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METAL β-DIKETONATES AND ALLIED DERIVATIVES

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Preface

This book aims to present a concise account of recent developments in the chemistry of metal β-diketonates. The book concentrates principally on four aspects of metal β-diketonates: their synthesis, the nature of bonding and aromacity, their chemical reactions and their physical properties, including spectroscopic, magnetic and structural characteristics. In addition to the conventional oxygen-bonded derivatives, the chemistry of carbon-bonded β-diketonate complexes has been dealt with in some detail. A brief account of the applications of metal β-diketonates, e.g., in n.m.r. spectroscopy as contact shift reagents, in laser technology, in solvent extraction, and in gas chromatographic techniques has been included, but these topics have not been dealt with in detail, as separate monographs or recent review articles cover these aspects adequately.

The increasing interest amongst scientists working in these fields can be judged by the fact that there are now more than a hundred research papers published annually on different facets of the fascinating chemistry involved. A portion of the book deals with the allied chemistry of metal thio-β-diketonates. These studies have been advancing at an even faster pace in recent years and are bringing to light, amongst other facets, an interesting comparative chemistry of metal–oxygen and metal–sulphur bonds.

There are no exhaustive recent review articles or books available on these topics and the present book should therefore prove useful to students, teachers and research workers in academic institutions as well as to industrial organisations. In consideration of the wide audience for the book, an attempt has been made to begin with the basic fundamentals of each topic; even undergraduate students who are interested in metal β-diketonates may be able to follow the subject without difficulty. In addition, the book should prove to be of great value to advanced students and research workers in these as well as some allied fields.

One of the authors (R. C. Mehrotra) has been involved in some aspects of the chemistry of metal β-diketonates for the last two decades. He would like to place on record his indebtedness to a number of able and persevering research colleagues for their dedicated efforts in furthering the knowledge. The authors are grateful to many persons, too numerous to be mentioned individually, for contributions of various types including generous help in supplying reprints and for granting permission to reproduce a few original structures and figures which have been published elsewhere and have been incorporated in the present volume.

Finally, the authors wish to thank the University Grants Commission (India) for their generous financial support in the form of a Senior Research Fellowship to one of the authors (Dr D. P. Gaur) and other expenses involved in the preparation of the manuscript.

January 1978

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Contents

CHAPTER 1

Metal β-Diketonates: Introduction

Amongst the most widely studied coordination compounds are the complexes of β-diketones, which appear to have been investigated with virtually every metal and metalloid in the periodic table. The coordination ability of β-diketones is now well established; a large number of β-diketones are known to form metal complexes, and further potential ligands are prepared continually by organic chemists.

The chemistry of metal β-diketonates in a sense reflects the different eras in the development of inorganic chemistry as a whole. Starting with the synthesis of these derivatives for the first time in 1887, the nature of bonding was soon elucidated by the classical work of Werner followed by later studies in the schools of Morgan and Sidgwick who drew attention to the predominant chelating character of these ligands. A new dimension was added to the understanding of the nature of bonding in these interesting derivatives by Calvin and Wilson who in 1945 suggested the presence of aromaticity in the diketonate ring; this aspect was later pursued by Collman and others. With increasing applications of sophisticated structural determination techniques in the 1950s, the classical work of Cotton and Holm (1958) on trimeric nickel bis(acetylacetonate) opened a new chapter in this direction also. The work of Lewis and coworkers (1962–1969) has further demonstrated a newer bonding mode of these interesting ligands with some platinum metals.

Apart from the bonding and structural aspects, the capacity of these ligands to form inner coordination compounds with a variety of metals provided inorganic chemists with what were at one time rare examples of electropositive metal ions in combinations depicting characteristics of covalent compounds, i.e. solubility in organic solvents and volatility. These special characteristics have been extensively exploited in solvent extraction and gas–liquid chromatographic techniques. Current interest in metal β-diketonates also arises from their application as contact shift reagents for better resolution of the nuclear magnetic resonance (n.m.r.) spectra of a variety of complex organic molecules, in laser technology, and in the polymer industry.

Livingstone and coworkers in 1964 introduced a new series of metal thio-β-diketonates by replacing carbonyl oxygen atoms of β-diketonates with sulphur atoms. Since then thio-β-diketonate derivatives of a large number of metals have been investigated.

1.1 General Chemistry of β-Diketones

During the past two decades there has been growing interest in the metal (and organometal) derivatives of β-diketones, and the number of novel ligands employed for the purpose, as well as new compounds of previously known ligands, have multiplied dramatically. It may be worthwhile at this stage to describe briefly the chemistry of β-diketone ligands themselves before going into a detailed account of their metal derivatives.

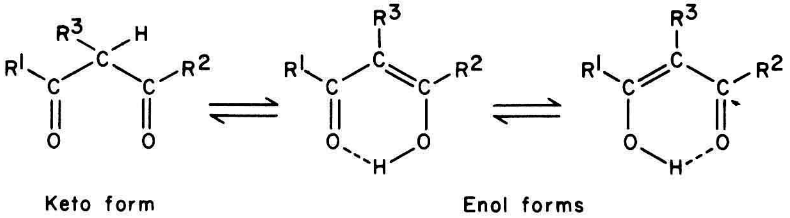


Fig. 1.1. Tautomerism of β-diketones.

β-Diketones are capable of keto–enol tautomerism (Fig. 1.1). The hydrogen atom of the CHR^3 group is activated by the adjacent C=O groups, and a conjugate system can arise by a prototropic shift. These tautomers exist in equilibrium with each other, and structurally they possess a *cis* configuration and a *syn* (cisoid) conformation. Under appropriate conditions the enolic hydrogen atom of the ligand can be replaced by a metal cation to produce a six-membered chelate ring (Fig. 1.2) thereby shifting the keto–enol equilibrium in favour of the enol form.

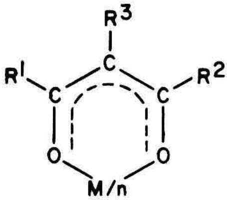


Fig. 1.2. Chelate ring.

Since a large number of β-diketones having various substituents R^1, R^2, and R^3 are known, abbreviations are used for selected ligands of principal interest (Table 1.1).

The keto–enol tautomerism of a wide variety of β-diketones has been studied over many years, by techniques such as bromine titration [1–3], exchange with deuterium [4], polarographic measurements [5], energy of enolization [6, 7], and u.v. [8–10], i.r. [11–21], Raman [22], and n.m.r. [23, 24] spectroscopy. It has been generally accepted that the enolic form is favoured in non-polar solvents, and simultaneous conjugation and chelation through hydrogen-bonding is responsible for the stability of the enol tautomers.

The proportion of the enol tautomers generally increases when an electron-withdrawing group, e.g. chlorine, is substituted for hydrogen at an α-position in β-diketones (see Table 1.1). The enolization also increases [25, 26] when the ligands are fluorinated or contain an aromatic ring. Substitution by a bulky group (e.g. alkyl) at an α-position tends to produce steric hindrance between R^3 and R^1 (or R^2) group protons particularly in the enol tautomer, and this together with inductive effects of the alkyl groups often brings about a large decrease in the enol proportion [27–29]. It should be noted that no enolization is possible if both hydrogen atoms of the α-carbon atom are substituted; formation of chelates with metal ions would obviously not be possible with such systems.

No attempt is made at this stage to cover all the literature on the chemistry of β-diketones since the relevant chemistry of the ligands will be discussed in detail with that of their metal derivatives.

A general method of synthesis of a wide variety of β-diketones is the well-known Claisen condensation according to which a ketone containing an α-hydrogen atom undergoes acylation with an acid anhydride, an acid chloride, or an ester in the presence of a base, e.g. sodium metal, sodium ethoxide, sodium hydride, or sodium amide. An acidic reagent like boron trifluoride has also been found to be effective for acylation of a ketone to form β-diketones.

The methods of synthesis of β-diketones were reviewed in 1954 by Hauser *et al.* [30], and more recently by Mushak *et al.* [31]. Only a few typical and important examples are given in Fig. 1.3.

Much of the work more recently published deals with improvements to the preparative methods already reported along with a few new methods of synthesis [32–41]; the presence of some of the β-diketones in natural products has also been shown by plant chemists [42–47].

1.2 Historical Background of Metal β-Diketonates

In the following brief history of the chemistry of metal β-diketonates, an attempt is made to cover relevant work reported from 1887 to 1960. This limiting year 1960 has been chosen since almost all basic conceptual break-throughs in the chemistry of this group of compounds appear to have been accomplished by then. Further, about 1960 there was a rapid increase in the

TABLE 1.1. Enol contents and boiling points of some β-diketones

Structural formula	Compound	Abbreviation for anion	Enol content (%)	B.p. (°C/mm)
$R^1COCHR^3COR^2$	General β-diketone	A	—	—
$(CH_3CO)_2CH_2$	Acetylacetone (Pentane-2,4-dione)	acac	81·4	140
$(CH_3CO)_2CH(Y)$	3-Y-Pentane-2,4-dione	Yacac	94 (Y = Cl) 46 (Y = Br) 30 (Y = Me)	— — —
$(CH_3CO)CH_2(COC_6H_5)$	Benzoylacetone (1-Phenylbutane-1,3-dione)	bzac	100	260–262
$(C_6H_5CO)_2CH_2$	Dibenzoylmethane (1,3-Diphenylpropane-1,3-dione)	dbzm	110	219–221/18
$[(CH_3)_2CHCO]_2CH_2$	Diisobutyrylmethane (2,6-Dimethylheptane-3,5-dione)	dim	95·8	199–201
$(CH_3)_3CCOCH_2COCH_2CH_3$	2,2-Dimethylheptane-3,5-dione	—	93·4	203–204
$(CH_3)_3CCOCH_2COCH(CH_3)_2$	2,2,6-Trimethylheptane-3,5-dione	—	97	206–208
$[(CH_3)_3CCO]_2CH_2$	Dipivaloylmethane (2,2,6,6-Tetramethylheptane-3,5-dione)	dpm or thd	98	214–216
$CF_3COCH_2COCH_3$	Trifluoroacetylacetone (1,1,1-Trifluoropentane-2,4-dione)	tfac	97	107
$(CF_3CO)_2CH_2$	Hexafluoroacetylacetone (1,1,1,5,5,5-Hexafluoropentane-2,4-dione)	hfac	100	70
$C_6H_5COCH_2COCF_3$	Benzoyltrifluoroacetone (1,1,1-Trifluoro-4-phenylbutane-2,4-dione)	btfac	—	224
$CF_3COCH_2COC(CH_3)_3$	Pivaloyltrifluoroacetone (1,1,1-Trifluoro-5,5-dimethylhexane-2,4-dione)	ptac	—	138–141

$CF_3CF_2CF_2COCH_2COC(CH_3)_3$	Heptafluorodimethyloctanedione (1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyloctane-4,6-dione)	fod	—	33/207
$CF_3CF_2COCH_2COCF_3$	Octafluorohexanedione (1,1,1,5,5,6,6,6-Octafluorohexane-2,4-dione)	ofhd	—	85
$CF_3CF_2CF_2COCH_2COCF_3$	Decafluoroheptanedione (1,1,1,5,5,6,6,7,7,7-Decafluoroheptane-2,4-dione)	dfhd	—	99–105
$(C_4H_3S)COCH_2COCF_3$	2-Theonyltrifluoroacetone	Ttfac	—	425–432 (m.p.)
$(C_4H_3O)COCH_2COCF_3$	2-Furoyltrifluoroacetone	Ftfac	—	19–21 (m.p.)

$$\mathrm{RCOOR'+CH_3COR''} \xrightarrow[\mathrm{NaNH_2\ or\ NaH}]{\mathrm{Na,\ NaOR}} \mathrm{RCOCH_2COR''+R'OH}$$

$$\mathrm{(CH_3CO)_2O+CH_3COCH_3} \xrightarrow[\mathrm{CH_3ONa}]{\mathrm{BF_3}} \mathrm{CH_3COCH_2COCH_3+CH_3COOH}$$

$$\mathrm{RCOCl+H_2C{=}C(OMgX)C_6H_2(CH_3)_3} \quad \text{(Mg derivative of acetomesitylene)}$$

$$\downarrow$$

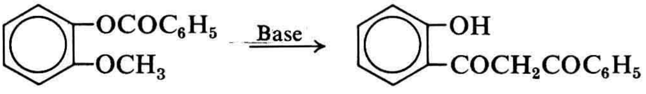
$$\mathrm{RCCl(OMgX)CH_2COC_6H_2(CH_3)_3} \longrightarrow$$

$$\mathrm{RCOCH_2COC_6H_2(CH_3)_3+MgXCl}$$

$$\mathrm{RCOCH_3+CF_3COOC_2H_5} \xrightarrow[\mathrm{NaNH_2,\ NaH}]{\mathrm{NaOC_2H_5}} \mathrm{RCOCH_2COCF_3+C_2H_5OH}$$

$$\mathrm{RCOCHR''COR'} \xrightarrow[\mathrm{C_2H_5O^-}]{\mathrm{CH_3O^-}} \mathrm{RCOCR''C(R)O^-} \xrightarrow{\mathrm{ClOF_3}} \mathrm{RCOCFR''COR'}$$

(R = R′ = alkyl, aryl; R″ = alkyl or H)



(Base = Na, K_2CO_3, NaOH, NaOEt, $NaNH_2$, etc.)

$$\mathrm{RCHXCHXCOR'} \xrightarrow{\mathrm{alc.KOH}} \mathrm{RCOCH_2COR'}$$

(Chalcone halide)

Fig. 1.3. Typical syntheses of β-diketones.

number of publications in the area, and all these are more conveniently dealt with separately in the chapters dealing with different aspects of the chemistry of metal β-diketonates.

The first series of publications in the field appears to be by Combes [48–51] who during 1887–1894 described the synthesis of acetylacetonates of sodium, beryllium, magnesium, aluminium, lead, iron, copper, nickel, and cobalt. Claisen *et al.* [52–54] reported during 1888–1893 the preparation of copper β-diketonates. In addition to Griner [55] and Curtiss [56], another important investigator in the nineteenth century was Urbain [57–60] who during 1896–1899 prepared tetrakis(acetylacetonates) of thorium and cerium and hydrated tris(acetylacetonates) of lanthanum, yttrium, and gadolinium. Conrad and Gast [61] (1898), Chabrie and Rengade [62] (1900), and Gach [63, 64] (1900) succeeded in preparing β-diketonates of iron(III), cobalt(III), chromium(III), scandium(III), manganese(III), and copper(II).

The penetrating insight of Werner [65] is exemplified by the formulation that he assigned to the complex potassium monochlorobis(acetylacetonate)-platinum(II), which he synthesized in 1901. The structure, in which one of the acetylacetone groups is bonded in the normal manner through a six-membered chelate ring and the other is attached through the active methylene 3-carbon atom, was confirmed in 1962 by an X-ray structural determination [66]. During 1901–1902, Bouveault and Bongert [67, 68], Hantzsch and Desch [69, 70], and Kohler [71] reported the synthesis of aluminium and copper β-diketonates.

Some interesting observations were made by Dilthey [72–78] during 1903–1906 on the reactions of metal halides with acetylacetone. The formation of an ionic species $B(acac)_2{}^+Cl^-$ was observed in the reaction of boron trichloride with acetylacetone, whereas boron trifluoride gave a neutral product $B(acac)F_2$. This ionic species $B(acac)_2{}^+Cl^-$, as well as a similar derivative, $Si(acac)_3{}^+Cl^-.HCl$, obtained by the reaction of silicon tetrachloride with acetylacetone, formed compounds of the type $[B(acac)_2]^+[MCl_4]^-$ and $[Si(acac)_3]^+[MCl_4]^-$ with $FeCl_3$ and $AuCl_3$. In 1903 Rosenheim *et al.* [79] investigated the reaction of titanium tetrachloride with acetylacetone in ethereal medium and reported the formation of an addition product with ether, formulated as $Ti(acac)Cl_3.Et_2O$. In 1904 Dilthey [76] repeated the above synthesis in solvents like ether, chloroform, and glacial acetic acid, and isolated in every case a product the analysis of which corresponded to $Ti(acac)_2Cl_2$. The product was given the formula $[Ti(acac)_3]_2TiCl_6$, which is a trimer of $Ti(acac)_2Cl_2$, by analogy with the products $Si(acac)_3Cl.HCl$ and $Zr(acac)_3Cl$ obtained in the corresponding reactions with silicon and zirconium tetrachlorides. This interesting formulation, made mainly on the basis of analogy and quoted in textbooks [80, 81] and treatises [82, 83], was found to have no real basis when Mehrotra and coworkers [84–86] showed by molecular weight measurements in benzene and by chemical and conductivity methods that the product is a monomeric non-electrolyte which can be represented simply as 6-coordinated $Ti(acac)_2Cl_2$. These preliminary observations were further confirmed in later publications [87–90].

A few references [91–110] traced between 1904 and 1914 deal with the synthesis of β-diketonates of magnesium, calcium, strontium, barium, beryllium, zinc, cadmium, aluminium, iron, cobalt, cerium, scandium, etc. For example, Tanatar and Kurovskii [99] in 1909 described the preparation of acetylacetonates of calcium, strontium, barium, beryllium, and zinc from basic salts of these elements and acetylacetone. Meyer and Winter [101, 102] prepared scandium tris(acetylacetonate) from the corresponding trihalide and acetylacetone. Rosenheim and Garfunkel [104] reported the preparation of zinc and cadmium acetylacetonates. These workers also isolated a complex of the type $M[Co(acac)_2(NO_2)_2].0{\cdot}5H_2O$ (M = Na, Ag).

Significant contributions in the field were made by Morgan and coworkers [111–134] who published about two dozen papers on metal β-diketonates during 1914–1928, along with the chemistry of acetylacetonates of a number of elements known up to 1914. These workers suggested that β-diketone ligands add 'wings' to the metal atoms, and they also gave a preliminary idea regarding the stability and structure of metal acetylacetonates. For example, it was suggested that the stability of acetylacetonates of elements with different valencies follows the order: univalent < bivalent < tervalent < quadrivalent. Tervalent and quadrivalent metal acetylacetonates were assumed to involve octahedral and cubic structures respectively. The absorption spectra of a few of these derivatives were also studied. Morgan and Drew [113] in 1920 observed the reduction of selenium(IV) to selenium(II) when the tetrachloride was treated with acetylacetone thereby resulting in the formation of C-bonded selenium(II) acetylacetonate. The corresponding tellurium tetrachloride, however, gave the C-bonded $Te(acac)_2Cl_2$. A study was also made of the bactericidal activity of different tellurium β-diketonates, among which the dipivaloylmethanate derivative was the most effective [120–122].

Morgan and Drew [123, 129] observed that, whereas tin tetrachloride reacts with acetylacetone at room temperature and under refluxing conditions to form $SnCl_4.acacH$ and $Sn(acac)_2Cl_2$ respectively, the corresponding germanium tetrachloride gives $Ge(acac)_2Cl_2$ only. The product of reaction between MoO_3 or $MoO_3.2H_2O$ and acetylacetone, which had been reported as $Mo(acac)_2$ by Gach [63], was shown by Rosenheim and Bertheim [91] and later by Morgan and Castell [134] to be really $MoO_2(acac)_2$.

A number of articles also appeared during the 1920s [12, 135–161]. For example, Werner [135, 136] in 1918–1921 prepared a derivative of the type $[Co(en)_2(acac)]X_2$ which could be resolved into optically active isomers. Sidgwick and Brewer [140] in 1925 studied the β-diketonates of alkali metals in detail. Reihlen *et al.* [141] were in 1925 the first group of workers to study the effect of electrophilic substitution in the metal acetylacetonate ring, and a product of the type $Cr[CH_3CO(CBr)COCH_3]_3$ was reported when chromium tris(acetylacetonate) was treated with bromine. The first report of an X-ray crystallographic study was published in 1926 by Sarkar [145] who suggested the presence of four molecules in each single cell of aluminium tris(acetylacetonate) which belongs to the C_{2h} space group. He also reported [146–149] the preparation of triaquo-acetylacetonate complexes of lanthanum, gadolinium, and europium. Ephraim and Ray [158] in 1929 investigated the reflectance spectra of praseodymium tris(acetylacetonate) and its aquo complex in the molten state and in solvents such as alcohol and carbon disulphide.

Important contributions during the 1930s were made by Rosenheim *et al.* [162–165], Menzies *et al.* [166–173], Emmert *et al.* [174–179], and a few others [180–201], who prepared β-diketonate derivatives of a number of elements. For example, Rosenheim *et al.* synthesized acetylacetonates and related derivatives of vanadium, molybdenum, tantalum, etc. Menzies *et al.*

prepared β-diketonates of thallium(I), organothallium(III), and organoplatinum(IV) moieties. Thallous acetylacetonate [166] was prepared from its hydroxide and acetylacetone, whereas dialkylthallium β-diketonates [169, 170, 173] were prepared from the corresponding ethoxide and β-diketones. Trimethylplatinum acetylacetonate was prepared by the reaction of trimethylplatinum(IV) chloride with thallium(I) acetylacetonate.

Emmert *et al.* synthesized β-diketonates of bi- and tervalent iron, and made an observation that, whereas ferrous acetylacetonate [176, 179] is oxidized by air in alcoholic medium to give $Fe(acac)_2OR$, the corresponding ferric tris(acetylacetonate) is reduced by phenylhydrazine to ferrous acetylacetonate coordinated to two molecules of phenylhydrazine. Booth and Smiley [183] in 1933 showed the formation of 1 : 1 adducts between beryllium acetylacetonate and ethyl acetoacetate with sulphur dioxide, but no reaction appeared to occur between magnesium or aluminium ethyl acetoacetate and sulphur dioxide. Servigne [186, 187] described the preparation of potassium acetylacetonate which was volatilized *in vacuo*. On the basis of X-ray measurements and optical properties, Cox and Webster [191] in 1935 assumed a planar configuration for the 4-coordinated copper(II) β-diketonates. Finn *et al.* [195] in 1938 studied the electric polarization of acetylacetonates of beryllium, zinc, copper, aluminium, iron, chromium, cobalt, zirconium, and thorium, and suggested these derivatives to be polar in character.

Although the rate of publication appears to have slowed down during the 1940s, references can be found to papers that appeared mostly during the latter part of the decade [202–233]. An important observation made during this period was that of Calvin and Wilson [210] (1945), who ascribed aromatic character to the six-membered ring (Fig. 1.4) on the basis of stability constant measurements on copper ethyl acetoacetate.

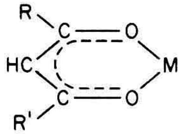


Fig. 1.4. Aromatic character of chelate ring.

In a series of articles in *Inorganic Synthesis*, Young *et al.* [82, 213–216] in 1946 described a detailed procedure for the preparation of β-diketone derivatives of a few elements. Marsh [218] in 1947 claimed the isolation of tris(acetylacetonates) of lanthanum, neodymium, gadolinium, and ytterbium, which were reported to be free from water of crystallization. Marsh also measured the molar volumes of all these complexes. Calvin and Bailes [212] in 1946 investigated the polarographic reduction of a few β-diketonates of copper(II). During 1949 Morgan [229] investigated i.r. spectra of metal β-diketonates for the first time, and the next report on this aspect appeared