A REACTION PRODUCT OF NICKEL ACETYLACETONATE

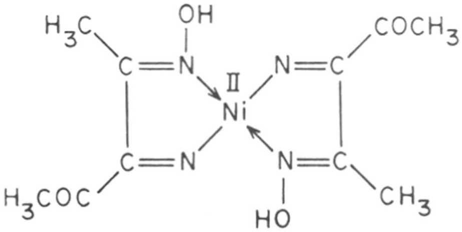
Nickel acetylacetonate has been reported to undergo a complicated reaction in the presence of nitrite ions and ammonium acetate in slightly acidic medium[85,86]. A highly crystalline red compound obtained by this reaction was found to have an empirical formula $Ni(C_5H_7N_2O_2)_2$. Two structures have been suggested[85,86] (structures I and II, Fig.28) for this diamagnetic compound, which is monomeric in chloroform. Infrared spectrum of the compound was compatible with either of the representations. However, mainly on the basis of diamagnetism, the investigators favoured structure II. Structure I involves oxygen as one of the donor atoms and this atom less readily brings about spin-pairing.

Mass spectrometry has been very successfully used recently in structure elucidation of metal complexes[87,88]. It was, therefore, hoped that the mass spectrum of this compound would help decide on the two structures.

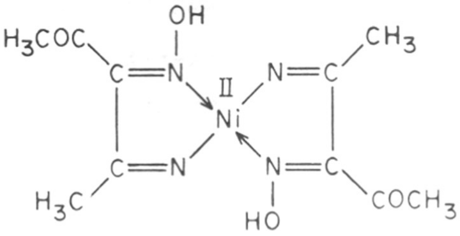
Mass spectrometry is one of the most potent means of structure determination of organic compounds[89,90].



I



II



III

Fig. 28

The advent of direct inlet system has widened its scope and in recent years the mass spectra of a number of metal complexes have been recorded[91-97]. MacDonald and Shannon[98] rationalized the mass spectra of a wide span of metal acetylacetonates, in terms of ion reactions. These investigations brought out the effect of valency change of the central atom on the mode of ion dissociation of the complexes.

The mode of dissociation of a metal complex ion may be markedly dependent on the valency states normally assumed by the metal concerned. If a radical ion $(X\text{-}M\text{-}Y)^{+\cdot}$, where M is a metal atom of valency state n, loses a radical $Y^{\cdot}$, the resulting positive ion $(X\text{-}M)^{+}$ is equivalent to the radical ion $(X\text{-}M)^{+\cdot}$, where M is now in the valency state (n-1), an electron being supposed to pass from the group X into the metal atom[96]. The lower valent radical so formed can then undergo further radical ion reactions. Alternatively, the initial radical ion $(X\text{-}M\text{-}Y)^{+\cdot}$ might lose a neutral molecule, e.g. XY, giving $(M)^{+\cdot}$, in which M now has valency state (n-2).

There are many examples of unit change in the valency of the metal atom of an ion with consequent reversal of the odd- or even- electron character of the ion, which influence the nature of its dissociation reactions[98]. Occurrence or non-occurrence of change in valency correlates well with the established chemistry of the metals[98]. When the metal atom concerned can readily take over different valency states, such valency changes may be an important factor contributing to the driving force of such reactions[97].

The mass spectrum of the nickel compound (Fig.29) showed a very intense molecular ion at m/e 312. The molecular ion pattern is consistent with the isotopic content and the presence of only one nickel atom in the molecule. Occurrence of two major isotopes of nickel differing in two mass units (58 and 60) has been helpful in distinguishing nickel-containing and nickel-free species.

The electron induced fragmentation of the compound studied appears quite different from that of metal acetylacetonates for which step-wise loss of the ligand from the molecular ion was found to be the major fragmentation mode[98,99]. In the mass spectrum of the nickel compound studied here, the first major peak observed is at m/e 227. This appears to be formed by the loss in one step of 85 mass units ($C_3H_3NO_2$) from

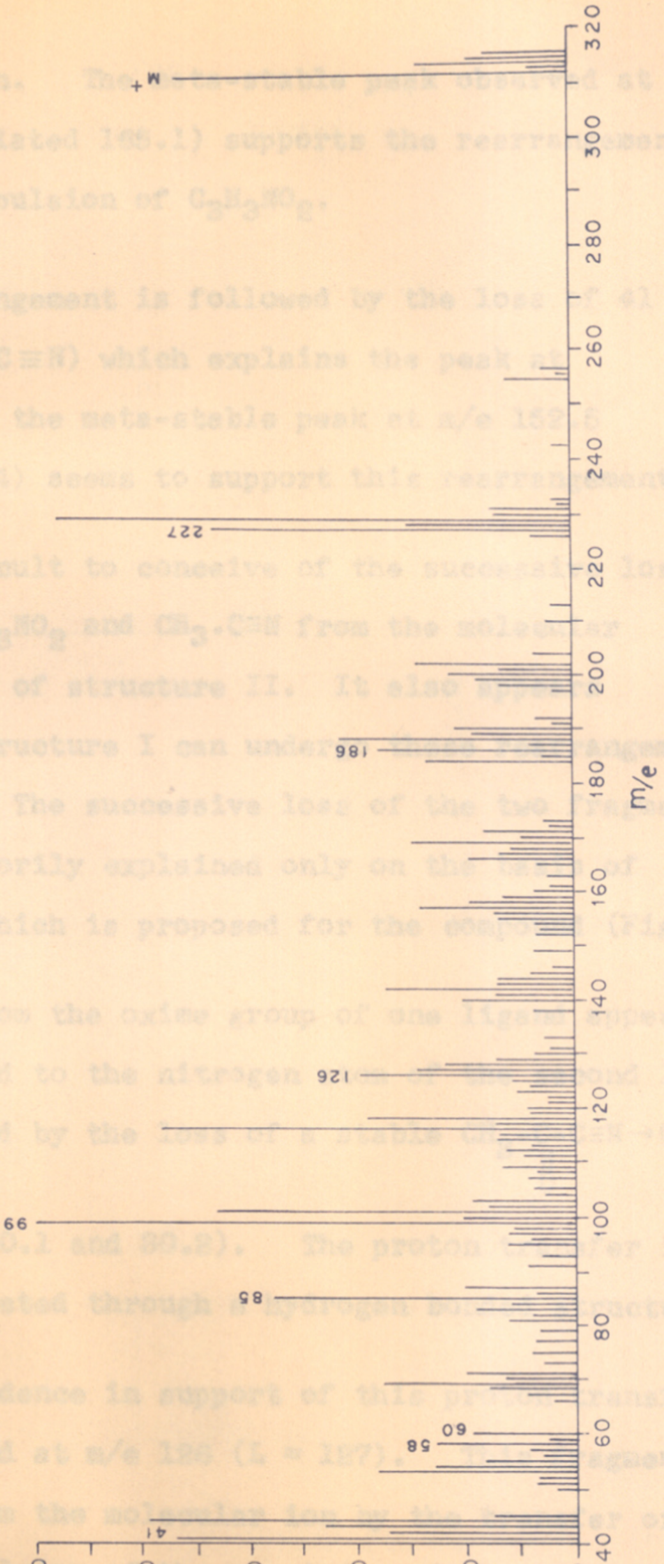
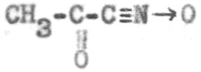


Fig. 29. Mass spectrum

the molecular ion. The meta-stable peak observed at m/e 165.5 (calculated 165.1) supports the rearrangement involving the expulsion of $C_3H_3NO_2$.

This rearrangement is followed by the loss of 41 mass units ($CH_3.C\equiv N$) which explains the peak at m/e 186. Again the meta-stable peak at m/e 152.5 (calculated 152.4) seems to support this rearrangement.

It is difficult to conceive of the successive loss of fragments $C_3H_3NO_2$ and $CH_3.C\equiv N$ from the molecular ion on the basis of structure II. It also appears unlikely that structure I can undergo these rearrangements in succession. The successive loss of the two fragments can be satisfactorily explained only on the basis of structure III, which is proposed for the compound (Fig.28).

A proton from the oxime group of one ligand appears to be transferred to the nitrogen atom of the second ligand, which is followed by the loss of a stable  $CH_3-\underset{\underset{O}{\|}}{C}-C\equiv N\rightarrow O$ molecule (Figs.30.1 and 30.2). The proton transfer is probably facilitated through a hydrogen bonded structure.

Further evidence in support of this proton transfer is the peak observed at m/e 126 (L = 127). This fragment seems to be formed from the molecular ion by the transfer of proton followed by expulsion of the remainder of the ligand.

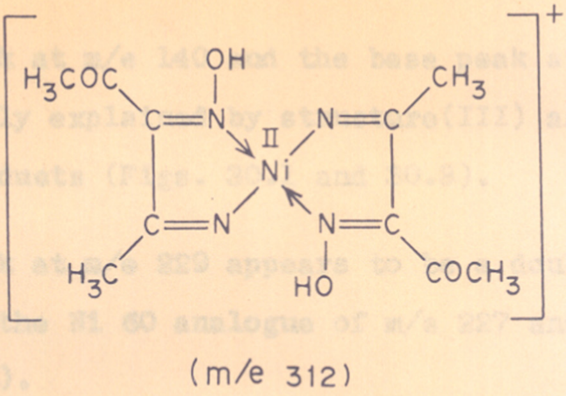


Fig. 30·1

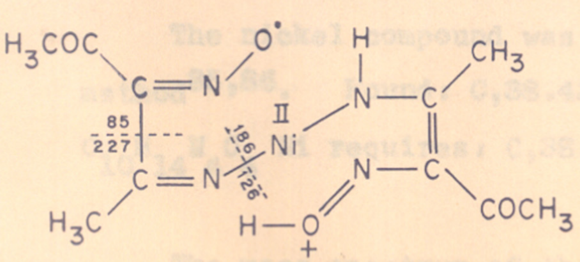


Fig. 30·2

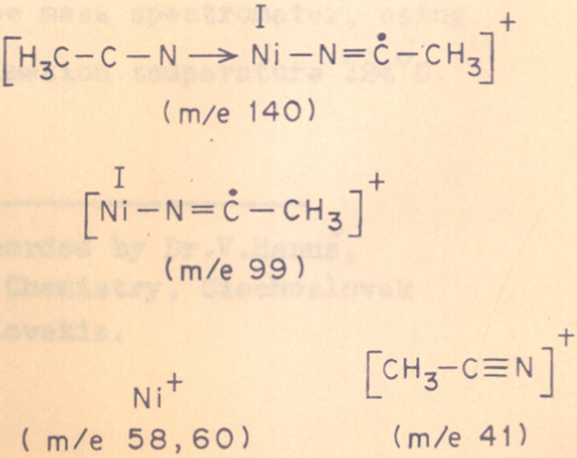


Fig. 30·3

The peak at m/e 140 and the base peak at m/e 99 are adequately explained by structure(III) as straight cleavage products (Figs. 30.1 and 30.3).

The peak at m/e 229 appears to be a doublet arising partly from the Ni 60 analogue of m/e 227 and partly from(M^+ - 83).

Structure(III) proposed can equally well explain the infrared spectral data and the diamagnetism. However, further confirmation seems desirable.

Experimental

The nickel compound was prepared by reported method[85,86]. Found: C,38.43; H,4.61; N,18.02; Ni,18.91%. $C_{10}H_{14}N_4O_4$ Ni requires: C,38.37; H,4.48; N,17.91; Ni,18.77%.

The mass spectrum of the compound was obtained* with an M Ch 1303-USSR, Sector type mass spectrometer, using 100 ev electrons and at sublimation temperature 124°C.

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* The spectrum was kindly recorded by Dr.V.Hanuš, of the Institute of Physical Chemistry, Czechoslovak Academy of Sciences, Czechoslovakia.

SUMMARY

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Two new nitrating agents, aluminium nitrate in acetic anhydride and concentrated nitric acid in acetic anhydride, have been introduced as nitrating agents for robust and labile metal acetylacetonates alike. Aluminium nitrate has been used also in a single-step preparation of aluminium nitroacetylacetonate. Metal nitroacetylacetonates have been employed as intermediates (in the place of non-existent nitroacetylacetone) in condensation reaction with hydrazine, leading to 4-nitro-3,5-dimethylpyrazole.

Bromine in the presence of calcium carbonate has been used successfully for the bromination of acetylacetonates of beryllium, aluminium and chromium. This method was, however, found unsuitable for acetylacetonates of metals which are easily reduced to stable lower oxidation states.

Using a solution of thiocyanogen in ethylene dichloride, aluminium and beryllium acetylacetonates have been thiocyanated.

Attempts to mercurate the metal chelates of β-dicarbonyl compounds using mercuric acetate led to the preparation of diacetoxymercuri derivatives of the respective ligands.

Complexes of uranyl (UO_2^{++}) with acetoacetanilide and acetoacet.orthochloroanilide were found to contain an excess molecule of the ligand. Thermogravimetric studies showed that the 'excess' molecule of the ligand is attached less firmly than the other two molecules. Infrared spectral evidences point to a seven-coordinate structure for these complexes.

Metal chelates of ethylenediaminetetracetic acid have been prepared by ligand replacement, starting from metal acetylacetonates.

Close similarity of the ultraviolet and visible spectral bands of copper chelates of β-diketones, β-ketoester, β-ketoamide and β-ketoanilides, has been shown as evidence of a common structural pattern for all the chelates. It has been brought out that no relation exists between the position of an ultraviolet spectral band and the stability of the metal chelate (stabilities of three copper chelates have been compared by the polarographic technique). Some of the reported assignments of the bands of copper chelates of β-diketones could be checked. The visible spectral band of the chelates showed appreciable red shift with increasing coordinating power of the solvents used. This has been explained, from the point of view of crystal field-ligand field theory, as due to adduct formation with the solvents. Different degrees of intensification of the visible band of metal chelates in pyridine have been shown as arising from different adduct ratios; 1:1 ratio leading to an acentric square pyramidal structure (hence the high intensity) and 1:2 ratio to a centric hexacoordinate structure (low intensity). The broad visible spectral band has been resolved in each case into its gaussian components. Adduct ratios of two of the copper chelates with pyridine have been determined spectrophotometrically (by the mole-ratio method) in chloroform.

The elegant proton magnetic resonance spectral method has been used in determining the keto-enol equilibrium of acetoacet.diethylamide. PMR spectrum of the beryllium chelate of acetoacet.diethylamide has been recorded and studied for comparison.

Nickel acetylacetonate undergoes a complex reaction in the presence of nitrite ions and ammonium acetate. From the mass spectrum of the resulting compound, a structure has been proposed for it.

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N. Thankarajan

(N. THANKARAJAN)

National Chemical Laboratory,
Poona-8.