
C H A P T E R - I I I

ACETYLACETONATE PRECURSOR ROUTE
IN CERAMIC PREPARATIONS

CHAPTER - III

ACETYLACETONATE PRECURSOR ROUTE IN CERAMIC PREPARATIONS

3.1 INTRODUCTION

It has been pointed in the previous chapter that the major difficulty in direct synthesis by ceramic route is the unavoidable occurrence of alkaline earth carbonates as starting materials or intermediate in thermal decomposition of the carboxylates. This is because of the fact that alkaline earth oxides absorb moisture and carbon dioxide from the atmosphere or form peroxide in variable amounts depending on the thermal treatment in oxide synthesis. Obviously search for well characterizable compounds of the constituent metals must be continued till we get suitable precursor which can be prepared in pure form and on thermal treatment yields an oxide without passing through an intermediate carbonate stage. Acetylacetonate has been chosen in the present study as the candidate ligand for this purpose.

3.2 GENERAL CHEMISTRY OF β -DIKETONES

Since the outstanding work of Urbain¹ and Werner² on β -diketone complexes, the study of metal 1,3 diketonates has been actively pursued. Many compounds of metal ions with 1,3 diketones, RCOCH_2COR , are known. Because of their chara-

characteristic properties,³ the metallic derivatives of 1,3 diketones have been found useful not only in laboratory operations but also in the development of chemical theory.

The chemistry of such compounds has focussed much interest in such diverse areas as spectral studies, solvent extraction, gas chromatography, column and thin layer chromatography, NMR shift reagents, laser technology and in polymer industry.^{4,5} Significant developments have taken place in the field of chemistry of fluorinated 1,3 diketones and their metal chelates.

3.2.1 β -Diketones

β -diketones exist in two tautomeric forms, keto and enol (Fig. 3.1).

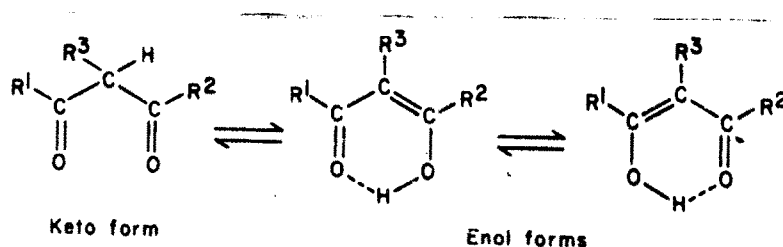


Fig. 3.1 Tautomerism of β -diketones

The hydrogen atom of the CHR^3 group is activated by the adjacent $\text{C}=\text{O}$ groups and a conjugate system can arise by a prototropic shift. The tautomerism exists in equilibrium with each other, and structurally they possess a cis-configuration and a syn-conformation. Under appropriate conditions the enolic hydrogen atom of the ligand can be replaced by

metal cation to produce a six membered chelate ring (Fig.3.2) thereby shifting the keto-enol equilibrium in favour of the enol form

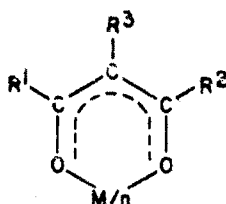


Fig. 3.2. Chelate ring

The keto enol tautomerism of different variety of β -diketones has been studied with the help of various techniques such as UV, IR Raman and N.M.R. spectroscopy, polarographic measurements, energy of enolisation and exchange with deuterium. The enolisation generally increases when the electron withdrawing group such as chlorine is substituted for the hydrogen at α position and it also increases when the ligand is fluorinated.^{6,7} In case of enol tautomer the substitution by bulky group at an α position produces the steric hindrance between F^3 and R^1 group protons. This together with inductive effect tend to decrease the enol proportion.^{8,9} In case of acetylacetone the enol % is 81.4 and the B.P. is $140^\circ\text{C}/\text{mm}$.¹⁰

3.2.2 Historical Background of Metal β -Diketonates

In case of β -diketonates their continuous flow of research work reported from 1887 to 1960. The first series of publications in the field appears to be by Combes¹¹⁻¹⁴

from 1887-1894 which describes the synthesis of acetylacetonates of sodium, magnesium, aluminium, lead, iron, cobalt, copper, nickel and beryllium. In nineteenth century the Griner,¹⁵ Curtiss¹⁶ and Urbain¹⁷⁻²⁰ described the method for the preparation of tetrakis (acetylacetonates) of thorium and cerium and hydrated tris (acetylacetonates) of lanthanum yttrium and gadolinium. During 1903-1906 Dilthey^{21,22} observed the reactions of metal halides with acetylacetonates. After four years Tanator and Kurovskii²³ described the preparation of acetylacetonates of calcium, strontium, barium, beryllium and zinc from basic salts of these elements.

Effect of electrophilic substitution in metal acetylacetonate ring was first reported in 1925. At the same time the X-ray crystallographic study was published by Sarkar.²⁴ In 1945 Calvin and Wilson²⁵ described the aromatic character of six-membered ring on the basis of stability constant measurement. Physical properties and the analytical applications was studied in 1950. During 1951-1960 X-ray crystallographic studies of iron, beryllium, copper, nickel, platinum, cerium and yttrium β -diketonates were published by various research workers.

3.2.3 Classification of Metal β -Diketonates

Metal β diketonates may be conveniently divided into four groups depending upon the mode of bonding of ligand to metal atoms as (i) oxygen-bonded; (ii) carbon bonded, (iii) both carbon and oxygen bonded and (iv) olefin bonded²⁶

Oxygen bonded β -Diketonate complexes are further divided into two groups :

- (1) β -Ketoenolates as unidentate ligands
- (2) β -Ketoenolates as bidentate ligands.

β -Ketoenolates as Bidentate Ligands

In this case the metal cation replaces the enolic hydrogen of the ligand and six-membered chelate ring is formed as shown in figure 3.3.

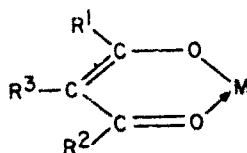


Fig. 3.3 β -ketoenolate as a bidentate ligand

Since the enolate ion carries a single negative charge, metal atom can react with one or more enolate ions to give either neutral or charged molecules, depending on the coordination number (m) and valency (n) of the central metal atom. This type of bonding gives rise to three different types of derivatives.

(1) When $m = 2n$

When the coordination number(m) of the metal ion is double the primary valence(n), the metal β diketonate so formed behaves as an inner complex or neutral molecule. The examples of this class of compounds (figure 3.4) are

$\text{Al}(\text{acac})_3$, $\text{Th}(\text{acac})_4$, $\text{Fe}(\text{acac})_3$, $\text{Be}(\text{acac})_2$. In these complexes metal atoms are coordinatively saturated. These derivatives show solubility in common organic solvents and volatility.

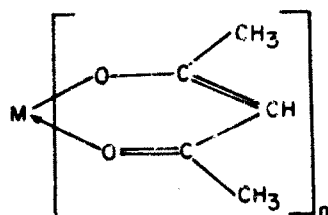


Fig. 3.4 Structure of $\text{M}(\text{acac})_n$

(2) When $m > 2n$

If the coordination number is more than double the primary valence, the molecule so formed behaves as a Lewis acid and achieves the desired coordination either by polymerization or by the adduct formation. Example of this type is metal β diketonates formed from the large bivalent ions of transition elements (Fig. 3.5). The various examples of such complexes are reported such as $\text{Ni}(\text{acac})_2 \cdot 3\text{H}_2\text{O}$, $\text{Co}(\text{acac})_2 \cdot 4\text{H}_2\text{O}$, $\text{Mn}(\text{acac})_2 \cdot \text{bipy}$, $\text{Zn}(\text{acac})_2 \cdot (\text{NH}_3)_2$.

These complexes generally behave as covalent compounds and the coordination number of the metal towards the oxygen is generally

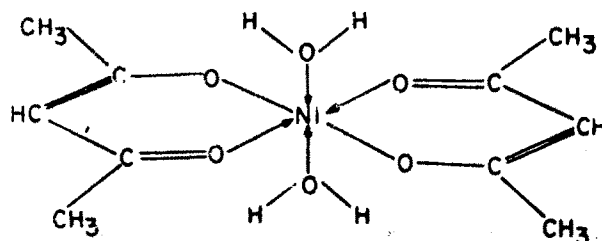
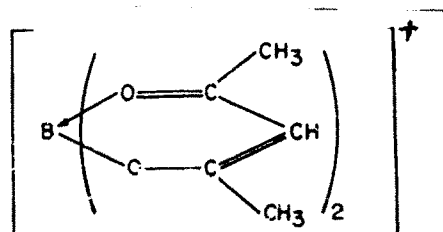


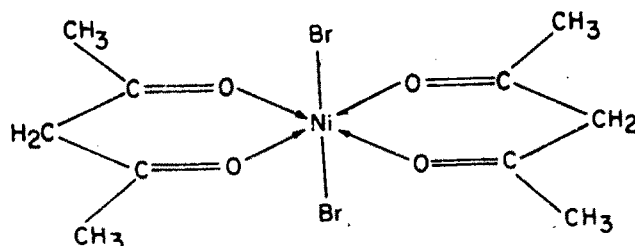
Fig. 3.5 Structure of $\text{Ni}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$

(3) When $m < 2n$

This type of complex ion may be formed if the coordination number of the metal ion is less than double the primary valence (Fig.5.6). The common examples of this type are $\text{Si}(\text{acac})_3$, $\text{Sn}(\text{acac})_2\text{Cl}_2$, $\text{Me}_2\text{Sn}(\text{acac})_2$, $\text{BuSn}(\text{acac})_3$ etc.

Fig. 3.6 Structure of $\text{B}(\text{acac})_2^+$ (4) β -Diketone as Neutral Ligand (Keto form)

These are the metal complexes in which both carbonyl groups of the ligand act as donor atoms are rather rare e.g. $\text{NiBr}_2(\text{acacH})_2$ and $(\text{acacH})_2(\text{SnCl}_2)^{2+} \text{SnCl}_6^{2-}$ X-ray analysis of $\text{NiBr}_2(\text{acacH})_2$ shows an octahedral structure (Fig.3.7) in which neutral acetylacetonone (keto form) is bonded to the metal through the oxygen atom.

Fig.3.7 β -diketone as a neutral ligandCarbon-bonded β -Diketonate Complexes

The metal-carbon bond in these complexes is quite stable. Examples of these are β diketonates of sulphur,

selenium, tellurium, gold and mercury.

3.2.4 Types of Metallic Derivatives of 1,3 Diketones

The metal derivatives of 1,3-diketones may be classified as follows :

(1) Simple Salt

The simple salts containing 1,3 diketone ion are like Na^+ , $\text{O}-\text{C}(\text{CH}_3)=\text{CH}-\text{CO}-\text{CH}_3$.²⁷ In this type the chelation is not the most dominating tendency. This shows typical salt like properties.²⁸

(2) Nonelectrolytes

Whenever the coordination number (CN) of the metal atom is twice that of its oxidation state (OS), the chelate compound formed is a nonelectrolyte or an inner complex compound of the first order. These are generally illustrated for the 2-4 pentanedione compounds (acetylacetonates).²⁹

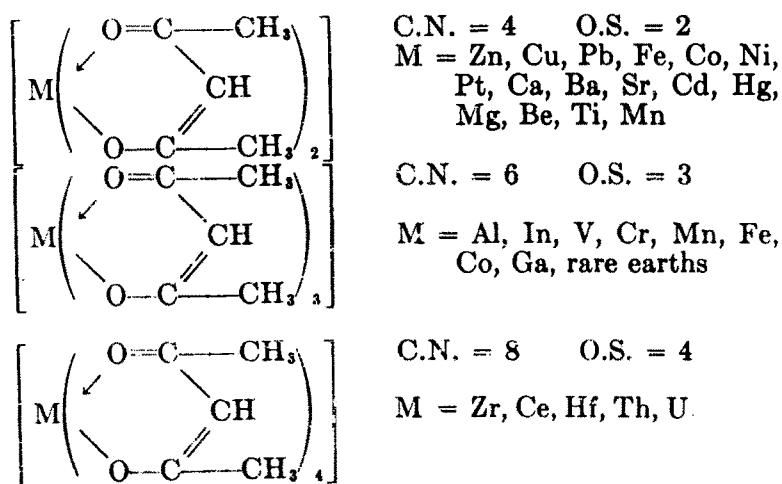


Fig. 3.8 Structures for 2.4 pentanedione

This type is an important type of 1:3 diketone. There are various nonelectrolytes such as $\text{BF}_2(\text{C}_5\text{H}_7\text{O}_2)$, $(\text{CH}_3)_2\text{Au}(\text{C}_5\text{H}_7\text{O}_2)$, $(\text{C}_3\text{H}_7)_2\text{Tl}(\text{C}_5\text{H}_7\text{O}_2)$, $\text{MO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$ $\text{M} = \text{U Mo}$ and $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_2(\text{NH}_3)_2$.

(3) Complex Ions containing 1,3-Diketones

(a) Simple salts

Whenever 1,3 diketones are the only coordinated groups and the coordination number is less than twice the value of the oxidation state, complex cations may result³⁰

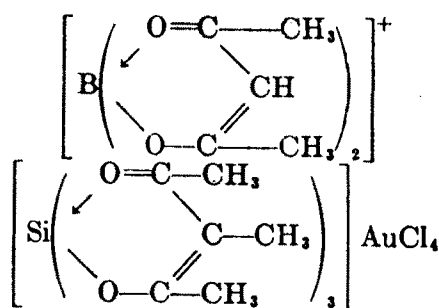
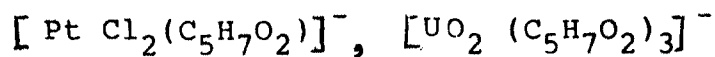


Fig. 3.9 Structure for B and Si pentanedione

(b) Mixed types

If one or more 1,3 diketone units are present in a complex ion as well as other uni- or multidentate groups.



3.2.5 Preparation of Metal Derivatives of 1,3 Diketones

Preparation of 1,3 diketones may be grouped into several classes.

(1) Direct Reaction of 1,3 Diketones with Metal Salts

(a) In Aqueous solutions

The reaction between 1,3 diketone and a metal salt will come to an equilibrium short of completed reaction because of increase in concentration of free acid in solution unless the metal chelate is extremely insoluble. For overcoming this difficulty the pH control of the solution with the help of buffer is necessary. pH is also controlled by adding gradually the weak base.³¹⁻³³ Generally the metal acetates are used for the preparations of β diketonates.^{34,35} The use of buffer has disadvantage of adding extraneous ions, which may contaminate the product. And this difficulty is avoided by the homogeneous generation of ammonia.

(b) In Nonaqueous solution

In this type both the metal halide and the 1,3 diketone are soluble in an inactive organic solvent such as benzene, reaction can be brought to completion by warming, so that the insoluble hydrogen halide is formed in reaction medium.³⁶⁻³⁸

(2) Reaction of soluble salt of 1,3 Diketone with a soluble salt of metal

This method is very similar to method I. This method involves dissolving the 1,3 diketone in water by adding the minimum required amount of aqueous ammonia or sodium carbonate.³⁹⁻⁴² This reaction lacks the pH control which may be essential under the reaction conditions the number of

substances other than the desired neutral chelate can be formed.

(3) Incorporation of Solvent Extraction with Method 1 or 2

For the extraction of 1,3 diketone compound, various investigators have suggested the addition of an immiscible liquid to an aqueous reaction mixture.^{32,39,43,44} Since metal hydroxides and such species as $MChX$, $MChOH$, MCh_3^- are seldom soluble in an organic medium, the extraction liquid separates the desired compound from these contaminants. For the separation of one metal from others the careful adjustment of pH is required.

(4) Reaction of 1,3 Diketone with Metal oxide, Hydroxide, carbonate, or Basic carbonate

(a) In Aqueous Solution : This is the reaction between 1,3 diketone and suspension of a hydrous oxide or hydroxide.⁴⁵ This reaction is slow.

(b) In Inert Solvent : In this type the excess of a liquid 1,3-diketone or solution of a solid 1,3 diketone in an inert solvent can be refluxed with an oxide, carbonate, or basic carbonate of the metal.^{46,47} By using this method vanadium oxy (acetylacetonate) is prepared.

(5) Reaction of 1,3 Diketone with a Metal

This procedure is usually carried out in an anhydrous inert medium. It has been used for obtaining derivatives

of alkali metals,⁴⁸⁻⁵⁰ alkaline earth metals,⁵¹ copper⁵², aluminium⁵³ and lead.⁵⁴

This procedure is particularly useful for obtaining (a) compounds of very active metals, (b) anhydrous compounds and (c) compounds of metal in lower states of oxidation.

(6) Miscellaneous Method

Some of the reactions that have been used for the preparation of metal derivatives of 1,3 diketones cannot be classified as any of the above general types. Derivatives of metals in lower oxidation states have been prepared by the reduction of materials exhibiting higher oxidation states e.g. uranium(IV) acetylacetonate by reduction of uranium(VI) compound with hydrogen sulfide.⁵⁵ Manganese(III) acetylacetonate by reduction of manganese(IV) chloride with acetylacetone.⁵⁶

Purification of Metal Derivatives of β -Diketone

It is necessary to purify such compounds after they are formed. Distillation, sublimation and crystallization are the methods generally available for this purpose. Generally the crystallization is the method which is most frequently used.

3.3 ACETYLACETONE COMPLEXES AND THE RELATED METAL IONS

There are various remarkable properties exhibited by many acetylacetonates, such as their solubility in anhydrous organic solvents, their stability on heating and their

anomalous colours have lead to believe that in these compounds the metal atoms are combined with the unsaturated organic complex not only with their principal valence but also by means of their residual affinity or auxillary valence.

Univalent organic complexes as shown in formula (I) consist of an open chain of the five atoms. Its intimate association with the metal is assumed to arise from the general tendency to form six membered ring (formula II), the metal atom serving as the connecting link between the end of organic group.

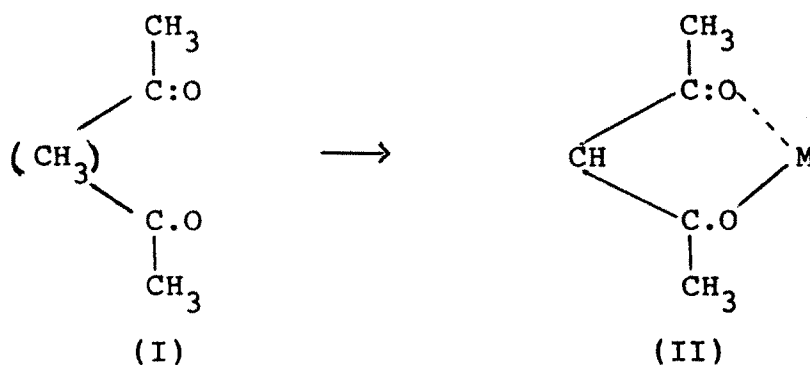


Fig. 3.10 Influence of symmetry on stability of metal acetylacetonate

Types of Acetylacetonates⁵⁷

(1) Complexes of Univalent Metals

Lithium and thalium acetylacetonates are most stable and decomposed by heating at 160°C Na, K, Cs char on heating unstable in solution or in moist air. They decomposed by hot water water into acetone and alkali acetate. Ag acetylacetonate decomposes at room temperature with the liberation

of silver. The important properties of the acetylacetonate of univalent metal justifies the contents the dissymmetry lead to instability.

Bivalent metal

The compound of this series which may possess either a tetrahedral or a planar configuration are on either alternative more symmetrical than the acetylacetonates of the univalent metals. They also display higher stability.

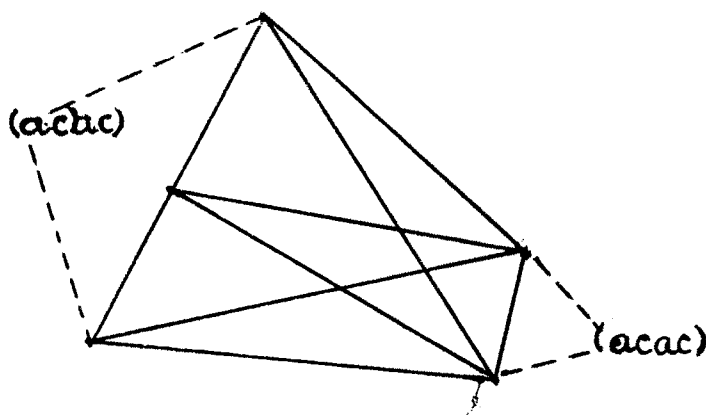


Fig. 3.11 Octahedral symmetry

The acetylacetonate of metal of the second series of the periodic table have all been prepared. Those of the alkaline earth metals are more stable than the corresponding compounds of the alkali metals.

Tervalent element

The case of boron is of great interest. The element resembles carbon in having a very small atomic volume and probably on this account it also resemble carbon in having

maximum coordination number 4 as exhibited by fluoboric acid. $H(BF_4)$ and its salt Boron accordingly associates only with two acetylaceton radical and produce general formula $(BAC_2)_x$ where x is insoluble radicle.

Tetravalent metal

Tetravalent metal which are most stable example of this class undoubtedly possess octahedral symmetry although they have not been resolved into their enantiomorphous components. Many members of rare earth metals such as lanthanum samarium, neodymium, praseodymium and cerium have yielded fairly stable acetylaceton.

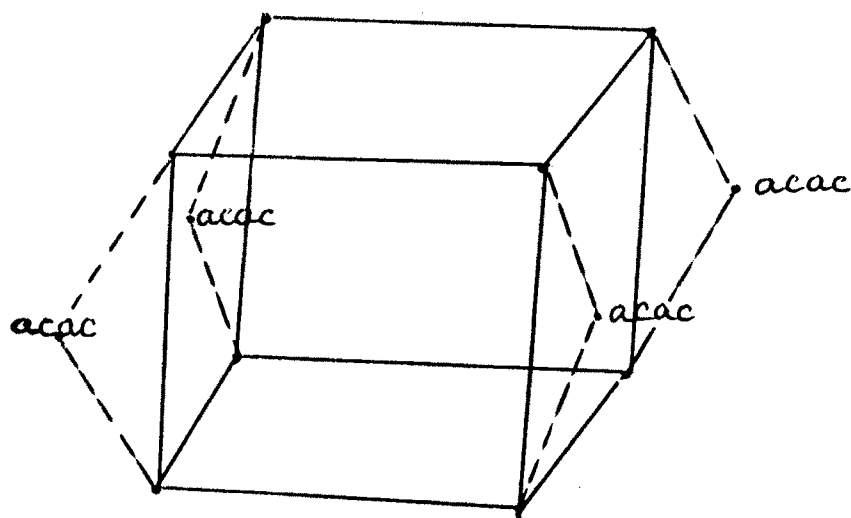


Fig. 3.12 Cubic symmetry

The chemical analyses and measurements of the absorption spectra of 2,4-pentanedione $CH_3COCH_2COCH_3$ (acetylaceton), Grossman⁵⁸ and Acly and French^{59,60} indicate that the enol form is present in water at 25°C to the extent of 15 to 20 per cent and in 95 per cent alcohol to the extent of 55.7 per cent.

The 2,4-pentanedione and also the other 1,3 diketones exist in the enol form. They probably have a cyclic structure with hydroxyl hydrogen coordinated to the carbonyl oxygen.

With the help of Raman effect⁶¹ exchange reaction with deuterium⁶² and by the polarographic oxidation reduction measurements⁶⁴ the tautomerism has been studied.

3.4 PREPARATION OF METAL ACETYLACETONATES

(1) Yttrium Acetylacetonate

The method was reported by Stites, and Mccarty used for the preparation of yttrium acetylacetonate.⁶³

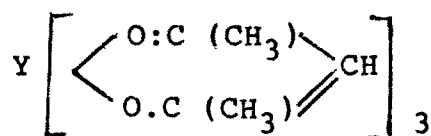


Fig. 3.13 Yttrium acetylacetonate

The weighed quantity of yttrium oxide was dissolved in the minimum amount of dilute hydrochloric acid and the pH of the solution adjusted with the help of dilute ammonium hydroxide to the value of approximately 5.0 as measured by the glass electrode. A solution of the ammonium acetylacetonate was prepared by adding concentrated ammonium hydroxide together with the required water for solution to an amount of the freshly distilled acetylacetone which was 50% in excess of that required for complete reaction with the rare earth oxide. The solution of the ammonium acetylacetonate was

added slowly with stirring to yttrium chloride solution. The pH of the reaction mixture was maintained at 11 times at a value just below that of the pH of the corresponding yttrium hydroxide by the addition of either dilute ammonium hydroxide or hydrochloric acid as required. The mixture was stirred for long time to obtain the conversion of any basic acetylacetonate to the normal compounds and to allow for completeness of the reaction. The yttrium acetylacetonate was precipitated at pH 6.2. The crystalline precipitate of yttrium acetylacetonate was obtained which was filtered and air dried.

In preparing the acetylacetonate it was observed that if the solution was too acidic no precipitation observed and if too basic gelatinous product was obtained so pH control is the most important factor.

(2) Lanthanum Acetylacetonate

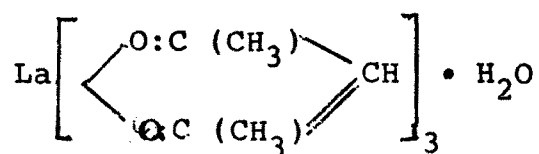


Fig. 3.14 Lanthanum acetylacetonate

The lanthanum acetylacetonate was prepared by the procedure mentioned above for the preparation of yttrium acetylacetonate by using lanthanum oxide.

(3) Barium Acetylacetonate

Barium acetylacetonate was prepared by the procedure used by the Tanatar and Kurovsk⁶⁴

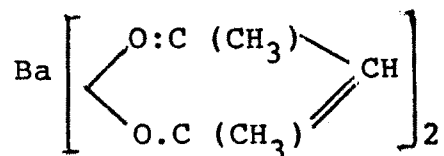


Fig. 3.15 Barium acetylacetonate

The weighed quantity of crystalline barium hydroxide was dissolved in water and then after dissolving all the quantity of barium hydroxide in warm water, the clear solution was kept on hot plate for heating. To this hot solution alcoholic acetylacetonate was added. After heating for some times the solution was filtered. The filtrate gave small flakes of barium acetylacetonate.

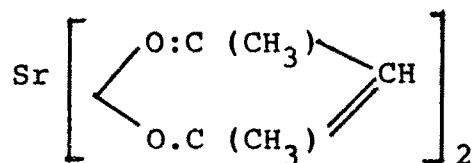
(4) Strontium Acetylacetonate

Fig. 3.16 Strontium acetylacetonate

Weighed quantity of the strontium nitrate was dissolved in distilled water. The solution of ammonium acetylacetonate was added slowly with constant stirring. And at pH 8 the white crystalline precipitate of strontium acetylacetonate was formed. After digestion, filtration and drying of the precipitate it was then recrystallized from carbon

tetrachloride and dried at 60°C. A solution of ammonium acetylacetonate was prepared by adding concentrated ammonium hydroxide together with sufficient water for the solution to an amount of the freshly distilled acetylacetone.

(5) Copper Acetylacetonate

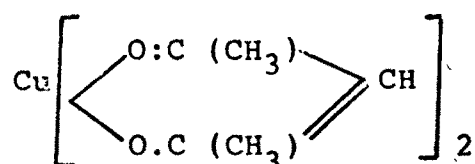


Fig. 3.17 Copper acetylacetonate

Weighed quantity of the copper nitrate was taken and to this the distilled water was added. After dissolving all the quantity of the copper nitrate into the distilled water, solution became clear. To this clear solution slight excess of (ligand) acetylacetone was added and the pH was raised slowly to 6.5 with the help of aqueous ammonia. After complete precipitation the solution was allowed to stand for some time. The blue precipitate was collected on filter paper and allowed to dry at room temperature.

3.5 GENERAL PROPERTIES OF METAL ACETYLACETONATES

(1) Yttrium Acetylacetonate

The formula of yttrium acetylacetonate was determined by estimating yttrium by spectrophotometric method with Arsenazo M⁶⁵ and the acetylacetonate determined by evaporating with perchloric acid.

The yttrium acetylacetonate $Y(acac)_3$ is pale cream coloured, needle like crystalline material. The melting point is $114^{\circ}C$.⁶⁶ It is soluble in 50% ethanol. The product $Y_2(acac)_3$ analyses to 34.434% Y and 65.56% acetylacetonate ion against the theoretical value Y 34.448% and acetylacetonate ion 65.59%.

(2) Lanthanum Acetylacetonate

The formula of lanthanum acetylacetonate was determined by estimating lanthanum by spectrophotometric method by using Alizarine as a reagent⁶⁷ and acetylacetonate ion as mentioned above.

Lanthanum acetylacetonate $La(acac)_3 \cdot H_2O$ is a white coloured crystalline hydrate. The reported melting point of the lanthanum acetylacetonate are $151^{\circ}C$, $142^{\circ}C$ and $185^{\circ}C$.⁶⁶

The product lanthanum acetylacetonate $La(acac)_3 \cdot H_2O$ analyses to 46.8% La, 50.11% acetylacetonate ion, and 3% water of crystallization against the theoretical values La 46.9%, acetylacetonate ion 50.10% and H_2O 3%.

(3) Barium Acetylacetonate

The formula of the barium acetylacetonate was determined by estimating barium as barium sulphate by standard gravimetric procedure⁶⁸ and acetylacetonate ion as mentioned above.

Barium acetylacetonate $Ba(acac)_2 \cdot H_2O$ is a pale cream coloured, flaky, crystalline compound. It is soluble in 50% ethanol.

The product $\text{Ba}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ analyses to 40.92% Ba, 59% acetylacetonate, and 10.72% water of crystallization against the theoretical value Ba 40.955%, acetylacetonate 59.04% and 10.73% H_2O .

(4) Strontium Acetylacetonate

The formula of strontium acetylacetonate was determined by estimating strontium gravimetrically as strontium sulphate⁶⁹ and acetylacetonate ion as mentioned above.

$\text{Sr}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ is a white coloured crystalline material. It is slightly soluble in ethanol.

The product $\text{Sr}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$ analyses to 27.22% Sr, 61.57% acetylacetonate ion and 11.18% water of crystallization against the theoretical value Sr 27.24%, acetylacetonate ion 61.56% and H_2O 11.19%.

(5) Copper Acetylacetonate

The formula of copper acetylacetonate was determined by estimating copper with EDTA titration⁷⁰ and acetylacetonate ion determined by the method mentioned above.

$\text{Cu}(\text{acac})_2$ is a bluish coloured crystalline material. The reported melting point is 236°C .⁷¹

Copper acetylacetonate $\text{Cu}(\text{acac})_2$ analyses to 24.28% of Cu and 75.71% of acetylacetonate ion against the theoretical value 24.30% of Cu and 75.70% of acetylacetonate ion.

3.6 INFRARED SPECTRA OF METAL ACETYLACETONE

IR spectroscopy is a powerful and versatile tool in the structural studies. The metal acetylacetonates, their dehydrated species and ultimate oxide residues can be identified and analysed. By inspecting the thermal profile it is possible to verify the course of conversion of anhydrous complex to the oxide. In case there is any definite intermediate step corresponding to an identifiable species, there will be an indication in the thermal profile. Acetylacetonate is a clean ligand which gives a well characterizable complex and involves only oxygens as coordinating atoms. This is likely to give oxides directly. The IR spectra of the metal complexes are discussed below.

The spectra of suspected carbonates and desired end point oxides are already discussed in the previous chapter.

The salient feature of the metal complexes are (a) the broad and strong absorption band due to structural, associated or adsorbed water, (b) characteristic carboxyl frequencies, (c) frequencies corresponding to M-O band. I.R. spectral data of complexes are shown in fig. 3.18 and the frequencies are tabulated along with probable origins (Table 3.1).

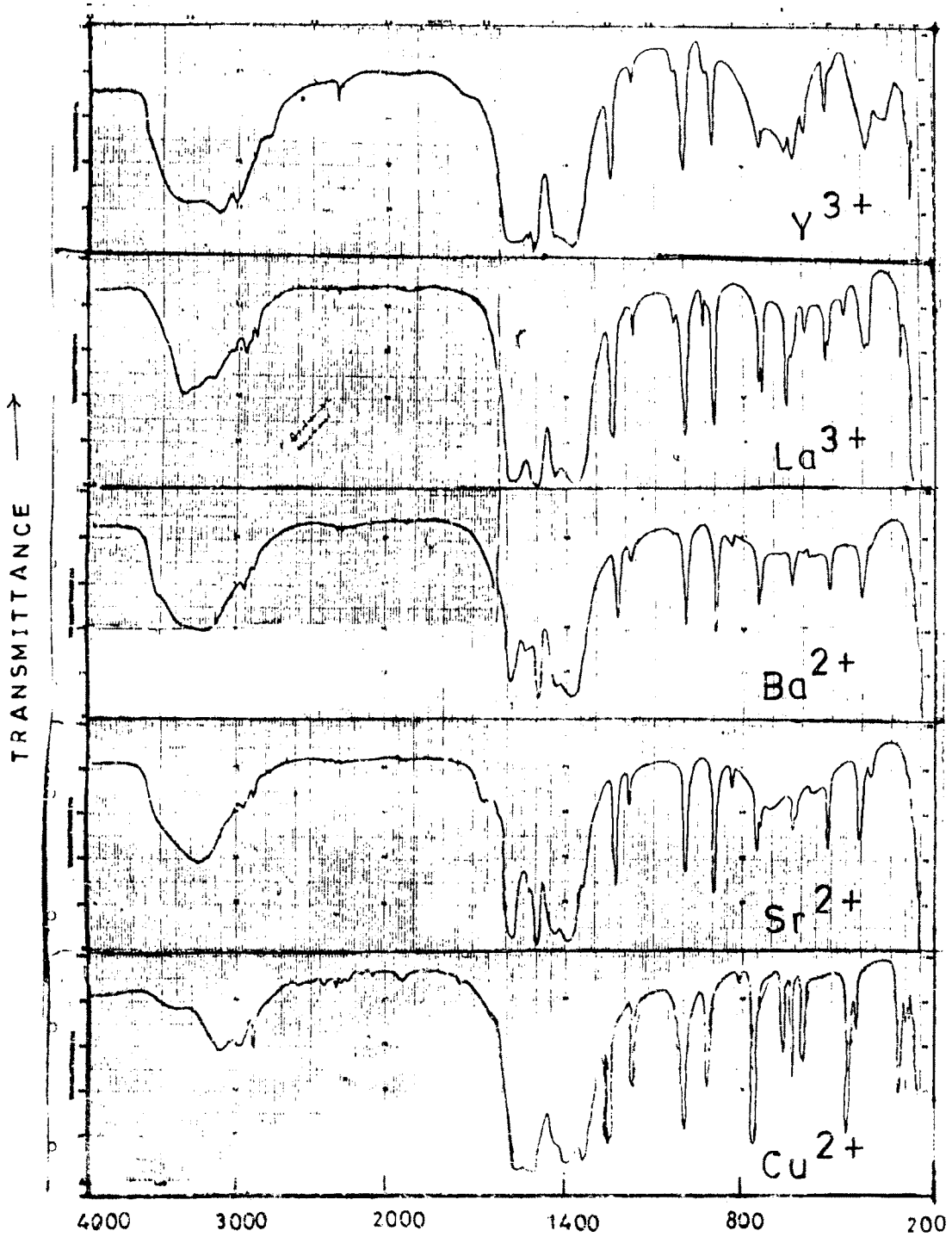
3.7 THERMAL ANALYSIS OF METAL ACETYLACETONATE

As reported earlier metal oxalates show a complex pattern of decomposition on heating in air. Thermogravimetry

Table 3.1 : IR spectral data for metal acetylacetonates

Y (acac) ₃	La (acac) ₃	Ba(acac) ₂	Sr(acac) ₂	Cu(acac) ₂	Predominant mode
3300-3500	3350-3500	3300-3500	3300-3500	3300-3500	Due to structural and absorbed water.
3030	3040	3080	3080	3072	ν (CH)
3000	2970	2995	2970	2988	ν (CH ₃)
2900	2940	2970	2940	2970	
	2900	2938	2904	2930	
1560	1592	1610	1595	1577	ν (C—C) + ν (C—C)
1540	1560	1545	1540	1552	Combination
1524	1521	1517	1515	1530	ν (C—O) + ν (C—C)
1460	1460	1457	1455	1460	ν (CH) + ν (C—C)
1400	1390	1415	1411	1413	δ (CH ₃)
1270	1260	1250	1250	1276	ν (C-CH ₃) + ν (C—C)
1190	1190	1190	1200	1200	δ (CH) + ν (C-CH ₃)
1020	1020	1018	1013	1020	Pr (CH ₃)
948	958	918	913	940	ν (C—C) + ν (C—C)
923	920				
760	758	782	760	770	π (CH)
757	750				
680	675	686	650	660	ν (C-CH ₃) + ring def.+ (Mo)
650	660	-	-	655	π (CH ₃ -C C O)
610	610	-	-	616	ring deformation
400	410	415	430	440	ring deformation

FIG. 3-18 — INFRARED ABSORPTION SPECTRA OF
METAL ACETYLACETONATES



is used to record the weight changes. Use of D.T.A. D.S.C. to know the endothermic or exothermic nature of chemical decompositions and physical changes and investigations of kinetics of thermal change are the possible techniques for further investigation for further changes. Acetylacetonate complexes of several metals have been studied in some detail in this manner. However, the main emphasis of studies of acetylacetonates are directed towards the investigation of volatility at higher temperature. With this bias, the study has been concentrated in these cases where the complexes volatilize. Fluorinated ligands are therefore, extensively studied⁷² and much of the work in the area are markedly high temperature gas chromatography.⁷¹ It is observed that most of the literature reports on acetylacetonate complexes do not cover the thermal analysis. In our study acetylacetonates of Ba^{2+} , Sr^{2+} , Cu^{2+} , Y^{3+} and La^{3+} are the precursors hence we have investigated the thermal behaviour of these complexes. The thermal analysis of metal acetylacetonates proceeds with a change leading to formation of metal oxides as the ultimate product and the corresponding organic component goes away without showing any distinct feature which can be attributed to particular decomposition product. The smooth thermogram has therefore no distinct diagnostic feature indicating the volatile component. Our interest in the reaction is concentrated on the residual component and in establishing conditions under which a clean oxidic phase

is obtained. Hence the thermal profile is analyzed by keeping in mind motive of establishing the temperature at which ceramic oxide is formed quantitatively. Tables 3.2 to 3.7 give observation on weight loss and figures 3.19-3.20 give the thermal profile of the five acetylacetonates.

(1) Yttrium Acetylacetonate $Y(acac)_3$

Yttrium acetylacetonate does not contain any associated or structural water so from 25-250°C does not show any change in weight and completely horizontal trace is present within this temperature range. It starts to decompose from 250°C and gives finally yttrium oxide at 700°C. The yield is quantitative.

(2) Lanthanum Acetylacetonate $La(acac)_3 \cdot H_2O$

Lanthanum acetylacetonate contains one molecule of water. It loses one molecule of water within the temperature range 25-200°C. Within the temp. range 200-362°C present is $La(acac)_3$. From 362°C lanthanum acetylacetonate decomposes and at 700°C it gives lanthanum oxide. The yield is quantitative.

(3) Barium Acetylacetonate $Ba(acac)_2 \cdot 2H_2O$

Barium acetylacetonate is a very pale cream coloured, flaky, crystalline compound. It loses two molecules of water at 125°C. This ionic compound requires fairly high temperature of the order of 625°C for the formation of oxide.

The thermal decomposition of $\text{Ba}(\text{acac})_2$ does not involve any intermediate step giving barium carbonate and therefore, the difficulty encountered in oxalate decomposition is overcome in this method of forming ceramic preparations. This establishes that acetylacetonates of barium is a suitable precursor. The yield is quantitative.

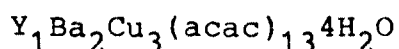
(4) Strontium Acetylacetonate $\text{Sr}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$

Strontium acetylacetonate contains two molecules of water. It loses two molecules of water at 125°C . This ionic compound requires high temp. of the order of 700°C for the formation of oxide. In thermal decomposition intermediate step giving carbonate is absent. This also establishes the suitability of this complex as a precursor.

(5) Copper Acetylacetonate $\text{Cu}(\text{acac})_2$

Copper acetylacetonate does not contain any associated or structural water and between $150-275^\circ\text{C}$. The blue compound darkens and finally gets completely converted to black copper oxide. The yield is quantitative.

(6) Thermal Analysis of Mixed Acetylacetonate



Mixed acetylacetonate complex loses four water molecules from barium acetylacetonate at 125°C . It forms copper oxide from the copper acetylacetonate within the temperature range $275-400^\circ\text{C}$. It shows yttrium and barium oxide formation above 700°C and gives the product $(\text{Y}_2\text{O}_3 + 4\text{BaO} + 6\text{CuO})$

Table 3.2 T.G.A. data for Yttrium acetylacetonate complex

Wt. of the sample taken : 28.8 mg.

Obs.No.	Temp.in °C	Time in min.	Wt.in mg	Change in wt. ΔW
1	32.5	10.0	28.8	0.0
2	62.5	20.0	28.8	0.0
3	100.0	30.0	28.8	0.0
4	125.0	40.0	28.8	0.0
5	162.5	50.0	28.8	0.0
6	200.0	60.0	28.0	0.0
7	225.0	70.0	28.8	0.0
8	262.5	80.0	28.2	0.6
9	300.0	90.0	27.4	1.2
10	325.0	100.0	27.0	0.4
11	362.0	110.0	26.6	0.4
12	400.0	120.0	26.0	0.6
13	430.0	130.0	25.2	0.8
14	462.5	140.0	24.6	0.6
15	500.0	150.0	23.6	1.0
16	525.0	160.0	23.0	0.6
17	550.0	170.0	22.0	1.0
18	575.0	180.0	21.2	0.8
19	600.0	190.0	20.0	1.2
20	625.0	200.0	19.0	1.0
21	650.0	210.0	16.0	3.0
22	675.0	220.0	14.0	2.0
23	700.0	230.0	13.0	1.0
24	725.0	240.0	13.0	0.0

Table 3.3 T.G.A. data for Lanthanum acetylacetonate complex.

Wt. of the sample taken : 23.0 mg.

Obs. No.	Temp. in °C	Time in min.	Weight in mg.	Change in wt. ΔW
1	32.5	10.0	23.0	0.0
2	62.5	20.0	23.0	0.2
3	100.0	30.0	22.8	0.4
4	125.0	40.0	22.0	0.4
5	162.5	50.0	22.0	0.0
6	200.0	60.0	22.0	0.0
7	225.0	70.0	22.0	0.0
8	262.5	80.0	22.0	0.0
9	300.0	90.0	22.0	0.0
10	325.0	100.0	22.0	0.0
11	362.0	110.0	22.0	0.6
12	400.0	120.0	21.4	0.4
13	430.0	130.0	21.0	0.8
14	462.5	140.0	20.2	0.8
15	500.0	150.0	19.4	0.8
16	525.0	160.0	18.6	0.4
17	550.0	170.0	18.4	0.6
18	575.0	180.0	17.8	0.6
19	600.0	190.0	17.2	1.2
20	625.0	200.0	16.0	1.0
21	650.0	210.0	15.0	1.0
22	675.0	220.0	14.0	1.5
23	700.0	230.0	12.5	0.0
24	725.0	240.0	12.5	

Table 3.4 T.G.A. data for Barium acetylacetonate complex.

Wt. of the sample taken : 49.0 mg.

Obs. No.	Temp. in °C	Time in min.	Weight in mg.	Change in wt. Δ W
1	32.5	10.0	49.0	1.0
2	62.5	20.0	48.0	2.0
3	100.0	30.0	46.0	2.0
4	125.0	40.0	44.0	0.0
5	162.5	50.0	44.0	0.0
6	200.0	60.0	44.0	0.0
7	225.0	70.0	44.0	0.0
8	262.5	80.0	44.0	0.0
9	300.0	90.0	44.0	0.8
10	325.0	100.0	43.2	2.0
11	362.0	110.0	41.2	2.8
12	400.0	120.0	38.4	2.8
13	430.0	130.0	35.6	2.4
14	462.5	140.0	33.2	3.2
15	500.0	150.0	30.0	1.2
16	525.0	160.0	31.2	3.6
17	550.0	170.0	24.8	2.4
18	575.0	180.0	22.4	1.6
19	600.0	190.0	20.8	0.8
20	625.0	200.0	20.0	0.0
21	650.0	210.0	20.0	0.0
22	675.0	220.0	20.0	0.0
23	700.0	230.0	20.0	0.0
24	725.0	240.0	20.0	0.0

Table 3.5 T.G.A. data for Strontium acetylacetonate complex.

Wt. of the sample taken : 12.8 mg.

Obs. No.	Temp.in °C	Time in min.	Weight in mg.	Change in wt. ΔW
1	32.5	10.0	12.8	0.2
2	62.5	20.0	12.6	0.8
3	100.0	30.0	11.8	0.6
4	125.0	40.0	11.2	0.0
5	162.5	50.0	11.2	0.0
6	200.0	60.0	11.2	0.0
7	225.0	70.0	11.2	0.0
8	262.5	80.0	11.2	0.0
9	300.0	90.0	11.2	0.0
10	325.0	100.0	11.2	0.6
11	362.0	110.0	10.6	0.6
12	400.0	120.0	10.0	0.2
13	430.0	130.0	9.8	0.08
14	462.5	140.0	8.6	1.2
15	500.0	150.0	7.8	0.8
16	525.0	160.0	7.0	0.4
17	550.0	170.0	6.6	0.6
18	575.0	180.0	6.0	0.6
19	600.0	190.0	5.4	0.6
20	625.0	200.0	4.8	0.2
21	650.0	210.0	4.6	0.4
22	675.0	220.0	4.2	0.4
23	700.0	230.0	4.0	0.0
24	725.0	240.0	4.0	

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Table 3.6 T.G.A. data for Copper acetylacetonate complex.

Wt. of the sample taken : 31.5 mg.

Obs. No.	Temp. in $^{\circ}\text{C}$	Time in min.	Weight in mg.	Change in wt. ΔW
1	32.5	10.0	31.5	0.0
2	62.5	20.0	31.5	0.0
3	100.0	30.0	31.5	0.0
4	125.0	40.0	31.5	3.5
5	162.5	50.0	28.0	4.0
6	200.0	60.0	24.0	6.6
7	225.0	70.0	17.4	5.8
8	262.5	80.0	11.6	2.0
9	300.0	90.0	9.6	0.0
10	325.0	100.0	9.6	0.0
11	362.0	110.0	9.6	0.0
12	400.0	120.0	9.6	0.0
13	430.0	130.0	9.6	0.0
14	462.5	140.0	9.6	0.0
15	500.0	150.0	9.6	0.0

Table 3.7 T.G.A. data for the mixture of acetylacetonate 99
 $Y_1Ba_2Cu_3(acac)_{13} \cdot 4H_2O$

Wt. of the sample taken : 31.0 mg.

Obs. No.	Temp. in $^{\circ}C$	Time in min.	Weight in mg.	Change in wt. ΔW
1	32.5	10.0	31.0	0.0
2	62.5	20.0	31.0	1.0
3	100.0	30.0	30.0	0.5
4	125.0	40.0	29.5	0.0
5	162.5	50.0	29.5	0.0
6	200.0	60.0	29.5	2.5
7	225.0	70.0	27.0	2.0
8	262.5	80.0	25.0	2.0
9	300.0	90.0	23.0	0.0
10	325.0	100.0	23.0	0.0
11	362.0	110.0	23.0	0.0
12	400.0	120.0	23.0	0.0
13	430.0	130.0	23.0	0.6
14	462.5	140.0	22.4	1.4
15	500.0	150.0	21.0	1.6
16	525.0	160.0	19.6	1.6
17	550.0	170.0	18.0	2.0
18	575.0	180.0	16.0	1.0
19	600.0	190.0	15.0	1.6
20	625.0	200.0	13.4	0.0
21	650.0	210.0	13.4	1.4
22	675.0	220.0	12.0	0.0
23	700.0	230.0	12.0	0.0
24	725.0	240.0	12.0	0.0

Table 3.8 : Chemical changes during thermal analysis.

(1) Yttrium acetylacetonate $Y(acac)_3$

Weight of the sample taken : 28.8 mg.

Temp.range	Expected wt.	Obtained wt.	Formula	Cause
25-275°C	28.8 mg	28.8 mg	$Y(acac)_3$	
275-700°C	Continuous change in wt.			
Above 700°C	13.7 mg	13.0 mg		

(2) Lanthanum acetylacetonate $La(acac)_3 \cdot H_2O$

Weight of the sample taken : 23.0 mg

Temp.range	Expected wt.	Obtained wt.	Formula	Cause
25 - 200°C	Continuous	22.0 mg	$La(acac)_3$	Loss of water
200-362°C	22.0 mg	22.0 mg		
362-700°C	Continuous change in wt.			
Above 700°C	12.6 mg	12.5 mg	La_2O_3	

(3) Barium acetylacetonate : $Ba(acac)_2 \cdot 2H_2O$

Weight of the sample taken : 490 mg

Temp.range	Expected wt.	Obtained wt.	Formula	Cause
25 - 125°C	Continuous change in wt.	Continuous change in wt.		Loss of water
125°C	44.0 mg	44.0 mg	$Ba(acac)_2$	
125-500°C	No change in wt.			
1000°C			BaO	

(4) Strontium acetylacetonate : $\text{Sr}(\text{acac})_2 \cdot 2\text{H}_2\text{O}$

Weight of the sample taken : 12.8 mg

Temp.range	Expected wt.	Obtained wt.	Formula	Cause
25 - 125°C	Continuous change in wt.	Continuous change in wt.		Loss of water
135-362°C	11.3 mg	11.2 mg	$\text{Sr}(\text{acac})_2$	
362-500°C	10.0 mg			

(5) Copper acetylacetonate : $\text{Cu}(\text{acac})_2$

Weight of the sample taken : 31.5 mg

Temp.range	Expected wt.	Obtained wt.	Formula	Cause
25 - 150°C	31.5 mg	31.5 mg	$\text{Cu}(\text{acac})_2$	
275-500°C	9.5	9.6	CuO	

(6) $\text{YBa}_2\text{Cu}_3\text{C}_7$ mixed acetylacetonate

Weight of the sample taken : 31.0 mg

Temp.range	Expected wt.	Obtained wt.	Formula	Cause
25 - 125°C	Continuous change in wt.	Continuous change in wt.		Loss of H_2O from $\text{Ba}(\text{acac})_2$
175-400°C	,,	,,		$\text{Cu}(\text{acac})_2$ - CuO
400-700°C	,,	,,	$\text{Y}_2\text{O}_3 + 4\text{BaO}$ + 6 CuO	$\text{Ba}(\text{acac})_2$ - BaO $\text{Y}_2(\text{acac})_3$ - Y_2O_3

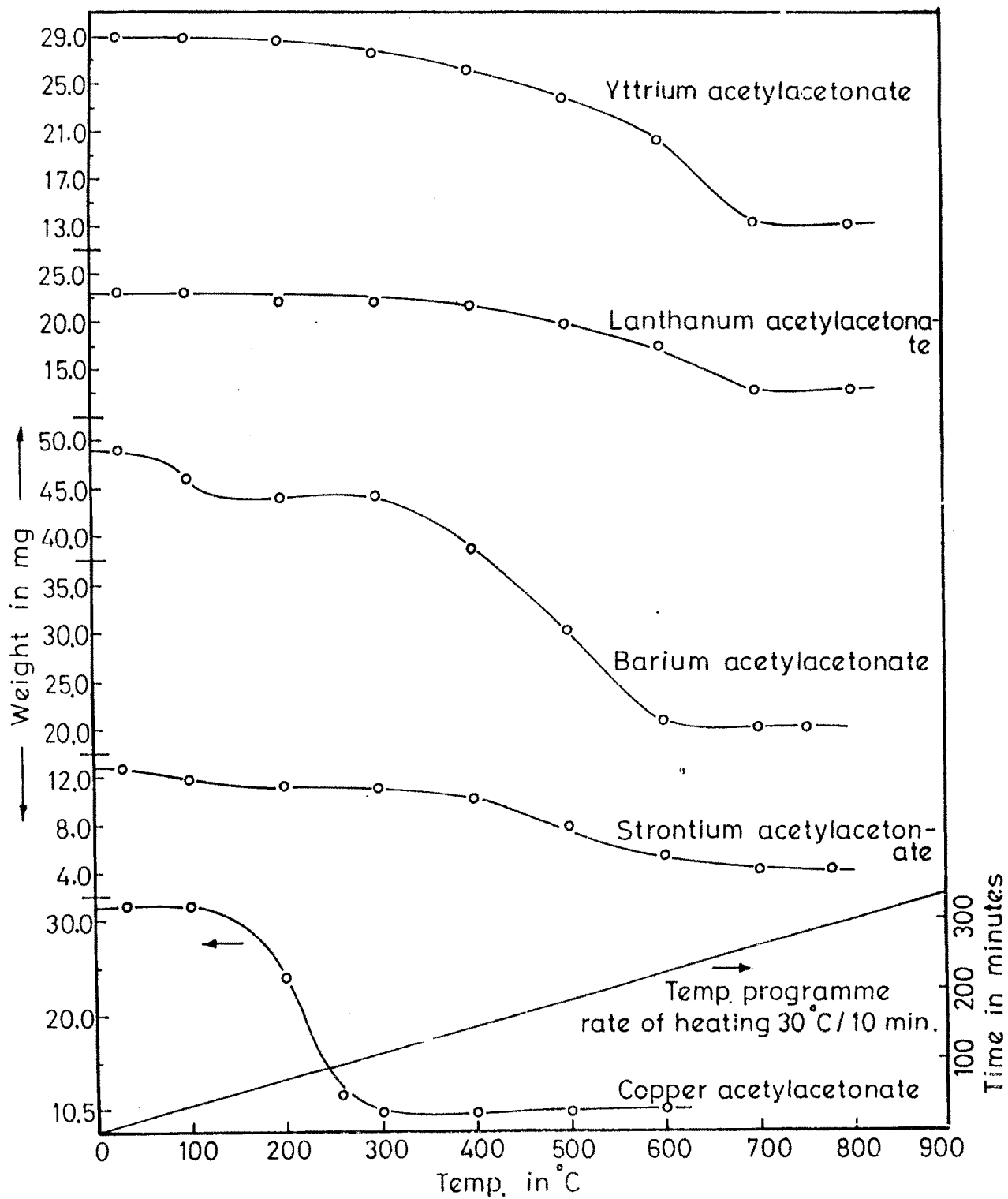


Fig. 3-19 TGA of metal acetylacetonates

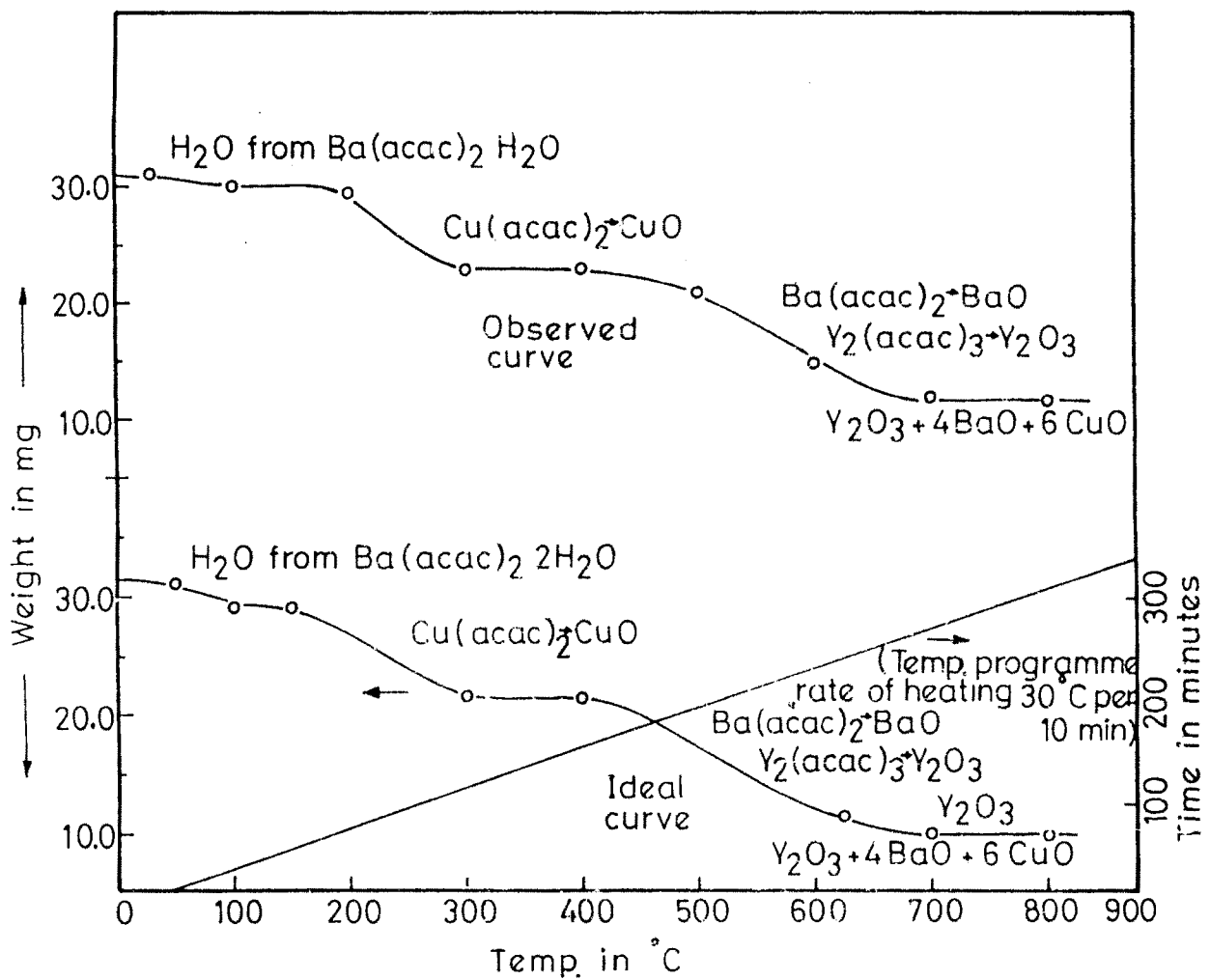


Fig. 3-20 TGA of mixed metal acetylacetonates
(mixture of $\text{Y}_1\text{Ba}_2\text{Cu}_3(\text{acac})_{13} \cdot 4\text{H}_2\text{O}$).

3.8 CONCLUSION

The study of T.G.A. profile, coupled with I.R. spectroscopy indicated that the metal acetylacetonates under study quantitatively yield metal oxides without involving formation of any intermediate which resists the decomposition to oxide. The conversion to oxide is 100% and no trace of carbonate is detected. As is known that carbonates of alkali metals if present resist decomposition, it was inferred that at no stage there is carbonate formation. Considering the above aspects following conclusions can be drawn :

- (1) All the constituent metal acetylacetonates $Y(acac)_3$, $La(acac)_3 \cdot H_2O$, $Ba(acac)_2 \cdot 2H_2O$, $Sr(acac)_2 \cdot 2H_2O$ and $Cu(acac)_2$ are stable, well characterizable starting materials which can be obtained in pure form.
- (2) The preparatory techniques of metal acetylacetonates are simple and the complexes are in a convenient forms for handling i.e. they are granular, microcrystalline, nonhygroscopic and kinetically stable materials.
- (3) The acetylacetonates on heat treatment gave pure oxide quantitatively.
- (4) There is no formation of carbonate as an intermediate.
- (5) There are no any side reactions at any stage in the entire procedure.

These points go in favour of choosing acetylacetonate route as a suitable method in the preparation of ceramic oxidic materials. This route circumvents the disadvantages of direct synthesis by using carbonates or using those route in which carbonate is an intermediate. Acetylacetonate route can be compared with another precursor route using nitrates. However, nitrates of yttrium and lanthanum are hygroscopic and difficult to handle. Copper nitrate is extremely hygroscopic and corrosive.

The thermal decomposition of nitrate give fumes of nitrogen oxide and due to hygroscopicity direct weighing of nitrates containing desired amount of the metal is difficult. This comparison establishes that acetylacetonate precursor route is the suitable and convenient procedure.

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