STUDIES ON METAL CHELATES AND CHELATE POLYMERS

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-: : CONTENTS : :-

Page

PART I

PART II

PART III

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PART I

INTRODUCTION

INTRODUCTION

The study of coordination compounds has gained increasing importance with the application of knowledge derived from the electronic structure of the atom and the theory of quantum mechanics. This study has also been aided by a variety of recent refined physical methods of investigation~~s~~. The field has grown so greatly that the study of coordination compounds now includes large portions of organic chemistry and some areas of biochemistry. The rapid growth of interest in the field can be visualised from the large and varied amount of published material[1-18]. The structure of complex molecules is a fascinating field of science and many physical methods, for example, X-ray crystallography, magnetic anisotropy, electron diffraction and spectroscopy have been used as ~~a~~ means of exploring such complex structures. Equally significant aspect of this study is the nature of the bonds involved in such compounds.

Infrared spectroscopy has been successfully employed to decide between alternate structures of complex organic molecules. For example, penicillin and even such complex structure as a part of protein molecule[19-21] have been studied by this method. Subsequently, this method has been utilized for the elucidation of the structures of inorganic compounds. This can be seen from the large volume of reported literature. Many reviews and books have been published[22-28].

Metal complexes of β-diketones with practically all metals and non-metals have been reported[29,30]. Anilides of β-keto acids (as also amides and esters) are capable of forming the same type of metal derivatives as the β-diketones. The term β-dicarbonyl compounds embraces all these ligands. A general introduction on metal chelates of β-dicarbonyl compounds and chelate polymers will now be presented.

Metal chelates of β-dicarbonyl compounds

The 1,3-dicarbonyl compouhds, through their ability to enolize, form stable chelate rings with a large number of metals. In many instances, the compounds so obtained are non-ionic, insoluble in water, soluble in nonpolar solvents and also volatile. Acetylacetone has received considerable attention for a long time, while dibenzoylmethane, benzoylacetone, acetoacetic ester etc. have gained importance in this regard only recently. Thenoyltrifluoroacetone has received considerable attention because of the great stability of its compounds. The metal complexes of acetylacetone and other β-diketones have been reviewed recently by Harris and Livingstone[31]. Most of the metal chelates are neutral complexes of the types $[M^{II}(acac)_2]$ (M^{II} = Be, Cu, Zn, Cd etc; acac = acetylacetonate), $[M^{III}(acac)_3]$ (M^{III} = Al, Cr, Fe, Co etc.) and $[M^{IV}(acac)_4]$ (M^{IV} = Zr, Hf, Ce, Th, Pu). Many of these compounds show exceptional stability; the beryllium complex, for example, boils without decomposition at 270°C at atmospheric pressure. Wilkins and Wittbecker[61] utilised this remarkable stability in the preparation of beryllium containing polymers. The chelates of Si(IV), Ti(IV) and B(III) are of interest, since they are rare examples of these elements in cationic complexes. The complex $[Si(acac)_3]Cl.HCl$, by its resolution into optical enantiomers, has been proved to possess an octahedral structure with three chelate rings[32]. Partial resolution of the neutral complexes $[M(acac)_3]$ (M = Cr, Co) has been also effected by Dwyer and Gyarfas[33] and by Moeller and Gulyas[34].

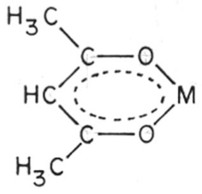
Other β-diketones, for instance, benzoylacetone and dibenzoylmethane form metallic complexes similar to those formed by acetylacetone. It has been found that when one of the H atoms of the central methylene group of acetylacetone is substituted by an isopropyl or sec-butyl group, the β-diketone does not give the usual coloured metal chelates with Cu(II) and Fe(III). However, α-n-alkyl and α-isobutyl substituted acetylacetones give normal complexes[35]. It would seem that steric hindrance between the isopropyl or sec.butyl groups and the H-atoms of the terminal methyl groups of the β-diketone interferes with the planar configurations of the chelate ring and thereby lowers the stability of the complex[36]. The stability of the metal derivatives is related to the acid dissociation constants of the β-diketones[37]. Fluorine substitution on the terminal carbon atoms of acetylacetone increases the amount of the enol form, relative to the keto form in aqueous solution[38,39].

Such β-diketonic compounds which are soluble in organic compounds have achieved considerable importance as agents for the separation of metal ions through the techniques of solvent extraction. If two metals in aqueous solution are in equilibrium with a diketone, if the equilibrium constants are different and if the complexes are soluble in a solvent immiscible with water, the metals can be separated by liquid-liquid extraction[40]. Huffman and Beaufait[41] using thenoyltrifluoroacetone as the complex former, separated zirconium and hafnium in this way. The distribution coefficient of the zirconium complex is about twenty-timesthat of the hafnium; so, excellent separation was achieved. This extraction technique can also be used to determine the formulae of complexes and the degree of hydrolysis of metal ions in aqueous solution as was shown by Connick and McVey[42] in their study of the zirconium ion. Steinbach and Freiser[43] have suggested that the complexing agent (acetylacetone, in their example) can serve also as the solvent for the complex. Using this technique, they have carried out the analytical separation of zinc and copper.

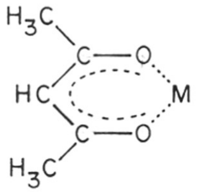
The nature of the metal chelate ring, particularly the type of bonding present in the ring system, the influence of these ring systems on the rest of the molecule and the 'aromaticity' of such rings have been controversial subjects. Calvin and Wilson[44] suggested that the unexpected stability of some of these chelates might be ascribed to their aromatic character. Holm and Cotton[45], however, pointed out that aromaticity is unreasonable on the basis of symmetry and energy of the metal orbitals available for π bonding. Double bonding between metal and oxygen in some acetylacetonates has been postulated from their study of visible and ultraviolet spectra by Basu and Chatterji[46]. From a comparison of the M-O distances (1.90A^{o}) in the Ni(II), Cu(II) and Co(III) chelates, Shkolnikova and Shugam[47] concluded that strong π bonding between the metal and the ligand does not occur. On the basis of electronic spectra of these chelates, Barnum[48], on the other hand, suggested that there is significant π bonding between the ligands and metal ion.

A study of the infrared spectra of the complexes M(acac)$_2$ (M = Be, Co, Ni, Cu, Zn, Pd) reveals that M-O stretching force constants increase in the order

$Zn \simeq Co < Ni < Cu < Pd$ and the C=O force constants decrease in the same order. It is suggested that the strong metal chelates have the structure (I) and weak chelates the structure (II). In (I) π-electrons as well as d-electrons of the metal tend to be more or less localised in the chelate ring whereas in (II) the π-electrons are localised more in the ligand[49].

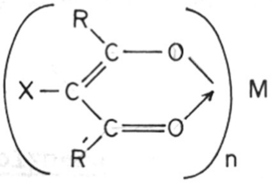


(I)



(II)

A metal ion when chelated, will cause the electrons in an organic ligand to be redistributed and, as a result, the reactivity at some point in the chelate ring itself, in an adjacent ring system or in a pendant functional group in the chelate molecule, will be altered to some extent. In addition to the location of the reaction centre with respect to the metal ion, a number of factors such as magnitude of the positive charge on the metal ion and the charge displacement that occurs on chelation, control the extent to which the chelated ligand reactivity is affected[50]. Electron withdrawal by the metal ion can weaken a bond and result in its rupture or facilitate attack by a nucleophile. Metal acetylacetonates undergo reactions characteristic of aromatic systems. Direct substitution of the H-atom on the central C-atom of the chelate ring in metal chelates produces complexes of the general type[51] (III).



III (n = 2 or 3; X = Cl, Br, I, SCl, SCN)

Collman and co-workers[52] have extensively studied the non-destructive reactions of β-diketone metal complexes chiefly metal acetylacetonates. The electrophilic substitution reactions of relatively stable inert tris-acetylacetonates of chromium(III), cobalt(III) and rhodium(III) have been investigated. Halogenation, nitration, thiocyanation, acylation, formylation, chloromethylation and aminomethylation take place at the central carbon of the chelate rings. Tri-substituted chelates are obtained in all cases except acylation and formylation. Unsymmetrically and partially substituted chelates have been prepared.

Nitration of stable acetoacetanilide chelates of chromium(III), aluminium(III) and beryllium(II) has been achieved in this investigation. The separation of geometrical isomers of chromium(III) acetoacetanilide and the studies on some metal chelates of acetoacetanilide have been also carried out. Details of this work will be presented in Part II of this thesis.

Coordination Polymers

The term 'coordination polymer' in its broadest sense can be applied to any macromolecular entity which contains coordinate covalent bonds[53]. Although progress has been very limited in the production of technologically useful materials, studies on coordination polymers reveal that good thermal stability may be associated with chelation[54]. Present activity is primarily directed on the synthesis and characterisation of systems heavy in organic ligands. Two categories of coordination polymers are easily recognised, one in which the coordinated metallic element is an integral part of the backbone and a second in which the metallic element is coordinated to a polymer repeating unit containing donor groups. Most of the known coordination polymers fall in the first group and a majority of them can be considered natural coordination polymers..

In many cases, it has been observed empirically that chelation with metal ions greatly enhances the thermal stability of organic ligands. Fernelius and Bryant[55] have shown that many metal acetylacetonates can be distilled without decomposition. The boiling point of acetylacetone is 139°C, whereas its thorium(IV) chelate distils at 260°-270°C (10mm) and the nickel(II) chelate at 220°-235°C (11mm). Similarly, ethylenediamine is destroyed rapidly by hot concentrated nitric acid, but when coordinated to cobalt(III), it is not attacked even on heating for many hours. The bis-ketoimine[56-58] is destroyed by heating to moderate temperatures but its copper complex is decomposed only slowly at 380°C.

Many attempts have been made during the past decade to incorporate these properties, especially heat stability into plastic organic materials by inclusion of metal ions.

Synthetic Methods

The preparative methods used for chelate polymers are based largely on the standard methods of organic polymer synthesis. They may be divided into three general categories: (a) those resulting when metal ions and suitable multi-dentate ligands are linked together, (b) those obtained by incorporation of metal ions into preformed polymeric ligands having coordination sites and (c) those formed by polymerisation of coordination monomers. However, it should be mentioned that linear polymers, such as gold and nickel cyanide, are known, in which metal atoms are linked by coordinate bonds but where chelate structures do not occur.

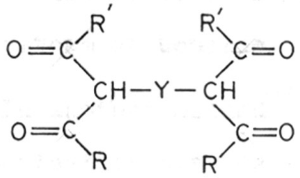
Metal ions and suitable multi-dentate ligands

Linear polymers have been obtained by the use of bifunctional groups which are bis-chelating agents. Nearly all the studies on polymers formed by coordination have utilised four coordinate metal ions (Ni^{2+}, Cu^{2+}, Zn^{2+}, Be^{2+}) and bis-bidentate chelating groups. Sowerby and Audrieth[59] have summarised bis-chelating ligands that have been proposed as bases for the production of coordinate polymers. Bailar[60] in his review enumerated some basic principles to be kept in mind in attempts to prepare coordination polymers.

Chelate polymers of bis-β-diketones will be reviewed as examples of bis-ligand polymers.

A great variety of bis-diketones has been used, in which the diketone functions are connected through the terminal carbon atom. $R.COCH_2.COCH_2.YCH_2.CO.CH_2.COR$.

or usually through the central carbon atom. (IV)



IV

Bis-1,3-diketones have been studied extensively by Wilkins and Wittbecker[61] and have been continued by Fernelius[62] and his students, Bailar[63-66] and his students, Charles[67-72] and his collaborators, Kluiber and Lewis,[73] Drinkard, Ross and Wiesner[74] and others. The methods employed for the preparation of such polymers are essentially the same as those used to prepare monomeric complexes of 1,3-diketones. For example, the method of Bailar and Oh[75] consists of mixing the ketones and a soluble metal salt in proper proportions in a water-organic solvent mixture and adjusting the pH until the chelate precipitates. It is necessary to add an organic solvent such as alcohol, dioxane or dimethylformamide, because of the insolubility of the ligand in water. The success of this method depends upon pH, rate of addition of the base, rate of stirring, temperature and reaction time. In some cases, polymers are obtained simply by the addition of an excess of an aqueous solution of metal acetate to a dioxane solution of the bis (β-diketone). The highly insoluble precipitate is purified by extraction with water followed by an organic solvent such as alcohol, acetone or benzene.

In another method[61,62,75] the technique of melt polymerisation has been employed. It consists of heating the metal acetylacetonate with a bis-β-diketone and distilling off the liberated acetylacetone under vacuo. The first method gives powders, while the second produces amorphous glassy materials. Oh and Bailar[75] obtained beryllium polymer, $(C_{17}H_{18}O_4)_4Be_3$, of low molecular weight by the melt polymerisation technique, in which the ketone is 2-phenyl-1,1,3,3-tetracetyl propane. Fernelius[62] prepared beryllium complexes of sebacoyl diacetophenone in the same way. Klüber and Lewis[73] combined the two diketo functions into a single bis-diketone molecule in which the two functional units are connected by chains such as $-(CH_2)_X-$, $-NH(CH_2)_xNH-$ or $-O(CH_2)_xO-$. From such tetraketones they obtained cyclic monomers and dimers which upon heating rearranged into polymers of high molecular weights.

Glukhov[76] reported the preparation of a series of chelate polymers of Be, Mg, Ca, Zn, Cu, Co and Fe with various bis-β-diketone derivatives of acetylacetone. He found that beryllium polymers were the most stable to heat, for they decomposed only at 350°.

Korshak[77-81] and his co-workers have published a series of papers on the synthesis and properties of the chelate polymers of metals with various tetraketones. The chelate polymers have been obtained as coloured amorphous powders, sparingly soluble or completely insoluble in the usual organic solvents. The beryllium compounds are more soluble than others. The thermal stability of the polychelates increases with increase in the number of phenyl groups in the initial tetraketones. The thermal properties of the polymers also depend on the metal ion, the stability diminishing in the sequence: $Cu > Be > Ni > Co > Zn > Mn > Cd$. Degradation of the polymers starts at 250°-$400^\circ C$ with various specimens. Molecular weight determination indicated that the degree of polymerisation did not exceed 25. It has been shown[82] that the thermal stability of chelate polymers based on bis-β-diketones is more clearly linked with the flexibility of the macromolecular chain than with solubility. X-ray examination established[83] that a decrease in molecular weight is accompanied by an increased degree of order in the molecular structure.

A polynuclear beryllium complex of naphthazarin[84] and metal derivatives of 2,5-dihydroxy benzoquinone[85], 1,6-dihydroxy phenazine[86] have also been reported.

A series of compounds derived from bis-α-amino acids has been prepared[87]. It is clear that if a trivalent ion such as Co^{3+} with a coordination number of six, is used, three dimensional crosslinked structures are possible, in addition to linear polymers. These might show greater chemical stability but would not be expected to exhibit plasticity. An attempt[88] has been made to utilise tridentate compounds, such as bis-imino diacetic acid in order to prepare linear polymers but the products had poor thermal stability. The molecular weights were too low to show plastic behaviour and the polymers were precipitated from solution during formation before a high degree of polymerisation had been reached.

An interesting polymer has been prepared from copper and nickel salts of rubeanic acid[89,90].

Knobloch and Rauscher[91] reported the preparation of coordination polymers of copper(II) at liquid-liquid interfaces. Organic condensation polymers of high molecular weights have been prepared in solvent systems containing liquid-liquid interfaces by Conix[92] and more recently by Wittbecker[93]. Two outstanding features of these poly condensations are the rapidity of the chain propagation and the apparent growth of the chains well beyond the point of polymer insolubility. The procedure reported by Knobloch and Rauscher[91] utilises interfacial systems which consisted of an aqueous phase containing a cupric salt and an immiscible organic phase containing a bis-(1,3-carbonyl-enol) monomer. For the success of the technique it appears to be essential that the copper be present in the aqueous phase as a relatively unstable complex such as the tetrammine copper(II) complex ion. Under these conditions, polymers are rapidly produced at room temperature with reaction times of a few minutes.

The study of metal complexes of bis-8-hydroxy quinolines as plastic polymers has recently been undertaken by several investigators[63,94-97]. Korshak[94] and collaborators reported the synthesis of a number of coordination polymers of bis-(8-hydroxy-5-quinolyl)-methane as well as some mixed polymers. In a recent paper Berg and Alam[98] discussed the synthesis of coordination polymers of 8-8'-dihydroxy-5-5'-biquinolyl and the use of the ligand as analytical reagent for detecting metal ions in the micro-gram range. Horowitz[95] and Perros have prepared the coordination polymers of bis-(8-hydroxy-5-quinolyl)-methane by reacting the ligand with Mn(II), Co(II), Ni(II) and Zn(II) in solution, as well as by thermal polymerization. The thermal stability of each polymer in vacuum was studied by thermogravimetric analysis upto 1000°, and the decomposition temperature was found to be closely related to such periodic properties of the metal incorporated in the backbone of the polymer as ionic potential and electronegativity. Furthermore, when heated in vacuum, decomposition temperature of the polymers is directly related to the atomic number of the metal incorporated in the backbone of the polymer. Infrared spectra of the coordination polymers revealed that the frequency of the absorption band in the 1100 cm^{-1} region was dependent upon the ionic potential and other periodic properties of the metal ion.

Studies on some bis ligands like bis-(8-hydroxy-5-quinolyl)-methane, 8-8'-dihydroxy-5-5'-biquinolyl and purpurin will be reported in Chapter 1 (Part III).

A few titanoxane polymers are described in Chapter 2 (Part III). A brief review on some titanoxane polymers is now presented here.

Polytitanoxanes can be obtained by hydrolysis of titanium alkoxides, trialkyl siloxyhalotitanium compounds and trialkyl siloxy alkoxy derivatives of titanium[99]. Nesmeyanov, Freydlina and Braynina[100] investigated the partial hydrolysis of tetraethoxy titanium and obtained octaethoxy trititanoxane $(C_2H_5O)_8Ti_3O_2$. When heated under reduced pressure, it further polymerised to form a new polymer, m.p. 165-170°C. It has been shown in the hydrolysis and condensation reactions of tetrabutoxy- tetraheptoxy- and tetraphenoxytitanium, that the extent of the reaction is controlled by the quantity of water in the mixture[101]. Polymers formed with titanium tetra alkoxides and phenols or polyhydric alcohols have been described by Boyd[102].

The conversion of titanium tetrachloride or titanium tetra alkoxides to titanium carboxylates by reaction with RCOONa or RCOOH leads to $Ti(OH)_x(OOCR)_{4-x}$, with the value of x dependent on the reaction conditions[103-105]. On storage, the materials become insoluble, presumably by homocondensation. It has been suggested that the products after aging are linear polymers with tetra coordinate titanium in a titanium-oxygen backbone[104]. Similarly, the monomer, $Ti(CH_3COCHCOCH_3)_2(OC_3H_7)_2$ obtained in the reaction of titanium tetraisopropoxide and acetylacetone, yields on hydrolysis and drying an insoluble linear polymer with a titanium-oxygen backbone[104].

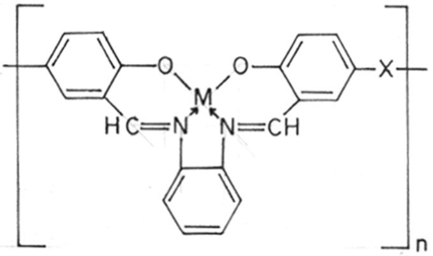
Polymers with backbone of silicon, titanium and oxygen have been prepared by cohydrolysis of alkyl or aryl chlorosilanes with titanium tetrabutoxide. The poly condensation at 200°C of the products formed by this reaction yields glassy polymers, soluble in ethanol or acetone or a mixture of ethanol and toluene[106]. Cohydrolysis of a mixture of $Ti(CH_3COCHCOCH_3)_2Cl_2$ and R_2SiCl_2 is reported to yield polymeric bis-

(acetylacetonato) titanium organo siloxanes[107]. The reaction of $Ti(C_9H_6NO)_2$ $(i\text{-}C_3H_7O)_2$ with $(C_6H_5)_2Si(OH)_2$ carried out in distilling benzene ~~also~~ yielded an insoluble yellow powder analysing to $[Ti(C_9H_6NO)_2O\ Si\ (C_6H_5)_2O]_x$. It decomposed above 275°C.[108]

Organic polymers as ligands

Production of polymers using preformed polymeric ligands has not been studied to any great extent. The introduction of the metal in a preformed polymer can be used either to reinforce an existing linear polymer or alternatively, to effect crosslinking. An interesting example of this is in tanning of leather by metal ions, which involves crosslinking and stabilizing of polypeptide polymers by coordination.

Linear polymers have been prepared[109-111] from Schiff's bases by mixing a solution of the polymer with a soluble metal salt, the insoluble polymer (V) being precipitated from solution.



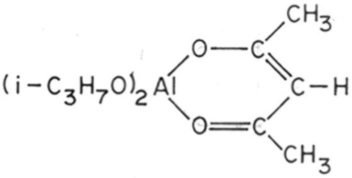
V X = SO_2 or CH_2

The heat stabilities of the polymers improved when $X = SO_2$. But in general, they were less stable than the corresponding monomeric chelates. Lions and Martin[112] have prepared polymeric Schiff's bases by the reaction of pyridine 2,6-dialdehyde and diamines such as ethylenediamine, hexamethylenediamine and benzidine. However, the polymer prepared from benzidine did not coordinate well, but the ones prepared from hexamethylene diamine and ethylenediamine reacted readily with iron(II) sulphate to give polymers of unknown molecular weight. These are insoluble ferromagnetic substances and stable upto 300°C. In these compounds, polyterdentate ligands are uncharged and consequently, the resultant polymer containing metal ions, is positively charged. Such materials might have ion-exchange properties but are unlikely to show useful mechanical properties. Analogous reactions have been carried out by Bayer[113] using polymeric Schiff's bases obtained from glyoxal and either 2,6-diamino-p-cresol or 2,4,6-triamino phenol. More recently[114] gummy products which decompose at about 150°C have been obtained from dimercaptals.

Goodwin and Bailar[115] used bis-salicylaldehyde but formed Schiff's bases with triethylene tetramine and diethylenetriamine. All these polymers are insoluble in non-polar solvents and decompose before melting.

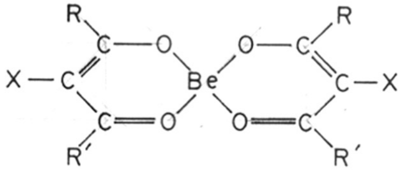
Polymerisation of coordination monomers

This method which has been used in forming coordination polymers consists in polymerising monomers containing coordinated metal ions. An interesting paper by Kugler[116] on the preparation of chelate polymers of aluminium shows that reaction between aluminium alkoxides and acetoacetic ester yields a compound in which a ketoester grouping is combined with the aluminium atom in a chelate ring. On hydrolysis, such systems split off ethyl alcohol and at high temperatures rearrangement takes place with loss of water and formation of a polychelate. Patterson and co-workers[117] described a series of chelate polymers of aluminium similar in structure to those obtained by Kugler[116]. The polymers are unstable towards moisture and are decomposed at elevated temperatures. Berlin and Matveeva[118] used aluminium with two coordination positions blocked by a molecule of diketone. (VI)



(VI)

When the monomer was heated with any variety of bis diketone, isopropyl alcohol escaped and polymerisation took place. The materials obtained were of low molecular weight. Klein and Bailar[119] have prepared beryllium-diketone polymers. The monomeric units are (VII)



(VII)

in which X represents $-COOC_2H_5-$, -OH or $-NH_2$. The monomer containing ester groups are converted to polymers and polyamides in melt system and those containing hydroxy or amino groups are polymerised by reaction with diphenyl dichlorosilane, terephthaloyl-chloride and diisocyanates. The polyesters, polyamides and some of the polymers prepared from the hydroxy monomers are glasses, soluble in non-polar solvents. However, these are not stable above 200°C.

Kenny[120] and Martin[121] employing melt polymerisation technique prepared polymers which are stable upto 350°C. Metal thiopicolinamides containing free amino groups, were reacted with bis-acid chlorides at 200°C. Infusible and insoluble powders were obtained in both instances.

Coordination polymers can be prepared when the ligand coordinated to a metal contains functional groups capable of undergoing conventional addition or condensation reactions. If the coordinated ligand, for instance, contains an ethylenic side chain, the unusual addition polymerisation may be possible. Arimoto and Haven[122] prepared vinyl ferrocene and showed that it undergoes homo- and co-polymerisation with vinyl monomers and dienes. A variety of copolymers have been obtained with trans-cinnamoyl ferrocene with a number of unsaturated compounds[123]. Marvel and Martin[124] have attempted free radical polymerisation of acrylate-containing basic beryllium carboxylates by benzoyl peroxide initiation. The products obtained, however, decomposed extensively at 200°C.

PART II

CHAPTER 1 : STUDIES ON ACETOACETANILIDE, ITS CHELATES, QUASIAROMATICITY AND ISOMERISM.

STUDIES ON ACETOACETANILIDE, ITS CHELATES, QUASIAROMATICITY AND ISOMERISM

Although the physical properties of metal chelates[1] have been studied extensively, it is relatively recent that investigations on the reactions of coordinated ligands have been carried out. Metal acetylacetonates exhibit the chemical behaviour expected for reactive aromatic systems and are readily substituted at the central carbon of the chelate rings by a variety of electrophiles[2,3]. However, studies on quasiaromaticity of β-dicarbonyl compounds seem to have been confined to acetylacetonates. For instance, the attempted nitration of Cr(III) chelates of benzoylacetone and dibenzoylmethane with copper nitrate-acetic anhydride mixture resulted in the destruction of these chelates[4].

The ligand, acetoacetanilide is chosen for the present study, since references to the chelates of acetoacetanilide are relatively few in the chemical literature. Chaplin and Hunter[5] in the course of their study on the "Associating effects of the hydrogen atom" by molecular weight measurement in naphthalene solution of some salicyl- and acetoacetanilides, isolated the copper chelate to support the enolic structure of acetoacetanilide.

This chapter deals with the isolation and infrared spectral studies of acetoacetanilide chelates of Cu(II), Be(II), Fe(III), Cr(III) and Al(III). Except the copper chelate[5], all the other metal chelates are synthesized for the first time. Attempts to prepare chelates of acetoacetanilide with other metals like Co(III) have been unsuccessful. The isolation of the nitration products of Be(II), Al(III) and Cr(III) acetoacetanilides is also reported here. Acetoacetanilide and some of its chelates are deuterated to establish various hydrogen modes in these compounds and the hydrogen bonding behaviour of the ligand in solution.

Since an unsymmetric bidentate ligand coordinated to a trivalent metal can exist in two geometrically isomeric forms, attempt has been made to separate *cis*- and *trans*- isomers of tris-(acetoacetanilidato)-chromium(III), by utilizing solubility differences in benzene and column chromatography on acid washed alumina. The inert complex has been separated into its two possible geometrical isomers, a deep green, *cis*-isomer, m.p., 204°C and a light green, *trans*-isomer, m.p., 226-27°C. The results of thermogravimetric studies on these geometric isomers are also included in this chapter.

Results and Discussion

Infrared spectra of acetoacetanilide and its metal chelates in the region 4000 cm^{-1} - 700 cm^{-1}

The infrared absorption maxima of acetoacetanilide and deuterated acetoacetanilide are tabulated in table I. Table II gives the absorption frequencies for bis-(acetoacetanilidato)-metal chelates as well as their deuteration products, while Table III reports those for tris-(acetoacetanilidato)-metal chelates (Figures 1-6).

The infrared spectrum of acetoacetanilide in nujol mull shows a strong absorption band at 3268 cm^{-1} and a medium band at 3145 cm^{-1}. These bands vary in frequency and intensity in the solution spectra and may be attributed to (the intermolecularly) bonded NH. The shoulder at 3067 cm^{-1}, however, can be assigned to C-H stretching vibration. On deuteration, a medium strong ND band was found at 2390 cm^{-1}. Two weak bands ascribable to CD_2 group were also observed at 2125 cm^{-1} and 2215 cm^{-1} (isotope ratio, 1.31). NMR spectrum of deuterated acetoacetanilide also shows that most of the methylene protons are deuterated, since the signal due to CH_2 at τ 6.48 decreases considerably. (Table V)

Table 1

Absorption frequencies (cm^{-1}) of acetoacetanilide and deuterated acetoacetanilide

Acetoacetanilide		Deuterated acetoacetanilide			Possible assignments
Nujol	$CHCl_3$ soln.	Nujol	Hexachloro-butadiene	$CHCl_3$ soln.	
3268s	3350sh	3280w	3280w	3325w	Bonded NH str.
3145m	3300m				
3067sh	3000b,m		3020w	3000w	C-H str. (aromatic)
2924*s,b		2930*s,b		2450w	
		2390s	2390s	2400m	N-D str.
		2215w	2215w		CD_2 str.
		2124w	2125w		
1946w		1946w			combination bands
1873w		1873w			
		1725sh			
1727vs	1710vs	1710vs		1710vs	C=O str.
1661vs	1675vs	1650vs		1675vs	Amide I
1597vs	1600s	1600s		1600s	Aromatic ring
1538b,vs	1550b,vs	1535m	1535m	1550s	Amide II
1502m	1500m	1505s	1505s	1500s	Phenyl vibration
1466*sh		1470*s	1470s	1470s	
1449vs	1445s			1445s	CH_3 deg.def.
	1420vw	1425vs,b	1425vs,b	1420s,b	Amide II'
1408s					CH_2 def.
1377*s		1380*s			
1366m	1365s	1360s	1360s	1365s	CH_3 sym.def.
1346w	1325s	1330s	1330s	1325m	
1330sh					
1316m	1315m	1315w	1315w	1311sh ~~1255m,b~~ 1255w	Amide III
1279m		1265s			
1238m	1235w	1215s			
	1175m	1175s		1175w	
1168vs	1160s	1168w			$-CH_2$ wag.
		1160w			
		1110w			
1080s	1090m	1077s		1075w	C-C str.
1027w	1025m	1060m		1055w	CH_3 rock
		1040m			
		1030s		1022w	

Table I (continued)

1006m				
967s	980w	960s		
		927s		Amide III'
905s	902m	908s	902m	C-CH_3 str.
868s		860m		CH_3-wag.
821w		855m		CH_3-rock
		820w		
757b,vs		752b,vs		CH O.P. def.
740b,sh				
708w ~~780w~~				
691b,vs		692b,vs		Aromatic mono-substitution

---

* Nujol peaks

s, strong; m, medium; w, weak; v, very; b, broad; sh, shoulder.

Table II

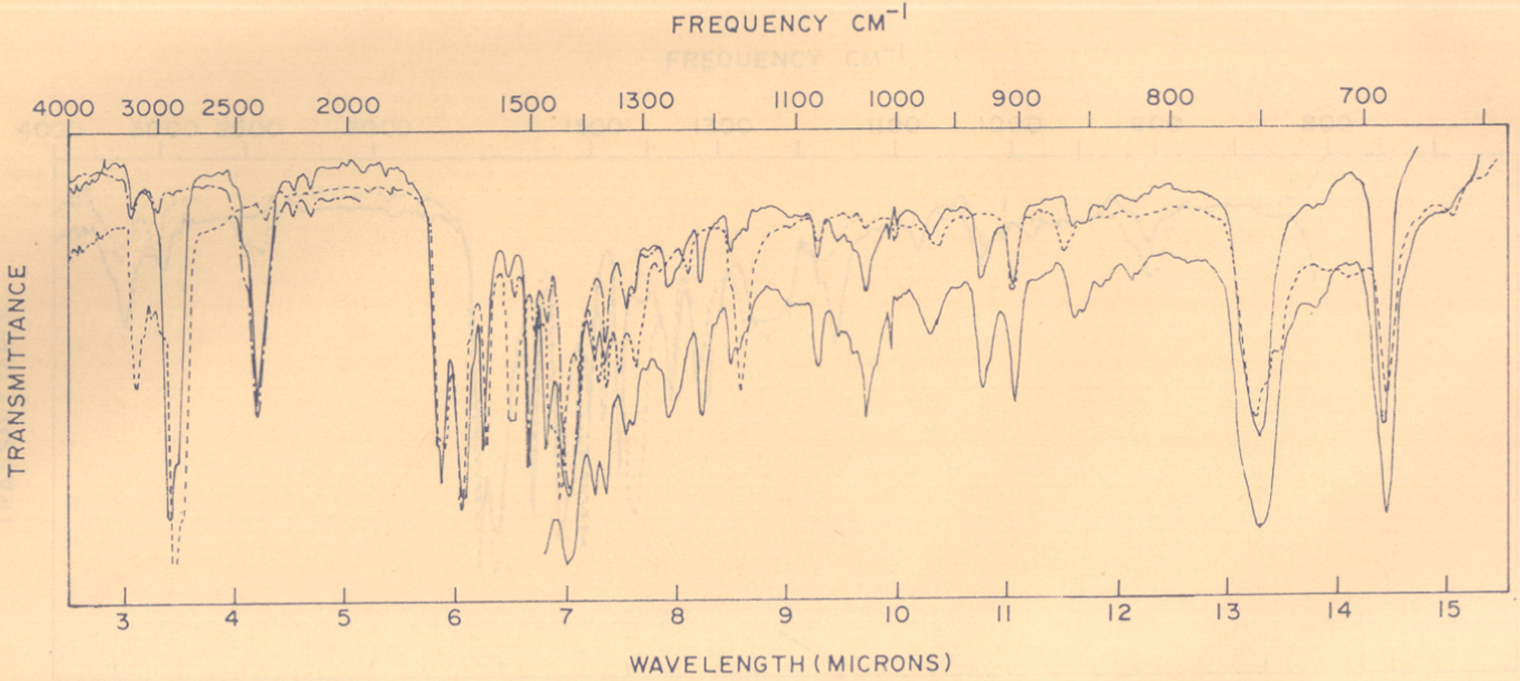
Absorption frequencies (cm^{-1}) of bis(acetoacetanilidato)-metal(II) chelates in nujol mull.

Copper	Deuterated copper	Beryllium	Deuterated beryllium	Possible assignments
3311m		3226w	3375w	NH-str.
3226w		3148sh		
2924*vs,b	2923vs,b	2924vs,b	2924vs,b	
	2335m		2337m	N-D str.
1618sh,	1600s	1608w	1600sh	Aromatic C-C
1603s	1590sh	1587sh	1590s	Amide I
1577vs	1550b,vs	1567vs,b	1560vs	C=C str. + C=O str.
	1540sh			
1529s		1548vs		Amide II
1502s	1505s	1501vs	1505sh	Phenyl vibration
			1495vs,b	
1466*m	1480s	1465*s	1450*s	
1437s	1445s	-	-	CH_3 deg.def.
1408m	-	1416s	-	
1377*m	1380*s	1384*s	1380*s	
1337s	1360s			
	1350s		1350s	Amide II'
	1330s	1333b,vs	1330s	CH_3 sym.def.
1319s	-	1305sh	-	Amide III
1266m		1272s		
1253m		1241s	1255m	
1182s	1185w	1188s		CH in plane def.
	1073w	1160m	-	
		1085w	1085m	
		1048s,b		Ring def. + BeO str.
1044s		1031s		
	1030s		1035b,s	
1029w				
998w		998sh	990m	CH_3 rock
971s,b		979vs,b		CH_3-C str.
	950s		960s	Amide III'
896m	895w	895w	890m	C-CH_3 str.
			874s	
846m		826s,b	812s,b	BeO str.+ C-CH_3 Str.
795w				
766s,b	755s,b	775w,b	773s,b	CH O.P. def.
752m		757s,b	725w,b	
743s	743m			
688s,b	688s,b	690s,b	692s,b	Mono substitution, Ring Def. + M-O str.

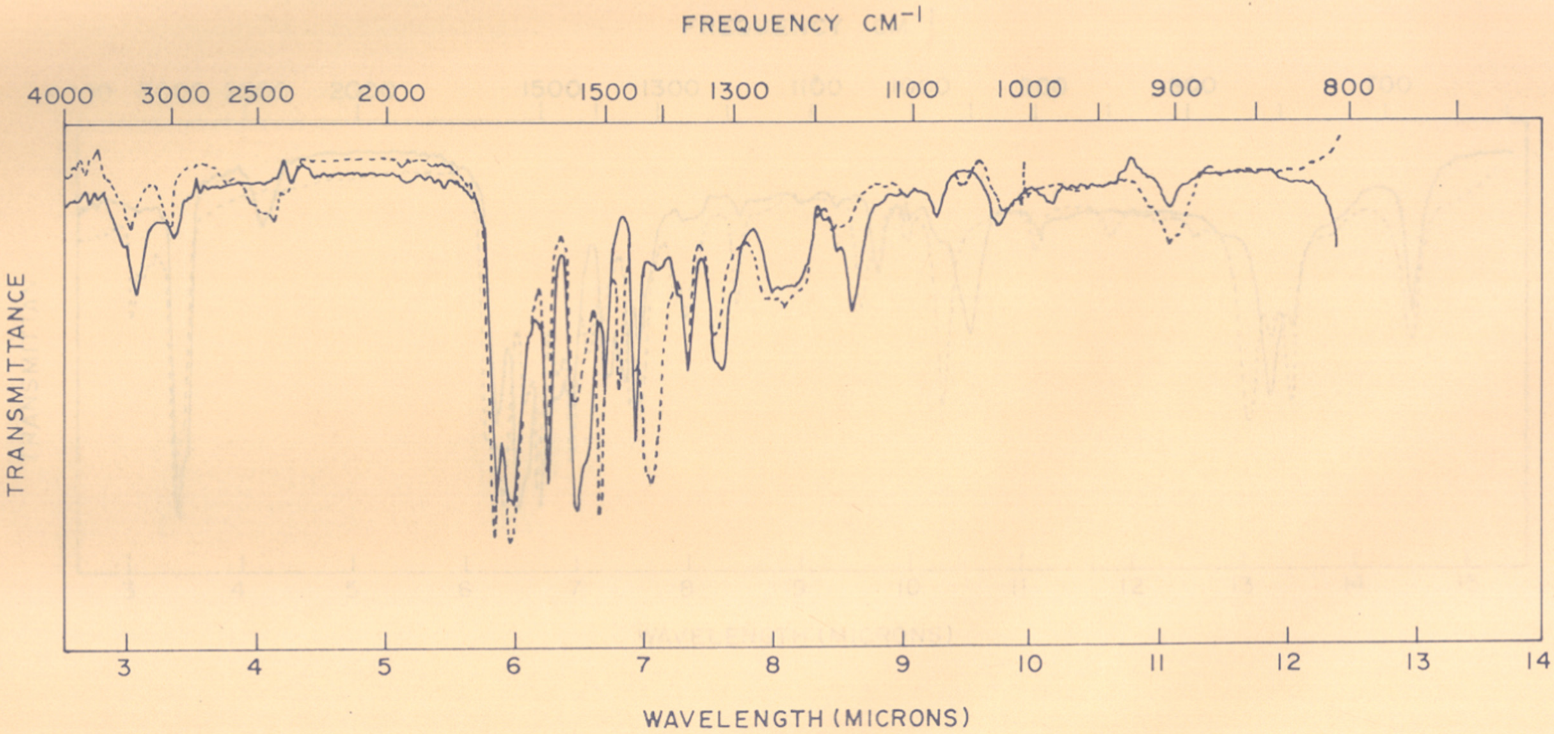
Table III

Infrared absorption frequencies (cm^{-1}) of tris-(acetoacetanilidato)-metal chelates in njuol mull.

Al(III)	Cr(III) <u>trans</u>- m.p.226°	Cr(III) <u>cis</u>- m.p.204°	Fe(III)	Possible assignments
3311w	3289m	3300w	3350s	NH str.
2924*vs,b	2924*vs,b	2924*vs,b	2924*vs,b	
1618w	1613w	1623sh	1608w	C=C + Amide I
		1618s		
1587s	1582vs	1587s	1587vs	C=C str. + C=O str.
1548s,b	1548vs] 1538vs]	1548vs	1548s	Amide II
1493vs	1493vs	1493m	1493vs	Phenyl vibration
1466*vs	1466*vs	1464*vs	1465*vs	
1441vs	1433s	1441sh	1433vs	CH_3 deg.def.
1416s	1408s	1408s	1407s	
1377*s	1377*m	1377*vs	1384*m	
1319vs,b	1348w	1319s	1305m	Amide III
1259s	1253s	1253s	1247s,b	
1182s	1188s	1182m	1181s	CH in plane def.
			1193w	
1155sh	1085w		1085w	
1050s	1048s	1048m	1044s	
1029m	1029s	1027m	1031s	
998w	998m		1002w	
971vs,b	968vs,b	967vs,b	966vs,b	
901w	901m		908m	
795w	793w		775w	
752vs,b	752vs,b	752w	766s,b	CH O.P. def.
			757w	
			743s	
		721w	732s	
690vs,b	690vs,b	690vs,b	688s,b	Mono substitution, Ring def.
			652w	+ MO str.
			652W	



FIG·1· INFRARED SPECTRA OF:- ------ ACETOACETANILIDE AND ——— DEUTERATED ACETOACETANILIDE IN NUJOL MULL ; —·—·— DEUTERATED ACETOACETANILIDE IN HEXA-CHLOROBUTADIENE.



FIG·2· INFRARED SPECTRA OF :- ——— ACETOACETANILIDE ; ------ DEUTERATED ACETOACETANILIDE (BOTH 3% W/V IN $CHCl_3$ IN 0·1 mm· CELL)

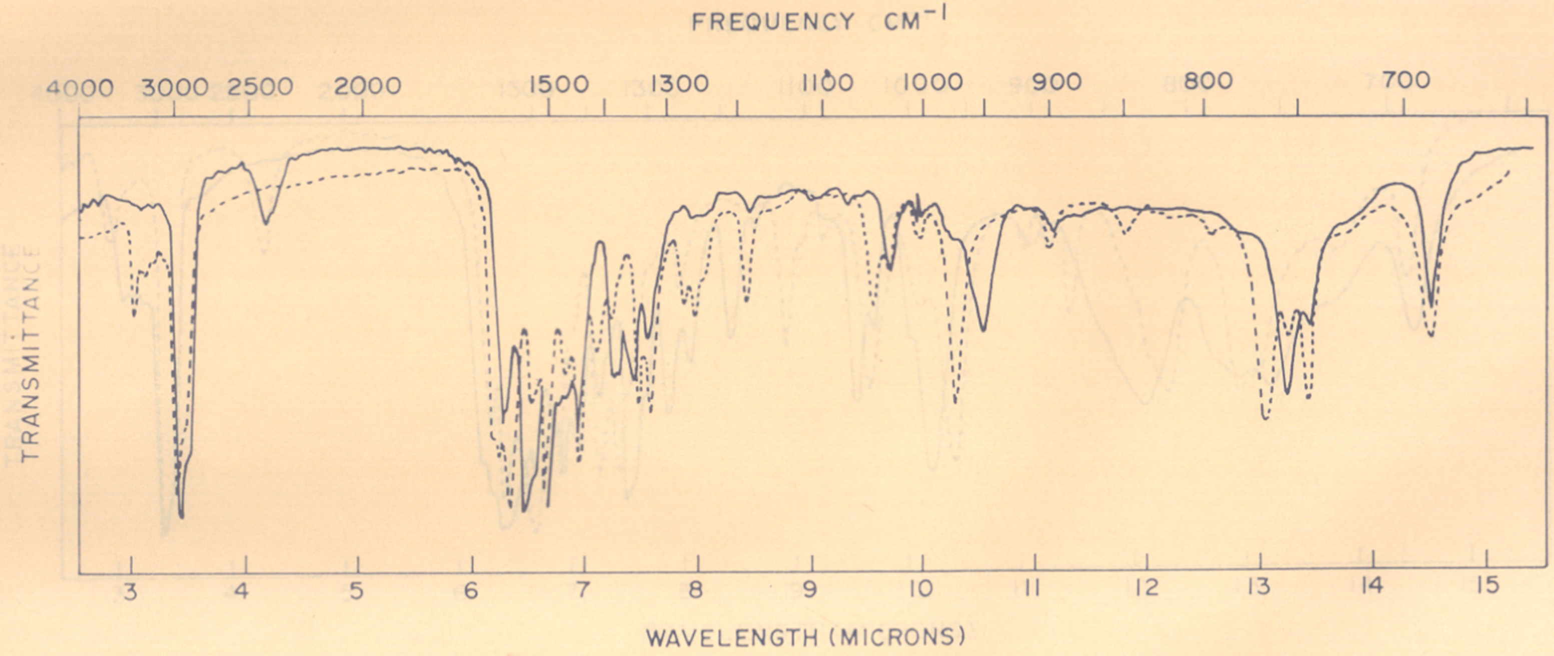


FIG. 3. INFRARED SPECTRA IN NUJOL MULL OF :- ——— DEUTERATED Cu (II) ACETOACETANILIDE;

------ Cu (II) ACETOACETANILIDE

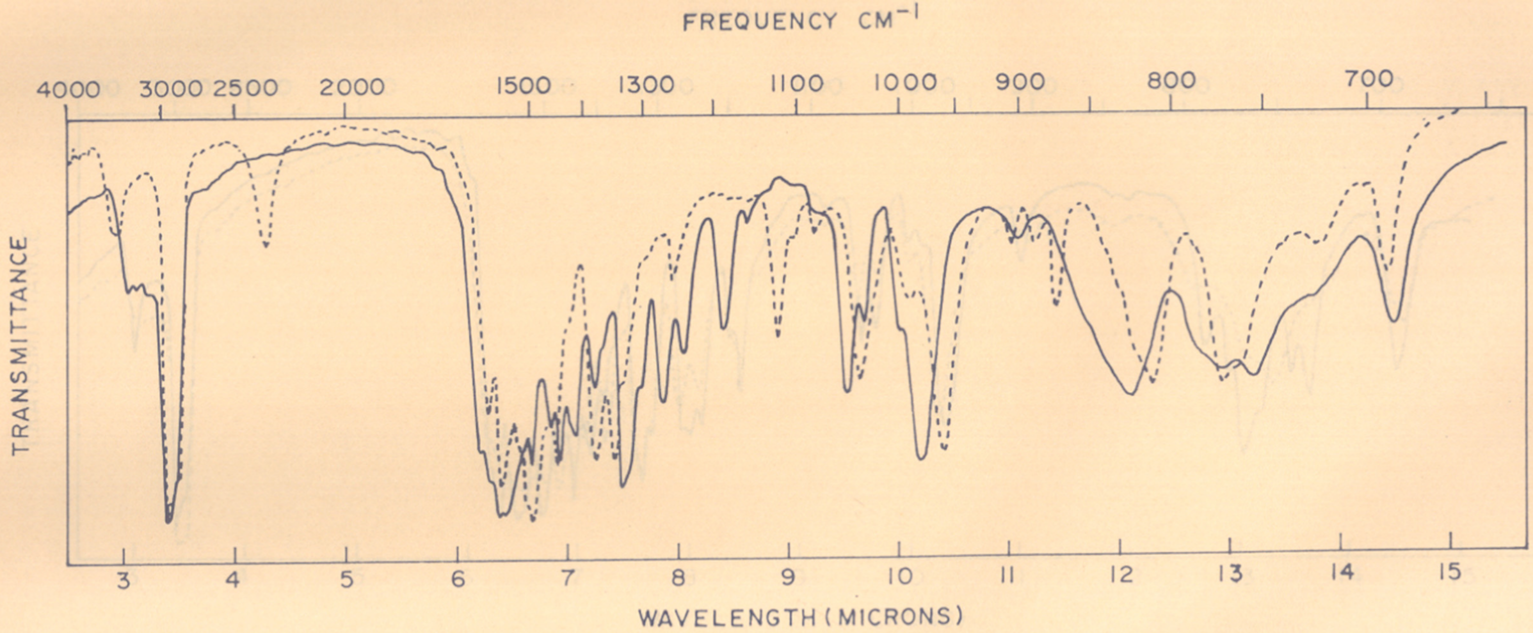
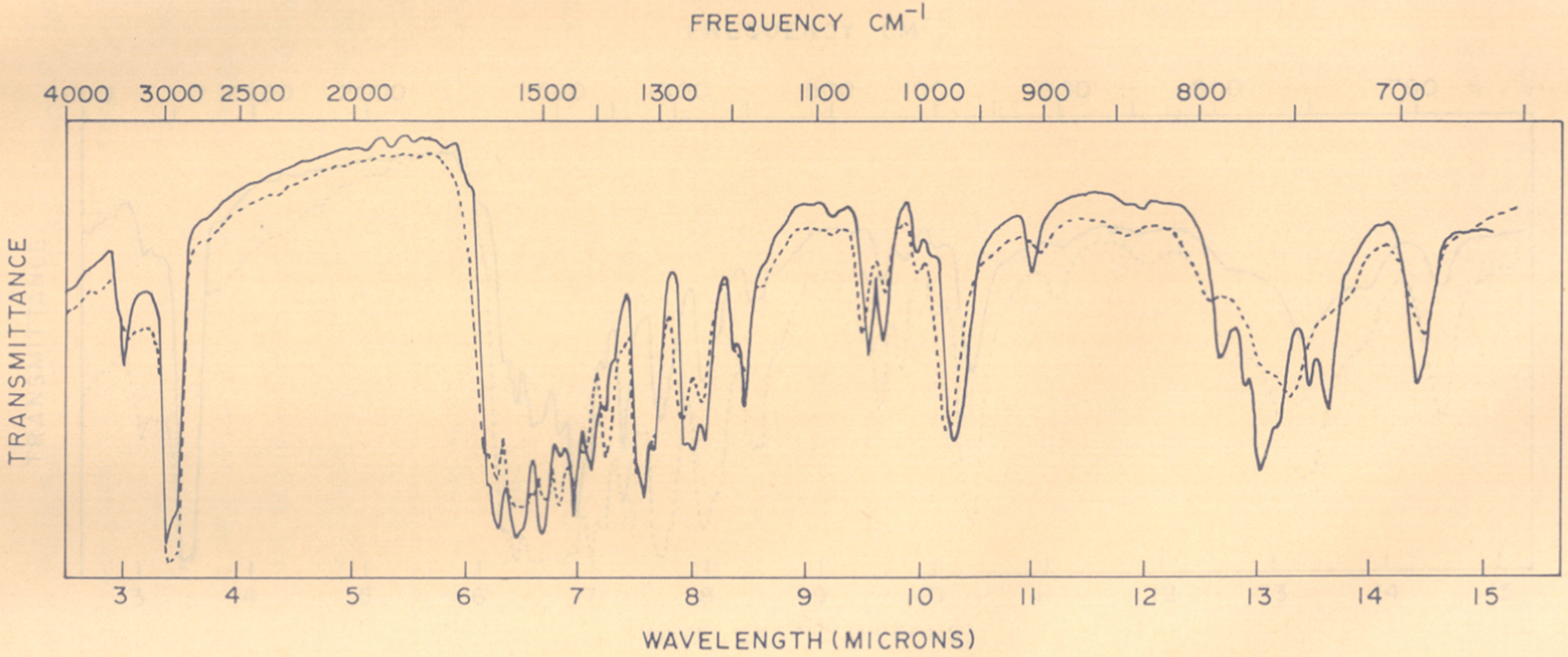


FIG. 4. INFRARED SPECTRA IN NUJOL MULL OF :- ——— Be (II) ACETOACETANILIDE;

- - - - - - DEUTERATED Be (II) ACETOACETANILIDE



FIG·5· INFRARED SPECTRA IN NUJOL MULL OF :- ——— Fe (III) ACETOACETANILIDE ;

------ Al (III) ACETOACETANILIDE

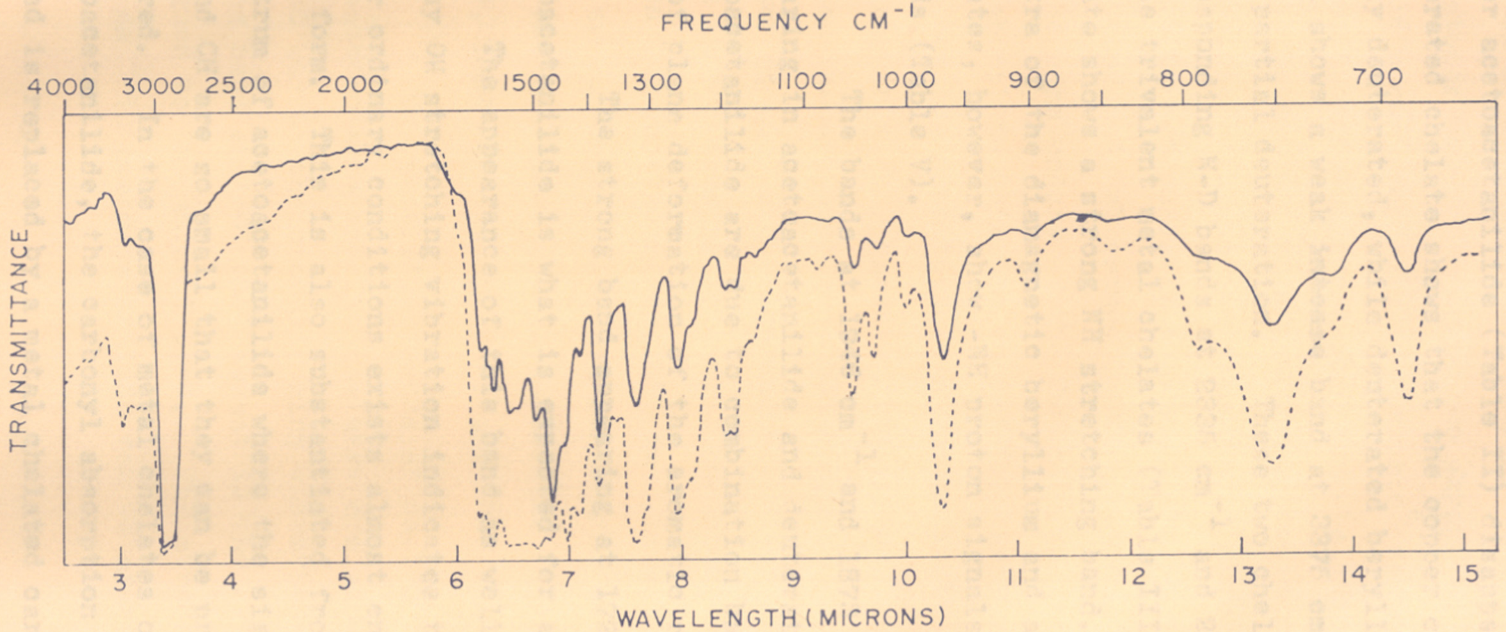


FIG.6· INFRARED SPECTRA IN NUJOL MULL OF :- ——— Cr (III) ACETOACETANILIDE m.p. 204°C· ; ----- Cr (III) ACETOACETANILIDE m·p 226°C·

The N-H stretching mode at 3311 cm^{-1} in the copper acetoacetanilide (Table II) disappearing in the deuterated chelate shows that the copper chelate is mostly deuterated, while deuterated beryllium chelate still shows a weak ~~intense~~ band at 3375 cm^{-1} indicating only partial deuteration. These two chelates show the corresponding N-D bands at 2335 cm^{-1} and 2337 cm^{-1}. Of the trivalent metal chelates (Table III), only iron chelate shows a strong NH stretching band. The NMR spectra of the diamagnetic beryllium and aluminium chelates, however, show -NH proton signals at low fields (Table V).

The bands at 1946 cm^{-1} and 1873 cm^{-1} appearing in acetoacetanilide and deuterated acetoacetanilide are due to combination bands of CH out of plane deformation of the aromatic ring.

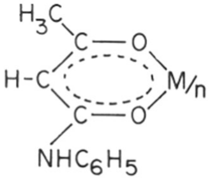
The strong band appearing at 1727 cm^{-1} in acetoacetanilide is what is expected for an unconjugated C=O. The appearance of this band as well as the absence of any OH stretching vibration indicates that acetoacetanilide under ordinary conditions exists almost entirely in the keto form. This is also substantiated from the NMR spectrum of acetoacetanilide where the signals due to OH and CH are so small that they can be practically ignored. In the case of metal chelates of acetoacetanilide, the carbonyl absorption of the ligand is replaced by a metal chelated carbonyl absorption at much lower frequencies. The infrared spectra of metal chelates of acetylacetone, ethylacetoacetate and other β-diketones usually exhibit two strong bands in the 1500-1650 cm^{-1} region[6-9]. Lecomte[6] assigned the uppermost band to a perturbed (or chelated) carbonyl and the lower band to perturbed carbon-carbon double bond. However, Martell and his co-workers[10] have rightly pointed out that it is not possible to assign the bands due to C=C and C=O groups in this region, since (a) the bond orders of the C=O and C=C are similar and both absorb in this region and (b) their relative positions are sensitive to a change in the metal. Further, in such a chelate ring system, coupling between these vibrational modes may be serious. Following Bellamy *et al.*[8] and Shigorin[9] the first strongest band found in the spectra of metal acetoacetanilides in this region and located at ca.1580 cm^{-1} is assigned empirically to a predominantly carbonyl stretching mode: 1577 (Cu II), 1567 (Be II), 1587 (Al III), 1587 Cr III, *cis*-), 1582 (Cr III, *trans*-) and 1587 (Fe III) cm^{-1}.

The absorption bands at ca.1600 cm^{-1} in acetoacetanilide and its chelates are assigned primarily to C=C and to the aromatic ring vibrations, while the strong band at 1661 cm^{-1} absent in the metal chelates is assigned to the amide I band. The strong band at 1538 cm^{-1} in acetoacetanilide can be attributed to amide II.

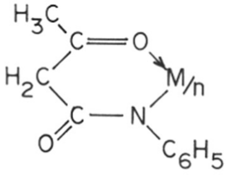
According to Miyazawa, Shimanouchi and Mizushima[11], the vibration responsible for this absorption is a mixture of N-H bending (ca. 60%) and C-N stretching (ca. 40%), although earlier they[12] postulated this band as having a more C-N than N-H character. Accordingly, the 1538 cm^{-1} band in acetoacetanilide can be assigned to a mixed vibration of CN stretching and NH in plane bending. The amide III band (CN stretching, NH bending) and CH_3-C stretching can be located at 1316 cm^{-1} and 1279 cm^{-1} respectively.

The amide II band in the chelated metal complexes is shifted: 1529 (Cu II), 1548 (Be II), 1548 (for trivalent metals) cm^{-1} respectively. The amide III band for metal chelates can be located at 1319 (Cu), 1305 (Be), 1319 (Al), 1319 (Cr, cis-), 1348 (Cr, trans-), 1305 (Fe) cm^{-1} respectively. On deuteration, the strong band appearing at 1425 cm^{-1} can be assigned to the corresponding absorption for amide II band in acetoacetanilide (amide II'). The amide III band, however, is quantitatively shifted to 927 cm^{-1} (isotope ratio, 1.3). Strong bands appearing in deuterated beryllium and copper chelates at ca.1350 cm^{-1} can be assigned to amide II'. Bands appearing at ca.950 cm^{-1} in deuterated copper and beryllium chelates correspond to the amide III'.

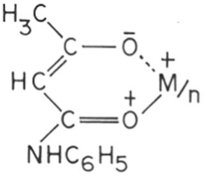
The strong absorption at 1502 cm^{-1} of acetoacetanilide shifted very little in the chelates and even on deuteration and can be assigned to the aromatic C=C vibrations. The strong bands at 1449 cm^{-1} and 1366 cm^{-1} (table I) and the corresponding bands in the chelates can arise from CH_3 asymmetric and symmetric deformations; the latter, however, is merged with the nujol peak in many cases. This leaves a strong band~~s~~ of acetoacetanilide at 1408 cm^{-1} which disappear~~e~~s on deuteration and can be assigned to CH_2 group adjacent to C=O; a band appearing at 1030 cm^{-1} in the deuterated acetoacetanilide seems to be the corresponding CD_2 band, since the isotope ratio (1408/1030) is 1.30. Difficulties are, however, experienced with the chelates, for instance, the copper chelate also shows a medium intense band at 1408 cm^{-1} shifted to a strong band at 1030 cm^{-1} {on deuteration} and the beryllium chelate shows a strong band at 1416 cm^{-1}, perhaps, also shifted and merged with the BeO stretching vibration in the deuterated chelate (the peak at 1030 cm^{-1} being broad). The other metal chelates also show this strong band: 1416 (Al III), 1408 (Cr, cis- and trans-) and 1407 (Fe III) cm^{-1}. Based on these results, one is tempted to suggest that there is significant contribution from structure II in such chelates.



I



II



III

However, such a structure is very unlikely since a free carbonyl band expected at ca.1700 cm^{-1} is absent and also in view of some recent visible and ultraviolet absorption spectral studies on a number of this type of chelates[13]. Hence it is apparent that this band is due to a combination of C=0 stretching and C-H in plane bending mode. The appearance of this at such a low frequency indicates that these chelates of acetoacetanilide are very weak type involving electrons of ligands only[10,23]. Wolf and Wetzel[14] from a study of a large number of chelate compounds of copper with amides of β-ketoacids particularly with anilides of β-ketoacids also concluded that the bonding between metal ion and enolate ion is mainly electrostatic in nature.

The bands at 1238 cm^{-1} and 1168 cm^{-1} in acetoacetanilide can be due to the twisting and wagging vibrations of methylene group. That the bands (table II) at 1188 (Be II), 1182 (Cu II), 1182 (Al III), 1188 (Cr III, trans-), 1182 (Cr III, cis-) and 1181 (Fe III) cm^{-1} respectively, can be assigned to a pure C-H in plane bending mode is well documented by the appearance of a strong absorption band at 874 cm^{-1} in the deuterated beryllium chelate (isotope ratio, 1.35).

But the copper chelate shows peculiarity, since the deuterated copper chelate does not show this band. The strong and broad bands at 1048 cm^{-1} and 826 cm^{-1} are due to the merging of Be-O stretching vibration[~~10~~ 23] with ring deformation and $C-CH_3$ bending vibrations. In the other metal chelates, the strong and broad bands at ca. 690 cm^{-1} can be assigned to a mixed vibration of metal-oxygen stretching with ring deformation.

Magnetic susceptibility data

The magnetic susceptibility data (given in Table IV) show that while the values of Cr(III) and Fe(III) chelates are what is expected for d^3- and d^5 spin only magnetic susceptibilities, the value for copper is low. Recently such subnormal magnetic moments of copper have been amply discussed[15]. The peculiarity of the infrared spectrum as well as the subnormal magnetic susceptibility of the copper chelate may be due to its structural differences from the other chelates.

Reactivity of chelated acetoacetanilide

To demonstrate the reactivity of the coordinated acetoacetanilide, nitration of the relatively stable chromium(III) chelate was attempted. A mixture of copper nitrate trihydrate and acetic anhydride was employed[4] to nitrate the chromium(III) chelate. Beryllium and aluminium nitro chelates were prepared in a single step reaction employing the metal nitrate and cold acetic anhydride[16].

Table IV

Magnetic susceptibility data

Compound	T^{o}_{K}	$\chi_g \times 10^6$	Dia.cor.	$\chi_M^{cor} \times 10^6$	μeff
Copper acetoacetanilide	304	1.327	165.9	718	1.336
Cr(III) acetoacetanilide	304	9.886	253.85	5194	3.833
Fe(III) acetoacetanilide	304	20.16	253.85	12043	5.434

Chromatography of the crude reaction product (chromium nitro acetoacetanilide) on alumina column resulted in the decomposition of the chelate. An yellow unstable metal and nitrogen free liquid (C, 63.43; H, 10.67%) was obtained. Polycaprolactum powder[17] (nylon powder), however, is found suitable for purification of these nitro chelates. Thin layer chromatography on calcium sulphate was used to examine homogeneity of these nitro chelates. Analysis showed that Be(II) and Cr(III) chelates are fully nitrated whereas Al(III) chelate is partially nitrated. The NMR* spectrum of the partially substituted nitro chelate of aluminium, perhaps due to low solubility in deuterated chloroform, did not show the signal in the vinyl region. (Table V)

The NMR spectrum of nitro chelate of Be(II) (Table V) confirms that the proton of the active methylene group in the chelate ring is replaced by a substituent. The nitro chelate of Be(II) acetoacetanilide exhibits ~~only~~ signals at 7.25 and at 2.49 corresponding to methyl and phenyl protons respectively and none in the vinyl region. The low field position of the methyl signal is probably due to a combination of electronegativity and anisotropy of the nitro group.

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* Chemical shifts are cited on the τ scale.

Table V

NMR spectral data of acetoacetanilide, its chelates and chelated nitroacetoacetanilides

Compound	Solvent	NH	Vinyl	Methylene	Methyl	Remarks and inference
Acetoacetanilide	$CDCl_3$	0.66		6.48(2)	7.83(3)	The vinyl (4.95) and the methyl signals (8.17) of the enol form appear like impurities. The phenyl protons show multiplicity and the integrated intensities of the peaks (τ = 2.4, 2.55 and 2.7) show the presence of five protons as expected.
Deuterated acetoacetanilide	$CDCl_3$	-	-	6.48 (~5%)	7.75	
Be(acacN)$_2$	Pyridine	-	4.75(1)		8.13(3)	The ratio of integrated intensities is in agreement with calculated values.
Al(acacN)$_3$	Pyridine	-	4.63 5.17		8.05 8.13	The spectrum strongly suggests the existence of isomeric forms as shown by two methyl and two vinyl signals.
Be(acacN)$_2$	DMSO	0.12	4.87		n.d.	The single proton signals of the vinyl and the NH groups suggests that the compound shifted to one isomeric form (probably trans-)
Al(acacN)$_3$	DMSO	0.33	4.978		n.d.	
Be(acacN-NO$_2$)$_2$	$CDCl_3$	-	-		7.25(3)	Lack of signals at the vinyl region shows complete substitution.

acacN stands for $C_{10}H_{10}O_2N$.

The values given in parenthesis are the ratios of the integrated intensities.

n.d. - not determined.

Isomerism of tris-(acetoacetanilidato)-chromium(III)

The *cis*- and *trans*-isomers of chromium(III) acetoacetanilide were separated by utilizing solubility differences in benzene and column chromatography on acid washed alumina and also by thin layer chromatography using acetone-benzene (1:1) solvent mixture. For separation by thin layer chromatography, different adsorbents (silica gel, neutral alumina, magnesium trisilicate) with different developing solvents were examined, but the ~~most~~ satisfactory separation was achieved with silica gel (adsorbent) and benzene-acetone mixture (developing solvent) only. In this particular combination, the difference between the *cis*- and *trans*- migrations was maximum. (Table VI).

Comparison of the mobilities of the *cis*- and *trans*-isomers indicates that the *trans*-isomer of the pair is more mobile.

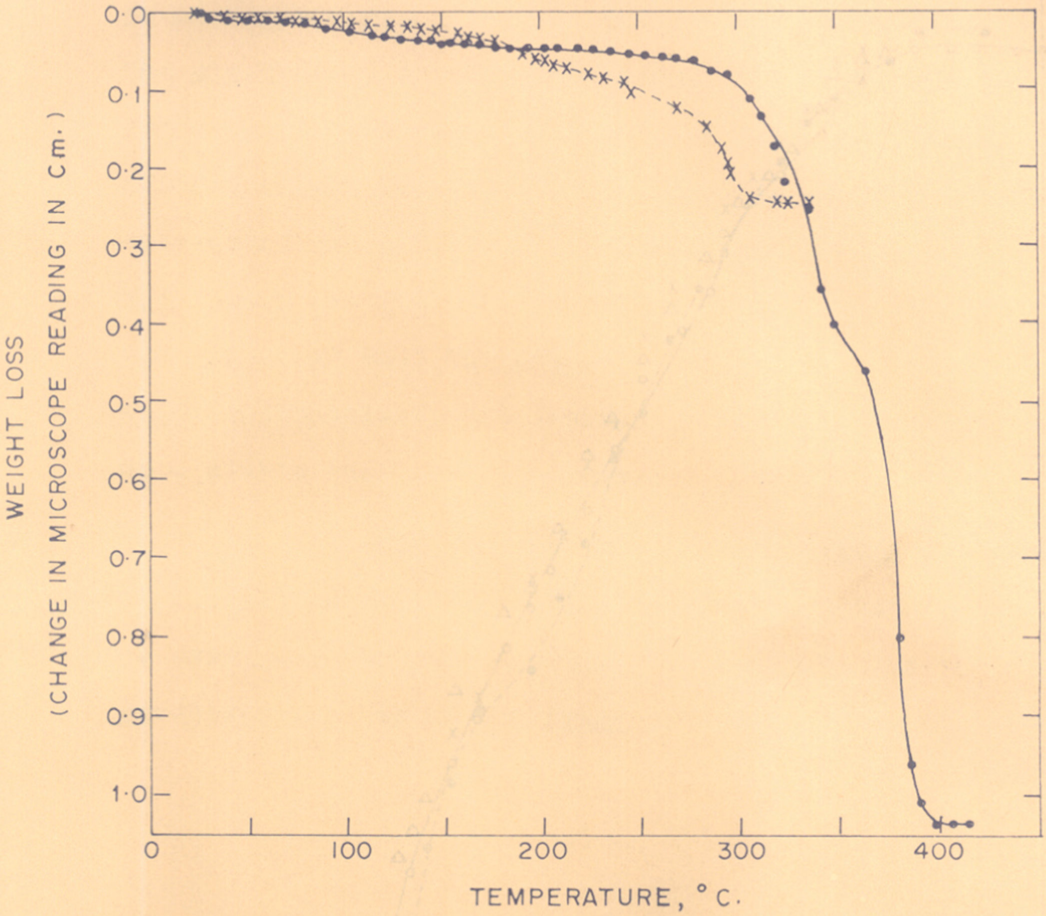
The infrared spectra of *cis*- and *trans*-isomers of chromium acetoacetanilide showed minor intensity differences. Thermogravimetric analysis of the *cis*- and *trans*-isomers in air and in nitrogen, however, showed differences in their stability.

It can be seen from the thermograms (figs. 7 and 8) that the *trans*-isomer is stable upto a temperature of 320°C in air and accelerated weight loss is observed only from 350°C onwards.

Table VI

TLC data of cis- and trans-isomers of Cr(III) acetoacetanilide

Adsorbent	Developing solvent	R_f cis-	R_f trans-	ΔR_f
Silica gel	$(CH_3)_2CO$	0.77	0.78	0.01
	CH_3OH	0.72	0.75	0.03
	$(CH_3)_2CO + C_6H_6$ (1:1)	0.58	0.71	0.13
	$C_6H_6 + CH_3OH$ (1:1)	0.73	0.79	0.06
Alumina	$(CH_3)_2CO$	0.76	0.77	0.01
	CH_3OH	0.78	0.82	0.04
	$(CH_3)_2CO + C_6H_6$ (1:1)	0.66	0.72	0.06
	$C_6H_6 + CH_3OH$ (1:1)	0.82	0.85	0.03
Magnesium trisilicate	$(CH_3)_2CO + C_6H_6$ (1:1)	No separation (0.65)		
	$C_6H_6 + CH_3OH$ (1:1)	No separation (0.77)		



FIG·7· THERMOGRAMS OF TRIS-(ACETOACETANILIDATO)-CHROMIUM(III) IN AIR; HEATING RATE, 2°C/MIN. •———• TRANS ISOMER (m·p· 226°C; Wt· 0·0247g·); x-------x CIS ISOMER (m·p· 204°C; Wt· 0·0241 g·)

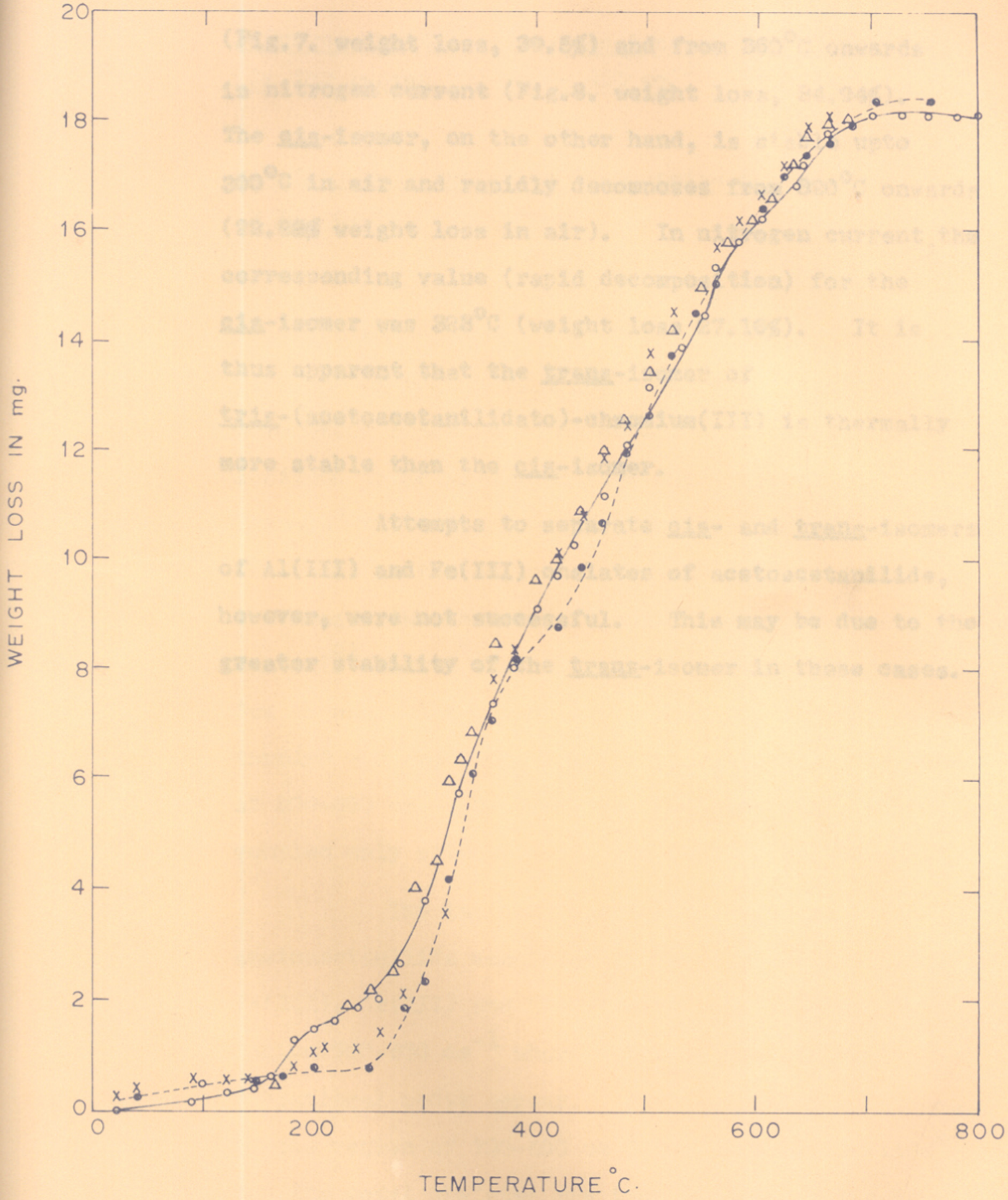


FIG. 8. THERMOGRAMS OF TRIS-(ACETOACETANILIDATO)-CHROMIUM(III) IN NITROGEN; HEATING RATE 4°C./MIN.

——— CIS ISOMER (m.p. 204°C. Wt. 0.0203 g.)

- - - - - TRANS ISOMER (m.p. 226°C.; Wt. 0.0202 g.)

(Fig.7. weight loss, 39.5%) and from 360°C onwards in nitrogen current (Fig.8. weight loss, 34.94%). The *cis*-isomer, on the other hand, is stable upto 300°C in air and rapidly decomposes from 320°C onwards (22.28% weight loss in air). In nitrogen current, the corresponding value (rapid decomposition) for the *cis*-isomer was 323°C (weight loss 27.16%). It is thus apparent that the *trans*-isomer of *tris*-(acetoacetanilidato)-chromium(III) is thermally more stable than the *cis*-isomer.

Attempts to separate *cis*- and *trans*-isomers of Al(III) and Fe(III) chelates of acetoacetanilide, however, were not successful. This may be due to the much greater stability of the *trans*-isomer in these cases.

Infrared spectra of acetoacetanilide metal chelates in the region 700 cm^{-1} - 400 cm^{-1}

Metal oxygen stretching frequencies in some metal acetoacetanilides

Recently infrared spectra of metal acetylacetonates, and metal γ-nitroacetylacetonates in the CsBr optics region were reported[10,18-20] and the absorption bands found at 600-300 cm^{-1} have been assigned to metal-oxygen stretching vibrations. Lecomte[6] first observed that in metal acetylacetonates the bands in the region of 700-590 cm^{-1} are sensitive to changes in the metal. Subsequently, Nakamoto and Martell[21] showed that the bands in this region arise due to coupled M-O and ring vibrations and due to coupled M-O and $C-CH_3$ bending vibrations. The bands at 500-400 cm^{-1}, however, are M-O stretching vibrations coupled only slightly with the $C-CH_3$ vibrations[22].

The infrared spectra in nujol mull of acetoacetanilide complexes of Cu(II), Be(II), Al(III), Fe(III), Cr(III) and Ti(IV) have been examined in the region 700-400 cm^{-1} where metal-oxygen stretching vibrational modes appear. The absorption bands found in the region of 700-400 cm^{-1} for acetoacetanilide[24] and its metal chelates are tabulated and given in Tables VII and VIII. (fig. 9-13) All the acetoacetanilide complexes exhibit a strong band between

Table VII

Infrared absorption frequencies (cm^{-1}) of metal acetoacetanilides (in nujol) in the region 700-400 cm^{-1} (CsBr prism)

HacacN*	Cu(acacN)$_2$	Be(acacN)$_2$	Fe(acacN)$_3$	Cr(acacN)$_3$ m.p.226°	Cr(acacN)$_3$ m.p.204°	Al(acacN)$_3$	Possible assignments
690s	690s	685s	687s	687s	687s	687s	M-O str. + ring defor.
635m	-		645m	637m	637m	637m	M-O str. + C-CH$_3$ bend
615m		606s	617m				
			588s	588sh	588sh	590sh	
563sh	565s			562vs	562vs	562vs	
554m	546m	544m	538vs	-	-	-	
523s	506vs		510m	508s	502b,s	495vb,s	
503s							
463w	474vs	510b,s	451vs	481b,vs	476b,vs	410b,vs	M-O Str.
413w	407m	417m	429w	429m	429m		
393m							
355m							

*acetoacetanilide

Table VIII

Infrared absorption frequencies (cm^{-1}) of metal acetoacetanilides* (in nujol) in the region of 700 - 400 cm^{-1} (CsBr prism)

$Ti(acacN)_2Cl_2$	$Ti(acacN)_3Cl$	$Ti(acacN)_3Br$	$Ti(acacN)_3I.HI$	Possible assignments
685s	687s	687s	687s	M-O str. + ring def.
			647s	
614s	621s	623s	621s	M-O str. + $C-CH_3$ bend
	562sh			
550sh	550sh	562sh	562sh	
546vs	556b,vs	556b,vs	556b,vs	
508m	508m	505m	508m	
465vs	470vs	472vs	474vs	M-O.str.
	443w	444w	453w	
	426w	424w	424w	

*Preparation of these compounds is described in Chapter 2.

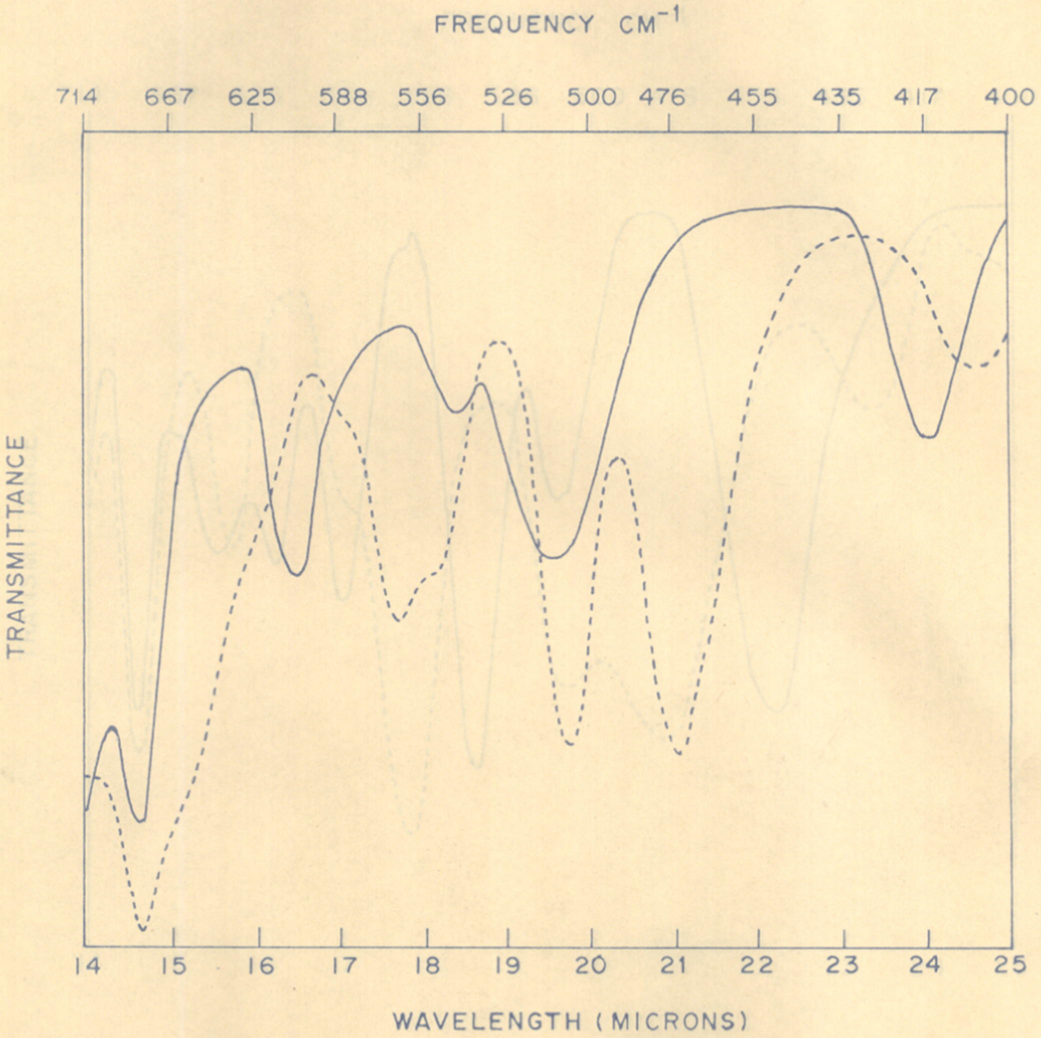
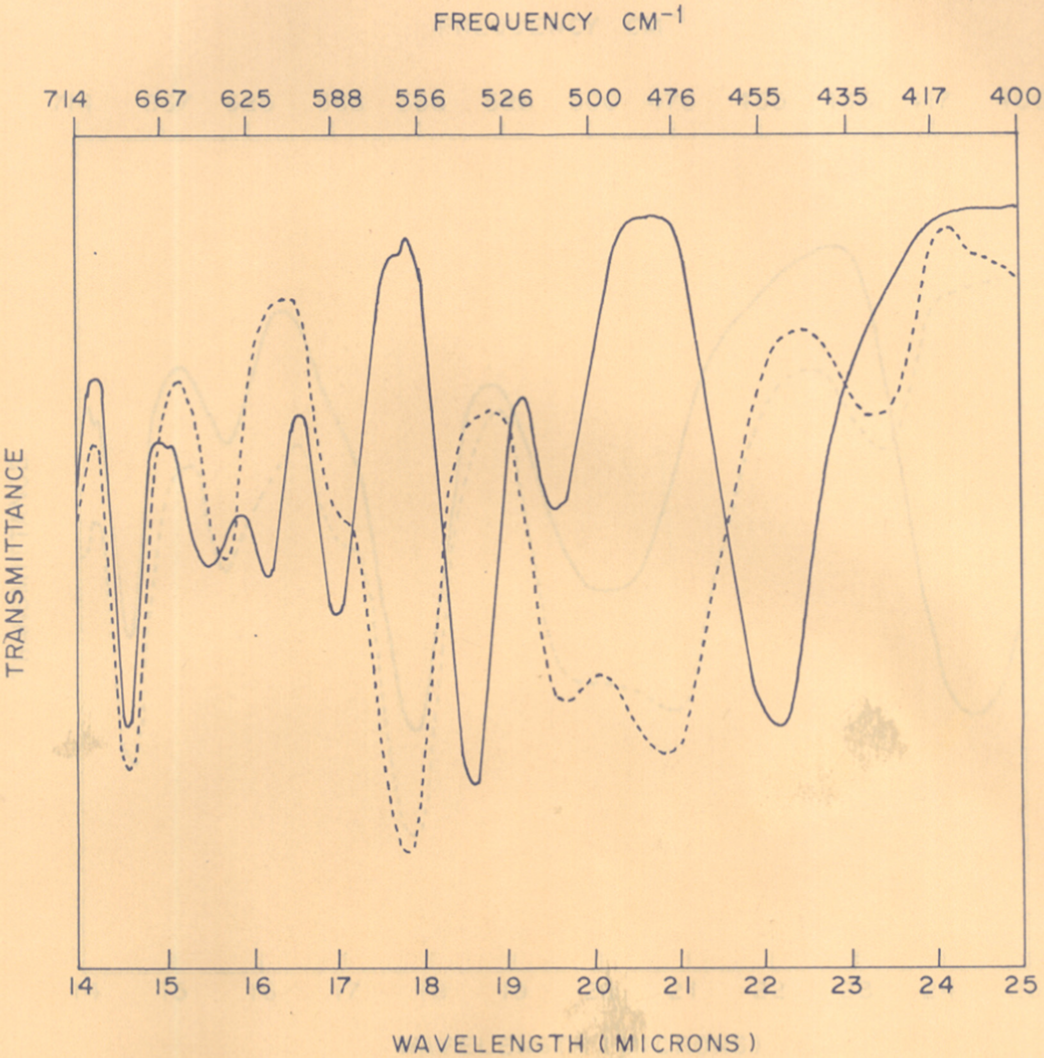


FIG.9. INFRARED SPECTRA IN NUJOL MULL OF: ——— Be (II) ACETOACETANILIDE; - - - - - - Cu (II) ACETOACETANILIDE



FIG·10· INFRARED SPECTRA IN NUJOL MULL OF:- ------ Cr (III) ACETOACETANILIDE· m·p· 226°C; ———— Fe (III) ACETOACETANILIDE

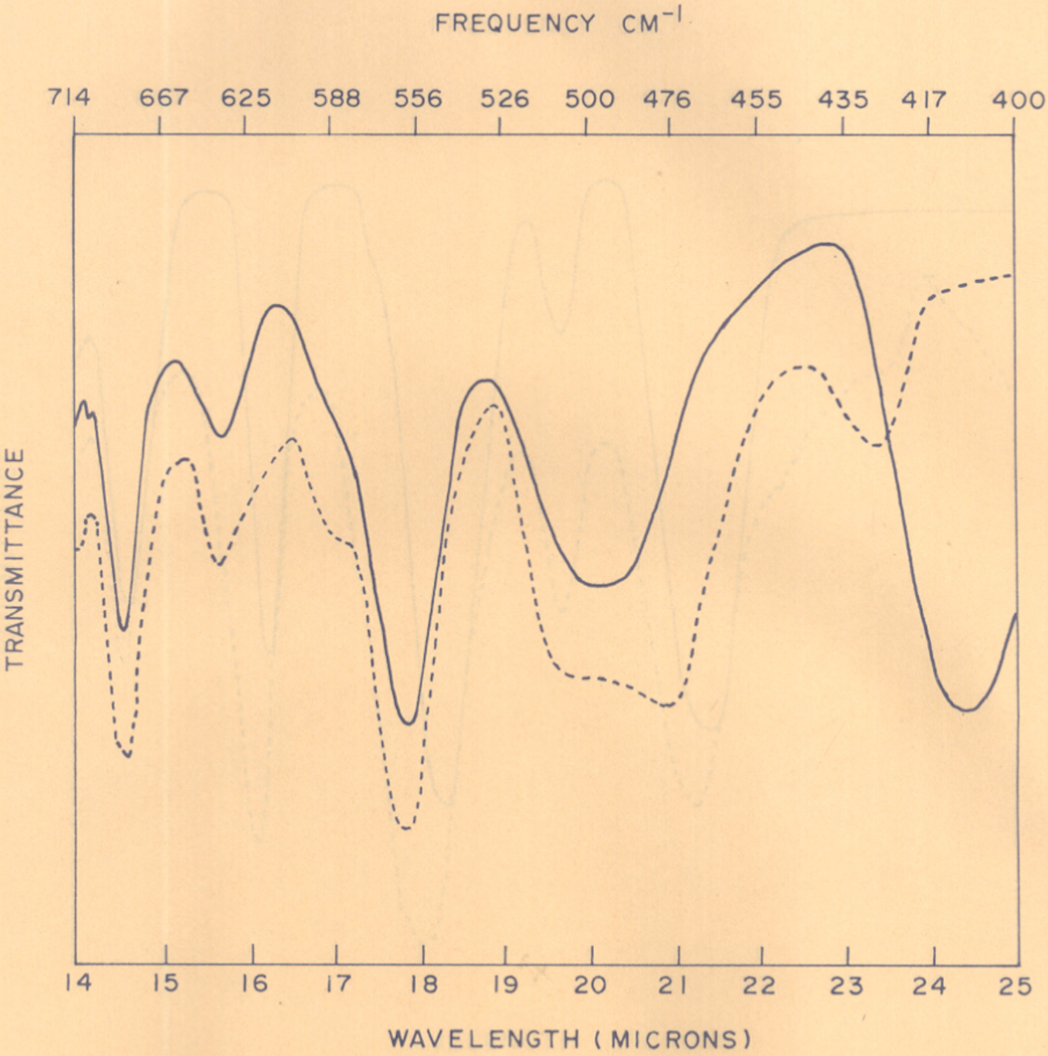


FIG. 11. INFRARED SPECTRA IN NUJOL MULL OF:- ----- Cr(III) ACETOACETANILIDE. m.p. 204°C; ———— Al(III) ACETOACETANILIDE

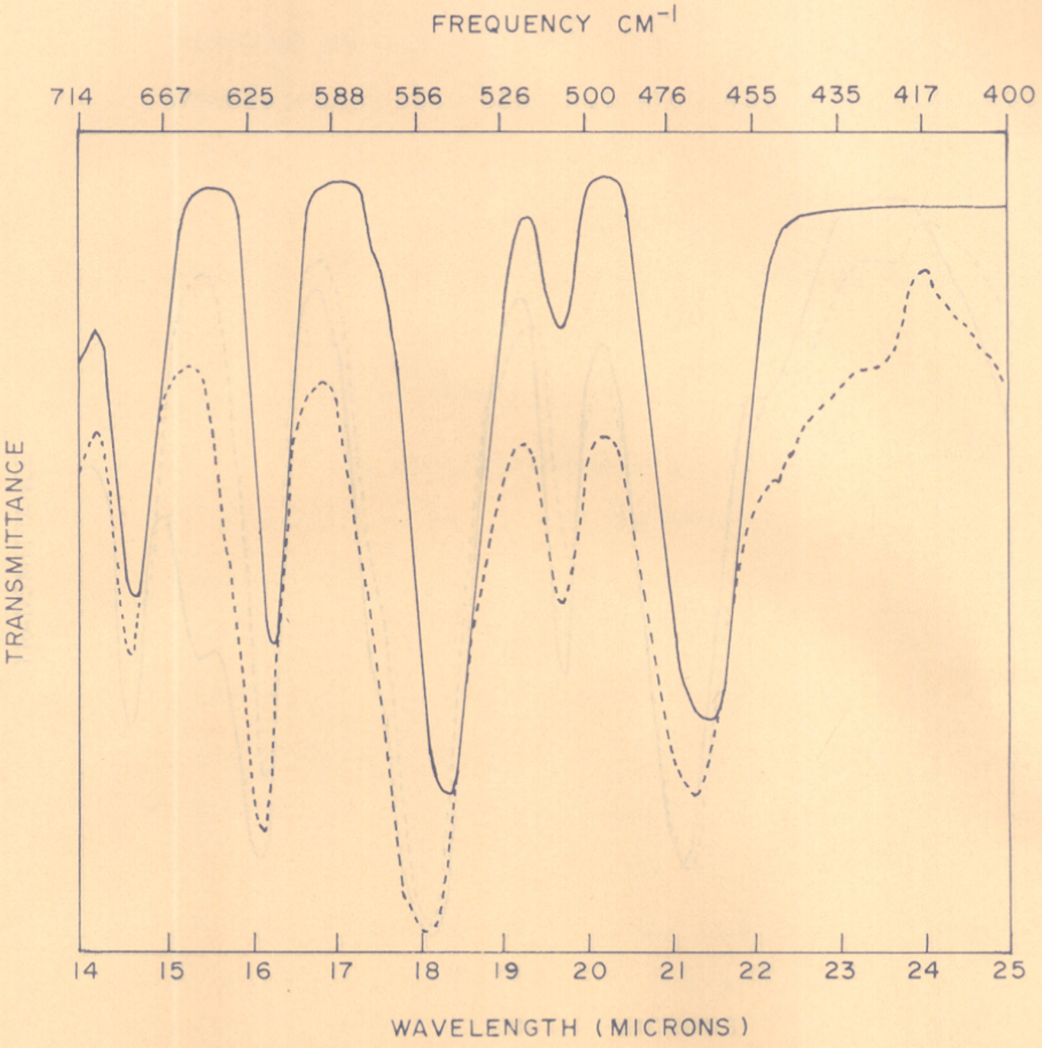
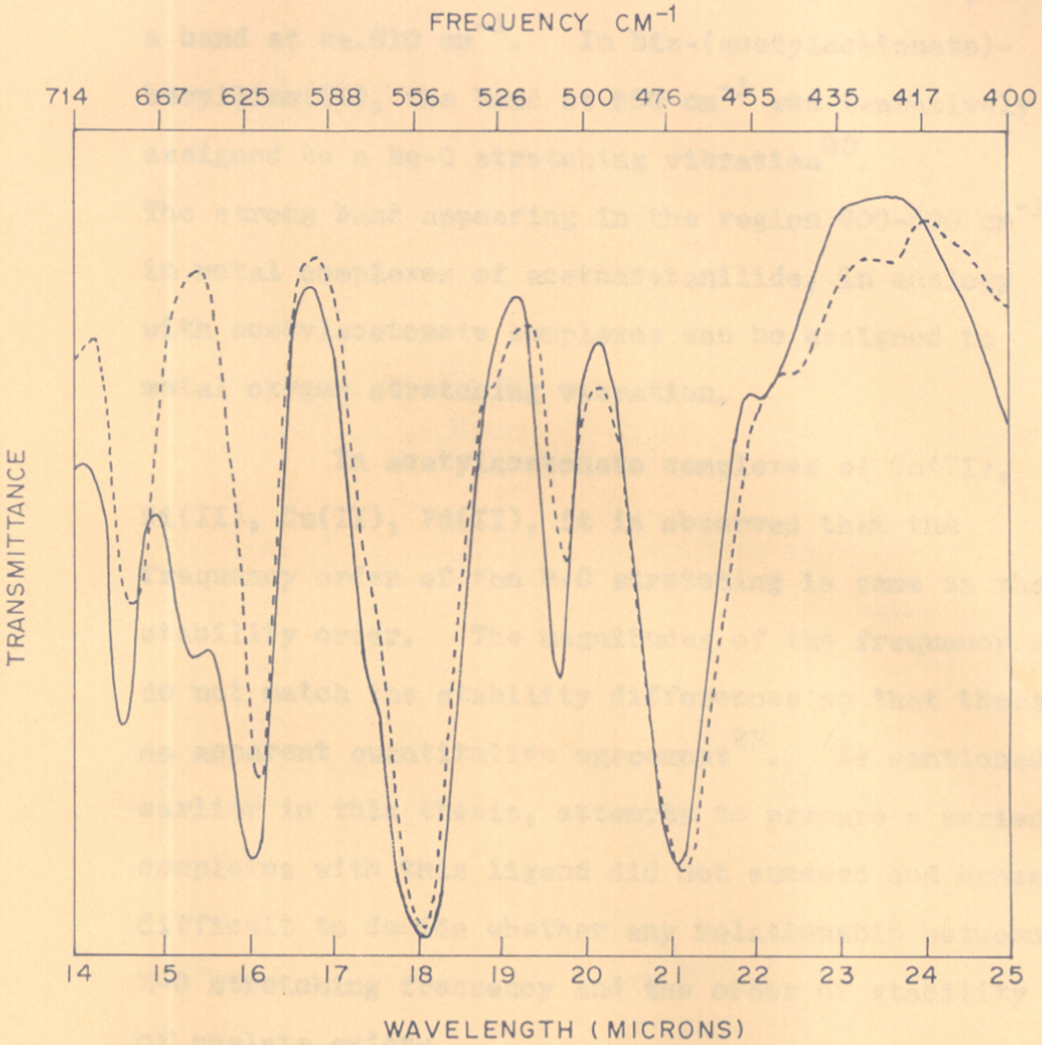


FIG. 12. INFRARED SPECTRA IN NUJOL MULL OF:- ----MONOCHLOROTRIS (ACETOACETANILIDATO) TITANIUM(IV) ; ———— DICHLOROBIS-(ACETOACETANILIDATO) TITANIUM(IV)



FIG·13· INFRARED SPECTRA IN NUJOL MULL OF:- - - - - MONOBROMOTRIS (ACETOACETANILIDATO) TITANIUM (IV); ——— MONOIODOTRIS-(ACETOACETANILIDATO) TITANIUM (IV)

400-500 cm^{-1}. The beryllium chelate, however, shows a band at ca.510 cm^{-1}. In bis-(acetylacetonato)-beryllium(II), the band at 500 cm^{-1} was tentatively assigned to a Be-O stretching vibration[23].
The strong band appearing in the region 400-500 cm^{-1} in metal complexes of acetoacetanilide, in analogy with acetylacetonate complexes can be assigned to metal oxygen stretching vibration.

In acetylacetonate complexes of Co(II), Ni(II), Cu(II), Pd(II), it is observed that the frequency order of the M-O stretching is same as the stability order. The magnitudes of the frequency shifts do not match the stability differences so that there is no apparent quantitative agreement[23]. As mentioned earlier in this thesis, attempts to prepare a series of complexes with this ligand did not succeed and hence it is difficult to decide whether any relationship between M-O stretching frequency and the order of stability of chelate exists.

In amides the band near 600 cm^{-1} is assigned to N-C=O deformation whereas the band near 500 cm^{-1} to a C-C=O deformation[24], a C-C deformation[25] and a NCO deformation[26]. The absorption bands appearing at ca.600 cm^{-1} in acetoacetanilide complexes may also arise out of coupled M-O and ring vibrations and due to coupled M-O and $C-CH_3$ bending vibrations.

EXPERIMENTAL

Copper acetoacetanilide - was prepared according to the method given by Chaplin and Hunter[5] and was recrystallised several times from acetone.

Found: C, 57.50; H, 5.01; N, 6.60; Cu, 14.6%.
Calcd. for $C_{20}H_{20}O_4N_2Cu$: C, 57.76; H, 4.85; N, 6.74; Cu, 15.29%.
The compound is soluble in chloroform and in acetone but insoluble in carbon tetrachloride and benzene. Solubility (29°C) in chloroform 0.16 g/100 ml. of solvent; in acetone 0.55 g/100 ml. of solvent.

Beryllium acetoacetanilide - was prepared as follows: Acetoacetanilide (7.09 g; 0.04 mole) was dissolved in 6N ammonia, little alcohol was added to get a clear solution. This clear solution was added to the beryllium nitrate solution (3.74 g; 0.02 mole) with stirring. The pH of the mixed solution was brought to 5.5-5.8. The precipitated beryllium acetoacetanilide was filtered, washed with hot water and dried. Yield, 5.9 g. (81.6%) Recrystallised from benzene and vacuum dried. M.P. 165°C.

Found: C, 66.97; H, 5.79; N, 7.0; Be, 2.60%.
Calcd. for $C_{20}H_{20}O_4N_2Be$: C, 66.45; H, 5.58; N, 7.75; Be, 2.49%.
Soluble in chloroform (3.22 g/100 ml.of solvent), and in benzene (0.16 g/100 ml.); insoluble in carbon tetrachloride.

Ferric acetoacetanilide - Ferric chloride hexahydrate (2.7 g; 0.01 mole) was dissolved in water (50 ml.) containing ca.3 g.of sodium acetate. The solution was filtered and to this was added acetoacetanilide (5.32 g; 0.03 mole) in alcohol (30 ml.) with stirring. A garnet red precipitate was obtained. This was collected on a filter under suction and washed with hot water and dried. Yield, 3.6 g; 61.6%. Crystallized from methanol and vacuum dried.

Found: C, 60.60; H, 4.91; N, 7.26; Fe, 9.46%.
Calcd. for $C_{30}H_{30}O_6N_3Fe$: C, 61.63; H, 5.17; N, 7.19; Fe, 9.55%.

Soluble in chloroform (0.17 g/100 ml. of solvent). Very sparingly soluble in benzene (0.05 g/100 ml.) and insoluble in carbon tetrachloride.

Aluminium acetoacetanilide - Acetoacetanilide (2.66 g; 0.015 mole) was dissolved in methanol (25 ml.). Aluminium isopropoxide (1.02 g; 0.005 mole) was added to this solution with stirring. The mixture was heated on the water-bath to dryness. Methanol (30 ml.) was added and again evaporated to dryness. White solid, insoluble in alcohol, benzene and chloroform. Yield, 2.5 g; 89.9%. Recrystallized from methanol and the product vacuum dried at 100°C for 2 hr. M.P. 206-7°C.

Found: C, 63.54; H, 5.64; N, 7.64; Al, 4.68%
Calcd. for $C_{30}H_{30}O_6N_3Al$: C, 64.83; H, 5.44; N, 7.56; Al, 4.86%.

Insoluble in carbon tetrachloride, but soluble in $CHCl_3$ (0.224 g/100 ml), methanol (3.83 g/100 ml) and very sparingly soluble in benzene (0.04 g/100 ml.)

Chromium acetoacetanilide - Chromium(III) chloride hexahydrate (1.33 g; 0.005 mole) was dissolved in water (50 ml.), 10 g of urea and acetoacetanilide (5.32 g; 0.03 mole) in alcohol (40 ml.) were added and the mixture was refluxed for 9 hours on water-bath. The product was collected on a filter while hot, washed with hot water and dried. Yield, 2.5 g; 86.2%. This compound was resolved into cis- and trans-isomers as outlined below.

The chromium compound is insoluble in $CHCl_3$ and CCl_4, sparingly soluble in hot benzene (0.08 g/100 ml) and soluble in methanol (2.03 g/100 ml).

Separation of cis- and trans-isomers

Chromium(III) acetoacetanilide was isolated from aqueous alcoholic solution in which it was almost completely insoluble. The crude reaction product was used without purification by recrystallisation since this would have led to loss of the more soluble cis-isomer. The isomers were separated[27,28] by utilizing solubility differences in benzene and column chromatography on alumina (acid-washed).

The crude reaction product (4 g.) was first purified by rapid chromatography on alumina (100 g. amount not critical). The material was put on the column in 50% benzene- 50% methanol solution and the *cis*- and *trans*-isomers of chromium(III) acetoacetanilide were eluted with pure benzene. Unreacted acetoacetanilide and other unidentified products remained on the column. After removing the benzene from the eluent by evaporation at room temperature, the more soluble *cis*-isomer was concentrated by extracting the residue with 20 ml. portions of hot benzene. The extraction was repeated several times until the extract was only slightly coloured. The residue from the benzene extract (less soluble *trans*-isomer) was purified by recrystallising twice from methanol and dried under vacuum at 100°C for 2 hours. (3.6 g.) light green m.p. 226-27°C.

Found: C, 61.67; H, 5.11; N, 7.04; Cr, 8.88%
Calcd. for $C_{30}H_{10}O_6N_3Cr$: C, 62.05; H, 5.21; N, 7.24; Cr, 8.96%.

The benzene was removed from the benzene extract (*cis*-isomer and some *trans*-isomer) by evaporating at room temperature. Separation of the *cis*-isomer was then achieved by careful chromatography on alumina (50-100 g. of alumina / 1 g. sample in a 20 mm. outside diameter tube). The sample was put on the column in 20% benzene and 80% methanol. The benzene content of the eluting solvent was increased in the order 20, 30, 40, 50 and finally 70% every 100 ml. of eluent. The *cis*-isomer was eluted with 70% benzene - 30% methanol. Early fractions contained *trans*-isomer. The *cis*-isomer was purified by recrystallization from benzene and dried under vacuum at 100°C for 2 hr.(75 mg.). deep green m.p.204°C.

Found: C, 61.75; H, 5.68%.

Separation of the *cis*- and *trans*-isomers by thin layer chromatography

Glass plates (160x40 mm.) were thoroughly cleaned, rinsed with distilled water and coated with a slurry of silica gel. The plates were air dried for 10 minutes and activated at 110°C for one hour. The activated plates were stored in a desiccator.

Saturated solutions of the *cis*- and *trans*-isomers in acetone-benzene were prepared and the plates were spotted first with individual isomers and then with a mixture of isomers, along the origin of the plate. The plate was air dried and introduced into a chromatographic jar containing the solvent and was developed by ascending technique[29]. The plate was removed when the solvent reached a height of 10 cm. and air dried. The positions of the isomers were marked and the R_f values determined.

Bis-(Y-nitroacetoacetanilidato)-beryllium(II) -

Acetoacetanilide (3.54 g; 0.02 mole) was dissolved with cooling and stirring in acetic anhydride (20 ml.). Beryllium nitrate solution (1.87 g; 0.01 mole) was added slowly with cooling. The mixture was stirred (for 2 hours) with cooling and then for 18 hours at room temperature. During stirring an yellow precipitate was formed. The mixture was decomposed with ice-water and sodium acetate. The yellow product was collected on a filter, washed with water several times and dried. Yield of the crude product 3.2 g (70.9%). It was purified first by recrystallisation from benzene and petroleum ether and then by chromatography on Nylon powder column with benzene as eluent. [Commercial nylon-6 beads were treated with hydrochloric acid at room temperature, washed, dried and pulverized to 100-200 mesh.] The solvent was evaporated and the product was vacuum dried. m.p. 98°C.

Found: C, 53.08; H, 3.78; N, 12,51; Be, 1.90%.
Calcd. for $C_{20}H_{18}N_4O_8Be$: C, 53.20; H, 4.02; N, 12.42; Be, 2.00%.

Tris-(Y-nitroacetoacetanilidato)-chromium(III) -

A slurry of finely divided copper(II) nitrate trihydrate (2.7 g; 0.01 mole) in acetic anhydride (50 ml.) was stirred for 15 minutes at 0°C. At the end of this time a portion of the copper nitrate had dissolved to form a deep blue solution. To this slurry was added

Cr(III) acetoacetanilide (1.09 g; 0.0017 mole) and the resulting slurry was stirred for 2 hours at 0°C. The cooling bath was removed and the mixture was stirred for another hour. The slurry was decomposed with a mixture of 300 ml. of ice-cold water and ca. 3 g of sodium acetate. The yellowish precipitate was collected on a filter and washed with water. It was purified by recrystallization from benzene and then by chromatography on Nylon column using benzene and methanol mixture as eluent. The solvent was evaporated and the product was vacuum dried. Yield 0.2 g; 17%. The compound softens at 150°C.

Found: C, 50.02; H, 3.85; N, 12.0; Cr, 7.10%.
Calcd. for $C_{30}H_{27}O_{12}N_6Cr$: C, 50.34; H, 3.80; N, 11.74; Cr, 7.27%.

Mono-(acetoacetanilidato)bis-(γ-nitroacetoacetanilidato)-aluminium(III)- Acetoacetanilide (2.57 g; 0.015 mole) was dissolved with cooling (0-5°C) and stirring in acetic anhydride (15 ml.). Powdered aluminium nitrate, hydrated (1.88 g; 0.005 mole) was added slowly with cooling. The mixture was stirred with cooling for 2 hours and at room temperature for about 18 hours. During stirring the solution acquired yellow colour. The mixture was poured into ice water containing sodium acetate and the yellow precipitate was collected on a filter, washed with water several times and dried. Yield of the crude product 2.8 g, 85.7%.

It was purified first by crystallising from benzene and petroleum ether and then by chromatography on Nylon powder column with benzene as eluent. The solvent was removed and the product was vacuum dried. m.p. 143-44°C.

Found: C, 56.32; H, 4.10; N, 10.90; Al, 4.22%.
Calcd. for $C_{30}H_{28}N_5O_{10}Al$: C, 55.80; H, 4.37; N, 10.86; Al, 4.18%.

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._[30] About 5 g. of calcium sulphate was slurried with 15 ml. of water and was used to coat three thoroughly cleaned plates (3.5x16 cm.). The coating was allowed to solidify and then activated in an oven at 110°C. for 2 hours, cooled in a desiccator over silica gel. The applicator used for obtaining uniform layer of 0.5 mm. and the technique adopted have been described in detail recently by Gupta and Sukh Dev[31]. When the solvent (benzene) front reached the 10 cm. mark the spot of the aluminium nitro acetoacetanilide had reached 8.5 cm. (R_f = 0.85).

The corresponding R_f values for the nitrochelates of beryllium and chromium were 0.90 and 0.93 respectively.

The spots did not show any sign of separation indicating the purity of these compounds.

Acetoacetanilide was purified by several recrystallizations from hot water, m.p. 86°C.
Found: C, 67.76; H, 6.21; N, 7.89%.
Calcd. for $C_{10}H_{11}O_2N$: C, 67.76; H, 6.27; N, 7.91%.

Deuteration - Solid deuterated acetoacetanilide was prepared by refluxing in a current of nitrogen, a solution of the compound in D_2O for 45 minutes. Cooled, filtered and dried under vacuum. Deuterated chelates of Cu(II) and Be(II) were obtained from dioxane solutions of the chelates by refluxing with D_2O for 2-4 hours. In the case of the copper chelate, a deep brownish green layer immiscible with the given solution was obtained. After separation, the solvent from the brownish green layer was removed under reduced pressure and the solid obtained was dried under vacuum.

Infrared spectra - were obtained by using a Perkin-Elmer Model 221 infrared spectrophotometer equipped with NaCl and CsBr optics. The instrument was calibrated using polystyrene film. The resolution of the instrument at maximum performance was about 15 cm^{-1} at 3000 cm^{-1} and 7 cm^{-1} at 1600 cm^{-1}.

N.M.R. - Spectra were measured on a Varian Associates Model A-60 spectrometer with TMS as internal standard.

Magnetic susceptibility - measurements were made at room temperature by the Gouy method using a semimicro analytical balance and electromagnet at a field strength of 6000 gauss/cm^2. The effective magnetic moment was calculated by the formula:

$$\mu_{eff} = 2.84\ (\chi_M^{cor} \times T)^{1/2}$$

where χ_M^{cor} is the corrected magnetic susceptibility. The diamagnetic corrections were estimated as usual.

Thermogravimetric analysis - The decomposition temperatures of the compounds were determined in a thermogravimetric balance using McBain-Bakr type Quartz spring[32] having sensitivity of 2.5 mg. per millimeter extension. About 25 mg. of the sample is required for the investigation. The extension of the spring was measured with a travelling microscope every two minutes while the temperature of the furnace was increased at a constant rate of about 2°C. per minute. The thermograms were obtained by plotting directly the change in the microscope reading representing the loss in weight against temperature. The actual weight loss at any stage was obtained from the change in the microscope reading and the spring constant which is 0.4106 mm. extension per mg.

Weight losses upto 500°C only were determined as the bucket employed was of aluminium. However, in the case of chromium isomers (fig. 8) using a platinum bucket, weight losses upto 800°C were determined on a thermobalance built by Bhabha Atomic Research Centre, Bombay.

CHAPTER 2 : ACETOACETANILIDE CHELATES OF TITANIUM(IV)

ACETOACETANILIDE CHELATES OF TITANIUM(IV)

Examples[33-41] have accumulated in the literature which reveal that two of the chlorine atoms of titanium tetrachloride are more easily replaced by ligands leading to dichloro titanium compounds. The attempt of Verma and Mehrotra[41] to prepare tetrasalicylaldehyde derivative by reacting together titanium tetrachloride and an excess of salicylaldehyde resulted in the isolation of the dichloro bis-chelated compound only. On the other hand, with zirconium and hafnium, the increase of coordination number to eight can readily occur and thus with acetylacetone, compounds of the type $[M(acac)_4]^0$, where acac stands for acetylacetone minus one hydrogen are easily obtained. By careful choice of reaction conditions, it is possible to replace chlorine atoms of zirconium tetrachloride in stages[42,43] to give $[Zr(acac)Cl_3]$, $[Zr(acac)_2Cl_2]$ and $[Zr(acac)_3]Cl$.

The reactions of titanium tetrachloride with acetoacetanilide have been studied, since search of the literature revealed that no work on acetoacetanilide chelates of titanium(IV) has been so far reported. The reaction medium chosen for the purpose was benzene. The isolation of the reddish-brown complex, dichloro bis-(acetoacetanilidato), titanium(IV) shows the easy and usual replacement of the two chlorine atoms of titanium tetrachloride. The replacement of a single chlorine atom leading to the isolation of trichloro mono(acetoacetanilidato)-titanium(IV) ~~was~~ has also ~~easily~~ been achieved.

In order to replace the two chlorine atoms in $Ti(acacN)_2Cl_2$, where acacN stands for the acetoacetanilide ligand anion, this compound was refluxed with an excess of acetylacetone when an interesting ligand exchange took place resulting in the formation of monochloro tris-(acetoacetanilidato)-titanium(IV) according to the following reaction:-

$$3Ti(acacN)_2Cl_2 + 2Hacac = 2Ti(acacN)_3Cl + Ti(acac)_2Cl_2 + 2HCl.$$

The same monochloro tris-(acetoacetanilidato)-titanium(IV) was also obtained when dichloro bis-(2,4-pentanediono)-titanium(IV) was refluxed with acetoacetanilide. The reaction may be represented according to the following equation:

$$Ti(acac)_2Cl_2 + 3HacacN = Ti(acacN)_3Cl + 2Hacac + HCl.$$

The success of this reaction led to attempts for the syntheses of monobromo-, and monoiodo-tris-(acetoacetanilidato)-titanium(IV) compounds.

Dibromo-* and diiodo-bis-(2,4-pentanediono)-titanium(IV) compounds were prepared, therefore, to serve as intermediates. The monobromo- and the monoiodo tris-(acetoacetanilidato)-titanium(IV) compounds were isolated by refluxing the dibromo- or the diiodo-(2,4-pentanediono)-titanium(IV) with acetoacetanilide in anhydrous benzene. However, the analytical data showed that the monoiodo compound contains one molecule of solvated hydrogen iodide. TGA data of these monohalogeno compounds will be discussed in this chapter.

Another approach towards the preparation of these chelates, through their addition compounds was also made. The isolation of the addition compounds $TiX_4.3HacacN$, where X = Cl or Br and the formation of the corresponding monohalogeno-tris-(acetoacetanilidato)-titanium(IV) chelates by heating the addition compounds will be also described in this chapter.

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* This compound was reported recently.
Fay, R.C. and Lowry, R.N., Inorg.Nucl.Chem.Letters, **3**, 117 (1967).

EXPERIMENTAL

Titanium tetrachloride was purifed and distilled before use. Titanium tetrabromide and tetraiodide were prepared according to the procedure of Brauer[44]. Dichloro bis-(2,4-pentanediono)-titanium(IV) was prepared by the reaction between titanium tetrachloride and acetylacetone in benzene according to the procedure of Doron[45]. All the solvents employed were purified before use.

Dibromo bis-(2,4-pentanediono)-titanium(IV) - Titanium tetrabromide (3.6 g; 0.01 mole) in dry benzene (50 ml.) was mixed with excess of acetylacetone in benzene (20 ml.) and refluxed till the reaction was complete (4 hr.). More than half the benzene was removed by distillation. After cooling the separated brown solid was filtered under nitrogen atmosphere and dried under vacuum. Yield, 2.2 g; 54.2%.

Found: C, 30.12; H, 3.42; Br, 39.02; Ti, 11.47%. Calcd. for $C_{10}H_{14}O_4Br_2Ti$: C, 29.59; H, 3.48; Br, 39.39; Ti, 11.80%.

Diiodo bis-(2,4-pentanediono)-titanium(IV) - The deep reddish-brown semi-solid obtained essentially in the above manner was poured into petroleum ether (60-80°C). The solid was collected on a filter under suction and washed with two 10 ml. portions of petroleum ether and dried under vacuum. Yield, 95%.

Found: C, 26.54; H, 3.35; I, 51.13; Ti, 8.39%. Calcd. for $C_{10}H_{14}O_4I_2Ti$: C, 24.03; H, 2.82; I, 50.79; Ti, 9.59%.

Dichloro bis-(acetoacetanilidato)-titanium(IV) - Titanium tetrachloride (1.89 g; 0.01 mole) in benzene (10 ml.) and acetoacetanilide (3.52 g; 0.02 mole) in benzene (30 ml.) were mixed together. A reddish-brown solution was immediately formed. The mixture was refluxed for 6 hr. The solid was collected on a filter under suction, washed with hot benzene several times, dried under suction for five minutes and finally dried under vacuum. Yield, 4.5 g; 95.5%.

Found: C, 49.3; H, 4.55; N, 5.89; Ti, 10.50; Cl, 15.5%. Calcd. for $C_{20}H_{20}O_4N_2Cl_2Ti$: C, 50.97; H, 4.28; N, 5.95; Ti, 10.16; Cl, 15.05%.

Trichloro mono-(acetoacetanilidato)-titanium(IV) - Titanium tetrachloride (2.85 g; 0.015 mole) in benzene (30 ml.) and acetoacetanilide (1.77 g; 0.01 mole) in benzene (20 ml.) were mixed together at 0°C and then refluxed for four hours. The reddish-brown product separated on cooling was collected on a filter under suction and washed with benzene and dried under vacuum. Yield, 3.0 g; 60.60%.

Found: N, 4.4; Ti, 13.98; Cl, 31.50%.

Calcd. for $C_{10}H_{10}O_2N.TiCl_3$: N, 4.24; Ti, 14.49; Cl, 32.20%.

Monochloro tris-(acetoacetanilidato)-titanium(IV) -

Method I

Dichloro bis-(2,4-pentadiono)-titanium(IV) (1.59 g; 0.005 mole) in benzene (30 ml.) was mixed with acetoacetanilide (1.77 g; 0.01 mole) in benzene (20 ml.). The mixture was refluxed for 2 hr., and cooled, ~~and~~ the separated product was collected under suction on a filter, washed with hot benzene and dried under vacuum. Yield of the orange-red solid, 1.59 g (51.96%), m.p., 216°C.

Found: C, 59.68; H, 5.17; N, 6.80; Ti, 7.86; Cl, 6.12%

Calcd. for $C_{30}H_{30}O_6N_3ClTi$: C, 58.86; H, 4.94; N, 6.87; Ti, 7.83; Cl, 5.79%.

Method II

A suspension of dichloro bis-(acetoacetanilidato)-titanium(IV) (1.88 g; 0.004 mole) in benzene (50 ml.) and 1.4 g. of acetylacetone (excess over the required quantity) were placed together in a flask and refluxed for 2 hr. Orange red solid formed was collected on a filter, washed with hot benzene and dried under vacuum. Yield, 0.8 g; 32.8%. m.p., 216-17°C.

Found: C, 59.14; H, 5.25; N, 6.85; Ti, 7.86; Cl, 5.7%

Monochloro tris-(acetoacetanilidato)-titanium(IV) -

(Repeated with quantities as per the equation
$\mathrm{Ti(acac)_2Cl_2 + 3HacacN = Ti(acacN)_3Cl + 2Hacac + HCl}$)

Dichloro bis-(2,4-pentanediono)-titanium(IV) (1.59 g; 0.005 mole) in benzene (40 ml.) and acetoacetanilide (2.66 g; 0.015 mole) in benzene (20 ml.) were mixed together and refluxed for 3 hr., cooled, collected on a filter under suction, washed with 10 ml. portions of benzene twice and vacuum dried. Yield of the reddish-brown compound, 3.0 (98%) m.p., 217°C.

Found: C, 60.67; H, 5.60; Cl, 6.27; Ti, 7.62%.

Monobromo tris-(acetoacetanilidato)-titanium(IV) -

Dibromo bis-(2,4-pentanediono)-titanium(IV) (1.22 g; 0.003 mole) in benzene (50 ml.) and acetoacetanilide (1.59 g; 0.009 mole) in benzene (20 ml.) were mixed together and refluxed for 3 hr. The orange-red solid separated was collected on a filter under suction, washed with 5 ml. portions of benzene twice and dried under vacuum. Yield, 2.0 g; 91.4%.; m.p., 211-12°C.

Found: C, 55.58; H, 4.78; Br, 13.05; N, 5.67; Ti, 7.1%

Calcd. for $C_{30}H_{30}O_6N_3BrTi$: C, 54.88; H, 4.61; Br, 12.17; N, 6.40; Ti, 7.30%.

Monoiodo tris-(acetoacetanilidato)-titanium(IV) -

Diiodo bis-(2,4-pentanediono)-titanium(IV) (1.25 g; 0.0025 mole) in benzene (50 ml.) and acetoacetanilide (1.33 g; 0.0075 mole) in benzene (20 ml.) were mixed together and refluxed for 6 hr. The reddish-brown solid separated was collected on a filter under suction, washed with 5 ml. portions of benzene, twice and dried under vacuum. Yield, 1.6 g; 77%. m.p., 218°C. (change at 135-7°C).

Found: C, 44.10; H, 3.44; N, 5.2; Ti, 5.32; I, 31.06%

Calcd. for $C_{30}H_{31}O_6N_3I_2Ti$: C, 43.30; H, 3.64; N, 5.06; Ti, 5.76; I, 30.50%.

Preparation of $TiCl_4$.3HacacN -

Titanium tetrachloride (0.95 g; 0.005 mole) in chloroform (20 ml.) was added dropwise to a solution of acetoacetanilide (2.66 g; 0.015 mole) in chloroform (30 ml.). Immediately, a deep red solution was obtained. Addition of petroleum ether precipitated the orange-red compound. It was collected on a filter under suction, washed with two 5 ml. portions of petroleum ether and dried under vacuum at room temperature. Yield, 2.9 g; 80.34%.

Found: N, 5.70; Ti, 6.39; Cl, 20.6%.

Calcd. for $C_{30}H_{33}O_6N_3TiCl_4$: N, 5.83; Ti, 6.64; Cl, 19.65%.

$TiCl_4$.3HacacN on heating at 140°C for 8 hr. yielded a reddish-brown product.

Found: C, 58.26; H, 5.47; N, 7.3%.

$TiBr_4$.2HacacN -

Titanium tetrabromide (7.2 g; 0.02 mole) in chloroform (50 ml.) and acetoacetanilide (7.09 g; 0.04 mole) in the same solvent (40 ml.) were mixed together at room temperature. Immediately, a deep red solution was obtained. Addition of petroleum ether (60°-80°C) precipitated deep red solid which was collected on a filter under suction, washed with petroleum ether and dried under vacuum.

Yield, 13.9 g; 96.25%.

Found: N, 4.01; Br, 45.2; Ti, 7.00%.

Calcd. for $C_{20}H_{22}N_2O_4TiBr_4$: N, 3.88; Br, 44.28; Ti, 6.63%.

$TiBr_4$.3HacacN -

Titanium tetrabromide (3.68 g; 0.01 mole) in chloroform (40 ml.) and acetoacetanilide (5.32 g; 0.03 mole) in the same solvent (30 ml.) were mixed together at room temperature. Immediately a deep red solution was obtained. Addition of petroleum ether (60°-80°C) precipitated a deep red solid which was collected on a filter under suction, washed with petroleum ether and dried under vacuum.

Yield, 7.5 g; 83.4%.

Found: N, 4.80; Ti, 5.45; Br, 34.48%.

Calcd. for $C_{30}H_{33}O_6N_3TiBr_4$: N, 4.67; Ti, 5.33; Br, 35.55%.

Results and Discussion

The reactions of acetoacetanilide with titanium tetrachloride in anhydrous benzene medium led to the isolation of three classes of derivatives - the trichloro mono-(acetoacetanilidato)-titanium(IV), dichloro bis-(acetoacetanilidato)-titanium(IV) and the monochloro tris-(acetoacetanilidato)-titanium(IV). Examples of the replacement of chlorine atoms in titanium tetrachloride by a β-dicarbonyl compound leading to trichloro-[33,40,46] or dichloro-chelates are well-known. However, the replacement of three chlorine atoms in titanium tetrachloride by three β-dicarbonyl functions leading to monochloro titanium(IV) chelates is not ~~wel~~ well-known. ~~However~~ The isolation of tris-(acetylacetonato)-titanium(IV) perchlorate by a solvent extraction procedure was reported recently by Reynolds[47]. Attempts to isolate the monochloro-compound by refluxing titanium tetrachloride with excess of acetoacetanilide in anhydrous benzene and also the tris-(acetoacetanilidato)-titanium(IV) perchlorate by the solvent extraction procedure described by Reynolds[47] were not successful. However, when dichloro bis-(acetoacetanilidato)-titanium(IV) was refluxed with acetylacetone in benzene an interesting rearrangement took place according to the equation mentioned previously resulting in the isolation of monochlorotris-(acetoacetanilidato)-titanium(IV). From the experimental data it can be seen that similar type of rearrangement takes place with dichloro-bis-(2,4-pentanediono)-titanium(IV) and acetoacetanilide. The yield of the product is essentially as per the equation mentioned before. Further, this novel rearrangement reaction can be successfully extended to the preparation of the monobromo- and the monoiodo-tris-(acetoacetanilidato)-titanium(IV) chelates.

The infrared absorption maxima of dibromo- and diiodo bis-(2,4-pentanediono)-titanium(IV) complexes, in nujol mull are presented in Table IX (Fig. 14). The position of the absorption bands in the spectra of these compounds is similar to that of the bands in dichloro bis-(2,4-pentanediono)-titanium(IV) recently reported by Tanaka and Okawara[48]. They have tentatively assigned the upper most band to a perturbed carbonyl vibration and the lower band to a perturbed C=C stretching mode. Accordingly the upper most band found in the spectra of dibromo- and diiodo-compounds in the 1600 cm^{-1} - 1500 cm^{-1} region and located at ca.1525 cm^{-1} can be assigned to a perturbed carbonyl stretching mode. The bands at ca.1515 cm^{-1} are due to perturbed C=C stretching modes.

Of the four absorption bands in the 1500 cm^{-1} - 1200 cm^{-1} region, the two appearing at ca.1420 cm^{-1} and at ca.1340 cm^{-1} are same as in

Table IX

Infrared absorption frequencies (cm^{-1}) of titanium(IV) chelates in nujol mull

$Ti(acac)_2Br_2$	$Ti(acac)_2I_2$	Possible assignments
2950*b,vs	2950*b,vs	
1530sh	1530sh	
1525vs	1520vs	C=O str.
1510s	1515vs	C=C str.
1480*s	1460*s	
1440s	1423m	CH_3 def.(asym)
1390m	-	
1380*s	1370*s	
	1340s	CH_3 def (sym)
1320vs	1310s	C-O str.
1300sh	1280s	C-C str.
1040vs	1025s	
1030sh	1010w	
955m	950w	
940s	935s	
820s	825m	CH O.P.def.
-	810w	
780w	795m	
-	730s	
680s	680s	

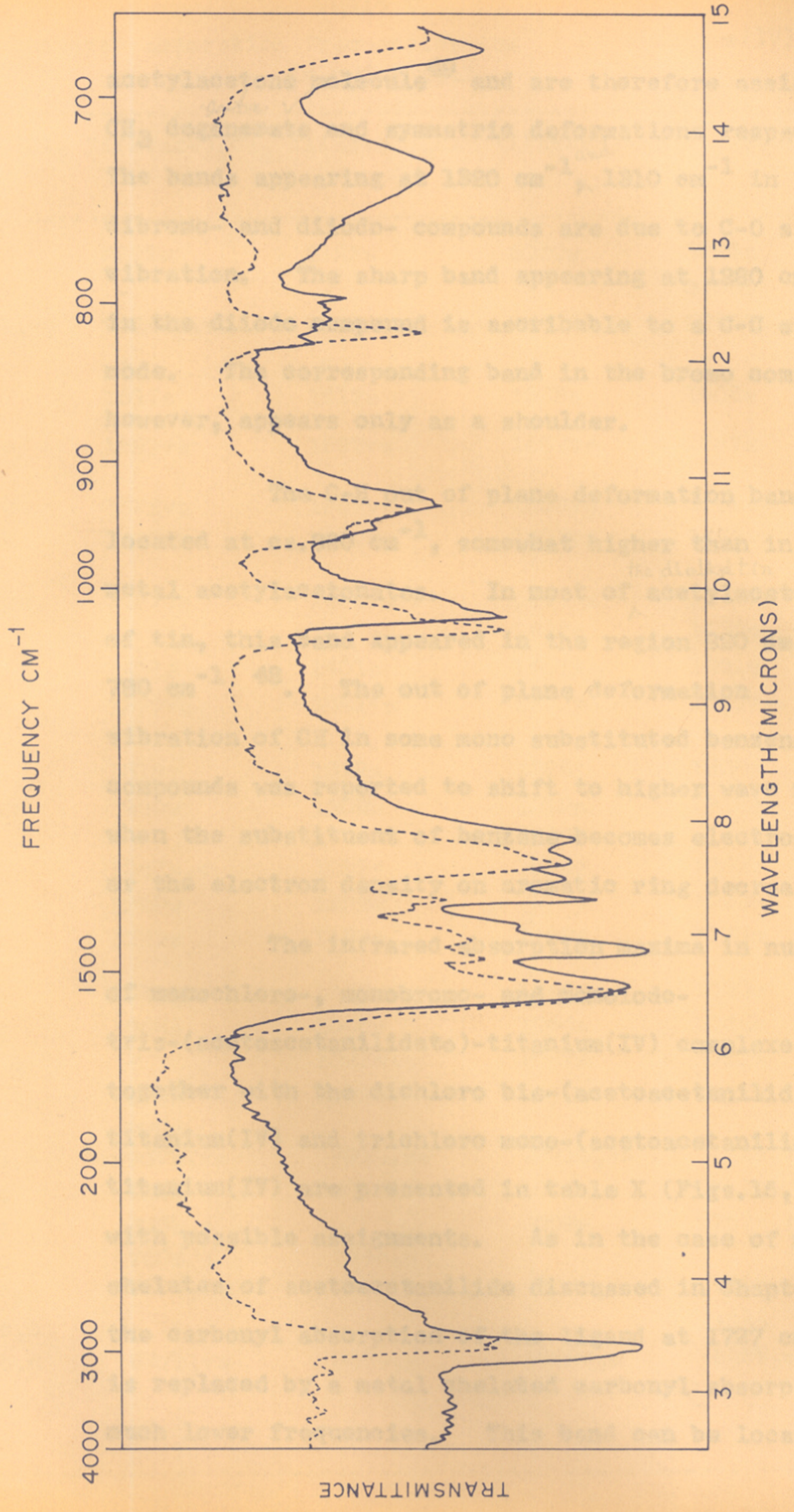


FIG.14· INFRARED SPECTRA IN NUJOL MULL OF :- —— DIIODO BIS(2,4-PENTANE DIONO)-TITANIUM(IV) ; ------ DIBROMO BIS (2,4-PENTANEDIONO) TITANIUM (IV) acetylacetone molecule[49] and are therefore assigned to CH_3 [illegible] ~~degenera~~te and symmetric deformations respectively. The bands appearing at 1320 cm^{-1}, and 1310 cm^{-1} in the dibromo- and diiodo- compounds are due to C-O stretching vibration. The sharp band appearing at 1280 cm^{-1} in the diiodo compound is ascribable to a C-C stretching mode. The corresponding band in the bromo compound, however, appears only as a shoulder.

The C-H out of plane deformation band was located at ca.820 cm^{-1}, somewhat higher than in the metal acetylacetonates. In most of the dialkyltin acetylacetonates, ~~of tin,~~ this band appeared in the region 820 cm^{-1} - 780 cm^{-1} [48]. The out of plane deformation vibration of CH in some mono substituted benzene compounds was reported to shift to higher wave number when the substituent of benzene becomes electronegative[50,51] or the electron density on aromatic ring decreases[52,53].

The infrared absorption maxima in nujol mull of monochloro-, monobromo- and monoiodo- tris-(acetoacetanilidato)-titanium(IV) complexes together with the dichloro bis-(acetoacetanilidato)-titanium(IV) and trichloro mono-(acetoacetanilidato)-titanium(IV) are presented in table X (Figs.15,16 and 16a) with possible assignments. As in the case of metal chelates of acetoacetanilide discussed in Chapter I, the carbonyl absorption of the ligand at 1727 cm^{-1} is replaced by a metal chelated carbonyl absorption at much lower frequencies. This band can be located at

Table X

Infrared absorption frequencies (cm^{-1}) of titanium(IV) chelates in nujol mull.

$Ti(acacN)Cl_3$	$Ti(acacN)_2Cl_2$	$Ti(acacN)_3Cl$	$Ti(acacN)_3Br$	$Ti(acacN)_3I.HI$	Possible assignments
3250m	3311m	3185w	3030w	3226m	NH str.
-	-	-	-	3106m	
2900*b,vs	2924*b,vs	2924*b,s	2890*b,s	2890*b,s	
1660m	-	-	-	-	
1600s	1617s	1617s	1608s	1608s	C=C + amide I
1575vs	1587vs	1597vs	1587vs	1587s	C=C str. + C=0 str.
1550vs	1558vs	1567vs	1558vs	1558vs	amide II
1490sh	1493vs	1502vs	1493vs	1493vs	Phenyl vibration
1460*vs	1457vs	1458vs	1449vs	1449vs	
-	-	-	1433s	1433sh	CH_3 deg.def.
-	1401s	1401s	1401s	1401s	
1375*vs	1377*s	1381*s	1377*s	1377*s	
	1333s				
1310s	1319s	1319s	1326s	1326s	
1300sh	1299w	1302m	1312s	1312s	Amide III
			1299m		
1240s	1247b,s	1253s	1250s	1247s	
-	1229w	1229m	-	1229m	
1175s	1182s	1182s	1188s	1178s	CH in plane def.
1080w	1085w	1085w	1080w	1080w	
1040s	1048s	1046s	1044s	1044s	
1025s	-	1031m	1027m	1027m	
-	998w	1002w	1002w	1002w	
	978s				
970b,s	967b,vs	971b,vs	971b,vs	971b,vs	
910m	910m	905w	901w	901w	
810m	796b,s	-	808m	787b,m	
780m	780m	784b,m			
760b,s	757b,vs	752b,m	797b,m	752b,m	CH O.P.def.
725b,m	-	-		734m	
685b,m	687b,vs	688b,m	688b,m	686b,m	Mono substitution, Ring Def. + MO str.

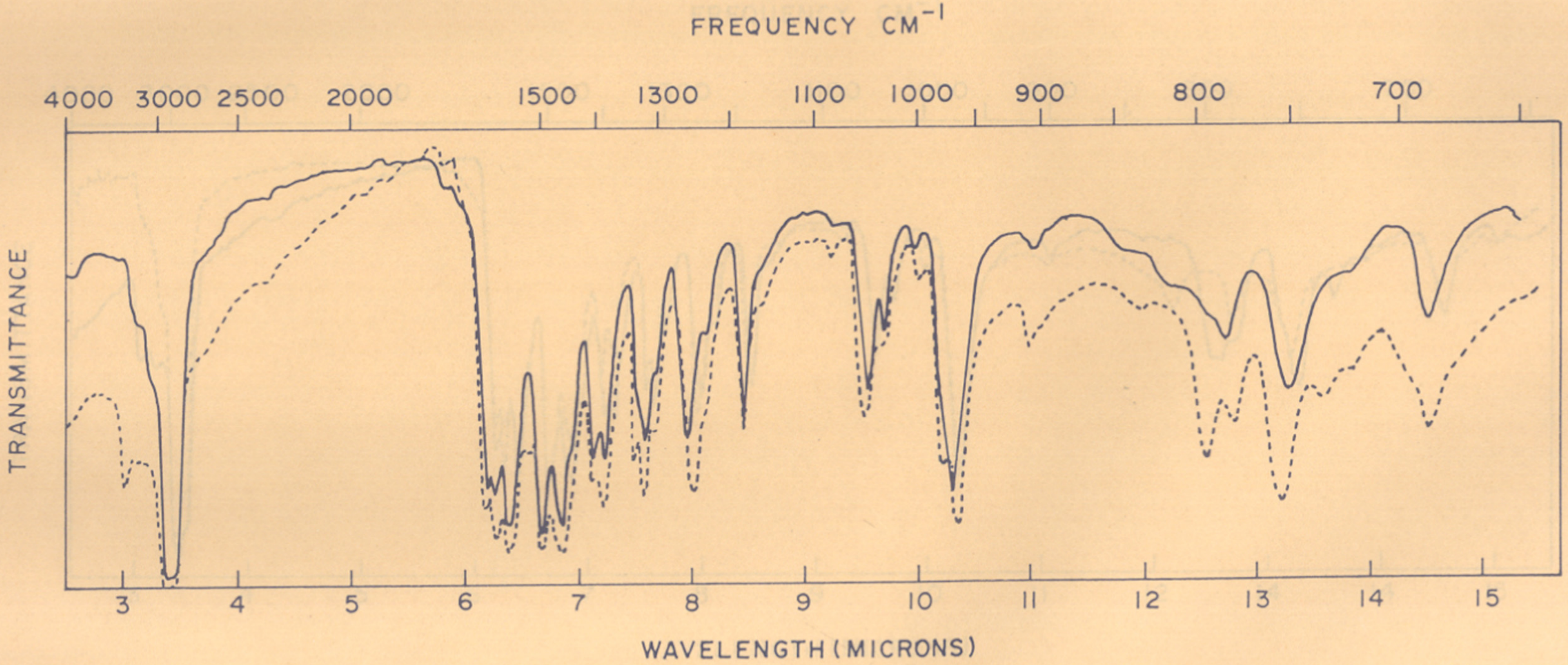
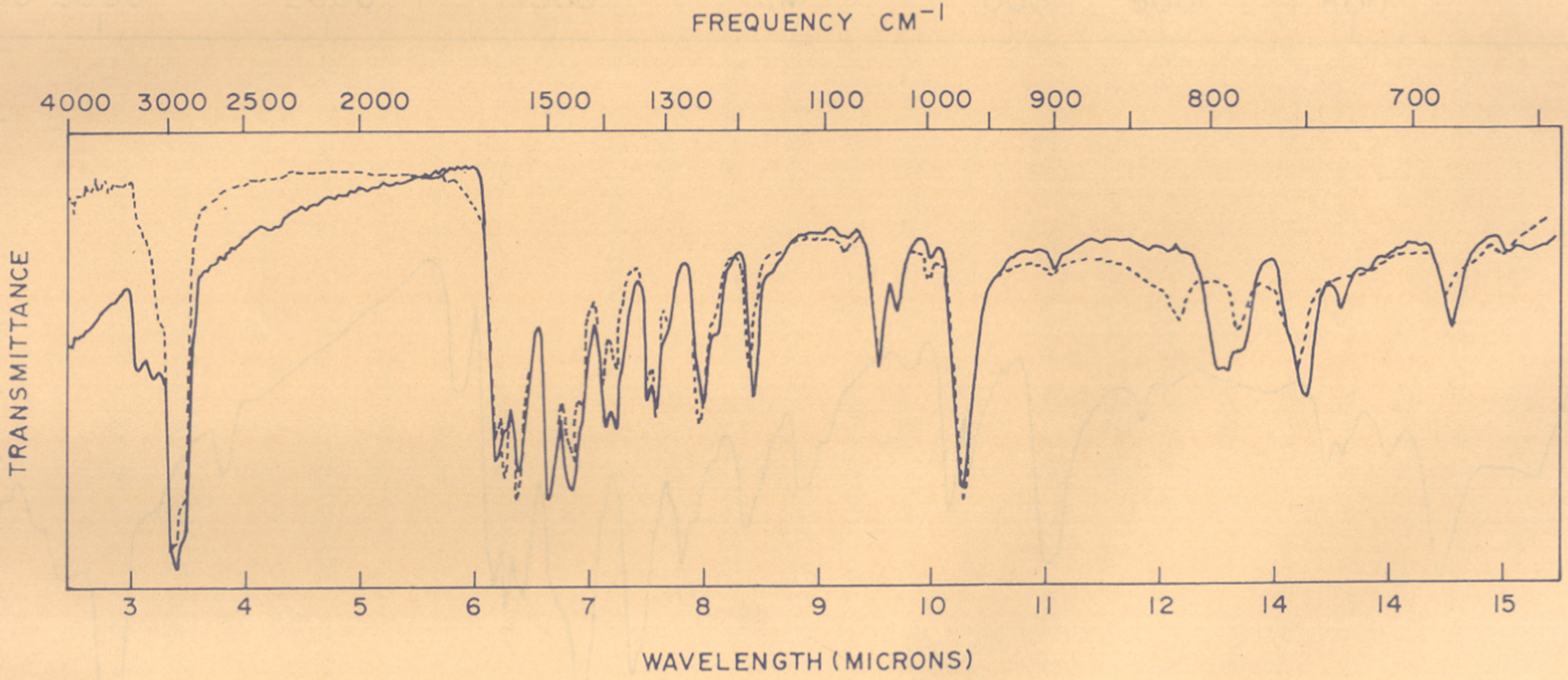


FIG. 15. INFRARED SPECTRA IN NUJOL MULL OF :- ——— MONOCHLOROTRIS (ACETOACETANILIDATO)-TITANIUM (IV) ; - - - - - DICHLOROBIS (ACETOACETANILIDATO) TITANIUM (IV)



FIG·16· INFRARED SPECTRA IN NUJOL MULL OF :- ——— MONOIODOTRIS (ACETOACETANILIDATO)-TITANIUM (IV) ; ----- MONOBROMOTRIS (ACETOACETANILIDATO) TITANIUM (IV)

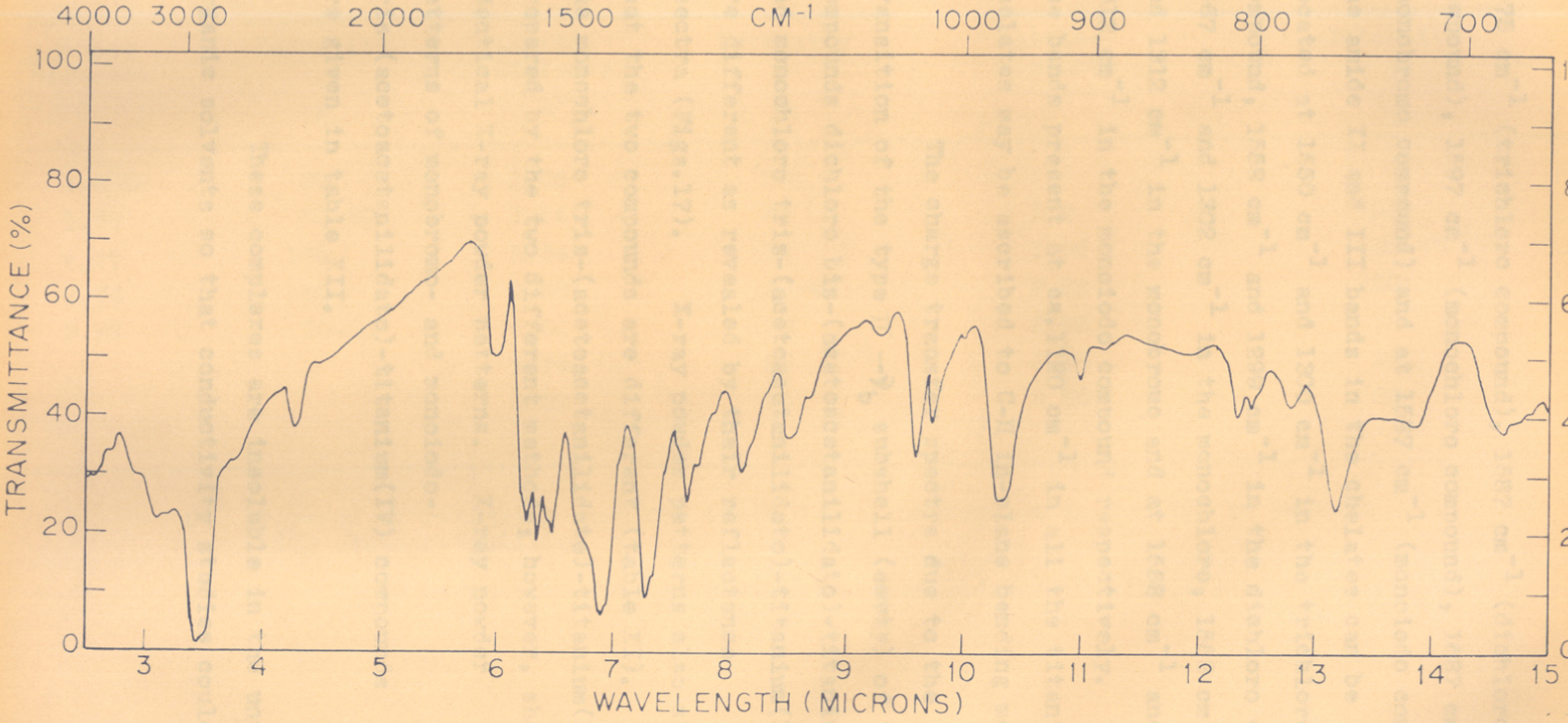


FIG. 16. a. TRICHLORO MONO-(ACETOACETANILIDATO)-TITANIUM (IV)

1575 cm^{-1} (trichloro compound), 1587 cm^{-1} (dichloro compound), 1597 cm^{-1} (monochloro compound), 1587 cm^{-1} (monobromo compound) and at 1587 cm^{-1} (monoiodo compound). The amide II and III bands in the chelates can be located at 1550 cm^{-1} and 1300 cm^{-1} in the trichloro compound, 1558 cm^{-1} and 1299 cm^{-1} in the dichloro compound, 1567 cm^{-1} and 1302 cm^{-1} in the monochloro, 1558 cm^{-1} and 1312 cm^{-1} in the monobromo and at 1558 cm^{-1} and 1312 cm^{-1} in the monoiodo compound respectively. The bands present at ca.1180 cm^{-1} in all the titanium(IV) chelates may be ascribed to C-H in-plane bending modes.

The charge transfer spectra due to the transition of the type $\pi \rightarrow \vartheta_b$ subshell (empty) of the compounds dichloro bis-(acetoacetanilidato)-titanium(IV) and monochloro tris-(acetoacetanilidato)-titanium(IV) are different as revealed by their reflectance spectra (Figs.17). X-ray powder patterns also show that the two compounds are different (table XI). The monochloro tris-(acetoacetanilidato)-titanium(IV) prepared by the two different methods, however, shows identical X-ray powder patterns. X-ray powder patterns of monobromo- and monoiodo-tris-(acetoacetanilidato)-titanium(IV) compounds are given in table XII.

These complexes are insoluble in the unusual organic solvents so that conductivity studies could not be

Table XI

X-Ray diffraction data of monochloro-and dichloro-(acetoacetanilidato)-titanium(IV) complexes

Monochloro tris(acetoacetanilidato)-titanium(IV)				Dichloro bis(acetoacetanilidato)-titanium(IV)	
a*		b*			
Lattice ~~distance~~ 'd' Values(Å) Å	Intensity %	~~Lattice~~ distance 'd' Values(Å). Å	Intensity %	~~Lattice distance~~ 'd' Values(Å). Å	Intensity %
1.08 ~~1.078~~	80	1.08	80		
1.68	50-60	1.55	30	1.4	50
2.27	100	1.64	80	1.96	40-50
2.74	80	2.06	30-40	2.52	100
3.78	10-20	2.25	100	3.15	20
		2.76	80	3.34	20
		3.02	20	3.56	20

a* prepared by refluxing dichloro bis(2,4-pentanediono)-titanium(IV) in benzene with acetoacetanilide.

b* prepared by refluxing dichloro bis(acetoacetanilidato)-titanium(IV) with acetylacetone.

Table XII

X-Ray diffraction data of monobromo-and monoiodo tris-(acetoacetanilidato)-titanium(IV) complexes

Monobromo tris(acetoacetanilidato)-titanium(IV) $Ti(acacN)_3Br$		Monoiodo tris(acetoacetanilidato)-titanium(IV) $Ti(acacN)_3I.HI.$	
~~Lattice distance~~ 'd' values(Å).	Intensity %	~~Lattice distance~~ 'd' values(Å).	Intensity %
2.06	100	2.0	100
2.965	100	2.74	100
3.58	40-50	3.28	40
3.995	40-50	3.84	80-90
4.36	80	4.18	40-50
4.83	80-90	4.445	20
5.135	80-90	4.885	20
5.395	70	5.30	20
6.26	80	5.52	90
6.620	100	5.875	90
7.285	50	6.08	10-20
7.53	20-30	6.45	"
7.64	20	6.60	"
7.85	10-20	6.865	"

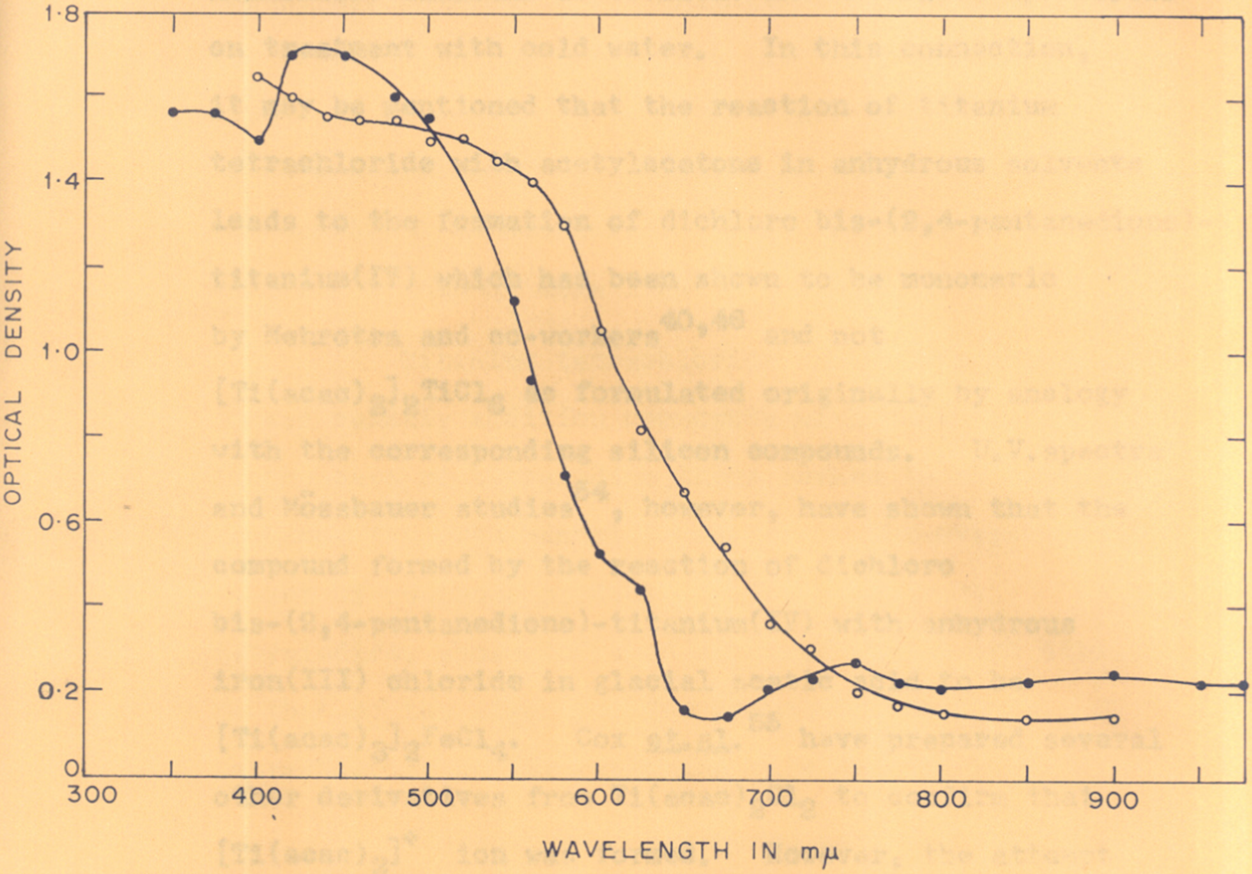


FIG. 17. ○———○ REFLECTANCE SPECTRUM OF DICHLOROBIS-(ACETOACETANILIDATO)-TITANIUM (IV) ; ●———● REFLECTANCE SPECTRUM OF MONOCHLOROTRIS-(ACETOACETANILIDATO)-TITANIUM (IV).

made to establish whether or not the compounds are ionic. It appears that the chlorine in the monochloro compound is covalent and undergoes hydrolysis on treatment with cold water. In this connection, it may be mentioned that the reaction of titanium tetrachloride with acetylacetone in anhydrous solvents leads to the formation of dichloro bis-(2,4-pentanediono)-titanium(IV) which has been shown to be monomeric by Mehrotra and co-workers[40,46] and not $[Ti(acac)_3]_2TiCl_6$ as formulated originally by analogy with the corresponding silicon compounds. U.V. spectra and Mössbauer studies[54], however, have shown that the compound formed by the reaction of dichloro bis-(2,4-pentanediono)-titanium(IV) with anhydrous iron(III) chloride in glacial acetic acid to be $[Ti(acac)_3]_2FeCl_4$. Cox *et. al.*[55] have prepared several other derivatives from $Ti(acac)_2Cl_2$ to confirm that $[Ti(acac)_3]^+$ ion was formed. However, the attempt to isolate the corresponding iron compound of dichloro bis-(acetoacetanilidato)-titanium(IV) was not successful.

The replacement of one more chlorine by acetoacetanilide raises the important question of coordination number of titanium. Examples of titanium having coordination number higher than six have been given by Nyholm[56] and recently by Muetterties[57] and by Frazer[58].

In the monohalogeno tris-(acetoacetanilidato)-titanium(IV) complexes, ~~that~~ if all the acetoacetanilide groups are bidentate, a coordination number of seven for titanium is implied. That all the groups are bidentate is confirmed by the infrared spectra, which are similar to the spectra of other acetoacetanilide complexes. Some difference would be expected if one or more ligands were unidentate.

Titanium tetrachloride and tetrabromide formed readily addition compounds with acetoacetanilide. In the case of tetraiodide, there seemed to be least tendency for such adduct formation. However, a small amount of resinous product was isolated, with tetraiodide, whose infrared spectrum was almost similar to that of the ligand. The adducts formed with tetrachloride and tetrabromide were deeply coloured.

The infrared absorption maxima observed for the complexes of titanium halides with acetoacetanilide are listed in table XIII. In these complexes there is a metal to oxygen bond as evidenced in the infrared spectra by an appreciable negative shift of the carbonyl stretching frequency. Such a shift of the carbonyl band to lower frequencies has been considered as an indication of coordination through the oxygen atom by many workers[59-61] . There was no appreciable change in the position of the

Table XIII

The infrared absorption frequencies (cm^{-1}) in Nujol mull of titanium tetrahalide adducts with acetoacetanilide

Acetoacetanilide (HacacN)	TiCl$_4$·3HacacN	TiBr$_4$·3HacacN
3268s	-	-
3145w	3200v,w	3200w
3067s,sh		
2924*vs,b	2900*b,vs	2900*b,vs
1946m	-	-
1873m	-	-
1727vs	1600s	1600s
1661vs	1575s	1580s
1597vs	1550s	1550s
1538b,vs	-	1500s
	1470sh,	
1466*s	1450*s	1450*b,vs
1449vs		
1377*s	1370*s	1370*vs
1346w		
1316s		
	1309s	1310s
		1300sh
1279m	-	
1238s	1245s	1250s
	1225sh	
1168vs	1175s	1175s
1080s	1075v,w	1080vw
1027w	1040s	1040s
1006m	1030m	1025m
967s	965s,b	970b,vs
905s		910w
868s		
821w		800b,w
757b,vs	750m,b	750b,m
740s	-	
708w		
691b,vs	690m,b	685b,m

amide(III) band in the complexes from that in the ligand. Archambault and Rivest[59,62] reported, however, a positive shift for the C-N stretching vibration in the titanium tetrahalide complexes with formamide and N,N-dimethyl formamide.

The shifts observed for the carbonyl band seem to decrease from the chloride complex to the iodide complex. This behaviour seems to be in agreement with the decreasing electronegativities and increasing steric hindrance of the halogens from chloride to iodide. In the case of the titanium tetrachloride addition complex, the observed shifts in the ketonic as well as the amide carbonyl frequencies indicate that both the carbonyls were involved in coordination. Furthermore, the sharp bands in the ligand at 905 cm^{-1}, and 868 cm^{-1} assigned to $C-CH_3$ stretching and CH_2 wag are absent in the spectra of the complexes.

The 1:3 adduct between $TiCl_4$ and acetoacetanilide on heating at 140° for 10 hr. yielded a reddish brown product with m.p. 216°C. The infrared spectrum and elemental analysis showed this to be monochloro tris-(acetoacetanilidato)-titanium(IV).

The titanium tetrabromide adduct, however, remained unchanged when heated at 140°C for several hours.

As mentioned earlier, elemental analysis indicated the presence of one HI attached to the monoiodo tris-(acetoacetanilidato)-titanium(IV). To confirm the presence of this attached molecule of HI, thermal analysis~~,~~ for the monohalogeno tris-(acetoacetanilidato)-titanium(IV) compounds was carried under similar conditions. Figure 18 shows the relationship between the temperature and the weight loss of the monohalogeno tris-(acetoacetanilidato)-titanium(IV) compounds when heated in air in the range 25°-310°C at a heating rate of 4°/min. Table XIV lists the percentage weight loss in the range 190°-310°C.

Weight loss in the early phase of the experiment (25°-190°C) is below 5% only. The thermal analysis curves for the three compounds are almost identical except for a break in the monoiodo compound at 230°C. At this temperature, the loss in weight for the monoiodo compound (14.69%) corresponds ~~to~~ nearly to the loss of one molecule of HI. It can be seen that there is considerable decomposition at this temperature (230°C) for the monochloro compound (35.40%) and the monobromo compound (28.25%) as indicated by the percentage losses. From the thermal analysis data, it appears that the monoiodo compound is more stable than the monobromo compound or the monochloro compound.

Table XIV

Percentage weight loss of monohalogeno tris(acetoacetanilidato)-titanium(IV) compounds (190°-310°., heating rate in air 4°/min.)

Temperature °C	$Ti(acacN)_3Cl$	$Ti(acacN)_3Br$	$Ti(acacN)_3I.HI$
190	6.39	3.77	2.45
200	7.38	4.24	2.45
210	16.71	7.54	3.42
220	26.56	17.89	7.35
230	35.40	28.25	14.69
235	36.39	30.13	18.58
240	37.37	30.53	19.59
250	42.29	31.08	20.57
270	45.24	32.03	23.51
300	49.17	35.31	30.37
310	50.16	35.79	33.31

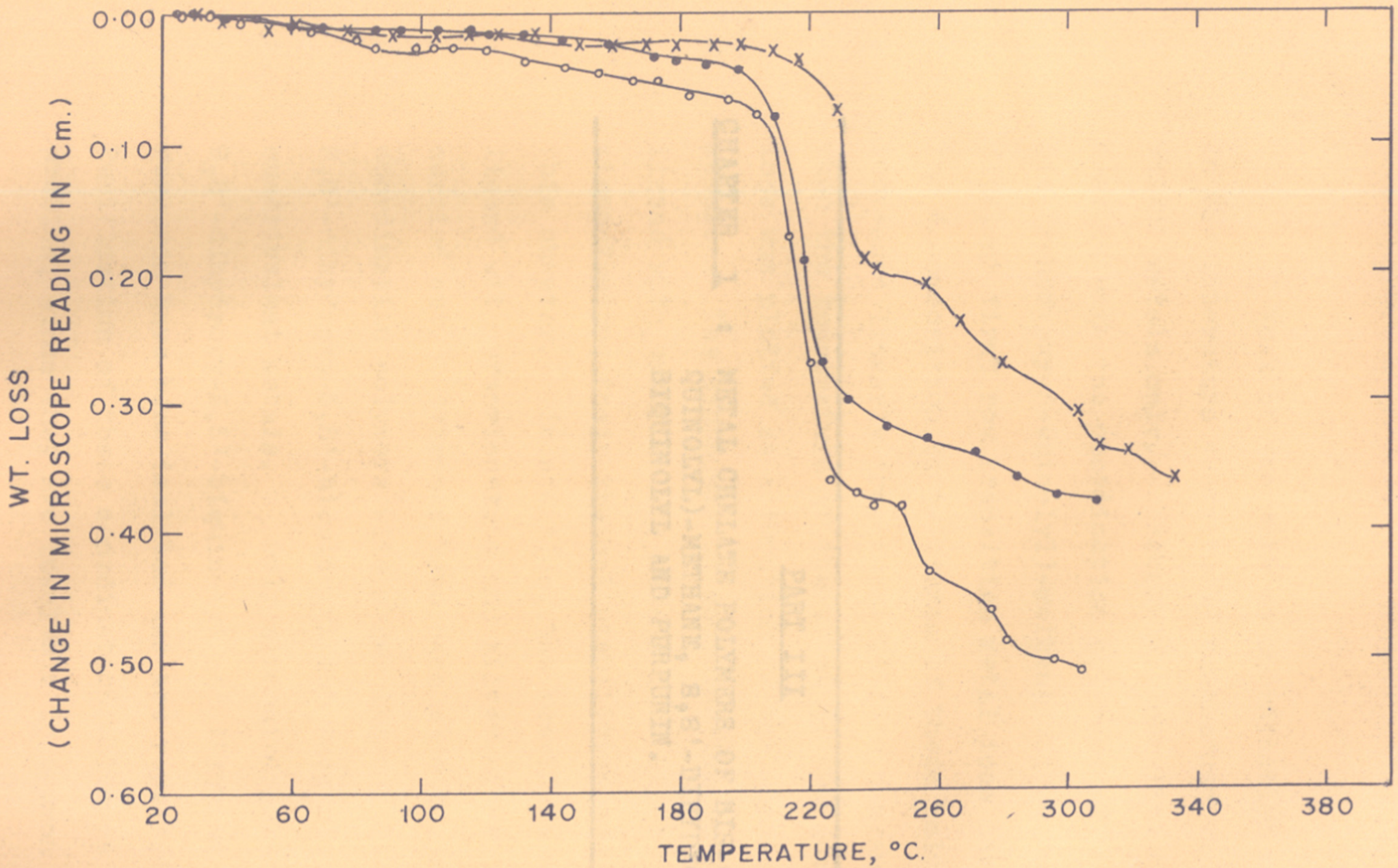


FIG. 18. THERMOGRAMS FOR MONOHALOGENOTRIS-(ACETOACETANILIDATO)-TITANIUM (IV) COMPLEXES.

o——o MONOCHLOROTRIS-(ACETOACETANILIDATO)-TITANIUM (IV). (Wt. 0·0248 g)

●——● MONOBROMOTRIS-(ACETOACETANILIDATO)-TITANIUM (IV). (Wt. 0·0259 g)

x——x MONOIODOTRIS-(ACETOACETANILIDATO)-TITANIUM (IV). (Wt. 0·0249 g).

PART III

CHAPTER 1 : METAL CHELATE POLYMERS OF BIS-(8-HYDROXY-5-QUINOLYL)-METHANE, 8,8'-DIHYDROXY-5,5'-BIQUINOLYL AND PURPURIN.

Metal Chelate polymers of bis-(8-hydroxy-5-quinolyl)-methane, 8,8'-dihydroxy-5,5'-biquinolyl and purpurin.

Most of the work on coordination polymers reported in the literature seems to be conneerned with di- and trivalent metals only. Recently, Horowitz and Perros[1] dealing with the coordination polymers of bis-(8-hydroxy-5-quinolyl)-methane with a number of divalent first row transition metal ions have shown that the decomposition temperatures of these polymers increased linearly from copper(II) to manganese(II) when the temperature at the start of the accelerated weight loss was plotted as a function of the atomic number of the metal. The synthesis of coordination polymers of this ligand with quadrivalent metals like titanium, tin and zirconium and their thermal stabilities are described in this chapter. In addition, the reactions of this bis-ligand with uranylacetate and silver nitrate have been carried out. Attempts have been made to prepare coordination polymers with other ligands like 8,8'-dihydroxy-5,5'-biquinolyl and purpurin with quadrivalent metals. Only zirconium polymer of 8,8'-dihydroxy-5,5'-biquinolyl and titanium polymer of purpurin have been isolated and are reported here. Purification of these coordination polymers has been a problem, since they are insoluble in common organic solvents.

EXPERIMENTAL

Bis-(8'-hydroxy-5-quinolyl)-methane prepared according to reported methods[1,2] melts at 280°C.

Found: C, 75.34; H, 4.54; N, 9.00%.

Calcd. for $C_{19}H_{14}O_2N_2$: C, 75.50; H, 4.64; N, 9.26%.

8,8'-Dihydroxy-5,5'-biquinolyl was prepared by the oxidation[3] of reagent grade 8-quinolinol with ferric sulphate. The method was same as followed by Berg and Alam[4]. The compound decomposed above 300°C.

Found: C, 75.63; H, 4.66; N, 9.21%.

Calcd. for $C_{18}H_{12}O_2N_2$: C, 75.0; H, 4.17; N, 9.37%.

Reaction between titanium tetrachloride and bis-(8-hydroxy-5-quinolyl)-methane

The reaction was carried out in a three-necked flask provided with a high speed vacu-o-stirrer and a pear-bulb fractionating column connected through a take-off condenser to a receiver. The quantities of the reagents were 0.95 g (0.005 mole) of titanium tetrachloride in dry benzene (15 ml.) and 1.51 g (0.005 mole) of the ligand in dimethylformamide (50 ml.). As heating and stirring continued, the titanium tetrachloride solution was added slowly to the ligand solution during a period of 40 min. and the hydrogen chloride generated was collected in the receiver containing potassium hydroxide solution.

After the reaction was complete, benzene was distilled off. The solid product obtained was collected and hydrolysed with water. An yellow product was obtained. It was extracted with alcohol and air-dried.
Yield, 1.0 g; 51.2%.

Reaction between titanium tetrabutoxide and bis-(8-hydroxy-5-quinolyl)-methane

The reaction was carried out in the same manner as above using ligand (3.02 g; 0.01 mole) in DMF (100 ml.) and titanium tetrabutoxide (3.40 g; 0.01 mole) in dry benzene (25 ml.). Yield of the yellow polymer, 3.9 g; 97.5%.

Reaction between titanium tetraethoxide and bis-(8-hydroxy-5-quinolyl)-methane

Ligand (1.50 g; 0.005 mole) in DMF (50 ml.) and titanium tetra ethoxide (1.14 g; 0.005 mole) in benzene (25 ml.) were reacted as before. Yield of the yellow polymer, 1.7 g; 89.0%.

Reaction between titanium tetraisopropoxide and bis-(8-hydroxy-5-quinolyl)-methane

Ligand (1.50 g; 0.005 mole) and titanium tetraisopropoxide (1.42 g; 0.005 mole) were reacted together. Yield, 1.80 g; 90%.

Reaction between dimethyl tin dichloride and bis-(8-hydroxy-5-quinolyl)-methane

A mixture of ligand (2.01 g; 0.0067 mole) in DMF (75 ml.) and dimethyl tin dichloride (1.47 g; 0.0067 mole) in benzene (40 ml.) was reacted as before. The mixture was refluxed for about half an hour, allowed to cool, filtered and the deep yellow filtrate was neutralised with a few drops of dilute ammonia.
The separated solid was collected on a filter, washed with water, and dried. It was further purified by extraction with alcohol and air-dried. Bright yellow product.
Yield, 1.85; 59.5%.

Reaction between zirconium oxychloride and bis-(8-hydroxy-5-quinolyl)-methane

Ligand (2.0 g; 0.0067 mole) in DMF (75 ml.) and zirconyl chloride octahydrate (2.1 g; 0.0067 mole) in DMF (25 ml.) were mixed together and refluxed.
The solid obtained was collected, washed with DMF and alcohol and dried. The bright yellow solid was further purified by extraction with alcohol and air-dried.
Yield, 2.1 g; 77.5%.

Reaction between zirconium tetrachloride and bis-(8-hydroxy-5-quinolyl)-methane

Zirconium tetrachloride (2.33; 0.01 mole) in DMF and the ligand (3.02 g; 0.01 mole) in DMF were reacted together as above. Bright yellow product. Yield, 3.8 g; 89.3%.

Reaction between uranyl acetate and bis-(8-hydroxy-5-quinolyl)-methane

Uranyl acetate dihydrate (2.83 g; 0.0067 mole) in DMF and ligand (2.0 g; 0.0067 mole) in DMF were mixed together and refluxed for 6 hr. The reddish-brown solid separated was collected on a filter, dried and extracted with alcohol. Yield, 3.3 g.

Found: C, 49.1; H, 3.87; N, 3.52; U, 35.73%.

Reaction between silver nitrate and bis-(8-hydroxy-5-quinolyl)-methane

Silver nitrate (1.70 g; 0.01 mole) in hot water (100 ml.) and the ligand (3.02 g; 0.01 mole) in hot DMF (100 ml.) were mixed. A deep green pasty mass was obtained. The mixture was kept on water-bath for 30 min. The product was collected on a filter, washed successively with hot DMF, water and alcohol and finally dried under vacuum. Yield, 3.2 g.

Found: C, 49.21; H, 4.42; N, 6.08; Ag, 21.1%.

Reaction between 8,8'-dihydroxy-5,5'-biquinolyl and zirconium oxychloride

Zirconyl chloride octahydrate (0.64 g; 0.002 mole) in DMF (25 ml.) and the ligand (0.58 g; 0.002 mole) in DMF (25 ml.) were mixed together. The orange-yellow solid obtained was collected on a filter, dried and extracted with alcohol.
Yield, 0.7 g; 78.3%.

Reaction between titanium tetrabutoxide and purpurin

Purpurin (1.79 g; 0.007 mole) in alcohol (100 ml.) and titanium tetrabutoxide (2.38 g; 0.007 mole) in benzene (25 ml.) were reacted together. Yield of the reddish violet solid, 2.2 g; 88.70%.

Results and Discussion

A number of experiments carried out to isolate polymers of titanium(IV) revealed some complexities in their isolation. For instance, when equimolar proportions of titanium tetrachloride in benzene and bis-(8-hydroxy-5-quinolyl)-methane in dimethylformamide (DMF) were reacted together, the polymer isolated was found to contain less chlorine than expected on the basis of replacement of two chlorine atoms. (Found: 7.82; required, 16.04%). The ratio of titanium to chlorine in this product was 1:1.42. Further the product, during drying under vacuum changed its colour from dark reddish brown to brown. When exposed to atmosphere it changed to brown, brownish-yellow and finally to yellow. Hence the compound obtained in the reaction was hydrolysed with water. The polymer thus isolated was found to retain DMF tenaciously. For instance, the infrared spectrum (Fig. 19) of the yellow product dried under vacuum at 100°C for two hours showed a strong band due to DMF at 6μ ($1667\ cm^{-1}$) region. DMF could not be removed completely even at elevated temperatures (120-160°C). Prolonged drying under vacuum at 170-180°C in a current of dry nitrogen resulted in slight decomposition of the product (titanium, found, 13.95; required, 12.2%). However, extraction of the product with ethanol was found, as evidenced from the I.R. spectrum (Fig.20), to remove DMF and give a polymer of reasonable purity.

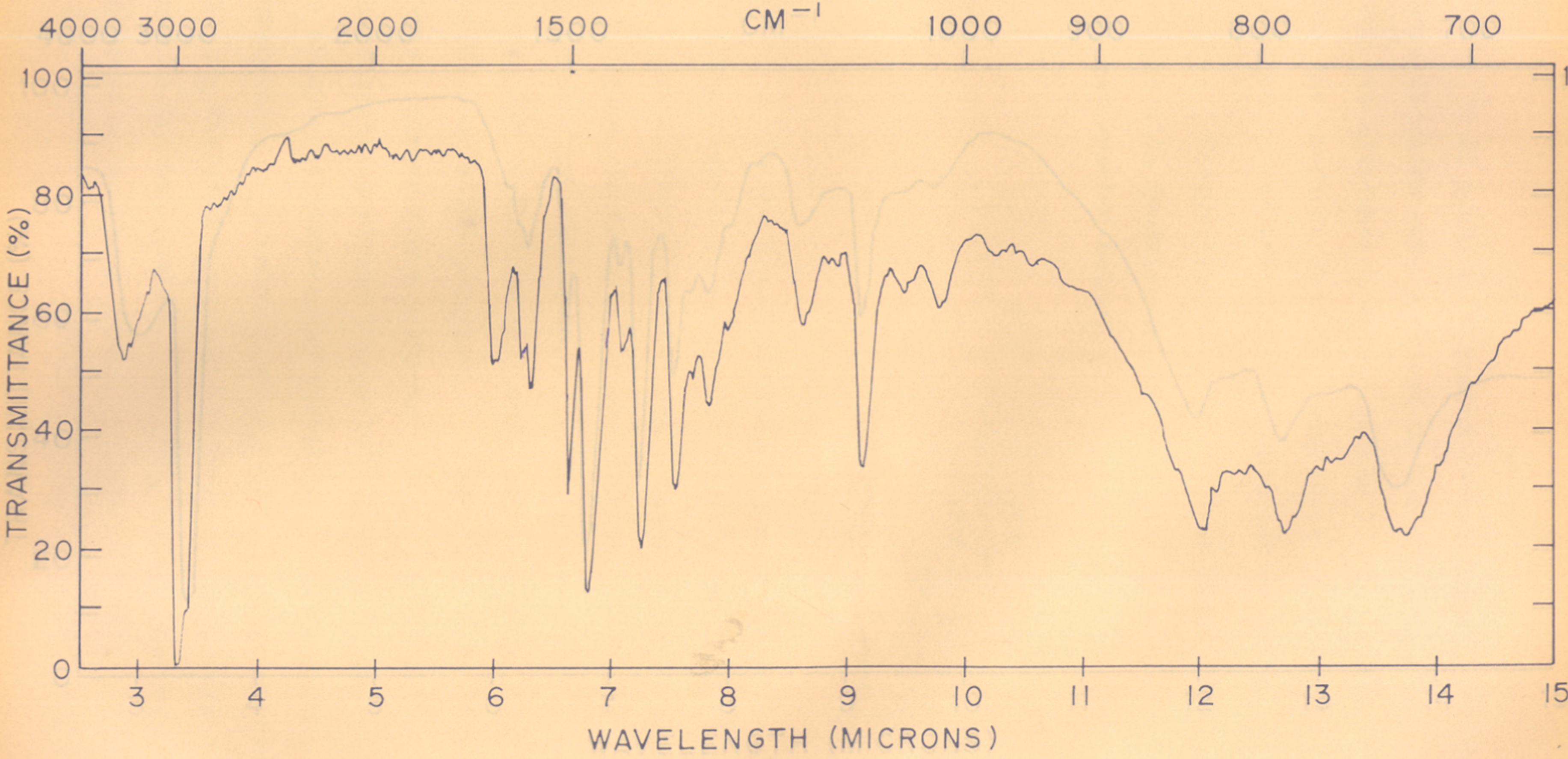


FIG. 19. IR SPECTRUM IN NUJOL MULL OF TITANIUM POLYMER OF BIS-(8-HYDROXY-5-QUINOLYL)-METHANE (BEFORE EXTRACTION WITH ALCOHOL).

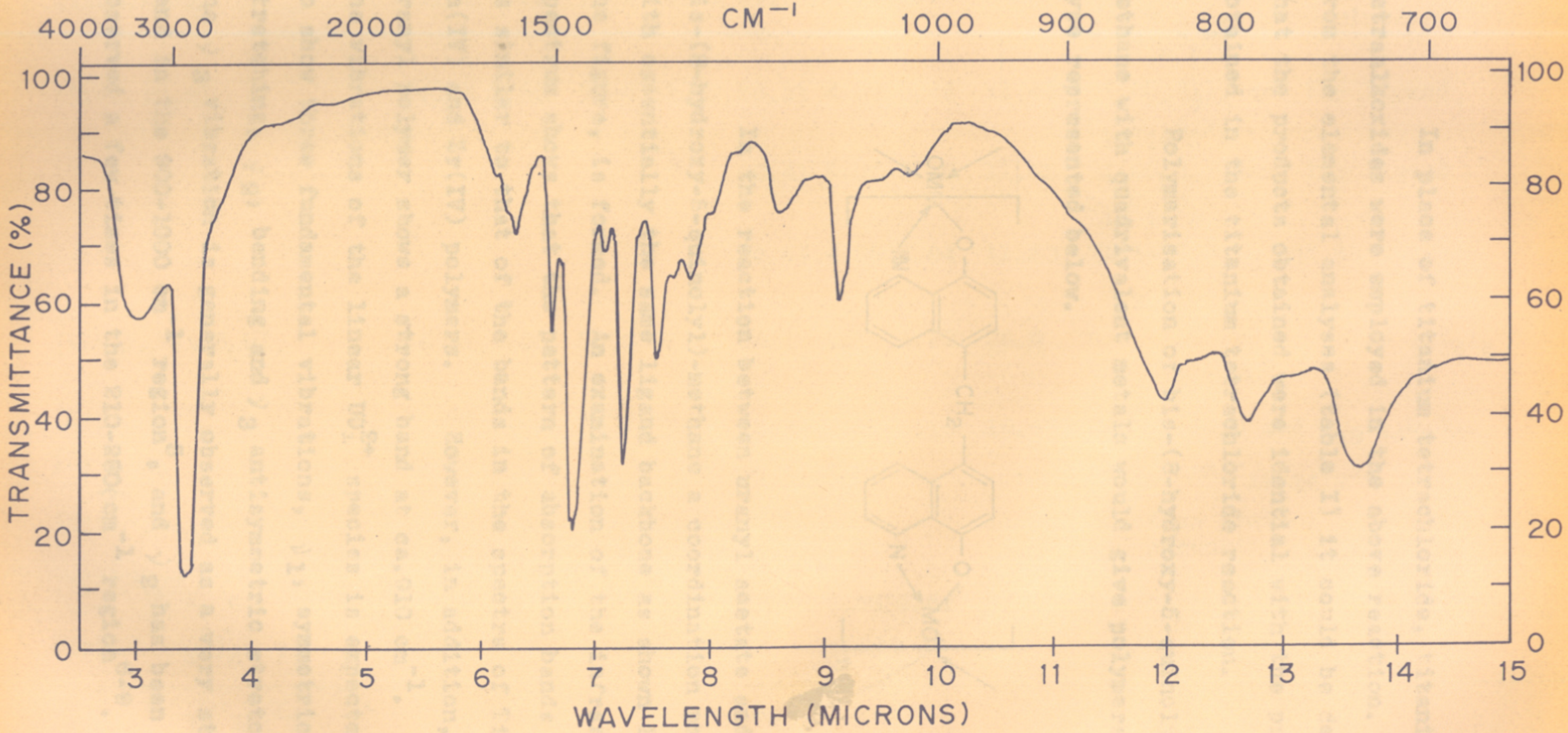
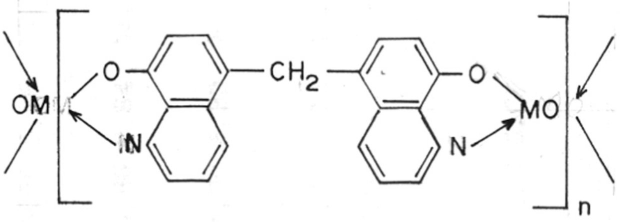


FIG. 20. IR SPECTRUM IN NUJOL MULL OF Ti-BIS (8-HYDROXY-5-QUINOLYL)-METHANE POLYMER (AFTER EXTRACTION WITH ALCOHOL).

In place of titanium tetrachloride, titanium tetraalkoxides were employed in the above reaction. From the elemental analyses (table I) it could be deduced that the products obtained were idential with the product obtained in the titanium tetrachloride reaction.

Polymerisation of bis-(8-hydroxy-5-quinolyl)-methane with quadrivalent metals would give polymers of the type represented below.



In the reaction between uranyl acetate and bis-(8-hydroxy-5-quinolyl)-methane a coordination polymer with essentially the same ligand backbone as shown in the figure, is formed. An examination of the infrared spectrum shows that the pattern of absorption bands (Table IV) is similar to that of the bands in the spectra of Ti(IV), Sn(IV) and Zr(IV) polymers. However, in addition, the uranyl polymer shows a strong band at ca.910 cm^{-1}. The vibrations of the linear UO_2^{2+} species is expected to show three fundamental vibrations, ν_1, symmetric stretching, ν_2, bending and ν_3 antisymmetric stretching. The ν_3 vibration is generally observed as a very strong band in the 900-1000 cm^{-1} region[5], and ν_2 has been observed a few times in the 210-280 cm^{-1} region[6-9].

Table 1

Elemental analyses of coordination polymers

Polymer	Calculated % C	H	N	M	Found % C	H	N	M	Remarks
$[TiOL.H_2O]_n$	59.71	3.69	7.33	12.53	59.02	3.56	7.10	12.20	Reaction product from $TiCl_4$ and bis(8-hydroxy-5-quinolyl)-methane, $C_{19}H_{14}O_2N_2$.
$[TiOL.2H_2O]_n$	57.03	4.03	7.00	11.97	56.31	4.37	6.89	11.40	$Ti(OC_4H_9)_4$ and the ligand $C_{19}H_{14}O_2N_2$.
					59.41	5.00	6.26	11.69	$Ti(OC_2H_5)_4$ and the ligand $C_{19}H_{14}O_2N_2$.
					54.54	4.86	6.84	11.63	$Ti(i\text{-}OC_3H_7)_4$ and the ligand $C_{19}H_{14}O_2N_2$
$[(CH_3)_2SnL.H_2O]_n$	54.01	4.32	5.99	25.42	54.12	4.32	5.33	24.6	Reaction product from $(CH_3)_2SnCl_2$ and $C_{19}H_{14}O_2N_2$.
$[ZrOL.H_2O]_n$	53.64	3.32	6.59	21.44	55.43	4.00	6.15	19.43	$ZrOCl_2.8H_2O$ and $C_{19}H_{14}O_2N_2$.
$[ZrOL.]_n$	56.02	2.98	6.88	22.40	55.71	2.91	-	-	$ZrCl_4$ and $C_{19}H_{14}O_2N_2$
$[TiOL'.2H_2O]_n$	47.47	2.85	-	13.85	46.59	3.50	-	14.00	Reaction product from $Ti(OC_4H_9)_4$ and purpurin $C_{14}H_8O_7$.
$[ZrOL''.2H_2O]_n$	50.32	3.29	6.52	21.23	48.84	4.28	6.68	21.90	Reaction product from $ZrOCl_2.8H_2O$ and 8',8'-dihydroxy-5,5'-biquinolyl, $C_{18}H_{12}O_2N_2$.
$[ZrOL''.3H_2O]_n$	48.31	3.60	6.26	20.40					

$L = C_{19}H_{12}O_2N_2$; $L' = C_{14}H_6O_7$; $L'' = C_{18}H_{10}O_2N_2$.

Table II

Percentage weight loss of coordination polymers (25°-500°C., heating rate in air 2°C/min).

Temp. °C	Weight loss of polymer, %				
	Ti	Zr	Sn	U	Ag
25	0	0	0	0	0
50	1.142	2.35	1.06	0.07	1.15
75	2.83	4.34	1.57	1.75	4.35
100	5.52	5.51	1.99	4.04	5.15
125	6.48	6.96	2.30	5.36	5.84
150	6.58	6.41	2.62	6.02	6.30
175	7.66	6.86	3.14	6.56	6.30
200	8.53	7.22	3.14	6.56	6.87
225	9.07	7.77	3.66	7.10	14.88
250	10.14	8.13	4.19	8.20	17.74
275	10.32	8.85	4.19	8.20	17.74
300	10.52	9.12	4.70	10.39	18.32
325	12.81	9.75	4.70	10.93	21.18
350	17.45	12.11	8.89	41.02	24.04
375	24.13	34.42	12.03	49.00	26.33
400	58.38	56.54	14.65	49.00	34.92
425	60.16	70.55	25.12	-	62.40
450			43.95		
475			49.72		

Table III

Temperature at start of accelerated weight loss for coordination polymers with bis(8-hydroxy-5-quinolyl)-methane

Coordination polymer	Atomic number	Decomposition temperature °C
Ti(IV)	22	330
Zr(IV)	40	380
Ag(I)	47	395
Sn(IV)	50	410
UO_2^{++}	92	340

Table IV

Infrared absorption frequencies (cm^{-1}) in nujol mull of bis(8-hydroxy-5-quinolyl)-methane and its metal coordination polymers

Ligand	Ti	Zr	Sn	U	Ag
3350s	3400m	3350w	3450m	3450m	
2950*b,vs	2900*b,vs	2900*b,vs	2950*b,vs	2900*b,vs	2924*b,vs
1620w	-	-	1600w	1650w	1650w
				1600w	1613m
1580m	1580m	1580m	1575m	1575m	1587m
1500s	1500s	1530s	1500s	1510s	-
1470*vs	1475*vs	1475vs	1470*b,vs	1480*vs	1466*vs
1420s	1425w	1420w	1410w	1420m	-
1365*vs	1375*vs	1380*s	1370*s	1380*s	1377s
	1325s	1330s	1325s	1330s	
1270s	1275m	-	1274w	1250w	1299w
1220s	1250sh		1242w		
1190s	-	-	-	-	-
1150m	1162w	1170w	1156m	1170w	1149w
			1124w	1140w	
	1090s	1100s	1095s	1100s	1080s
1075w	-	-			
1015w	1025w		1015w	-	975w
-	-	-	-	910b,s	-
830m	835m	840m	830m	835m	826s
780b,vs	785m	790m	785b,s	795m	780b,s
-	730m	735m	725m	730m	721s
695w	-	-	-	-	-

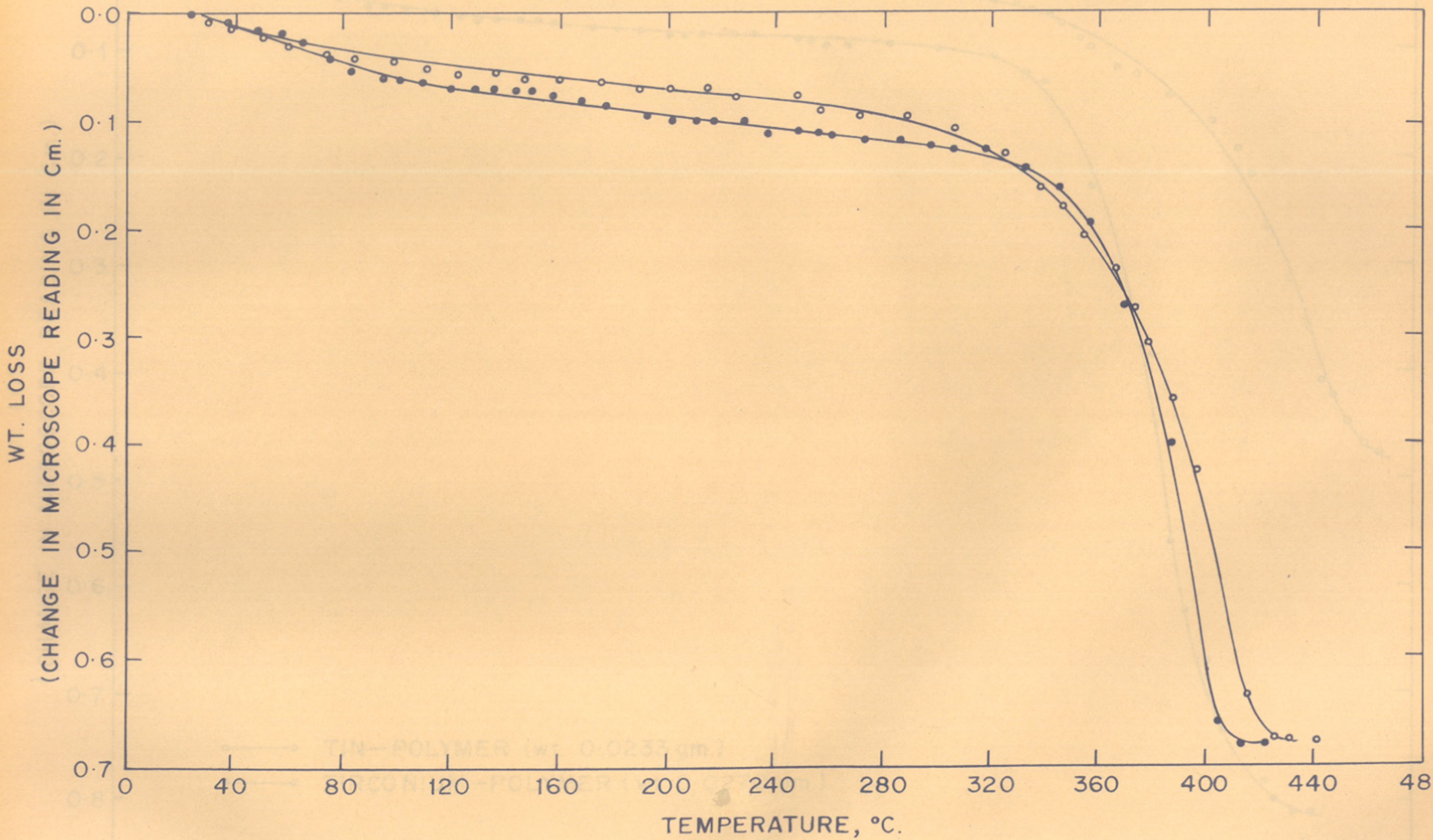


FIG. 21. THERMOGRAMS FOR Ti-BIS (8-HYDROXY-5-QUINOLYL)-METHANE POLYMERS. (HEATING RATE 2°C./MIN.; •——• TITANIUM POLYMER USING $Ti(OBu)_4$; Wt. 0·0274 gm., ○——○ TITANIUM POLYMER USING $TiCl_4$; Wt. 0·0290 gm.).

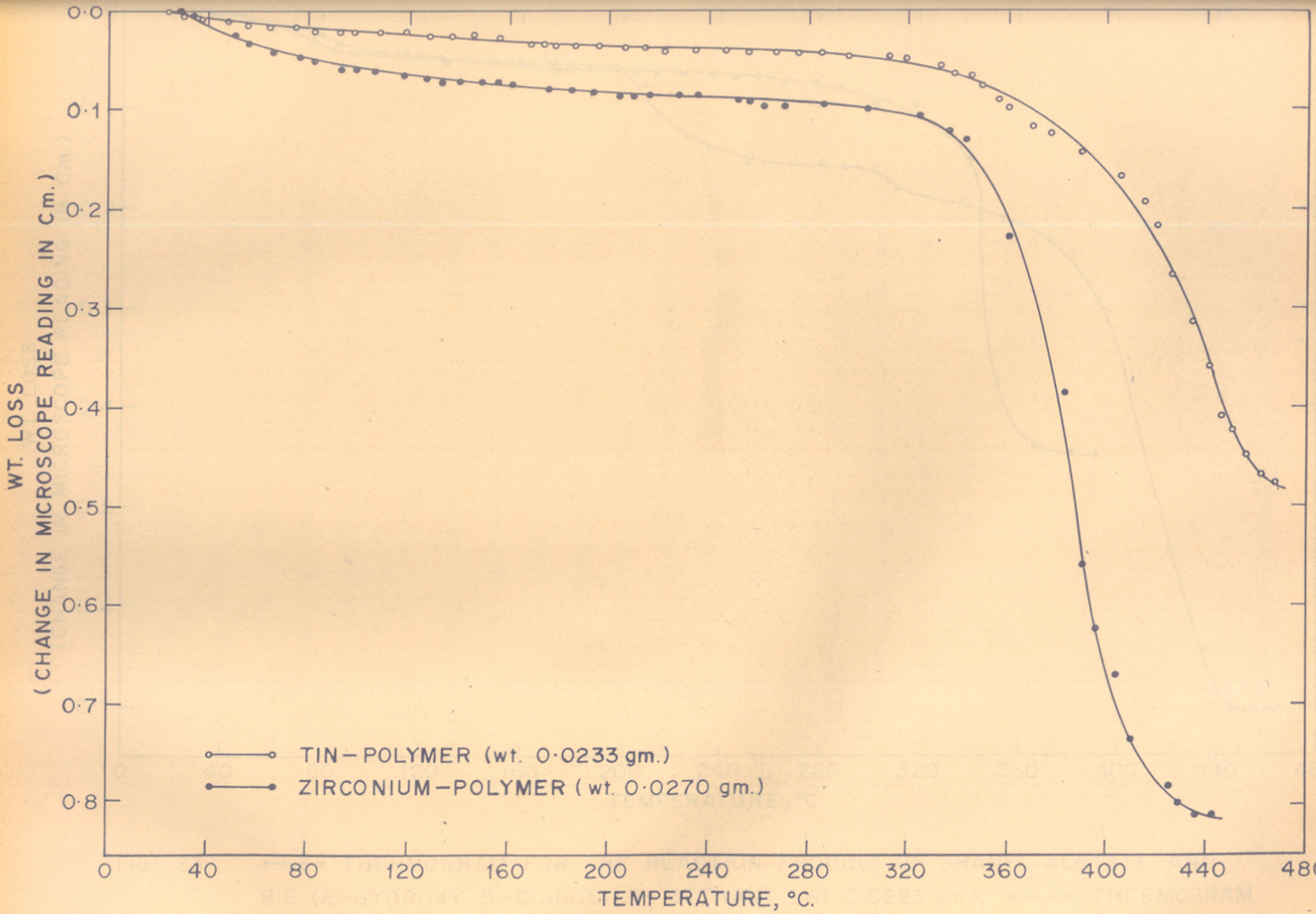


FIG. 22. THERMOGRAMS OF METAL BIS (8-HYDROXY-5-QUINOLYL)-METHANE POLYMERS. (HEATING RATE 2 °C./MIN.)

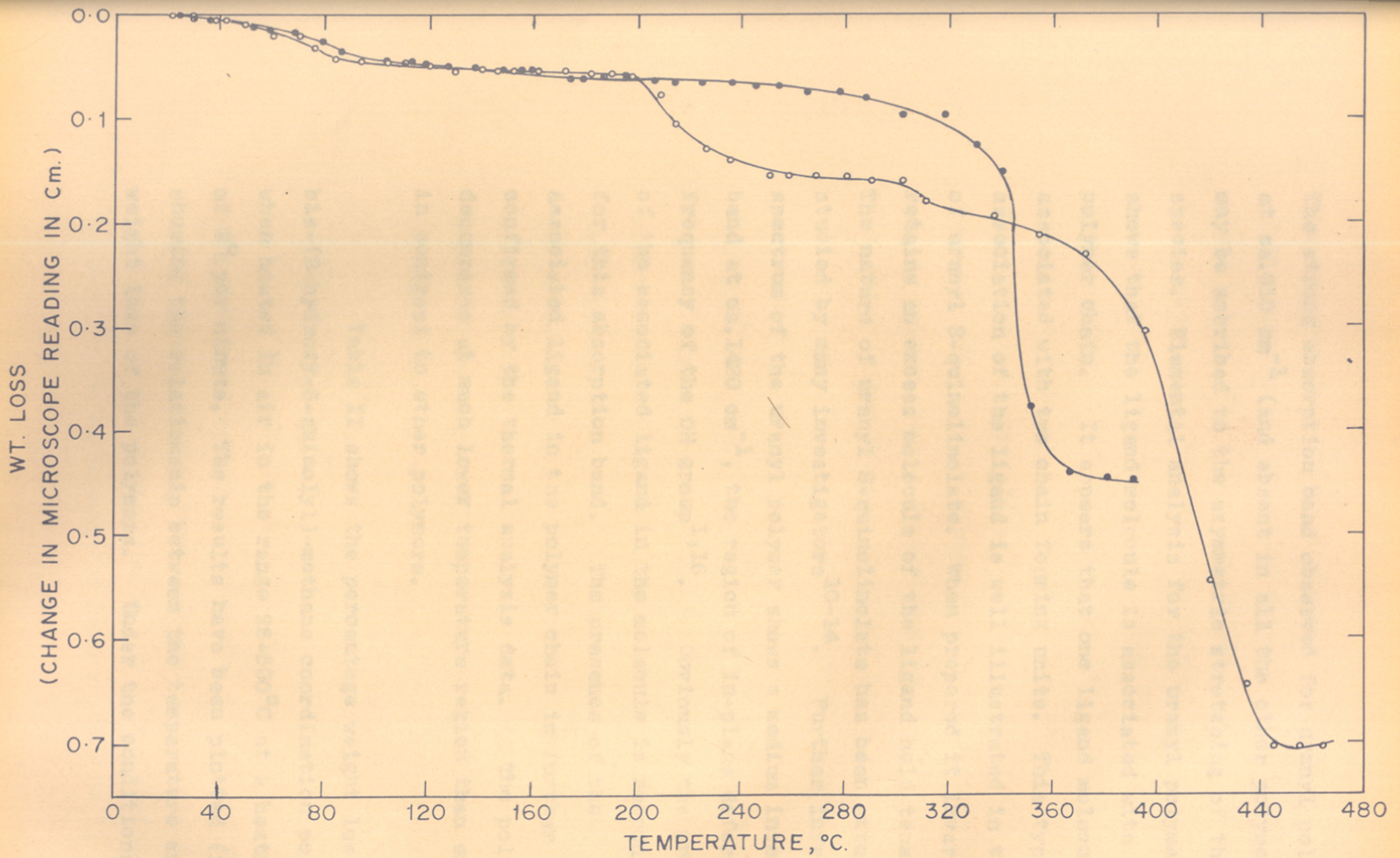


FIG. 23. ●—● THERMOGRAM FOR THE REACTION PRODUCT OF URANYL ACETATE AND BIS (8-HYDROXY-5-QUINOLYL)-METHANE (Wt. 0·0223 gm.), ○—○ THERMOGRAM FOR REACTION PRODUCT OF SILVER NITRATE AND BIS (8-HYDROXY-5-QUINOLYL)-METHANE (Wt. 0·0213 gm.). HEATING RATE 2 °C./ MIN.

The strong absorption band observed for uranyl polymer at ca.910 cm^{-1} (and absent in all the other polymers) may be ascribed to the asymmetric stretching of the uranyl species. Elemental analysis for the uranyl polymer shows that the ligand molecule is associated with the polymer chain. It appears that one ligand molecule is associated with two chain forming units. This type of association of the ligand is well illustrated in the case of uranyl 8-quinolinolate. When prepared it invariably retains an excess molecule of the ligand held tenaciously. The nature of uranyl 8-quinolinolate has been extensively studied by many investigators[10-14]. Further, infrared spectrum of the uranyl polymer shows a medium intense band at ca.1420 cm^{-1}, the region of in-plane deformation frequency of the OH group[1,15]. Obviously the presence of the associated ligand in the molecule is responsible for this absorption band. The presence of the associated ligand in the polymer chain is further confirmed by the thermal analysis data. The polymer decomposes at much lower temperature region than expected, in contrast to other polymers.

Table II shows the percentage weight loss of bis-(8-hydroxy-5-quinolyl)-methane coordination polymers when heated in air in the range 25-500°C at a heating rate of 2°C per minute. The results have been plotted (figs.21-23) showing the relationship between the temperature and weight loss of the polymers. Under the conditions employed, the polymers lost weight gradually in the early phase of the experiment indicating slow volatilisation of the bound water. The percentage weight loss in the temperature range 25-325°C was moderate. Rapid decomposition occurred in the range 350-450°C. However, the tin(IV) polymer lost 14% by weight of the organic portion, at this temperature range. The decomposition temperatures for the polymers are given in table III. It is apparent that the increasing atomic number results in enhanced thermal stability. The trend in the thermal stability is ~~of~~ in the order of Sn > Ag > Zr > Ti. However, uranium polymer decomposed at 340°C, presumably, due to the decomposition first~~,~~ of the free ligand attached to the polymeric unit.

The accelerated weight loss of the polymers may be attributed to the breaking up of the bonds at the metal ligand site. The decomposition mechanism~~,~~ involving the formation of bis-8-hydroxy quinoline (non-polymeric) chelates, seems to be improbable, because these chelates are volatile under conditions employed in the thermogravimetric analyses. Further, the presence of metal oxides in the residue suggests the rupture of the metal-ligand bonds.

The infrared absorption bands of bis-(8-hydroxy-5-quinolyl)-methane, along with those of the metal coordination polymers~~,~~ in nujol mull are given in table IV. The spectrum of the ligand contains a moderately strong absorption band at 3350 cm^{-1}, the region of OH Stretching vibration frequency. The weak band at 1620 cm^{-1}, the medium band at 1580 cm^{-1} and the strong band at 1500 cm^{-1} are due to C=N and C=C stretching vibrations of the quinoline ring[4]. The strong band at 1420 cm^{-1} in the ligand, is due ~~perhaps~~ to the OH deformation vibration. The strong band at 780 cm^{-1} and the medium band at 830 cm^{-1} are due to out-of-plane CH bending vibrations. In the finger print region (1350 cm^{-1} - 900 cm^{-1}) strong bands appear at 1270 cm^{-1} (C-C stretching), 1220 cm^{-1} and at 1190 cm^{-1} (CH in-plane) and a medium intense band at 1150 cm^{-1}.

The patterns of all the metal coordination polymers show an absorption band at 1570 cm^{-1} - 1580 cm^{-1}, somewhat displaced from the 1580 cm^{-1} frequency present in the ligand.

The strong band present in the ligand at 1420 cm^{-1} (OH vibration) is absent in the spectra of the coordination polymers. All spectra show weak bands in 1410 cm^{-1}-1425 cm^{-1} region. The appearance of a strong and sharp band at approximately 1100 cm^{-1} in the coordination polymers may be assigned to C-O stretching vibration at the C-O-M site[16]. There seems to be no apparent relationship between the frequency at ca. 1100 cm^{-1} and the atomic number of the central metal atom in these polymers.

The infrared absorption spectra of 8,8'-dihydroxy-5,5'-biquinolyl and its zirconium polymer (Table V) show evidence for the chelation of the ligand with the metal. On chelation, the -C=N- vibration of the quinoline ring of the ligand in the region 1580 cm^{-1} - 1600 cm^{-1} is displaced to 1565 cm^{-1} - 1575 cm^{-1}. The strong band at ca.1400 cm^{-1} attributed to in-plane deformation frequency of the OH group[1,15] disappeared and only a weak band appeared in the spectrum of the polymer. The strong absorption band at ca.1120 cm^{-1} in the polymer may be assigned to the C-O stretching vibration at C-O-M-site[16]. Thermal stability study of the zirconium polymer (Table VI, fig.24) shows that it is quite stable upto 420°C (heated in air at a heating rate of 2°C per minute). At 500°C, the percentage loss for the polymers is only 7.3. It is noteworthy that the percentage losses for some of the divalent metal coordination polymers[4] of this bis ligand in the temperature range of 280°-300°C are quite considerable (16%).

Infrared spectra of purpurin and its titanium polymer (Table V) show evidence for chelation of the ligand with metal. On chelation the carbonyl stretching frequency is shifted from 1626 cm^{-1} to 1560 cm^{-1}.

Thermal analysis for the coordination polymer of purpurin with titanium shows that it is stable upto 280°C. In the temperature region 280°-370°C, the decomposition of the polymer is very rapid and considerable. (Table VI, fig.24).

Table V

Infrared absorption frequencies (cm^{-1}) in nujol mull of 8,8'-dihydroxy-5,5'-biquinolyl and its zirconium polymer and purpurin and its titanium polymer

8,8'-Dihydroxy-5,5'-biquinolyl	Zr-8,8'-dihydroxy-5,5'-biquinolyl polymer	Purpurin	Ti-purpurin polymer
3300m	3300m	3330b,m	3400m
-	-	-	3150w
2900*b,vs	2900*b,vs	2941*b,vs	2900*b,vs
1650m	1650w		
1580s	1600w	1626s	1600w
	1570s	1587s	1560s
1500s	1500s		1500w
1460*s	1465*s	1471*s	1460*s
1400s	1400w	1449s	1400v,w
1380*s	1380*s	1379*s	1370*s
1360sh			
	1360sh	1333s	
	1310s	1307s	
1280s	1270w	1274w	1285s
-	1240w	-	-
1220w	1225w	1205m	1200s
1200s	-		
1180m		1176s	1160m
1150m	1155m		
1110w	1120s		
-	1080s	1075s	
1030w	1040m	1031m	
905m		971s	990s
		901w	900w
		885w	
		865w	
845s	840b,s		
840w			
830w	810m	810m	-
790s	795b,s	784s	
	745b,s	746s	735m
		728s	720b,m
715s	720m	704m	700w

Table VI

Percentage weight loss of coordination polymers (25°-500°C., heating rate in air 2°C/min.)

Temp. °C	Weight loss of polymer % Ti-purpurin polymer	 Zr-8,8'-dihydroxy-5,5'-biquinolyl polymer
25	0	0
50	2.03	0.21
75	4.42	0.50
100	7.16	0.72
125	8.13	0.90
150	9.53	1.29
175	10.34	1.48
200	11.05	1.65
225	11.58	1.75
250	14.14	1.79
275	16.00	1.93
300	60.09	1.96
325	65.04	2.00
350	65.66	2.13
375		2.17
400	65.66	2.45
425	-	3.14
450	-	4.96
475	-	5.93
500	-	7.30

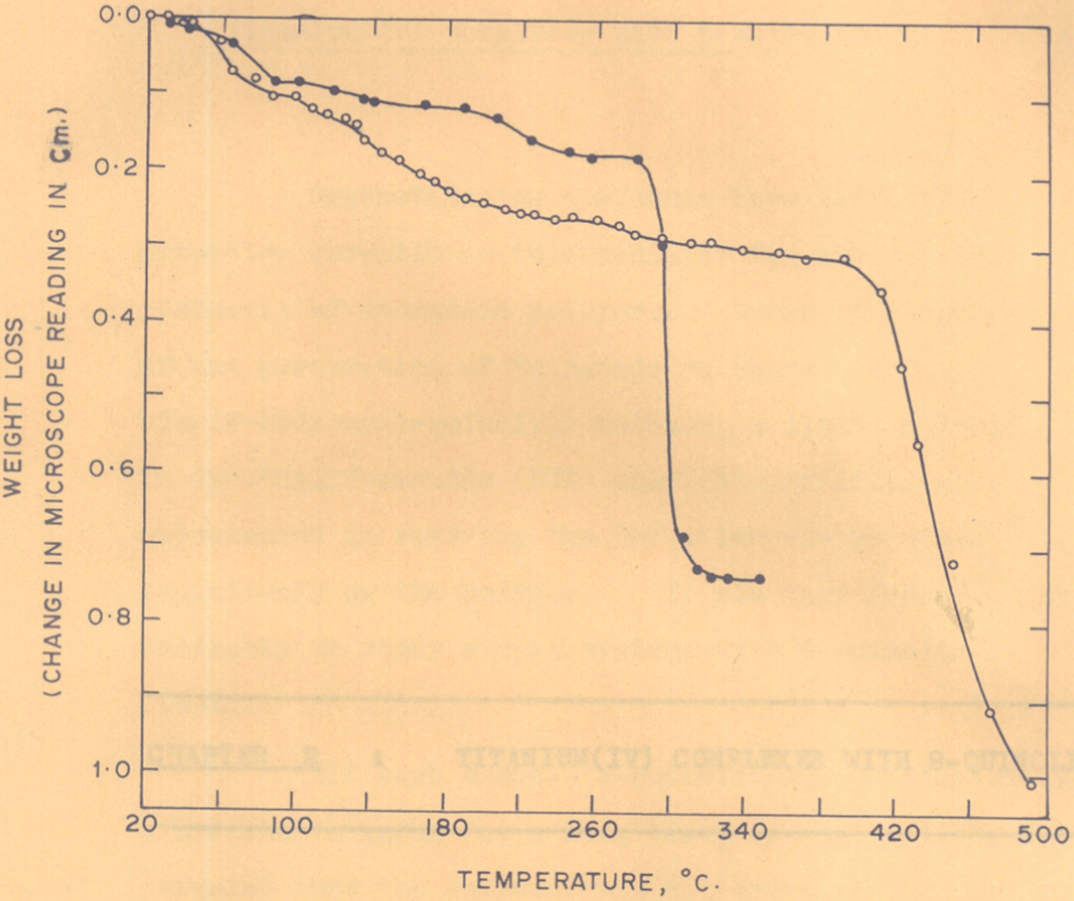


FIG. 24. ○———○ THERMOGRAM FOR Zr-8,8'-DIHYDROXY-5,5'-BIQUINOLYL POLYMER. (WT. 0·0354 g.);

●———● THERMOGRAM FOR Ti-PURPURIN POLYMER. (WT. 0·0276 g.)

HEATING RATE 2°C/MIN.

CHAPTER 2 : TITANIUM(IV) COMPLEXES WITH 8-QUINOLINOL

Titanium(IV) complexes with 8-quinolinol

Organotitanium compounds have attracted attention recently as intermediates for the possible synthesis of inorganic polymers. During the course of the preparation of inorganic polymers with bis-(8-hydroxy-5-quinolyl)-methane, a ligand soluble in dimethylformamide (DMF) only, difficulties were experienced in removing the DMF which was retained tenaciously by the polymer. It was therefore thought desirable to study simple systems with 8-quinolinol itself.

Although oxobis-(8-quinolinolato)-titanium(IV) dihydrate is known for a long time, search of literature revealed that the compound was not examined thoroughly. Berg and Teitelbaum[17] reported that quantitative precipitation of the orange yellow complex, $TiO(C_9H_6ON)_2.2H_2O$ takes place in slightly acid or alkaline medium. Early workers[18-20] studied the reactions of tetravalent titanium and 8-quinolinol from the stand point of estimation of titanium only. Thermogravimetric studies carried out by Borrel and Paris[21] and by Duval[22] contradicted the results of Berg and Teitelbaum[17]. Thus, according to Borrel and Paris[21], the compound containing two molecules of water was not stable and loss of water occurred at temperatures of 40°-50°C.

On the other hand, Duval[22] stated that the anhydrous complex was formed at temperatures in the region of 115°C and at this temperature, it was comparatively stable.

Attempts made in this investigation to obtain anhydrous oxobis-(8-quinolinolato)-titanium(IV) were not successful. Various polymeric products containing presumably Ti-O-Ti linkage were obtained. Attempts were also made to obtain titanoxane polymers by the hydrolysis of dialkoxybis-(8-quinolinolato)-titanium(IV). However, search of the literature revealed that Takimoto and Rust[23] had isolated diisopropoxybis-(8-quinolinolato)-titanium(IV) and obtained anhydrous $TiO(C_9H_6ON)_2$ by the hydrolysis of the alkoxy-compound. But the work reported here shows that the hydrolysed product contains one water molecule, $TiO(C_9H_6ON)_2.H_2O$. Furthermore, the products obtained from diethoxy-, diisopropoxy-, and dibutoxy-bis-(8-quinolinolato)-titanium(IV) chelates and the hydrolysis product from the reaction of titanium tetrachloride and 8-quinolinol, are the same as judged from their analyses and their infrared spectra.

EXPERIMENTAL

Solvents used for these preparations were purified and dried according to known methods. 8-Quinolinol was of Riedel-deHaën, C.P. grade. Titanium tetraalkoxides were prepared according to the procedures described by Bradley and co-workers[24-26].

T.G.A. Determined in a balance using McBain-Bakr type Quartz-spring[27].

V.P.C. recorded on Aerograph A 350B with hydrogen as carrier gas, column P, temperature 70°C.

Reaction between titanium tetrachloride and 8-quinolinol

8-Quinolinol (14.5 g; 0.1 mole) dissolved in benzene (75 ml.) was added slowly to titanium tetrachloride (9.5 g; 0.05 mole) in benzene (50 ml.) placed in a two-necked flask fitted with a stirrer and a reflux condenser. A bright red compound was immediately formed which was kept under mild reflux for one hour and a half before the compound was collected on a filter. It was washed with several portions of benzene and dried.

This product (1.0 g) was hydrolysed by keeping in contact with water (150 ml.) for 48 hours. The bright yellow product thus obtained was filtered, and dried at 110°C for 2 hours. (Product A)

Found: C, 59.00; H, 3.47; Ti, 13.57%.
Calcd. for $C_{36}H_{26}N_4O_7Ti_2$: C, 59.89; H, 3.63; Ti, 13.27%.

The above product was recrystallised from absolute alcohol (Product B).

Found: C, 61.39; H, 3.43; N, 7.96; Ti, 13.6%.
Calcd. for $C_{72}H_{50}N_8O_{13}Ti_4$: C, 60.63; H, 3.53; N, 7.86; Ti, 13.44%.

Reaction between titanium tetraethoxide and 8-quinolinol

To a solution of titanium tetraethoxide (2.28 g; 0.01 mole) in benzene (30 ml.) was added over a period of 25 minutes, 8-quinolinol (2.9 g; 0.02 mole) in benzene (40 ml.). Orange-yellow solution was formed immediately. The solvent and the liberated alcohol were removed under reduced pressure. An orange-yellow solid was obtained. Yield, 4.0 g; 93.9%.

Found: C, 62.53; H, 4.98; N, 6.20; Ti, 11.24%.
Calcd. for $C_{22}H_{22}O_4N_2Ti$: C, 62.03; H, 5.21; N, 6.58; Ti, 11.25%.

To 1.1 g of diethoxybis-(8-quinolinolato)-titanium(IV) was added 5-10 ml. of water. The crystals were filtered and dried to give 0.70 g of yellow amorphous powder (Product C).

Found: C, 57.12; H, 4.17; Ti, 12.20; N, 7.8%
Calcd. for $C_{18}H_{14}O_4N_2Ti$: C, 58.38; H, 3.81; Ti, 12.94; N, 7.60%.

Reaction between titanium tetraisopropoxide and 8-quinolinol

Similarly from titanium tetraisopropoxide (2.84 g; 0.01 mole) in benzene (30 ml.) and 8-quinolinol (2.9 g; 0.02 mole) in benzene (50 ml.) the diisopropoxy compound was prepared. Lemon yellow solid. Yield, 4.29 g; 94.5%.

Found: C, 63.34; H, 4.93; N, 6.57; Ti, 10.32%

Calcd. for $C_{24}H_{26}O_4N_2Ti$: C, 63.48; H, 5.77; N, 6.17; Ti, 10.54%.

This product was hydrolyzed as before (Product D).

Found: C, 57.12; H, 4.17; Ti, 12.20; N, 7.85%.

Reaction between titanium tetrabutoxide and 8-quinolinol

This reaction was carried out in a three-necked flask provided with a high speed vacu-o-stirrer and a pear-bulb fractionating column connected through a take-off condenser to a receiver for the alcohol evolved during the reaction. The quantities of the reagents were 1.99 g (0.007 mole) of n-butyl titanate in 25 ml. of dry benzene and 2.04 g (0.014 mole) of 8-quinolinol in 100 ml. dry xylene. As heating, stirring and distillation of alcohol proceeded, the solution acquired a red colour. Benzene solution of n-butyl titanate was added slowly while stirring was continued during a period of half an hour. Benzene and butyl alcohol were distilled off quantitatively. (The V.P.C. showed that the quantity of butyl alcohol collected into the distillate was 1.12 g, theoretical value is 1.04 g.). The mixture was cooled and 2.1 ml. of water 50 ml. of dry petroleum ether (40°-60°C) were added with stirring. The hydrolysis product was collected on a filter under suction, dried under vacuum, immediately recrystallised from absolute alcohol and dried.

Yield, 2.0 g; 77.2%. (Product E)

Found: C, 58.56; H, 3.71; N, 7.90; Ti, 12.44%

Calcd. for $C_{18}H_{14}O_4N_2Ti$: C, 58.38; H, 3.81; N, 7.60; Ti, 12.94%.

Dibutoxy bis-(8-quinolinato)-titanium(IV) was also isolated by the addition of petroleum ether (40°-60°) to a small portion of the reaction mixture. The solid separated was collected on a filter, washed with a little petroleum ether and dried under vacuum.

Found: Ti, 10.10%.

Calcd. for $C_{26}H_{30}O_4N_2Ti$: Ti, 9.94%.

Reaction between diisopropoxy bis-(8-quinolinolato)-titanium(IV) and catechol

Diisopropoxy bis-(8-quinolinolato)-titanium(IV) in benzene and catechol in benzene were mixed in 1:2 proportions. Immediately a deep red solution was formed.

The mixture was refluxed for 3 hr. Isopropyl alcohol and half the volume of benzene were removed under reduced pressure. Addition of petroleum ether (60°-80°C) resulted in the precipitation of an orange-red solid. It was collected on a filter, washed with ether and dried under vacuum. Yield, 90.42%.

Found: C, 64.88; H, 4.97; N, 4.96; Ti, 8.25%
Calcd. for $C_{30}H_{22}O_6N_2Ti$: C, 65.01; H, 4.00; N, 5.06; Ti, 8.60%.

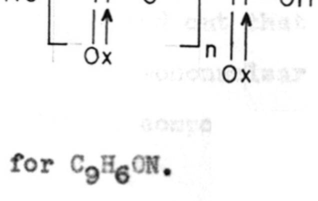
Reaction between diisopropoxy bis-(8-quinolinolato)-titanium(IV) and acetic anhydride

Diisopropoxy bis-(8-quinolinolato)-titanium(IV) in benzene and acetic anhydride were mixed in 1:2 proportion and refluxed for 2 hr. The orange red solid obtained was filtered, washed with petroleum ether and dried under vacuum. Yield, 72.02%.

Found: C, 60.22; H, 4.43; N, 7.22; Ti, 12.27%
Calcd. for $C_{40}H_{30}O_9N_4Ti_2$: C, 59.62; H, 3.75; N, 7.0; Ti, 11.9%.

Results and Discussion

Attempts to obtain anhydrous $TiO(C_9H_6ON)_2$ by drying oxobis-(8-quinolinolato)-titanium(IV) dihydrate at 110°C were unsuccessful. Prolonged drying results in slight decomposition of the product and at the same time water is not completely removed as shown by the presence of a medium intense band at ca.3500 cm^{-1} in the infrared spectrum of the dried product. Hence the compound was dried at 110°C for 2 hours only, (Product A) and was recrystallised from absolute alcohol (Product B). On the basis of elemental analysis, the product B can be formulated as anhydrous oxobis-(8-quinolinolato)-titanium(IV), $TiO(C_9H_6ON)_2$. But the infrared spectrum (Fig. 26) of this product showed bands at 3450 cm^{-1} (OH stretching) and at ca.1600 cm^{-1} (OH bending) indicating the presence of OH groups. The presence of OH groups in the spectrum together with the presence of strong and broad bands at ca.825 cm^{-1} and at ca.735 cm^{-1} suggests polymeric structure for the complex perhaps of the type



where Ox stands for C_9H_6ON.

When the value of n = 1, the elemental analysis for compound A agrees well with the above formulation. Similarly for the compound B, the values agree when n = 3.

The dialkoxy-bis(8-quinolinolato)-titanium(IV) complexes turn to yellow amorphous powders on addition of water. The change may be ascribed to the hydrolysis of unstable alkoxy groups and subsequent condensation with the formation of polymeric substances with Ti-O-Ti bonds[28]. Thermal analysis of the hydrolysed product showed that the compound is stable upto 280°C and rapid decomposition starts from 300°C onwards (Fig. 30). The limited solubility precluded the determination of molecular weight of the hydrolysis product.

The infrared absorption maxima in nujol mull of oxobis(8-quinolinolato)-titanium(IV) complexes are given in Table VII (Figs.25-29).

In the spectra of oxobis(8-quinolinolato)-titanium(IV) complexes, there is no band corresponding to Ti=O in the region of 900-1100 cm^{-1} expected for titanyl compounds[29]. Selbin[30] in his review on 'some recent developments in the chemistry of transition metal oxo cations' pointed out that on the basis of infrared spectra alone, mononuclear titanyl species are rare. The most likely compounds and their possible

Table VII

Infrared absorption frequencies (cm^{-1}) in nujol mull of bis(8-quinolinolato) titanium(IV) complexes

8-Quinolinol	Product A	Product B	Product C	Product D	Product E	Possible assignments
3350b,m	3350m	3450m	3400m,b	3460m,b	3425m	OH str.
2900*b,vs	2950*b,vs	2950*b,vs	2900*b,vs	2900*b,vs	2950*b,vs	
	1650v,w	1640w	1670w	1650m 1640m	1650w	
	1600v,w	1600m	1600m	1600m	1600m	OH bend?
1582s	1570s	1572s	1570s	1575s	1570s	C=N str.
1508vs	1490s	1500s	1495vs	1500vs	1495vs	
1466*b,vs	1450*vs	1480*vs	1450*vs	1470*vs	1470*vs	
1415s						OH in-plane def
1377*s	1370*vs	1370*vs	1370*vs	1375*vs	1375*vs	
	1317s	1322vs	1317vs	1317vs	1320vs	
1291sh	1267s					
1279vs	1270s	1275s	1260s	1267s	1265s	Benzene and pyridine ring vibration
1288vs	1225w	1228m	1225m	1225w	1220w	
1205vs,b						
1176sh	1175w	1170w	1170m	1175w	1175w	
1166s						
1139s						
1094s	1100s	1100vs	1100vs	1100vs	1100vs	C-O str.
1061s		1050w	1050w			
	1025w	1028w	1028m	1025w	1025w	
975s						
898s						O-H out of plane def.
867m		884s	860w			
821b,s	820vb,vs	839vb,vs	820vb,vs	820vb,vs	833vb,s	Ti-O-Ti str.
808sh	805sh	805sh		805sh	805sh	
785b,s	790sh	782s	780s	780m	780m	
743b,s	735vb,s	730vb,vs	740vb,vs	735vb,vs	733vb,s	Ti-O-Ti str.
711b,s						

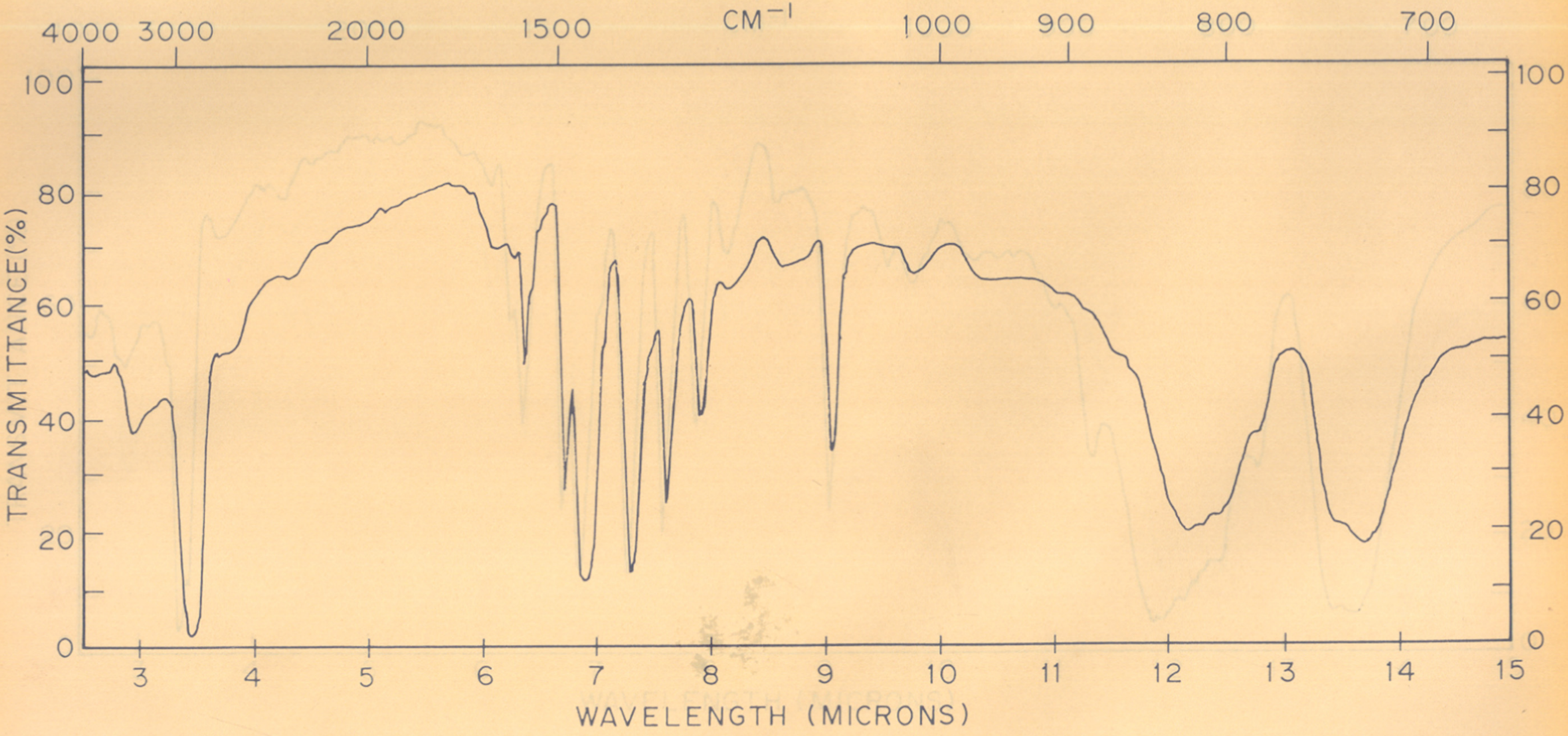


FIG. 25. IR SPECTRUM IN NUJOL MULL OF PRODUCT A.

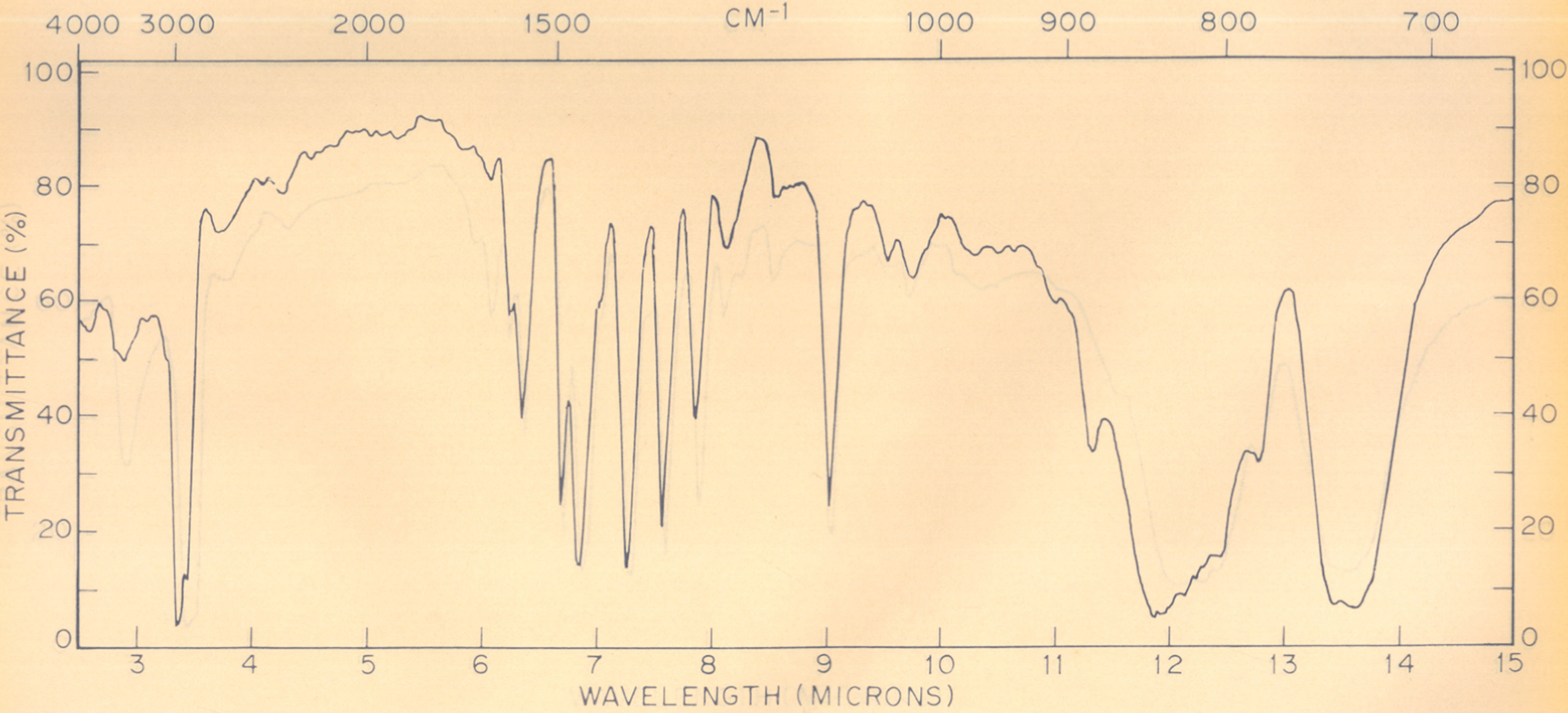


FIG. 26. IR SPECTRUM IN NUJOL MULL OF PRODUCT B.

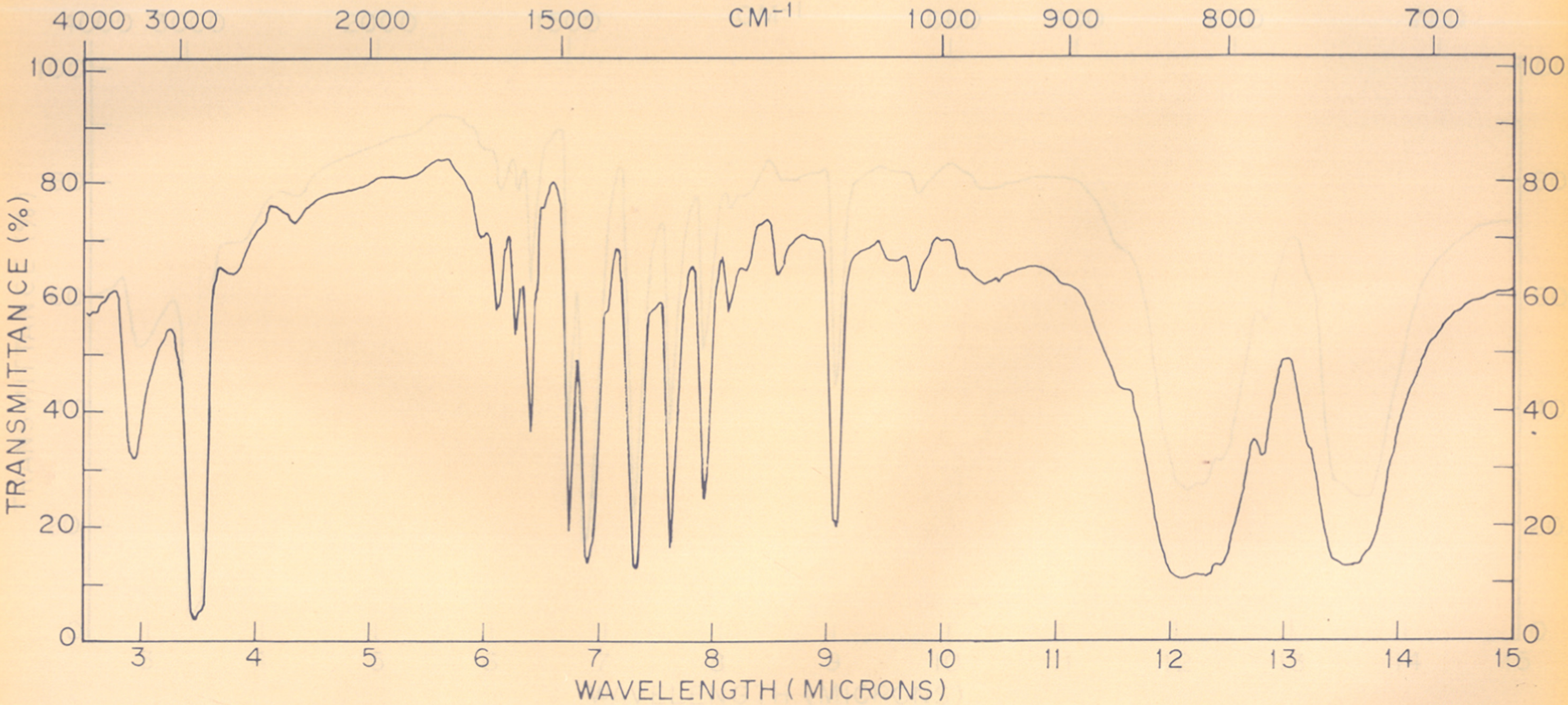


FIG. 27. IR SPECTRUM IN NUJOL MULL OF PRODUCT C.

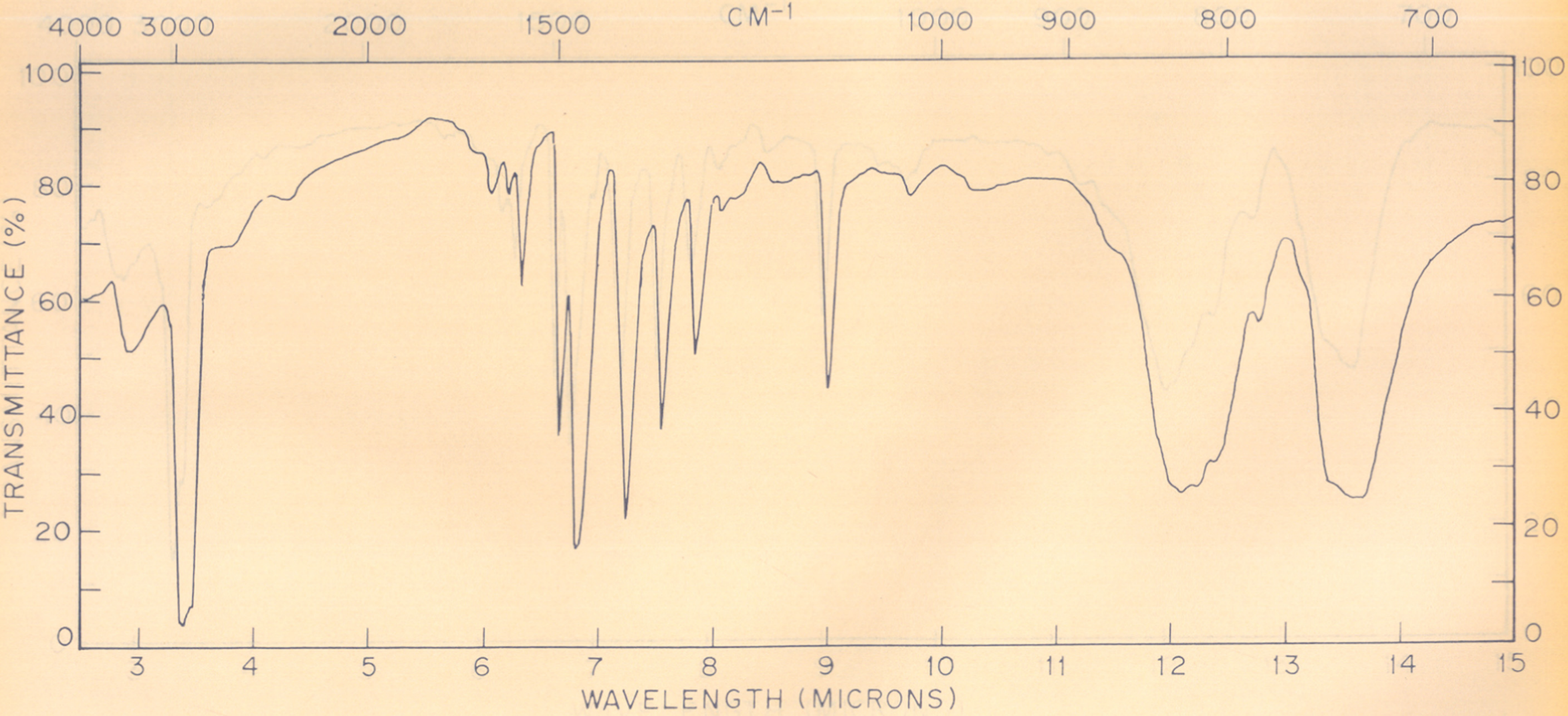


FIG. 28. IR SPECTRUM IN NUJOL MULL OF PRODUCT D.

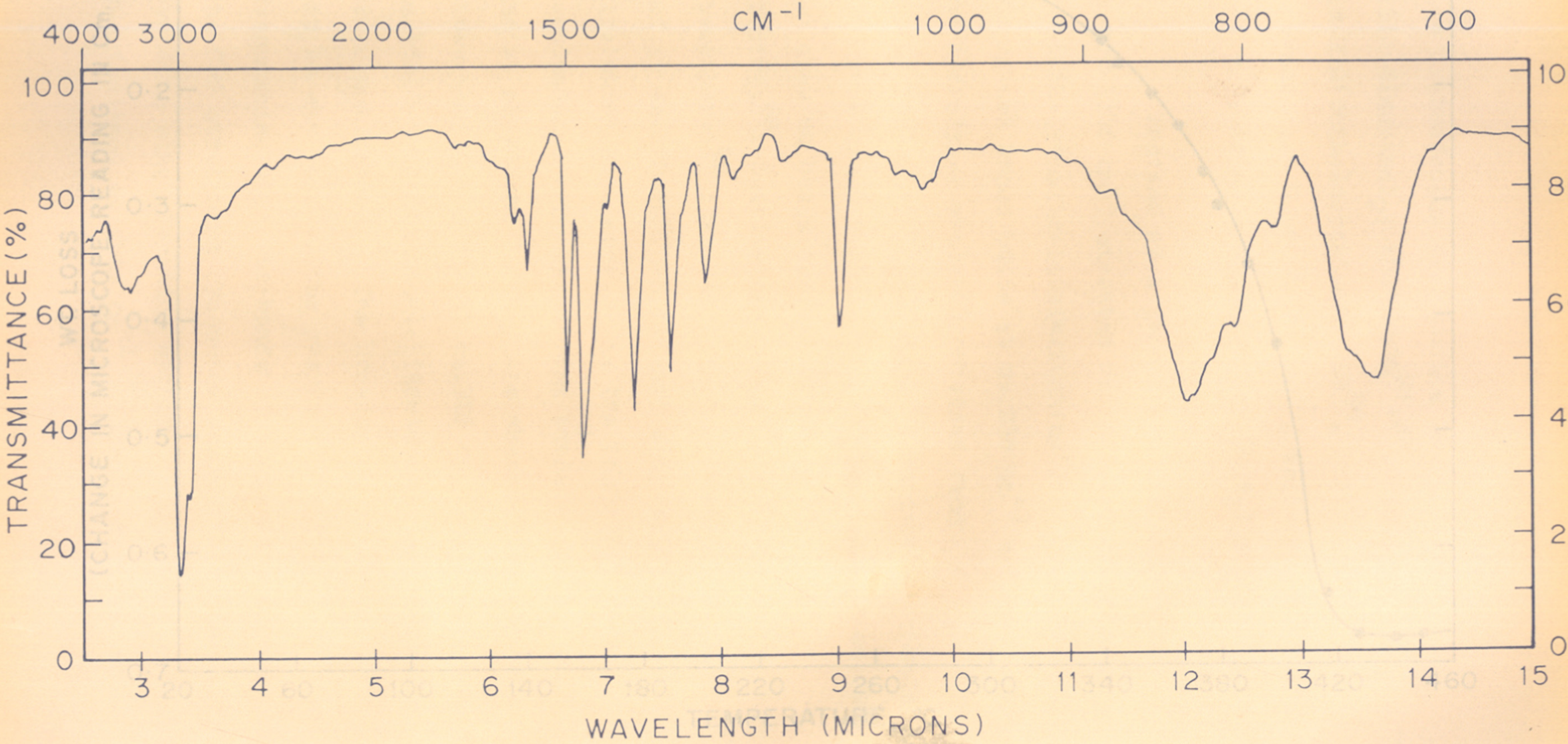


FIG. 29. IR SPECTRUM IN NUJOL MULL OF PRODUCT E.

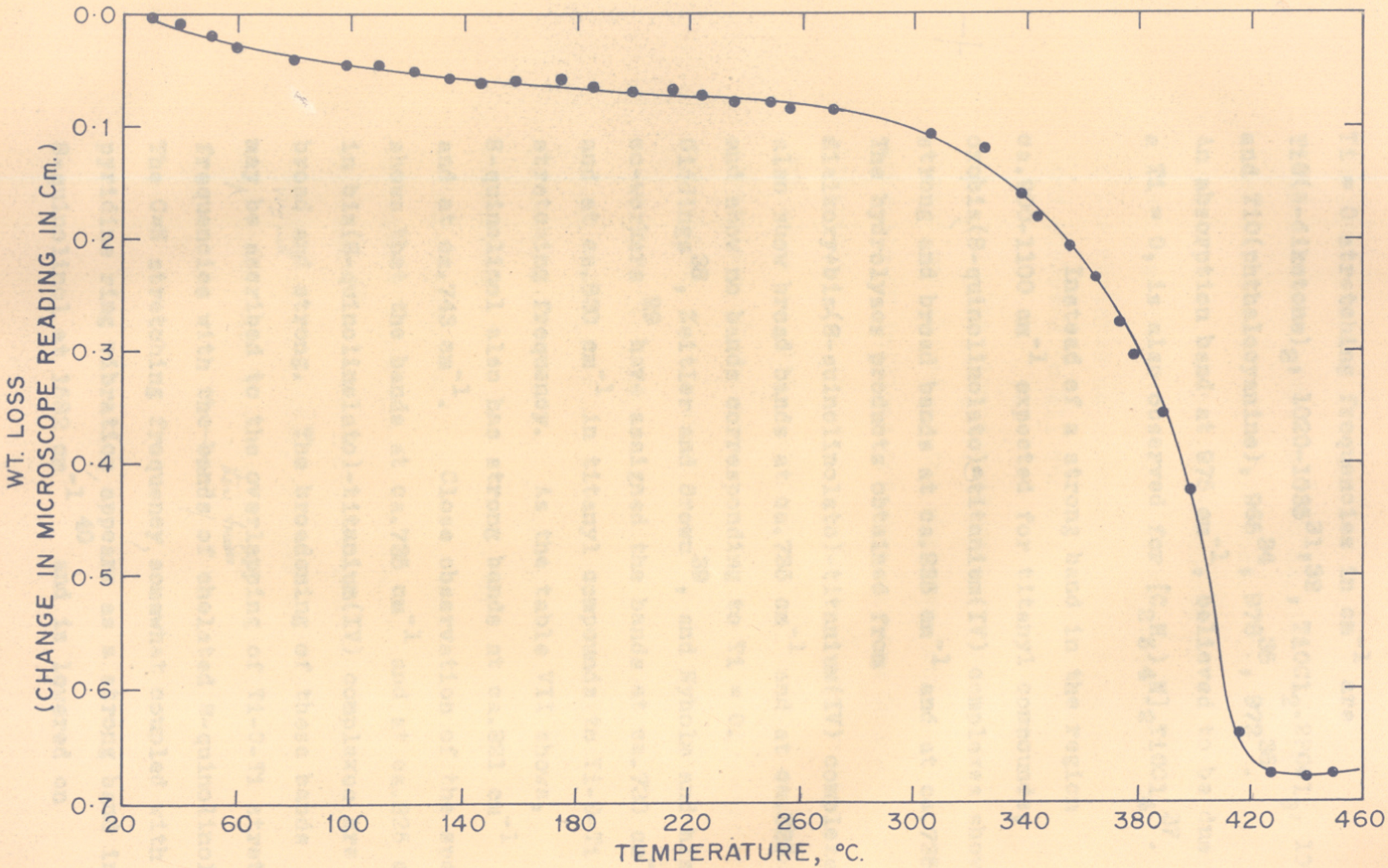


FIG. 30. THERMOGRAM FOR THE HYDROLYSIS PRODUCT OF DIALKOXYBIS-(8-QUINOLINOLATO) TITANIUM (IV). (PRODUCT E).

Ti = O stretching frequencies in cm^{-1} are $TiO(\beta\text{-diketone})_2$, 1020-1035[31,32], $TiOCl_2.2POCl_3$, 1078[33], and TiO(phthalocyanine), 965[34], 978[35], 972[36]. An absorption band at 975 cm^{-1}, believed to be due to a Ti = O, is also observed for $[(C_2H_5)_4N]_2TiOCl_4$[37].

Instead of a strong band in the region ca.900-1100 cm^{-1} expected for titanyl compounds, oxobis(8-quinolinolato)-titanium(IV) complexes show strong and broad bands at ca.825 cm^{-1} and at ca.735 cm^{-1}. The hydrolyses products obtained from dialkoxy-bis(8-quinolinolato)-titanium(IV) complexes also show broad bands at ca.735 cm^{-1} and at ca.825 cm^{-1} and show no bands corresponding to Ti = O. Giddings[38], Zeitler and Brown[39], and Nyholm and his co-workers [29] have assigned the bands at ca.730 cm^{-1} and at ca.830 cm^{-1} in titanyl compounds to Ti-O-Ti stretching frequency. As the table VII shows, 8-quinolinol also has strong bands at ca.821 cm^{-1} and at ca.743 cm^{-1}. Close observation of the spectra, however, shows that the bands at ca.735 cm^{-1} and at ca.825 cm^{-1} in bis(8-quinolinolato)-titanium(IV) complexes are more broad and strong. The broadening of these bands may very well be ascribed to the overlapping of Ti-O-Ti stretching frequencies with ~~the bands~~ those ~~bands~~ of chelated 8-quinolinol. The C=N stretching frequency, somewhat coupled with pyridine ring vibration, appears as a strong band in 8-quinolinol at 1582 cm^{-1} [40] and is lowered on chelation to ca.1570 cm^{-1}. The other bands in the region from ca.1470 cm^{-1} to ca.1600 cm^{-1} arise mainly from C=C stretching vibrations. The C-O stretching frequency at C-O-M site discussed by some investigators[16] is shifted from 1094 cm^{-1} in the ligand to 1100 cm^{-1} in the chelates as expected. This is a characteristic band observed in all chelates of 8-quinolinol.

The strong band present at 1415 cm^{-1} in the ligand and absent in the chelates, can be assigned to the phenolic OH in-plane deformation, the OH out-of-plane deformation is apparent at 898 cm^{-1} in the ligand. The bands at 1279, 1166, 1139 cm^{-1} are characteristic vibrations of the ligand. Similar characteristic vibrations are observed for substituted pyridine ring[41].

The absorption band at ca.1600 cm^{-1} present in all the bis-(8-quinolinolato)-titanium(IV) compounds, however, cannot be assigned unequivocally to OH bending vibration, since this absorption band is present in the infrared spectrum (Fig.31) of dichloro-bis(8-quinolinolato)-titanium(IV) prepared according to the method described by Frazer[42]. The infrared spectra of 8-quinolinolato chelates of aluminium, gallium and indium also exhibit this absorption band at ca.1600 cm^{-1} [43].

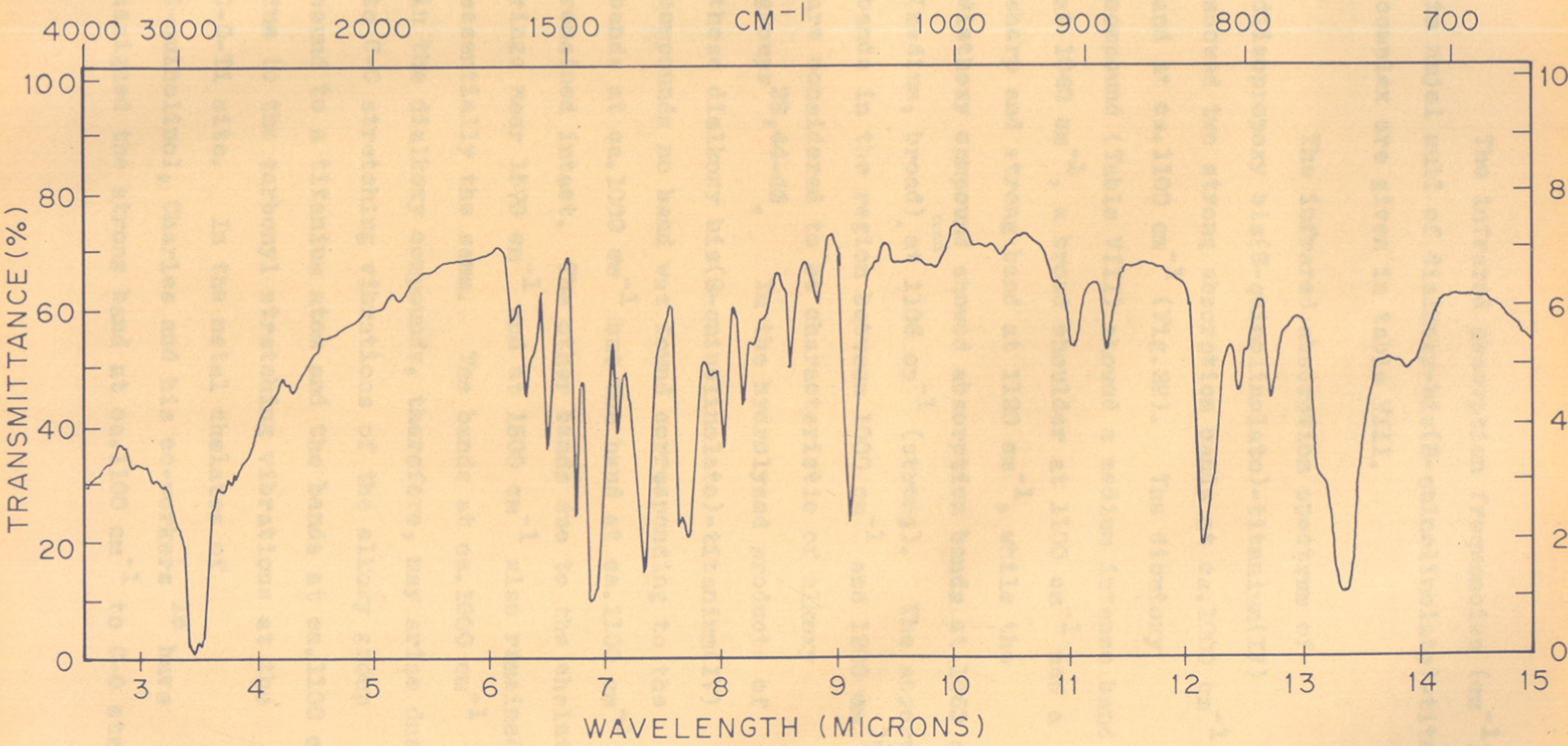


FIG. 31. IR SPECTRUM IN NUJOL MULL OF DICHLOROBIS-(8-QUINOLINOLATO) TITANIUM (IV).

The infrared absorption frequencies (cm^{-1}) in nujol mull of dialkoxy-bis(8-quinolinolato)-titanium(IV) complex are given in table VIII.

The infrared absorption spectrum of diisopropoxy bis(8-quinolinolato)-titanium(IV) showed two strong absorption bands at ca.1000 cm^{-1} and at ca.1100 cm^{-1} (Fig.32). The dibutoxy compound (Table VIII) showed a medium intense band at 1040 cm^{-1}, a broad shoulder at 1100 cm^{-1} and a sharp and strong band at 1120 cm^{-1}, while the diethoxy compound showed absorption bands at 1060 cm^{-1} (medium, broad) and at 1106 cm^{-1} (strong). The absorption bands in the region between 1000 cm^{-1} and 1200 cm^{-1} are considered to be characteristic of alkoxy groups[28,44-46]. In the hydrolysed products of these dialkoxy bis(8-quinolinolato)-titanium(IV) compounds, no band was found corresponding to the bands at ca.1000 cm^{-1} but the band at ca.1100 cm^{-1} remained intact. The other bands due to the chelate rings near 1570 cm^{-1} and at 1500 cm^{-1} also remained essentially the same. The bands at ca.1000 cm^{-1} in the dialkoxy compounds, therefore, may arise due to C-O stretching vibrations of the alkoxy group bound to a titanium atom and the bands at ca.1100 cm^{-1} due to the carbonyl stretching vibrations at the C-O-Ti site. In the metal chelates of 8-quinolinol, Charles and his co-workers [16] have assigned the strong band at ca.1100 cm^{-1} to C-O stretching

Table VIII

Infrared absorption frequencies (cm^{-1}) in nujol mull of dialkoxy-bis(8-quinolinolato)-titanium(IV) complexes

$Ti(OC_2H_5)_2(OX)_2$	$Ti(OC_3H_7)_2(OX)_2$	$Ti(OC_4H_9)_2(Ox)_2$
2900*b,vs	2900*b,vs	2900*b,vs
1570s	1590w	1590s
	1570s	
1500s	1500s	1520s
1450*s	1450*s	1480*s
1367*s	1367*s	1380*s
1317s	1317s	1340s
1267m	1267s	1280s
	1217m	1240m
		1180m
	1136s	
1106s	1124s	1120s
	1100s	1100sh
	1050w	
1060b,m	1010sh	1040m
	1000s	
975w		980w
915m	850s	905w
825m	835m	835s
	820s	
	810m	815m
780m	795w	800b,m
	790m	
	775w	
745b,m	740b,s	750b,m
720b,m	720sh	

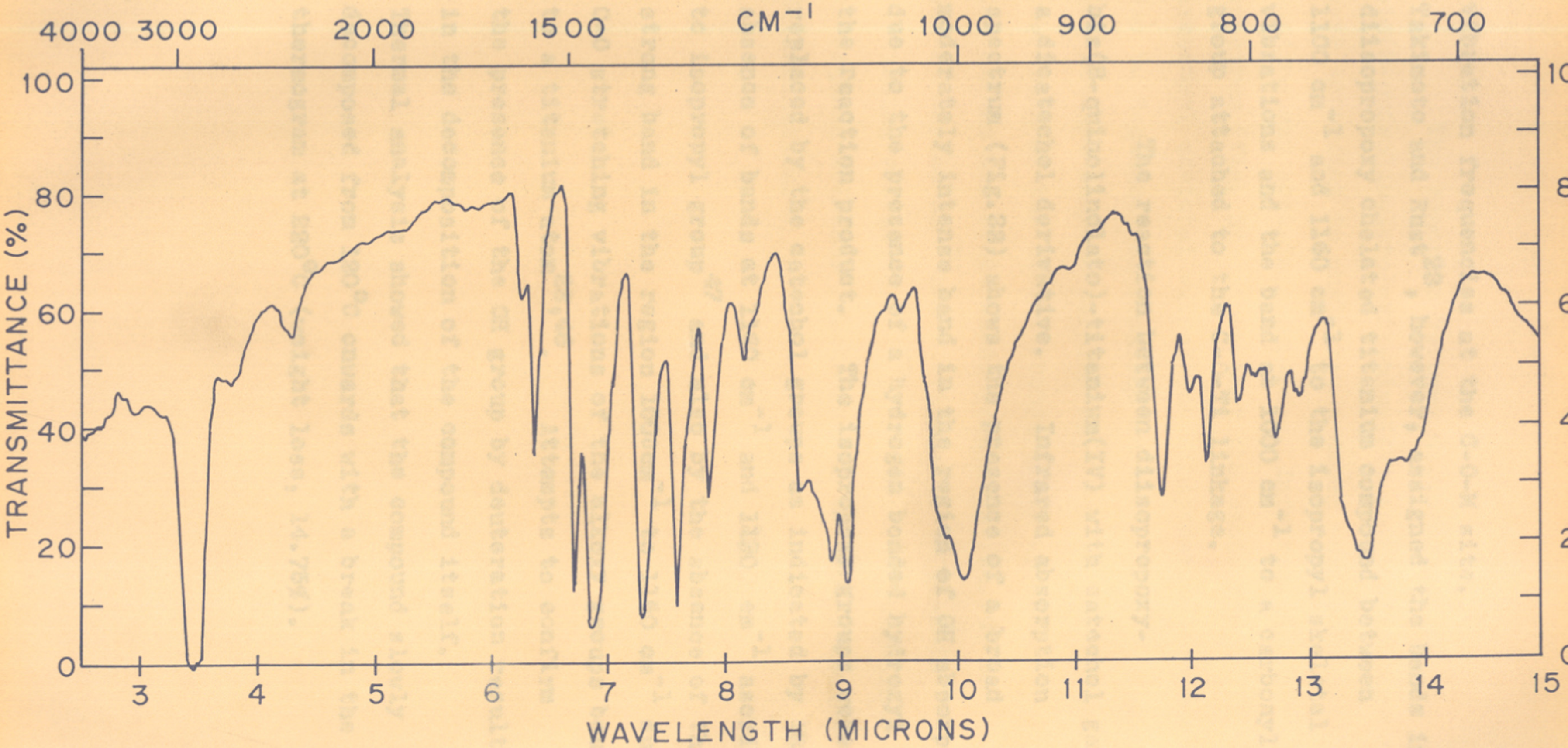


FIG. 32. IR SPECTRUM IN NUJOL MULL OF DIISOPROPOXYBIS-(8-QUINOLINOLATO) TITANIUM (IV).

vibration frequencies at the C-O-M site. Takimoto and Rust[23], however, assigned the bands in diisopropoxy chelated titanium compound between 1100 cm^{-1} and 1160 cm^{-1} to the isopropyl skeletal vibrations and the band at 1000 cm^{-1} to a carbonyl group attached to the C-O-Ti linkage.

The reaction between diisopropoxy-bis(8-quinolinolato)-titanium(IV) with catechol gave a dicatechol derivative. Infrared absorption spectrum (Fig.33) shows the presence of a broad moderately intense band in the region of OH absorption due to the presence of a hydrogen bonded hydroxyl in the reaction product. The isopropoxy groups were replaced by the catechol groups as indicated by the absence of bands at 1160 cm^{-1} and 1130 cm^{-1} ascribable to isopropyl group[47] and also by the absence of the strong band in the region 1000cm^{-1} to 1150 cm^{-1} due to C-O stretching vibrations of the alkoxy groups bound to a titanium atom[28,46]. Attempts to confirm the presence of the OH group by deuteration resulted in the decomposition of the compound itself. Thermal analysis showed that the compound slowly decomposed from 120°C onwards with a break in the thermogram at 220°C (weight loss, 14.75%).

The reaction between diisopropoxy bis(8-quinolinolato)-titanium(IV) and acetic anhydride gave according to analysis, a dimer having Ti-O-Ti bonding and acetate groups. Infrared spectrum (fig. 34) shows that the bands due to isopropyl skeletal vibrations disappeared, and those due to 8-quinolinol remained in tact. However, a new intense band at ca.1725 cm^{-1} due to the stretching vibration of the free carbonyl group appeared. The strong and broad bands present at ca.740 cm^{-1} and at ca.820 cm^{-1} are attributable to Ti-O-Ti stretching vibrations[29,38]. The Its low solubility in organic solvents precluded ~~its~~ molecular weight determination. of the compound

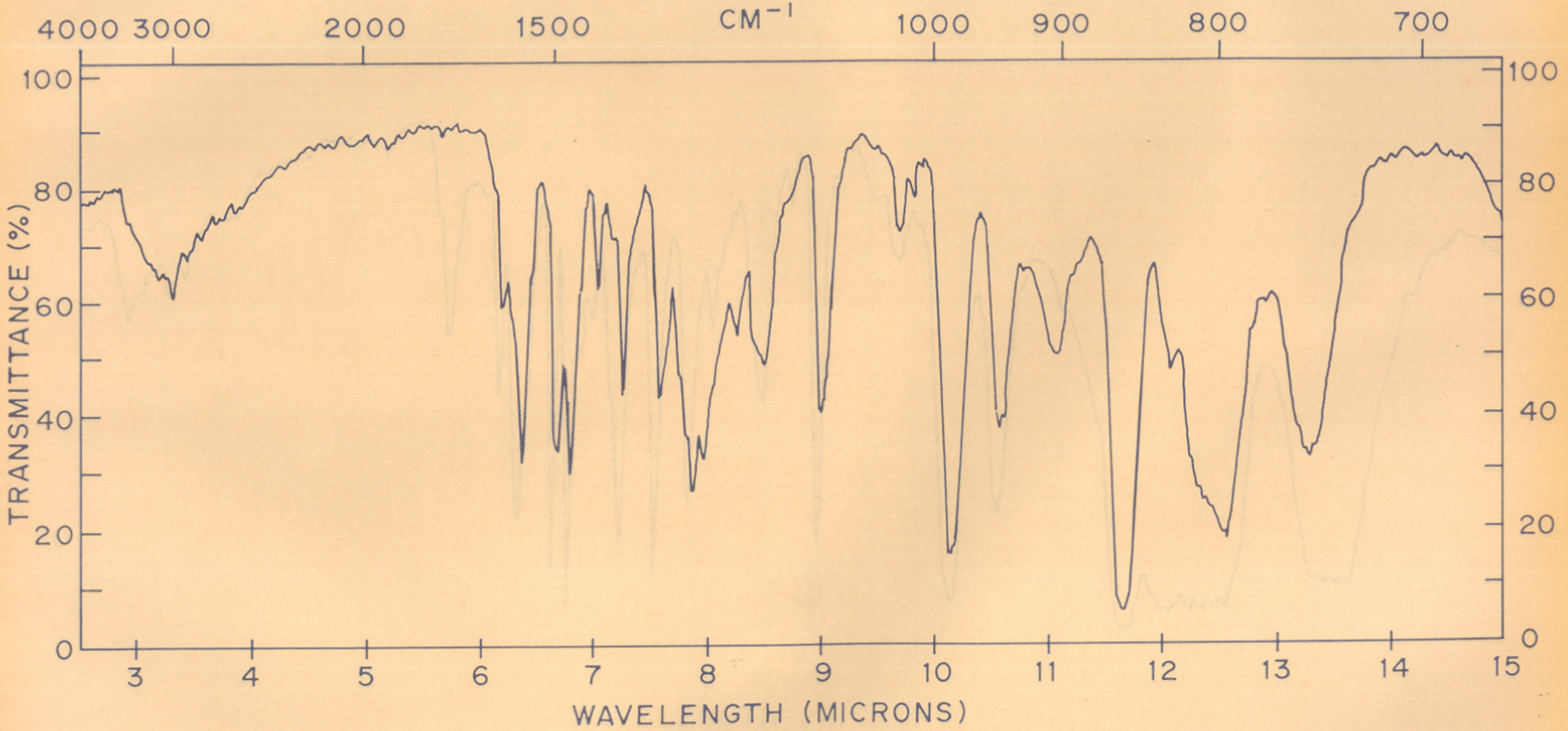


FIG. 33. IR SPECTRUM IN HEXACHLOROBUTADIENE, OF THE REACTION PRODUCT BETWEEN DIISOPROPOXYBIS (8-QUINOLINOLATO) TITANIUM (IV) AND CATECHOL.

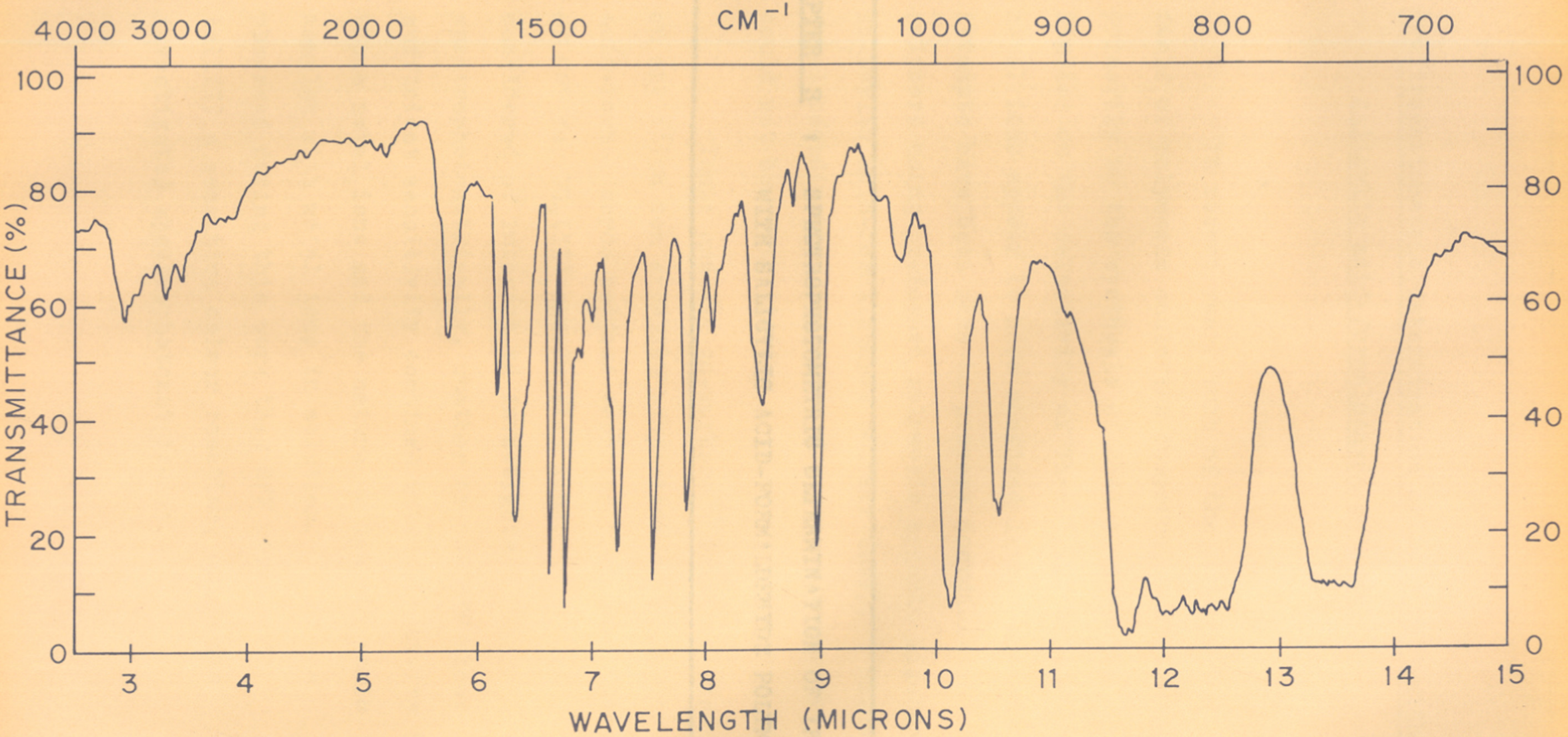


FIG. 34. IR SPECTRUM IN HEXACHLOROBUTADIENE, OF THE REACTION PRODUCT BETWEEN DIISOPROPOXYBIS (8-QUINOLINOLATO) TITANIUM (IV) AND ACETIC ANHYDRIDE.

CHAPTER 3 : SPECTROPHOTOMETRIC DETERMINATION OF IRON(III) WITH SALICYLIC ACID-FORMALDEHYDE POLYMER

Spectrophotometric determination of iron(III) with salicylic acid-formaldehyde polymers

In recent years much of the work in the field of polymeric chelating compounds was directed primarily to the synthesis of chelating resins[48]. Studies on the selectivity of these ligands towards metal ions appear to have received little attention. Attempts have been made to prepare coordination polymers using preformed polymeric organic ligands, e.g. salicylic acid-formaldehyde polymer (SFP). However, metal coordination polymers of reasonable purity could not be synthesised.

Tomic and his co-workers[49] in their study on chelation ion exchange properties of salicylic acid-formaldehyde polymer reported high selectivity of SFP for UO_2(II) and Fe(III) ions. It was considered of interest to investigate spectrophotometrically, whether or not SFP shows sufficient sensitivity combined with selectivity towards these metal ions and the nature of the polymeric complex with metal ions in solution. It was observed during this work that SFP gives with Fe(III) a sensitive colour reaction, which was investigated spectrophotometrically.

EXPERIMENTAL

The absorption measurements were made with Hilger's UVISPEK spectrophotometer. A Beckman model G pH meter was used for pH measurements. A pair of 1 cm. matched glass cells was used for all measurements. The reference cell contained distilled water except for the measurements of absorption spectrum of the complex in which case an appropriate blank was used whose preparation and composition were identical with the complex except that the metal was missing. All measurements were made at room temperature.

Salicylic acid-formaldehyde polymer was prepared according to the procedure described by Tomic and his co-workers[50]. A 0.5% reagent solution (prepared by dissolving in 1N sodium hydroxide solution) was employed in these investigations. The reagent solution has an yellow colour with absorption maximum at 306 mμ in the alkaline range (pH 7.0 and above) but in the pH range 4.3 - 7.0 it was colourless. In strongly acid solutions the reagent gets precipitated.

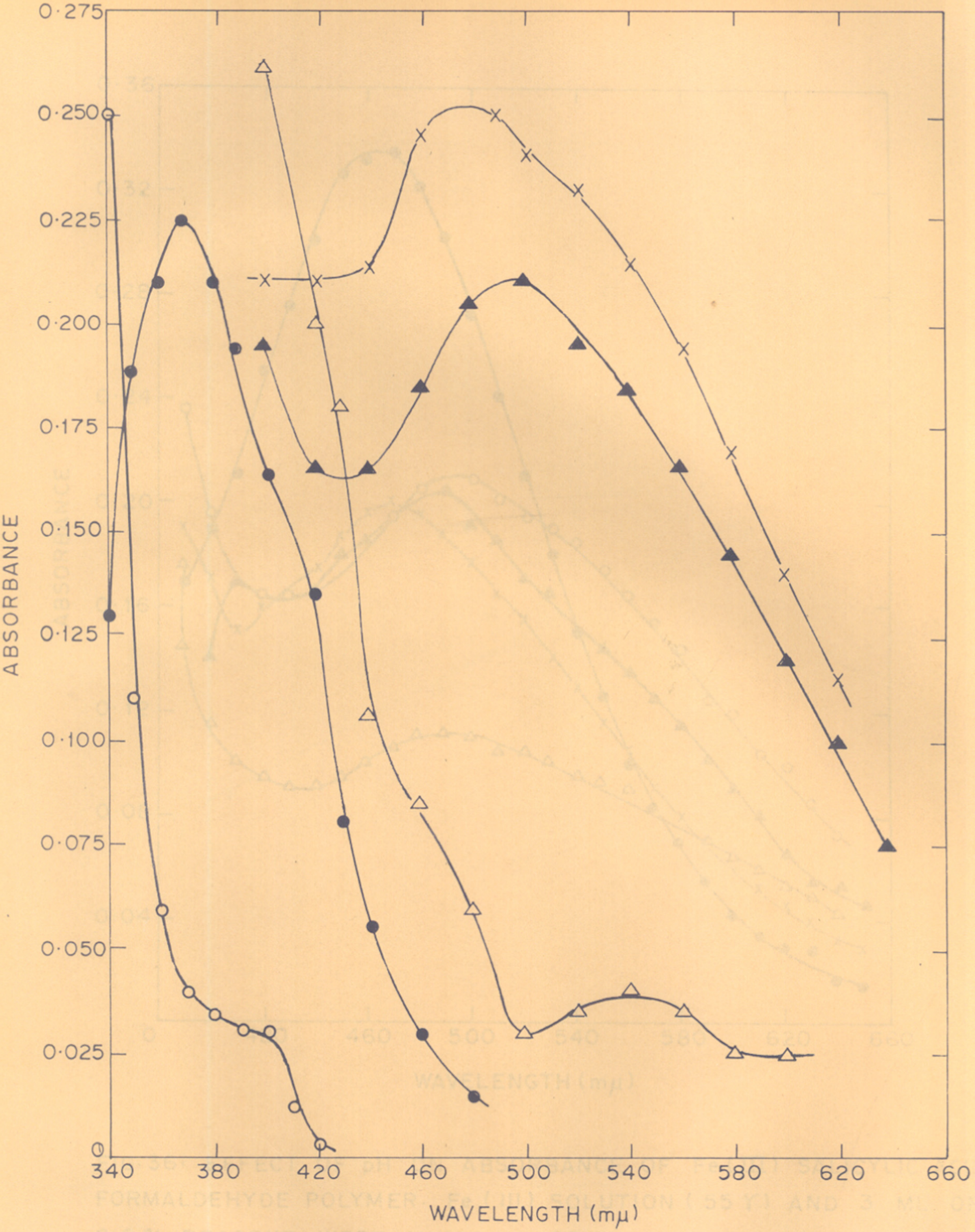
Standard Fe(III) solution A stock solution of iron(III) was prepared by dissolving A.R. $FeCl_3.6H_2O$ in distilled water containing hydrochloric acid. The Fe(III) content was determined gravimetrically using standard procedures[51]. This solution contained 5.28 mg/ml. of Fe(III). Working solutions were prepared from this stock solution by dilution with water containing hydrochloric acid.

Results and Discussion

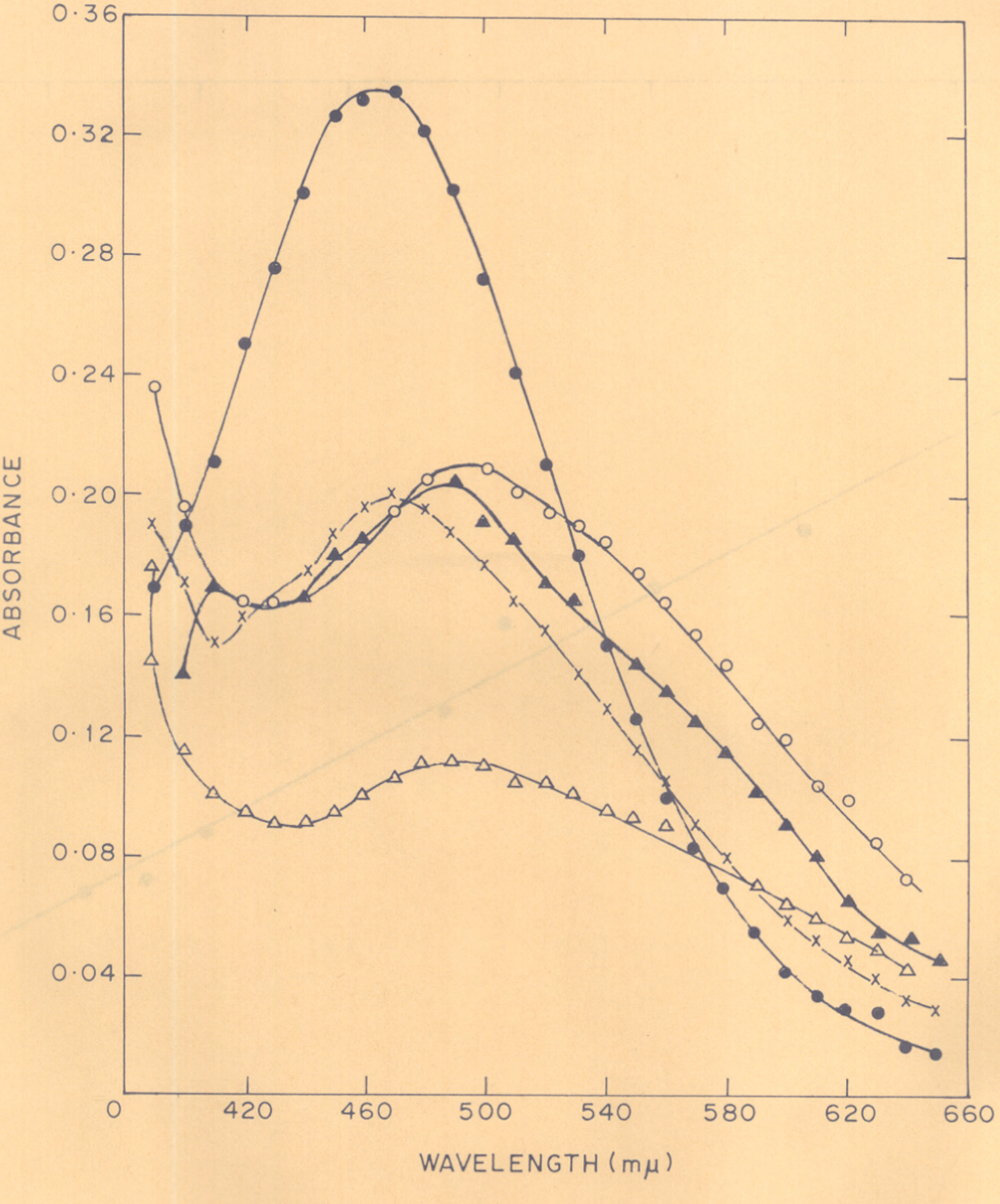
Salicylic acid-formaldehyde polymer reacts with several metals in acid or alkaline medium. The colours produced with Pd(II), Cu(II), Mn(II), UO_2(II), Mo(VI) and Re(VII), however, were not sensitive enough to utilise this ligand for spectrophotometric determinations of these metals. Only iron and titanium gave sensitive stable colour reactions. Figure (35) shows the absorption spectra of some of these metal chelate polymers in solution.

Many of the spectrophotometric reagents proposed for Fe(III) generally have the disadvantage that they cannot be used in the presence of appreciable amounts of fluoride[52]. SFP forms a stable violetish-pink colour with Fe(III) in the pH range 5.0 - 5.6 with absorbance maximum at 500 mμ. The reagent solution at this pH range and wave length has no absorption. The violetish-pink colour, however, was found to change with change in pH of the solution. At pH 10.0 an orange colour with absorption maximum at 470 mμ was formed. The effect of pH on the absorbance of the solution is shown in figure (36).

The plot of absorbance versus iron concentration in the range 2 γ - 40 γ is linear, indicating that Beer's law is applicable in this concentration range. (Fig.37). The sensitivity of the spectrophotometric determination of Fe(III) with SFP was of the order of 0.2 γ/ml.

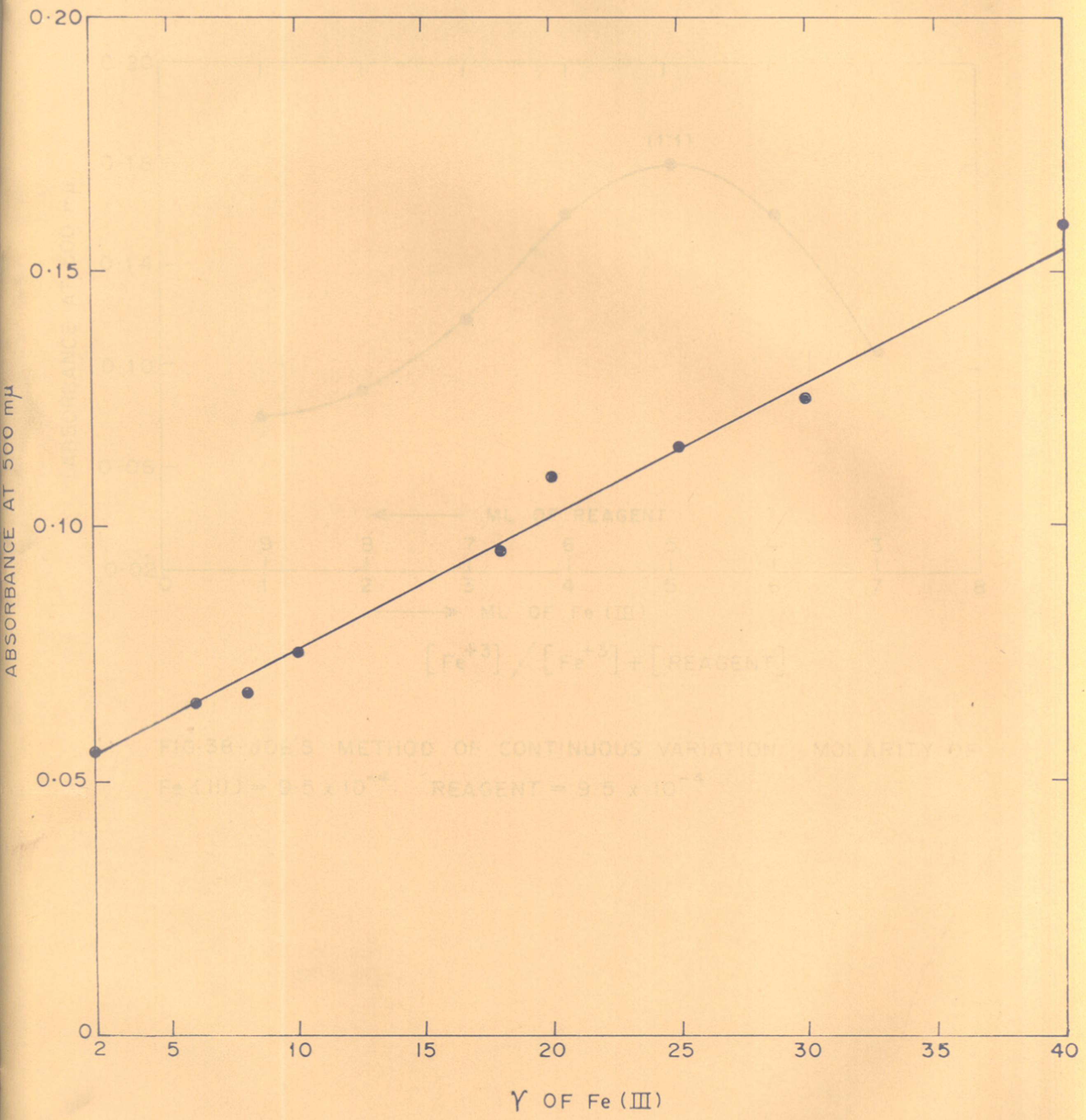


FIG·35· ABSORPTION SPECTRA OF METAL–SALICYLIC ACID–FORMALDEHYDE POLYMERS AT pH 5·5· ×——× Fe (II)–SFP AGAINST REAGENT BLANK· ▲——▲ Fe (III)–SFP AGAINST REAGENT BLANK. △——△ Cu (II)–SFP AGAINST REAGENT BLANK. ●——● Ti (IV)–SFP AGAINST REAGENT BLANK· ○——○ REAGENT AGAINST WATER BLANK·

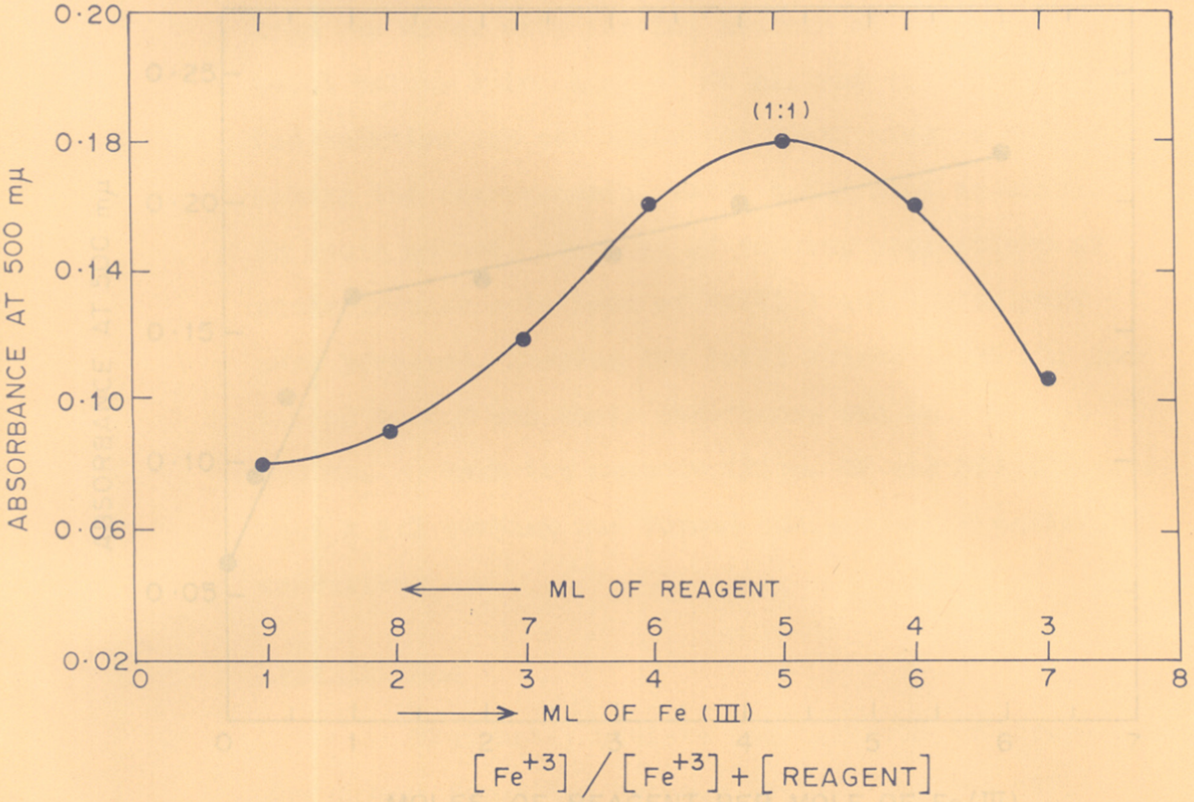


FIG·36· EFFECT OF pH ON ABSORBANCE OF Fe(III) SALICYLIC ACID-FORMALDEHYDE POLYMER· Fe(III) SOLUTION (55 γ) AND 3 ML OF 0·5 % REAGENT WERE MIXED IN 25 ML FLASK AT VARIOUS pHs.

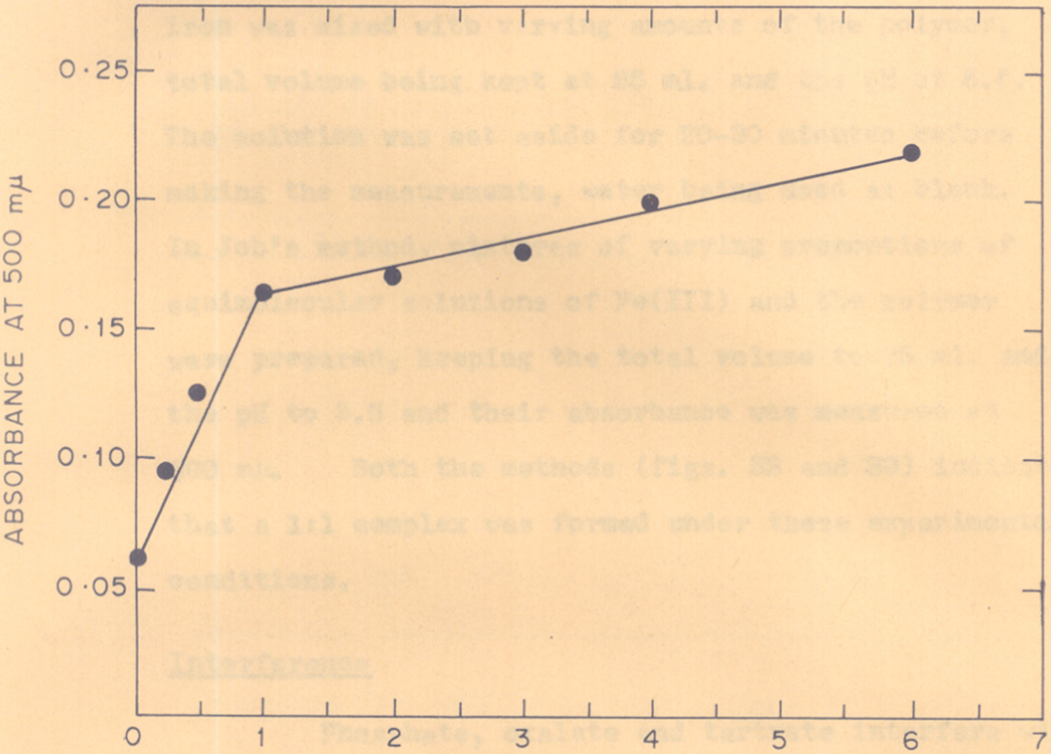
△——△ 4·8 ; ○——○ 5·6 ; ▲——▲ 7·0 ; ×——× 8·8 ; ●——● 11·0·



FIG·37· ABSORPTION–CONCENTRATION CURVE



FIG·38· JOB'S METHOD OF CONTINUOUS VARIATION· MOLARITY OF Fe (III) = $9{\cdot}5 \times 10^{-4}$· REAGENT = $9{\cdot}5 \times 10^{-4}$



MOLES OF REAGENT PER MOLE OF Fe(III)

FIG·39· MOLE RATIO METHOD· MOLARITY OF THE SOLUTIONS= $4·75 \times 10^{-3}$

The composition of the polymeric chelate was investigated by the mole ratio method[53] and by Job's method[54]. In the former method one mole of iron was mixed with varying amounts of the polymer, total volume being kept at 25 ml. and the pH at 5.5. The solution was set aside for 20-30 minutes before making the measurements, water being used as blank. In Job's method, mixtures of varying proportions of equimolecular solutions of Fe(III) and the polymer were prepared, keeping the total volume to 25 ml. and the pH to 5.5 and their absorbance was measured at 500 mμ. Both the methods (figs. 38 and 39) indicate that a 1:1 complex was formed under these experimental conditions.

Interference

Phosphate, oxalate and tartrate interfere with the colour formation between Fe(III) and the SFP. Amongst cations, Al(III), Cr(III), Ce(IV), Zr(IV), Th(IV), V(V), Cu(II), Ni(II), Ti(IV) and Fe(II) interfere.

Fluoride is tolerated upto 40 mg as indicated in table IX.

Table IX

Effect of fluoride on the colour intensity of SFP and Fe(III) solutions

(50 γ of Fe(III), 0.5 ml of 0.5%, reagent and varying amounts of hydrofluoric acid in a final volume of 25 ml. and at pH 5.5).

Fluoride (mg)	Optical density at 500 mμ
0	0.185
5	0.185
10	0.185
20	0.185
40	0.183
60	0.097

Procedure for Fe(III) determination

For the estimation of Fe(III) in trace quantities a solution approximately containing 2 γ - 40 γ is taken in a flask (10 ml.). A 0.5% reagent solution (0.5 ml.) is added and the pH adjusted to 5.5. The absorbance of the solution is measured at 500 mμ. Fe(III) present can be then read from the calibrated graph.

SUMMARY

SUMMARY

Review of the literature revealed that work carried out on acetoacetanilide is very meagre. The only reported compound of the ligand seems to be its copper complex. In the present work acetoacetanilide chelates of beryllium(II), chromium(III), aluminium(III) and iron(III) have been prepared and characterised. The salient features of the infrared spectra, in the NaCl prism region, of acetoacetanilide and its chelates with Cu(II), Be(II), Cr(III), Al(III) and Fe(III) have been discussed by comparison with spectra of deuterated acetoacetanilide and deuterated beryllium and copper acetoacetanilides.

The analyses of the keto and amide bands in acetoacetanilide and its deuterated product in solid as well as in solution, show that it exists largely in the diketo form. By comparison with the spectra of the ligand the coordination of the metal ion in these chelates is concluded to be through the two carbonyl groups. The NH stretching mode as well as the amide II and III bands were found to be very little affected on chelation.

Infrared spectra of some metal chelates of acetoacetanilide in the region 700 cm^{-1} - 400 cm^{-1} using

CsBr prism also have been examined. The metal oxygen stretching vibrational modes have been found in the 400 cm^{-1} - 500 cm^{-1} region in all these chelates.

Cis- and trans-isomers of the inert complex, tris-(acetoacetanilidato)-chromium(III) have been separated, utilizing solubility differences in benzene and column chromatography on acid washed alumina and also by thin layer chromatography using acetone-benzene (1:1) solvent mixture. TGA of the compounds revealed that the trans-isomer is thermally more stable than the cis-compound.

Attempts were made to demonstrate the quasiaromaticity of chelated acetoacetanilide by the isolation of nitro acetoacetanilides of beryllium(II), chromium(III) and aluminium(III). Based on the analytical data the nitration products isolated after purification have been formulated as bis-(γ-nitroacetoacetanilidato)-beryllium(II), tris-(γ-nitroacetoacetanilidato)-chromium(III) and mono-(acetoacetanilidato)-bis-(γ-nitroacetoacetanilidato)-aluminium(III). Although the physical measurements of these nitration products did not give very good concordance with the expected result, it is believed that nitration does take place. TLC of these products, however, did not show any separation into two or more spots.

Three types of acetoacetanilide chelates of titanium(IV) have been isolated - the trichloro mono-(acetoacetanilidato)-titanium(IV), dichloro-bis-(acetoacetanilidato)-titanium(IV) and the monochloro-tris-(acetoacetanilidato)-titanium(IV). The monobromo- and the monoiodo-tris-(acetoacetanilidato)-titanium(IV) chelates have been also isolated. However, analytical data indicated that the monoiodo compound contained one molecule of solvated HI. To clarify this point thermogravimetric study of these monohalogeno-tris-(acetoacetanilidato)-titanium(IV) complexes has been carried out. Infrared spectral evidence implies a coordination number of seven for titanium in these mono halogeno tris-(acetoacetanilidato)-titanium(IV) complexes.

Addition compounds of titanium(IV) halides with acetoacetanilide of the type $TiX_4.3HacacN$, where X=Cl, or Br have been prepared and attempts to isolate the corresponding monohalogenotris-(acetoacetanilidato)-titanium(IV) chelates, by heating the addition compounds have been made. Only the monochlorotris-(acetoacetanilidato)-titanium(IV) chelate could be obtained in this way.

Chelate polymers of bis-(8-hydroxy-5-quinolyl)-methane with titanium(IV), tin(IV) and zirconium(IV) have been synthesised. Zirconium polymer with

8,8'-dihydroxy-5,5'-biquinolyl and titanium polymer with purpurin have been also isolated. The thermal stabilities of these polymers have been evaluated in air in the temperature range 25°- 500°C.

Titanoxane polymers have been prepared by the (controlled) hydrolysis of dialkoxy-bis-(8-quinolinolato)-titanium(IV) and also by the hydrolysis of the reaction product of titanium tetrachloride and 8-quinolinol. The reactions of diisopropoxy-bis-(8-quinolinolato)-titanium(IV) with catechol, and acetic anhydride have been also carried out.

A sensitive method for the determination of microgram quantities of iron(III) in the presence of moderate amounts of fluoride has been evolved. The method is based on the formation of violetish-pink colour between salicylic acid - formaldehyde polymer and iron(III) in solution.

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