

NEW DEVELOPMENTS IN THE CHEMISTRY OF METAL-ACETYLACETONATE COMPLEXES

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New, direct and convenient, methods of synthesizing acetylacetonato metal complexes are described and their advantages highlighted. Two general methods of synthesis have been devised, (i) Acid-base and (ii) Electron-Transfer (REDOX) reactions enabling a large number of metal-acetylacetonate complexes, for example, $M(acac)_2$ ($M = Mn, Fe, Co, Ni, Cu, MoO_2^{2+}$ or UO_2^{2+} ; $(acac) = C_5H_7O_2$), $Mo_2O_7(acac)_4$, $M(acac)_3$ ($M = Cr, Mn, Fe$ or Ru) and $M(acac)_4$ ($M = Ce$ or Th), to be synthesized. REDOX reaction between acetylacetonone and a higher-valent transition metal ion also enabled the isolation of α, α, β -tetra-acetyethane as the oxidation product of acetylacetonone, for the first time, from such a reaction. Newer reactions involving some of these compounds are described and the scope of such reactions in the context of research in synthetic inorganic chemistry has been emphasised. Salient features of electron-ionization mass spectra of acetylacetonatometal compounds, in terms of molecular association and structure-fragmentation correlation are also highlighted.

Key Words : New General Routes to Acetylacetonatometals; Oxidation Product of Acetylacetonone; Newer Reactions; Mass Spectrometry

INTRODUCTION

ACETYLACETONE is the simplest of the β -diketones. The presence of β -carbonyl groups with at least a proton on the intermediate carbon, allows a keto \rightleftharpoons enol tautomerism to be operative in β -diketones (Fig. 1). The enolic proton (Fig. 1) can be replaced from the β -diketo-enols, with various ligands, under appropriate

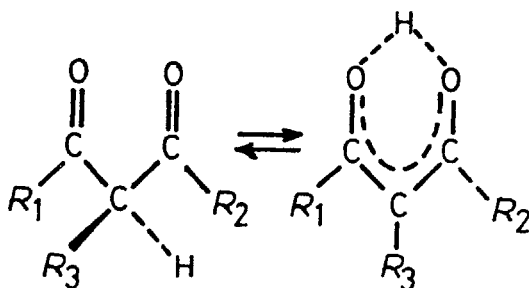


FIG 1 Keto-enol tautomerism with β -diketone

conditions. Although a variety of substituents can appear at R_1 , R_2 , R_3 of the β -diketones (Fig. 1), however, acetylacetonone (*Hacac*: $R_1, R_2, = \text{CH}_3$; $R_3 = \text{H}$) and compounds that are formed when the enolic proton is replaced by metals in several of their oxidation states from acetylacetonone (Fig. 2) constitute the subject matter of the present report.

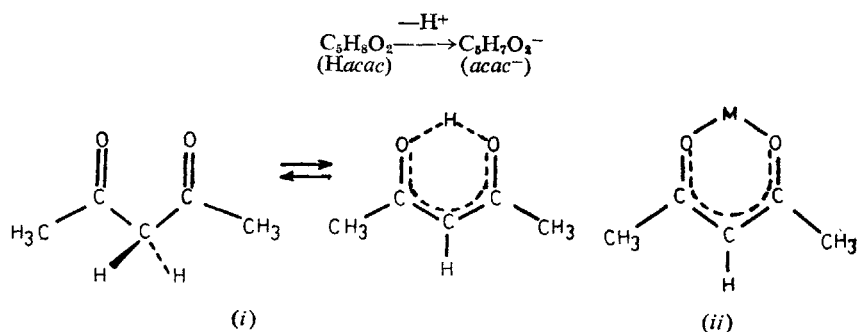


FIG 2 (i) Keto-enol tautomerism with acetylacetonone (ii) Metal-acetylacetonate

Metal-acetylacetonato complexes, as they are called, have been known and studied for almost a century yet much remains to be understood.¹ Complexes with acetylacetonone are known for all nonradioactive metals and metalloids and can broadly be grouped into two viz., the molecular and the ionic complexes. However, the present report is exclusively restricted to the ones which are molecular in nature. The types of molecular complexes and the corresponding metals for which they are known have been enlisted in Table I.

TABLE I

Metals for which different types of molecular complexes are known

$M(\text{acac})$: Li, Na, K, Cs, Cu, Ag, Tl
$M(\text{acac})_2$: Be, Ca, Ba, Zn, Hg, Cr, Mn, Fe, Co, Ni, Cu, Mg, Sr, Pd, Pt, Pb, UO_2^{2+} , VO^{3+}
$M(\text{acac})_3$: Sc, Y, Ce, Ln's, V, Cr, Mo, Mn, Re, Fe, Ru, Co, Rh, Ir, Al, Ga, In, Ce, Os
$M(\text{acac})_4$: Zr, Hf, Th, U, Pu, Ce

Metal acetylacetonate complexes are known for quite a long time so also their synthesis known for long. Evidently there exists more than one route to such complexes. But those synthetic routes had some limitations in scope owing to the involvement of several complications. Improvising newer and convenient synthetic routes in order to have a rather easy access to the chemistry of metal-acetylacetonates, therefore had been one of the primary concerns. Our interest in the synthetic inorganic chemistry have eventually led us to devise two new, direct and general methods—one based on (i) *ACID-BASE* and the other on (ii) *ELECTRON-TRANSFER* (redox) concepts. The essential features of the

newly devised methods, their advantages over the earlier ones alongwith a brief summary of various acetylacetonato-metals that have been successfully synthesized in our laboratory following the new routes are reported in this work. Also summarised herein are some newer reactions of acetylacetonato-metals and their scope, and the salient aspects of electron-impact induced positive ion mass spectrometry of a variety of the title compounds. No attempt, however, is made here to give an exhaustive coverage to every acetylacetonato-metal prepared, rather the contention is to approach their studies with special reference to their synthesis, newer reactions and EI-induced positive ion mass spectrometric investigations that will complement the work of various other groups reported earlier in this field.

But before we enter into a discussion on the problems encountered in the synthesis of acetylacetonato-metals and the new methods developed to circumvent such problems, it is appropriate to briefly enumerate the vast potential and immense importance that such complexes hold. The role of metal-acetylacetonates as catalysts in important organic reactions such as oligomerisation, polymerisation, hydrogenation, isomerisation of olefins, hydrosilylation of alkynes and coupling of organic halides,² is well recognised. Metal-acetylacetonato complexes have also found applications in various industrial processes, for example, in rubber technology for vulcanisation,³ in polymer^{4,5} plastic, and paints industries as additives and for metal planting from organic solvents³ and for extraction, separation of metals^{6,7,8} and also as semiconductors,⁹ antioxidants¹⁰ etc. Their ability, to function as probes in NMR spectroscopic studies, has rendered them a useful class of NMR shift reagents.^{11,12} Two important properties namely volatility and solubility in organic solvents are significant. While the former renders this class of compounds as suitable probes amenable to mass spectrometric studies, the latter causes them to be useful synthetic precursors for organometallic synthesis. In addition, it has been conclusively proved that metal-chelates of β -ketoenolate under certain specific conditions are capable of laser emission.^{13,14} Work¹⁵ in this regard has confirmed the fact that metal chelate anion is responsible for laser action in a number of such complexes. Metal acetylacetonates or for that matter β -ketonates have been also found to exhibit quenching effect of triplet state.¹⁶ It is believed that the effect is due to the presence of unsaturated ligands.¹⁶ Consequent upon the applied needs as well as the interests in academic research metal- β -diketonates, in general, and metal-acetylacetonates, in particular have thus always engaged the attention of various groups of workers over the years.

SYNTHESIS

As already mentioned in the introduction of this article, an easy access to pure metal-acetylacetonato compounds have always been a major difficulty owing to problems elaborated below.

Earlier methods,^{17,18,19} reported in the literature for the synthesis of metal acetylacetonato complexes may be discussed under the following heads :-

1. Metal-Acetate

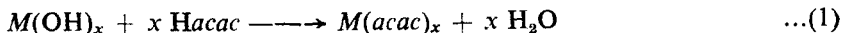
2. Metal Salt

3. Metal Carbonyl

Certain amount of caution, which we outline below, must be exercised in using any of the above-mentioned techniques. The metal-acetate method uses acetates in order to control the *pH*. Chances of end-product contamination by acetates, owing to the use of large excess of buffer, cannot be ruled out. The metal salt technique which is a modification of aqueous solution synthesis¹⁷ from metal salts, on the other hand, appeared to have some general usefulness and products in many cases could be obtained free from base contamination. But, since this procedure requires a metal salt to be soluble in strongly basic or amomniacal solution, formation of basic compounds¹⁸ on many occasions were unavoidable. While it is essential to exercise some caution in both of these procedure, the metal-carbonyl route was proved to be free from the afore-mentioned limitations and purity of the end product could thus be ensured. However, this technique has some other kinds of limitations viz., involvement of extra preparation steps in addition to the difficulties encountered in the handling of air-sensitive toxic metal carbonyl.²⁰ Taking note of the limitations and problems highlighted above, a search for easier general synthetic routes to acetylacetonato-metals was therefore warranted. With this background we embarked on a research programme aimed at improvising easily accessible routes to pure acetylacetonato-metals. Fortunately it has been possible for us to improvise two direct general methods (*vide supra*) for the purpose, the theme and scope of which will be developed in some details below.

ACID-BASE

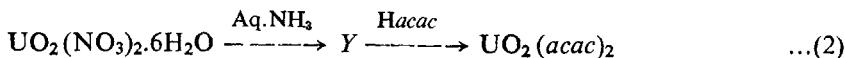
Acetylacetonone, because of the presence of active methylenic hydrogen, shows weak acidity and it was thought that an interaction of acetylacetonone (*Hacac*) with metal hydroxides or hydrated basic metal oxides would lead to an acid-base type of reaction thereby bringing about co-ordination of acetylacetonone with metal (Eqn. 1). Accordingly, based on this philosophy we were successful in obtaining a good number



of acetylacetonato-metals. The advantage of this method, unlike the earlier ones, are that it neither requires any extra preparation steps nor any external buffering agent for the maintenance of a requisite *pH*. The *pH* of the reaction medium was found to be controlled spontaneously at *ca* 5, a condition conducive to the successful synthesis of the desired compounds. The method, therefore, not only resulted in pure products but also ensured shorter reaction time. Further the method is direct, simple and easy to manipulate. Outlined below are the syntheses of several acetylacetonato-metals which were successfully achieved in our laboratory following this procedure.

(i) *Synthesis of Bis(acetylacetonato) metal(II)-Hydrates*²¹

(a) $M(acac)_2 \cdot nH_2O$ ($M = Co, Ni$ or $Cu, n = 2; UO_2^{2+}, n = 0$)—Freshly prepared alkali-free metal hydroxide $M(OH)_2$ ($M = Co, Ni$ or Cu) (20mmol) or a yellow precipitate (1.99mmol) resulting from addition of aqueous ammonia to a solution of uranyl nitrate (eqn. 2) was made to react with *ca* 10cm³ of over a steam-bath for *ca* 30min (1hr for $M = UO_2^{2+}$). A clear coloured solution or, in the case of nickel



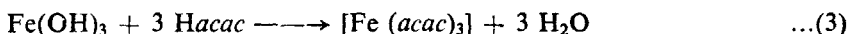
green-blue microcrystalline product, was obtained. The pH of the solutions recorded at this stage was found to be 5–6, a pH range conducive for metal-acetylacetonate formation. The solutions as obtained above were cooled to ice-bath temperature and the product was separated by filtration. Yields of the compounds are 90–95 per cent.

(b) $M(acac)_2 \cdot 2H_2O$ ($M = Mn(II)$ or $Fe(II)$)²¹—Bis(acetylacetonato) manganese(II) dihydrate, $[Mn(acac)_2] \cdot 2H_2O$, and bis(acetylacetonato) iron(II) dihydrate, $[Fe(acac)_2] \cdot 2H_2O$, have been synthesized following the general procedure described for those of other $[M(acac)_2] \cdot 2H_2O$ complexes described under (i) (a). The only difference was that the syntheses were carried out in the presence of 2.5–3.0cm³ 38 per cent formaldehyde solution to prevent undesirable oxidation of manganese(II) and iron(II).

(c) *Tetrakis(acetylacetonato) dioxo-μ-oxomolybdenum(V)*²², $[Mo_2O_3(C_5H_7O_2)_4]$ —Tetrakis(acetylacetonato) dioxo-μ-oxodimolybdenum(V), $Mo_2O_3(C_5H_7O_2)_4$, has been synthesized directly from the reaction of $MoO(OH)_3$ (6.1mmol) and acetylacetonone (60.0mmol) by refluxing in a round-bottomed flask for *ca* 3hr. The deep brown solution thus obtained was filtered and the filtrate was cooled in an ice-bath for *ca* 2.5hr to obtain brown microcrystalline $[Mo_2O_3(C_5H_7O_2)_4]$. The compound was washed with ethanol and dried *in vacuo*.

(ii) *Synthesis of Tris(acetylacetonato) Metal(III) $M(acac)_3$* ($M = Fe^{20}, Co^{20}, Mn^{23}$ or Ru^{24})

Novel synthesis of tris(acetylacetonato) iron(III) has been achieved in high yield directly from the reaction of iron(III) hydroxide with acetylacetonone under gentle warming over a steam-bath for 30min (eqn. 3)



Analogous methods have been used with success for the synthesis of $[Co(acac)_3]$ from $CoO(OH)$, $[Mn(acac)_3]$ from $MnO(OH)$ and $[Ru(acac)_3]$ from hydrated ruthenium oxide. The pH of the solution recorded immediately after the formation of the compound, was found to be *ca* 5 which concurs with that maintained by using a large amount of sodium acetate in the earlier methods of Synthesis of such compounds.

(iii) *Synthesis of Tetrakis(acetylacetonato) metals(IV), $M(acac)_4$ ($M = Ce^{25}$ or Th)*

The $Ce(acac)_4$ and $Th(acac)_4$ were synthesized directly from the reactions of hydrated Ce(IV) oxide and Th(IV) oxide, respectively, with acetylacetonone and finally concentrating the reaction solution over a steam-bath. The solutions so obtained were cooled to 0 °C in the case of Ce and to room-temperature in the case of Th to obtain crystalline $M(acac)_4$ ($M = Ce$ or Th) in very high yields.

ELECTRON-TRANSFER (REDOX)

The chelating ability of acetylacetonone has long been recognised and, based on some very recent studies^{23,26} on the synthesis of fluoro-metallates of Mn(III) from $KMnO_4$, its potential as a suitable reducing agent has also been proved beyond doubt. In view of this it was expected that the synthesis of acetylacetonato-metals might as well be possible from the reactions of higher-valent transition metals with acetylacetonone. As anticipated, the strategy worked in line with the contention enabling us to devise another direct general route to acetylacetonato-metals based on the concept of redox reaction. The reduction of higher valent metal ions by acetylacetonone and subsequent formation of the chelates owing to the presence of an excess acetylacetonone appear to be the driving forces for the reactions.²⁷ It is imperative to mention that an excess of acetylacetonone should be used so that, after the electron-transfer reaction between a metal ion and $Hacac$ is over, an appreciable amount of $Hacac$ is still available in the medium to act as ligands. The course of the reaction is observed to be such that it spontaneously maintains the pH conducive to the synthesis. Thus, here again like our acid-base method (*vide supra*) no additional buffer is required. The Redox method has been very successful for the synthesis of a number of acetylacetonatometals, as outlined below :

(i) *Synthesis of Tris (acetylacetonato) Metal(III), $M(acac)_3$ ($M = Mn(III)^{26}$ or $Cr(III)^{28}$)*

Tris (acetylacetonato) manganese(III), $[Mn(acac)_3]$ has been prepared starting from a hot aqueous solution of $KMnO_4$ and an excess of $Hacac$ with vigorous stirring over steam-bath for *ca* 5min and then cooling to room temperature. The dark brown-black shiny crystals of $[Mn(acac)_3]$ so obtained were filtered off and washed several times with small amounts of $Hacac$: water mixture and finally dried *in vacuo*.

The synthesis of $[Cr(acac)_3]$ required a somewhat vigorous reaction condition. A quantity of 2.0g powdered CrO_3 was added to 2.0g distilled acetylacetonone with constant stirring whereupon an exothermic reaction set in and the colour of the solution became dark violet. Stirring was continued for another 5–10 min after the addition was complete. The solution was heated over a steam-bath for *ca* 4hr in an open beaker and then allowed to cool for *ca* 1hr in a freezer. The dark

pink-violet shiny crystals of $[\text{Cr}(\text{acac})_3]$ were filtered off and washed several times with water and finally dried *in vacuo*.

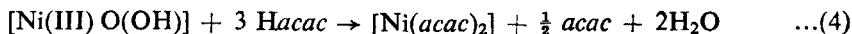
(ii) *Synthesis of Bis (acetylacetonato) Nickel(II) Dihydrate, $[\text{Ni}(\text{acac})_2] \cdot 2\text{H}_2\text{O}$* ²⁹

Synthesis of $[\text{Ni}(\text{acac})_3] \cdot 2\text{H}_2\text{O}$ was achieved from the reaction of $\text{NiO}(\text{OH})$. The $\text{NiO}(\text{OH})$ was prepared by oxidation of an alkaline suspension by bromine. The reaction of $\text{NiO}(\text{OH})$ with *Hacac* is an exothermic one and proceeds almost immediately. The reaction-mixture needs to be stirred continuously until the black $\text{NiO}(\text{OH})$ is converted completely to a blue-green product.

Isolation of $\alpha, \alpha, \beta, \beta$ -Tetraacetylene as the Oxidation Product of Acetylacetonate from Redox Reaction

Having achieved success^{26,28,29} in the synthesis of acetylacetonato-metals through the redox method, as demonstrated above, it was our concern to identify the oxidation product of *Hacac* in such a reaction. Incidentally there exists no firm evidence regarding the oxidation product of *Hacac* when it acted as a reducing agent until we published²⁹ our results first in 1983. Interest in ascertaining the identity of the oxidation product of *Hacac*, was not only to provide a concrete evidence for its identity but also to have an insight into the redox mechanism of such reactions. Our first success in this context came through the synthesis of $[\text{Ni}(\text{acac})_2] \cdot 2\text{H}_2\text{O}$ from $\text{NiO}(\text{OH})$ wherein work-up of the mother liquor, after separating $[\text{Ni}(\text{acac})_2] \cdot 2\text{H}_2\text{O}$, afforded colourless crystals. The compound was obtained in a very high yield and found to melt at 190 °C. The product was very sparingly soluble in water, benzene and ether. Its various physical and chemical properties (colour, m.p., solubility, reaction with FeCl_3 , and mass and NMR spectra) compare very well with those of a specimen prepared by the action of iodine upon sodium acetylacetonate.³⁰ Accordingly the identity of the compound has been established as $\alpha, \alpha, \beta, \beta$ -tetra-acetylene, $(\text{CH}_3\text{CO})_2\text{CH}-\text{CH}(\text{CH}_3\text{CO})_2$.

In an attempt to generalise the contention that electron-transfer reactions between higher-valent transition metal ions and acetylacetonate leading to the corresponding acetylacetonates, give $(\text{CH}_3\text{CO})_2\text{CH}-\text{CH}(\text{CH}_3\text{CO})_2$ as the oxidation product, we performed the reactions of *Hacac* with Mn^{7+} and Cr^{6+} following the procedures described in our previous paper^{26,28} Isolation of $(\text{CH}_3\text{CO})_2\text{CH}-\text{CH}(\text{CH}_3\text{CO})_2$ from each of the reactions, after separation of the corresponding $[\text{M}(\text{acac})_3]$ complex, was successful again owing to the oxidation of acetylacetonate. We therefore conclude that in the electron-transfer reactions of the types discussed above, acetylacetonate is oxidised to $\alpha, \alpha, \beta, \beta$ -tetraacetylene, $(\text{CH}_3\text{CO})_2\text{CH}-\text{CH}(\text{CH}_3\text{CO})_2$. In view of the products isolated from the reactions of Ni^{3+} (eqn 4), Mn^{7+} or Cr^{6+} with acetylacetonate, and the observed pH of the reaction medium, it is



felt that acetylacetonate first undergoes ionization giving $(\text{CH}_3\text{CO})_2\text{CH}^-(\text{acac}^-)$ and H^+ (cf. the observed pH) followed by the oxidation of $(\text{CH}_3\text{CO})_2\text{CH}^-$ ion to $(\text{CH}_3\text{CO})_3\text{C}^\cdot$ radical (with corresponding reductions of the metals) which dimerises

to yield $(\text{CH}_3\text{CO})_2\text{CH-CH}(\text{CH}_3\text{CO})_2$.²⁹ It may be mentioned in passing that this route to $\alpha, \alpha, \beta, \beta$ -tetraacetyethane is relatively simpler than the method described in the literature.³¹

NEWER REACTIONS

The synthetic potentiality of acetylacetonato-metal compounds as precursor in organometallic synthesis is well documented^{32,33} in the literature. Having achieved an easy access to such compounds by the methods reviewed in this article, the authors got interested in exploring a newer facet of application of acetylacetonato-metals as synthetic precursors for the synthesis of inorganic compounds which are otherwise very difficult to get an access to. As a part of one of our general programmes dealing with the fluoro-chemistry of metals and non-metals, it was anticipated that the reactions of such compounds with F^- in acidic medium would lead to the cleavage of metal-oxygen bond of β -ketoenolate complexes ultimately leading to newer synthetic routes to fluoro-metallates.³⁴ The strategy worked in line with the contention enabling us to obtain a good number of fluoro compounds of metals as highlighted below, in an unprecedented easy manner. It is believed that the success of the strategy largely depends on the presence of both H^+ as well as the stabilising ligand (F^- , in these cases) in the solution phase.²³

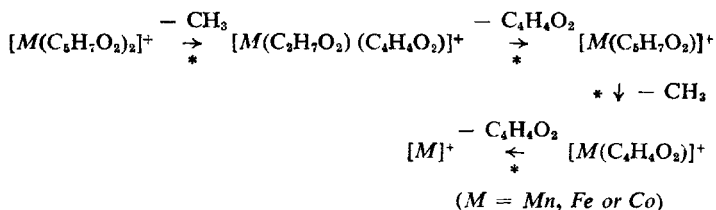
Thus the complexes $A_2[\text{NiF}_4]$ ($A = \text{NH}_4, \text{K}$ or Rb) and $A_2[\text{ZnF}_4]$ ($A = \text{NH}_4, \text{K}, \text{Rb}$ or Cs) have been synthesised,²⁷ from $[\text{Ni}(\text{acac})_2] \cdot 2\text{H}_2\text{O}$ and $[\text{Zn}(\text{acac})_2] \cdot \text{H}_2\text{O}$, respectively, with 40 per cent HF and AF, in a very high yields. Literature methods^{35,36,37} for the synthesis of $[\text{NiF}_4]^{2-}$ or $[\text{ZnF}_4]^{2-}$ complexes employ fusion of NiF_2 or ZnF_2 with stoichiometric amounts of alkali-metal or alkaline-earth metal fluorides *in vacuo* or in an atmosphere of dry HF. Such methods require not only MF_2 ($M = \text{Ni}$ or Zn) but also anhydrous HF which is difficult to handle, consequently limiting their accessibility.

The alkali-metal trifluoronicklate(II) monohydrates, $\text{ANiF}_3 \cdot \text{H}_2\text{O}$ ($A = \text{NH}_4, \text{Na}$ or K), are simple, yet show interesting properties. For example, the mere change of the counter cation in $\text{ANiF}_3 \cdot \text{H}_2\text{O}$ brings about very drastic and significant changes of magnetic properties. Although Machin and Nyholm reported³⁸ the analytical data and magnetic properties of $\text{ANiF}_3 \cdot \text{H}_2\text{O}$ about 25 years ago, there was no report on their synthesis until we published³⁴ a general procedure in 1985, as outlined below. In a typical procedure, $[\text{Ni}(\text{acac})_2] \cdot 2\text{H}_2\text{O}$ was reacted with AF ($A = \text{NH}_4, \text{Na}$ or K) and an excess of 40 per cent HF on a steam-bath. The light-green crystalline product obtained thereof on treatment with water was shown to be alkali-metal trifluoronicklate(II) monohydrate, $\text{ANiF}_3 \cdot \text{H}_2\text{O}$. In an attempt to explore the scope of the new synthetic procedure, similar reactions involving $[\text{VO}(\text{acac})_2]$,³⁹ $[\text{Cr}(\text{acac})_3]^{2-}$ ²⁸ or $[\text{Mn}(\text{acac})_3]^{2-}$ ²⁶ with NH_4F and 40 per cent HF were carried out and the products obtained were identified as $(\text{NH}_4)_4[\text{VOF}_4]$, $(\text{NH}_4)_2[\text{CrF}_5(\text{H}_2\text{O})]$, and $(\text{NH}_4)_2[\text{MnF}_5]$, respectively, thereby supporting our notion that the method can be used as a paradigm for other such syntheses.

MASS SPECTROMETRY

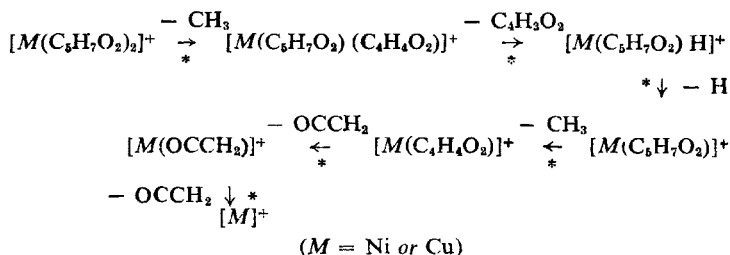
Since β -ketoenol-metal complexes have been such a commonly used commodity around the chemistry laboratories for half a century or more, it is but natural to expect that various physico-chemical⁴⁰ studies involving them were carried out. Low and sharp melting points of acetylacetonato-metals, however, rendered this class of coordination compounds suitable probes for mass spectrometric studies. Accordingly, a good amount of mass spectrometry of such compounds, mainly involving bis- and tris-chelates of higher metals,^{20,28,41,42,43} were carried out. In contrast, the corresponding heavy metal analogues, and tetrakis-chelates, the examples of which are only a few in number, have not received due attention. Although a hike in current interest in this area has been accentuated in some of the recent reports dealing with mass spectra of fluorinated β -diketonato complexes of Eu,⁴⁴ Pd,⁴⁴ UO_2^{2+} (Ref. 45), and Ce,⁴⁶ we are unable to discern any obvious reasons for taking no notice of the corresponding nonfluorinated acetylacetonato complexes in the previous mass spectrometric investigations. As a case in point, the mass spectrum of $\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$, an important compound of uranium has been reported²¹ only in 1986, while that of $\text{Ce}(\text{C}_5\text{H}_7\text{O}_2)_4$ is yet to be seen in print. Further it was commented^{41,43} that attempts to obtain good mass spectrum of acetylacetonato-metals were not always successful. In view of this and in a continuation of our work^{20,26,28} in this field, the mass spectrometric studies of several acetylacetonato-metals were undertaken. We present in this section of the article, the salient features of Electron-Impact induced positive ion mass spectrometric studies of acetylacetonato-metals of the types $M(\text{acac})_2^{21}$ ($M = \text{Mn, Fe, Co, Ni}$ or Cu), $M(\text{acac})_3$ $M = \text{Mn,}^{26} \text{Fe}^{20}$ or Cr^{28} and $M(\text{acac})_4$ ($M = \text{Ce}^{25}$ or Th). Also highlighted herein are the results of mass spectrometric studies of bis(acetylacetonato) dioxouranium(VI), $[\text{UO}_2(\text{acac})_2]^{21}$, bis(acetylacetonato) dioxomolybdenum(VI),²² $\text{MoO}_2(\text{acac})_2$, and tetrakis(acetylacetonato) dioxo- μ -oxomolybdenum(V), $\text{Mo}_2\text{O}_3(\text{acac})_4$,²² which were reported for the first time in 1986. Moreover, an attempt has also been made to internally compare the results of mass spectrometry of the related systems.

Mass spectrometrically, bis(acetylacetonato) metal, $M(\text{C}_5\text{H}_7\text{O}_2)_2$ ($M = \text{Mn, Fe, Co, Ni}$ or Cu) compounds may be classified into two groups with $M = \text{Mn, Fe, Co}$ forming one, and $M = \text{Ni}$ or Cu the other. The molecular ion in each case loses CH_3 to produce $[M(\text{C}_5\text{H}_7\text{O}_2) (\text{C}_4\text{H}_4\text{O}_2)]^+$. However, the subsequent fragmentation of $[M(\text{C}_5\text{H}_7\text{O}_2) (\text{C}_4\text{H}_4\text{O}_2)]^+$ with M being Mn, Fe or Co (Scheme 1) is distinctly different from that with M being Ni or Cu (Scheme 2). Whereas in the former case the fragment ion undergoes a loss of $\text{C}_4\text{H}_4\text{O}_2$ to produce the most dominant ion $[M(\text{C}_5\text{H}_7\text{O}_2)]^+$, in the latter case it fragments involving an extensive H migration to the metal, especially to give $[M(\text{C}_5\text{H}_7\text{O}_2)\text{H}]^+$, with the loss of $\text{C}_4\text{H}_3\text{O}_2$. Further H atom migration appears to be more facile in the case of $\text{Ni}(\text{C}_5\text{H}_7\text{O}_2)_2$ than the corresponding copper complex. Facile H migration in the case of nickel is rationalised in terms of the formation of a strong nickel-hydrogen bond and may be related to the catalytic activity of the metal in hydrogenation reaction.²¹



SCHEME 1

We believe hydrogen transfer to the metal, rather than to any oxygen atom of the other ligand as proposed by others,⁴⁷ as a likely alternative explanation because if H migration to any other sites were involved, this type of ion (cf. $[M(C_5H_7O_2)H]^+$) should be well observed for acetylacetonato complexes of other metals.



SCHEME 2

The fragment ion $[M(C_5H_7O_2)H]^+$ then loses H to produce $[M(C_5H_7O_2)]^+$ ($M = Ni$ or Cu) which undergoes a stepwise loss of CH_3 , $OCCH_2$, and again another $OCCH_2$ ultimately to give the $[M]^+$ ion (as shown in Scheme 2). While for $M = Mn$, Fe or Co , the ion $[M(C_5H_7O_2)]^+$ sequentially loses CH_3 and $C_4H_4O_2$ to produce the $[M]^+$.

A comparison of the Schemes 1 and 2 shows that the mode of fragmentation of the $[M(C_5H_7O_2)]^+$ ion is different in two cases. Thus, for $M = Mn$, Fe or Co , the $[M(C_5H_7O_2)]^+$ first expels CH_3 and then $C_4H_4O_2$ moiety to produce the bare $[M]^+$ ion however, for $M = Ni$ or Cu three steps are involved as depicted in the Scheme 2. Another point of difference lies in the appearance of the base peaks. Whereas the $[M(C_5H_7O_2)]^+$ is the most dominant fragment in the spectra of Mn , Fe and Co complexes, the molecular ion $[M(C_5H_7O_2)_2]^+$ appears to provide the base peak of the corresponding complexes of Ni or Cu . Enough metastable peaks have been observed in support of Schemes 1 and 2 to lend credence to the suggested mode of fragmentation. Mass spectra of bis(acetylacetonato) metal(II), with M being Mn , Fe , Co , Ni or Cu , were reported by earlier workers. It is in order to collate the mass spectrometric results of these compounds with those of the heavier metal analogues that we re-investigated the mass spectra of such compounds under analogous experimental conditions. The selective

*indicates metastable supported transitions.

acetylacetonates of heavy metals incorporated for the purpose mentioned above include $[\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2]$, $[\text{Mo}_2\text{O}_3(\text{C}_5\text{H}_7\text{O}_2)_4]$, $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2]$, and $[\text{Ce}(\text{C}_5\text{H}_7\text{O}_2)_4]$.

The mass spectrum of $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$ (structure shown in Fig. 3) showed a parent ion signal at m/z 328, due to $[\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2]^+$, followed by the signals at m/z 286 and 229 assigned to $[\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_3\text{H}_5\text{O})]^+$ and $[\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)]^+$, respectively, suggesting that the parent ion first loses CH_2CO and then $\text{C}_3\text{H}_5\text{O}$ to produce the ion $[\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)]^+$. It is important to note that, unlike the *bis* (acetylacetonato) complexes of first-row transition metals,²¹ the molecular ion of $[\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2]$ undergoes a loss of a ketene (CH_2CO) instead of a CH_3 radical.²² This difference may, in part, arise as a consequence of the fact that the former usually have *d* electrons so that valency changes become important, whereas in $[\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2]$ Mo atom has d^0 configuration. The $[\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)]^+$ ion, however, undergoes further fragmentation in two different ways, as evident from the appearance of signals of almost equal intensities owing to $[\text{MoO}_2(\text{C}_5\text{H}_5\text{O})]^+$ and $[\text{MoO}_2(\text{C}_3\text{H}_5\text{O})]^+$, respectively. Both of these fragments ultimately crack down to the bare ion $[\text{MoO}_2]^+$. The most probable fragmentation pattern, in line with the experimental observations, is shown in Scheme 3. The observation of a metastable ion peak at m^*/z 99.6 is consistent with the fragmentation $[\text{MoO}(\text{C}_3\text{H}_5\text{O})]^+$ (m/z 211) \rightarrow $[\text{MoO}_2\text{CH}_3]^+$ (m/z 145), and suggests the occurrence of a methyl transfer reaction from the ligand, presumably to one of the oxygen atoms already bound to the metal or to form a new Mo-CH₃ bond. A somewhat similar methyl shift has been observed²⁰ in the case of $\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3$ (*vide infra*).

The mass spectrum of $\text{Mo}_2\text{O}_3(\text{C}_5\text{H}_7\text{O}_2)_4$ appears to be more complicated than that of $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$. The compound $\text{Mo}_2\text{O}_3(\text{C}_5\text{H}_7\text{O}_2)_4$ (structure shown in Fig. 4) showed the molecular ion signal at m/z 636 due to $[\text{Mo}_2\text{O}_3(\text{C}_5\text{H}_7\text{O}_2)_4]^+$ suggesting that it did not undergo any association in the vapour state.

The molecular ion fragments in two distinctly different ways as shown in Scheme 4. While path I involves fragments containing bimetallic ions, path involves only monometallic fragments.

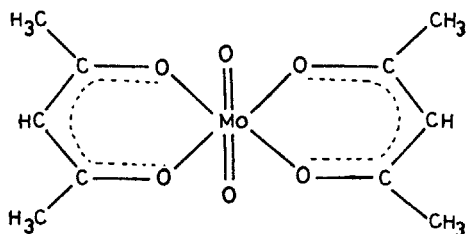
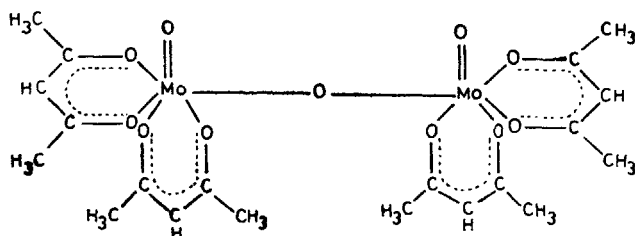
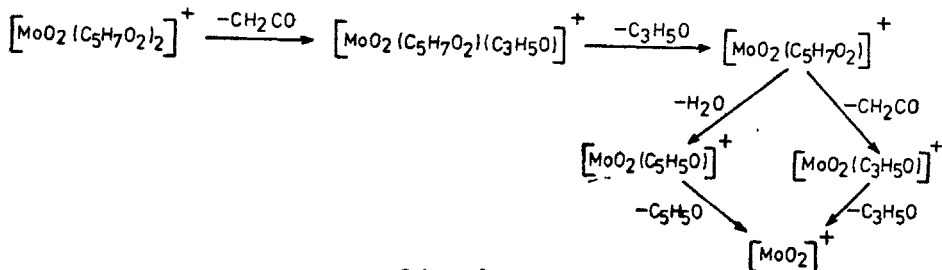
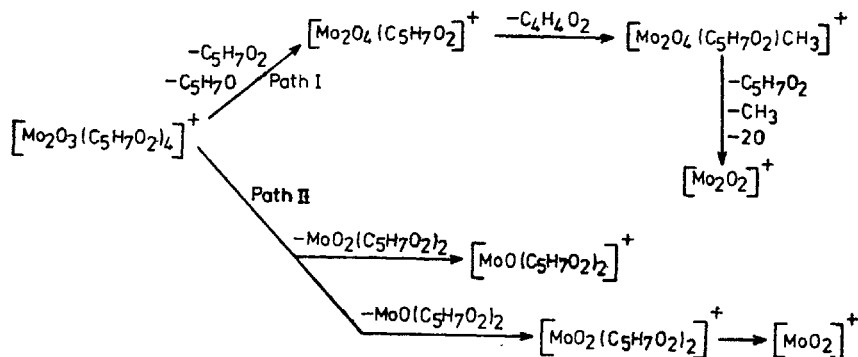


FIG 3 Structure of $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$

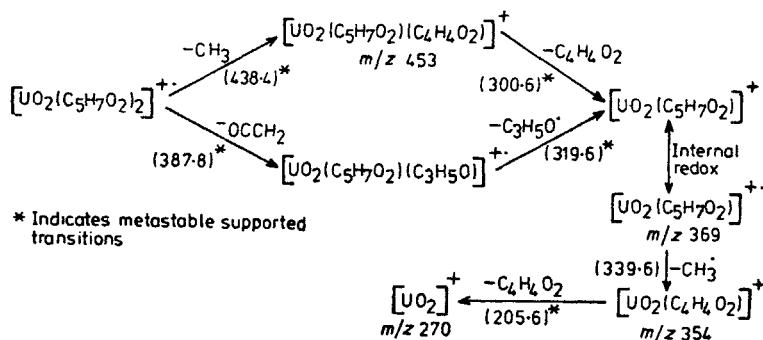
FIG 4 Structure of $\text{Mo}_2\text{O}_3(\text{C}_5\text{H}_7\text{O}_2)_4$ Scheme 3Scheme 4

Natural molybdenum contains a mixture of isotopes forming a characteristic pattern diagnostic for the presence of Mo in a given ion. The isotope pattern for ions containing two Mo atoms can be predicted by well-established methods,^{45,46,47} from the isotope distribution of the metal. The reported relative abundance data for the monometallic fragment ions are based on the heights of signals of the ions containing the isotope ⁹⁸Mo (23.8 per cent natural abundance), while the bimetallic fragment ions of compound $\text{Mo}_2\text{O}_3(\text{acac})_4$ are based on the ions where Mo_2 contributed 192 (13.1 per cent natural abundance by calculation) to the total mass of the fragment ion. Typical patterns for the bimetallic and monometallic fragment ions were observed in the respective cases. The parent ion, in accord with the path I, loses one $\text{C}_5\text{H}_7\text{O}_2$ moiety and $\text{C}_5\text{H}_7\text{O}$ moiety in

steps to produce $[\text{Mo}_2\text{O}_4(\text{C}_5\text{H}_7\text{O}_2)_2]^+$ ion. Whereas the loss of $\text{C}_5\text{H}_7\text{O}_2$ has been observed in the spectra of many acetylacetonatometals, the loss of $\text{C}_5\text{H}_7\text{O}$ from such compounds is rather rare though not unprecedented.⁵¹ It is believed that the strong tendency of Mo^{5+} to form $\text{Mo}=\text{O}$ causes fragmentation of the coordinated $\text{C}_5\text{H}_7\text{O}_2^-$ ligand leading to the expulsion of $\text{C}_5\text{H}_7\text{O}$ with the retention of one oxygen atom (as $\text{Mo}=\text{O}$). The fragment thus formed, then loses $\text{C}_4\text{H}_4\text{O}_2$ to yield $[\text{Mo}_2\text{O}_4(\text{C}_5\text{H}_7\text{O}_2)\text{CH}_3]^+$ which again, as observed for $[\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2]$, is a case of methyl shift from ligand to the oxo-oxygen already bound to the metal or directly to the metal itself. The ion $[\text{Mo}_2\text{O}_4(\text{C}_5\text{H}_7\text{O}_2)\text{CH}_3]^+$ ultimately breaks down to $[\text{Mo}_2\text{O}_2]^+$.

A perusal of the signals arising from the monometallic fragments reveals that the signal at m/z 312 assigned to the $[\text{MoO}(\text{C}_5\text{H}_7\text{O}_2)_2]^+$ ion forms the base peak of the spectrum of $[\text{Mo}_2\text{O}_3(\text{C}_5\text{H}_7\text{O}_2)_4]$. Unfortunately, no metastable peak for the transition $[\text{Mo}_2\text{O}_3(\text{C}_5\text{H}_7\text{O}_2)_4]^+ \rightarrow [\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2]^+$ could be observed. The other signals due to monometallic fragments correspond to those observed in the spectrum of $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$, but generally of much lower intensities, suggesting that the formation and subsequent fragmentation of the ion $[\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)]^+$ can not be totally ruled out. Metastable transition studies lend strong support to the proposed fragmentation pattern.

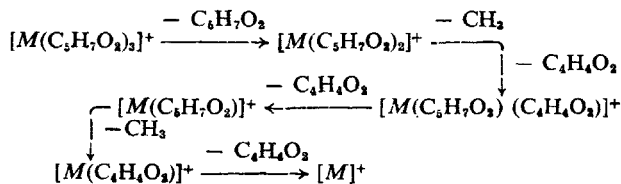
The EI-induced positive ion mass spectrum of $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2]$ exhibited parent ion signal at m/z 468 due to $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2]^+$ and no signal beyond m/z 468 thereby showing the absence of any molecular association in the gaseous state. The molecular ion, $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2]^+$; so obtained fragments (Scheme 5) to $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_4\text{H}_4\text{O}_2)]^+$ and $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)]^+$ with an equal probability via a methyl radical (CH_3) or a ketene (OCCH_2) loss, respectively. While CH_3 radical loss from the molecular ion $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2]^+$ involves simply the cleavage of C- CH_3 bond to produce the even electron ion $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_4\text{H}_4\text{O}_2)]^+$, the loss of an even electron species OCCH_2 from $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2]^+$ must involve a rearrangement in the ligand to give the odd-electron ion $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_3\text{H}_5\text{O})]^+$. The ions $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)(\text{C}_4\text{H}_4\text{O}_2)]^+$ and $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)]^+$ lose $\text{C}_4\text{H}_4\text{O}_2$ and $\text{C}_3\text{H}_5\text{O}$ species, respectively, to form the most dominant ion $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)]^+$, which



Scheme 5

again fragments in two different ways by the loss of H_2O and $\text{CH}_3\cdot$, respectively, to give $[\text{UO}_2(\text{C}_5\text{H}_5\text{O})]^+$ and $[\text{UO}_2(\text{C}_4\text{H}_4\text{O}_2)]^+$ ions. The weak nature of the signal at m/z 351 owing to the loss of H_2O points to a relatively lower ease of H_2O loss from the $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)]^+$ ion over the loss of a $\text{CH}_3\cdot$ radical. The loss of a $\text{CH}_3\cdot$ radical, at this stage, can be rationalised in the light of the valency change concept and accordingly the even electron ion $[\text{U(VI)} \text{O}_2(\text{C}_5\text{H}_7\text{O}_2)]^+$ changes to the odd-electron ion $[\text{U(V)} \text{O}_2(\text{C}_5\text{H}_7\text{O}_2)]^+$ which then expels a $\text{CH}_3\cdot$ radical to produce $[\text{UO}_2(\text{C}_4\text{H}_4\text{O}_2)]^+$. This even electron ion ultimately cracks down to bare $[\text{UO}_2]^+$. The last two steps of fragmentation involving loss of $\text{CH}_3\cdot$ and $\text{C}_4\text{H}_4\text{O}_2$ from the $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)]^+$ fragment resemble those generally observed for the corresponding $[\text{M}(\text{C}_5\text{H}_7\text{O}_2)]^+$ where $M = \text{Mn}$, Fe or Co , as discussed earlier. Methyl transfer from ligand to the uranyl (UO_2) centre, like in the case of $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$ or hydrogen transfer from ligand to the uranyl centre, like in the case $\text{M}(\text{C}_5\text{H}_7\text{O}_2)_2$ ($M = \text{Ni}$ or Cu), could not be observed in $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2]$. Like the *bis* (acetylacetonato) metals of first row transition metals, $\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$ exists as a monomer in the gaseous state without undergoing any association. As pointed out in the case of $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$, the difference between $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2]$ and $M(\text{acac})_2$ ($M = \text{Mn}$, Fe , Co , Ni or Cu) may, in part, owe its origin to the $5f^3 6d^0$ configuration of U in $\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$ as opposed to a d^n configuration in the latter. The unique feature of EI-mass spectrum of bis(acetylacetonato) dioxouranium(VI) $\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$, as against other $M(\text{acac})_2$ ($M = \text{Mn}$, Fe , Co , Ni or Cu), $\text{MoO}_2(\text{C}_5\text{H}_7\text{O}_2)_2$, and $\text{Mo}_2\text{O}_3(\text{C}_5\text{H}_7\text{O}_2)_4$ compounds is that it provides evidence for the simultaneous loss of $\text{CH}_3\cdot$ and ketene (OCCH_2) from the molecular ion. The most probable fragmentation pathway, in conformity with the experimental observations, $[\text{UO}_2(\text{C}_5\text{H}_7\text{O}_2)_2]^+$ is as depicted in Scheme 5.

In going from *bis* (acetylacetonato) metals to the corresponding *tris* (acetylacetonato) metals one finds some notable differences as emphasised in the following discussion. Mass spectrometrically the three compounds, namely $[\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_3]^+$, $[\text{Cr}(\text{C}_5\text{H}_7\text{O}_2)_3]^+$ and $[\text{Fe}(\text{C}_5\text{H}_7\text{O}_2)_3]^+$, included herein behave generally in an analogous manner. Their typical fragmentation pathway can be displayed as shown in Scheme 6. As evident from the fragmentation pattern, the $M(\text{acac})_2$ compound, like $M(\text{acac})_2$, show their respective molecular ion signals indicating an absence of any association in the vapour state.



SCHEME 6

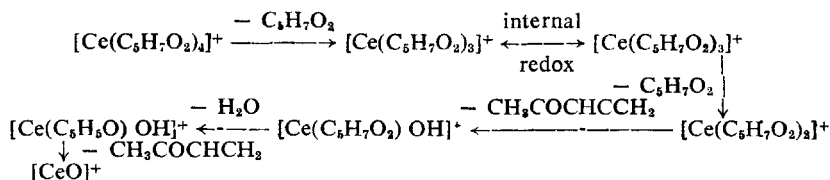
The molecular ion in each case, unlike those of $M(\text{acac})_2$ compounds, expels $\text{C}_5\text{H}_7\text{O}_2$ ligand. It may be recalled that the molecular ions of bis(acetylacetonato) metals generally lose a CH_3 group from one of the ligands. The fragment ion

$[M(C_5H_7O_2)]^+$ originated from the process $[M(C_5H_7O_2)_3]^+ \xrightarrow{-C_5H_7O_2} [M(C_5H_7O_2)_2]^+$, constitutes the base peak of the spectrum in each case. The fragment ion $[M(C_5H_7O_2)_2]^+$ then undergoes loss of CH_3 and $C_4H_4O_2$ in successive steps to produce the $[M(C_5H_7O_2)]^+$ ion which again repeats a similar sequence of fragmentation ultimately to produce the bare $[M]^+$ ion (*vide* Scheme 6). It may be mentioned in passing that the fragmentation of $[M(C_5H_7O_2)_2]^+$, irrespective of its origin either from the process $[M(C_5H_7O_2)_3]^+ \xrightarrow{-C_5H_7O_2} [M(C_5H_7O_2)_2]^+$, or from that of $[M(C_5H_7O_2)_2] \xrightarrow[+2e]{-2e} [M(C_5H_7O_2)_2]^+$, until the bare $[M]^+$ ion follows a similar pattern (*cf.* Schemes 1, 2 and 6). Experiments on metastable transition studies showed enough metastable peaks adducing strong support to the suggested mode of fragmentation of the compounds (Scheme 6). This general mode of fragmentation agrees well with those of similar compounds reported by some other workers. A significant point in this context, which needs a special mention here, is the observance of two metastable supported signals at m/z 170 and 71 assigned to $[Fe(CH_3)(C_5H_7O_2)]^+$ and $[Fe(CH_3)]^+$, respectively, in the case of $[Fe(C_5H_7O_2)_3]$ providing evidence for easy methyl migration (*cf.* $[MoO_2(acac)_2]$) from carbon to metal presumably favoured by the formation of a new bond between metal atom and CH_3 .

The tetrakis (acetylacetonato) metals, $M(acac)_4$, are very few in number (See Table) as opposed to a host of complexes of the types $M(acac)$ and $M(acac)_2$. Comparatively very little is therefore known on the mass spectrometry of the spectrometry of the $M(acac)_4$ class of compounds. As a case in point, for instance, *tetrakis* (acetylacetonato) cerium(IV), $Ce(C_5H_7O_2)_4$ has been known in the literature, however there is no reported existence of its mass spectrum until date.

The electron-impact induced positive ion mass spectrum of $Ce(C_5H_7O_2)_4$, recorded under conditions similar to those maintained for other compounds already described in this section, showed weak molecular signal at m/z 536 due to the formation of the odd-electron ion $Ce(C_5H_7O_2)_4^+$ in which Ce maintains +4 state. Absence of any signal beyond m/z 536 in the mass range covered, indicates the monomeric nature of the molecule in the gaseous state. The weak nature of molecular ion appears to be the common features of *tetrakis* (β -diketonato) complexes of metals irrespective of whether the β -diketonate is either $C_5H_7N_2^-$ (e.g. present work) or a fluorinated β -diketonate⁴⁶ with the metal being Ce⁴⁶ Zr or Th.⁵² This may at least, in part be due to the rapid decomposition of $[Ce(C_5H_7O_2)_4]^+$ to the even-electron ion $[Ce(C_5H_7O_2)_3]^+$ with the expulsion of $C_5H_7O_2$ radical. The signal due to $[Ce(C_5H_7O_2)_3]^+$ constitutes the most dominant peak, and in this respect there exists a very strong resemblance between $Ce(C_5H_7O_2)_4$ and $M(C_5H_7O_2)_4$, ($M = Zr$ or Th)⁴¹ or CeL_4^{48} ($L =$ fluorinated β -diketone). The *tris*-chelate fragment ion generally like CeL_3^+ as well as like those of *tris*-chelates of trivalent transition metals,^{41,42,43} but unlike that of

$[M(C_5H_7O_2)_2]^+$, suffers loss of an intact ligand radical $C_5H_7O_2$ to give $[Ce(C_5H_7O_2)_2]^+$. The corresponding $[M(C_5H_7O_2)_3]^+$ ($M = Zr$ or Th), in contrast, fragments to $M[C_5H_7O_2](OH)]^+$ expelling an even-electron neutral $CH_3COCHCCH_2$ which can be understood in terms of a loss familiar +3 state of Zr or Th thus the metal valency change becomes unimportant and leads to the loss of an even-electron neutral instead of a neutral radical. Further fragmentation starting from the ion $[Ce(C_5H_7O_2)_2]^+$



SCHEME 7

involves stepwise loss of three even-electron neutrals in the sequence $CH_3COCHCCH_2$, H_2O and $CH_3COCHCCH_2$, as shown in Scheme 7, until the bare $[CeO]^+$ ion is reached without invoking any internal reduction. The events starting from the fragmentation of $[Ce(C_5H_7O_2)_3]^+$ are just parallel to those observed⁴¹ in the case of $[La(C_5H_7O_2)_3]^+$ and enable us to state that this feature may be regarded as a typical one for tris-acetylacetonato-chelates of lanthanides. No methyl migration from ligand has been observed in the present case unlike in those of some other heavy metal cases viz. $[MoO_2(C_5H_7O_2)_2]$ and $[Mo_2O_3(C_5H_7O_2)_4]$. The cracking pattern beyond $[Ce(C_5H_7O_2)_3]^+$ till $[CeO]^+$ resembles only that of $[La(C_5H_7O_2)_3]^+$ but not those of the zirconium and thorium analogue. The step of fragmentation $[Ce(C_5H_7O_2)_3]^+ \rightarrow [Ce(C_5H_7O_2)_2]^+$ also resembles that of tris-chelates of the first row transition metals, however, the fragmentation beyond $[Ce(C_5H_7O_2)_2]^+$ does not do so.

CONCLUDING REMARKS

Following are the important points that emerge out of our research in the field of (acetylacetonato) metal chemistry :

(i) Acetylacetonato-metal complexes of the types $M(acac)_2$ ($M = Mn, Fe, Co, Ni$ or Cu), $[Mo_2O_3(C_5H_7O_2)_4]$, $[UO_2(C_5H_7O_2)_2]$; $M(acac)_3$ ($M = Cr, Mn, Fe$ or Ru) and $M(C_5H_7O_2)_4$ ($M = Ce$ or Th) are capable of being synthesized, without involving any buffer, exploiting either the ACID-BASE or the Electron-Transfer (REDOX) concept. Successful synthesis of a large number of the afore-mentioned compounds clearly demonstrates the scope of the newly developed methods.

(ii) $\alpha, \alpha, \beta, \beta$ -Tetraacetyethane, $(CH_3CO)_2CH-CH(CH_3CO)_2$, has been shown to be the oxidation product of acetylacetone in the REDOX reactions of higher-valent metal ions with acetylacetone leading to acetylacetonato-metals.

(iii) Newer reactions based on the interaction of (acetylacetonato)-metal with HF and alkali-metal fluorides leading to the synthesis and of fluorometallates, which are otherwise difficult to have an access to, have been described. Important in the context of research in synthetic inorganic chemistry, this novel route to fluoro-metallates can be regarded as a paradigm to the synthesis of such compounds.

(iv) Electron-impact induced positive ion mass spectra of a large number of acetylacetonato-metal compounds, with varying stoichiometry between metal and acetylacetonate, have been investigated enabling an internal comparison of their fragmentation behaviours. Comments have also been on molecular association of such compounds in the vapour state. The results cause us to recommend the direct insertion technique to be suitable for mass spectrometry of coordination compounds.

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