Pure & Appl. Chem., Vol. 60, No. 8, pp. 1349–1356, 1988.
Printed in Great Britain.

Chemistry of metal β-diketonates

Ram C. Mehrotra

Chemical Laboratories, University of Rajasthan, Jaipur 302004

<u>Abstract</u> - The chemistry of metal β-diketonates broadly follows the pattern of development of inorganic chemistry as a whole, since their first synthesis in 1887. Three types of metal β-diketonate complexes : (i) oxygen bonded, (ii) carbon bonded and (iii) both oxygen and carbon bonded have been synthesised by a variety of routes. Out of these, the reactions of various β-diketones and -ketoesters with simple and bimetallic alkoxides in different stoichiometric ratios in benzene medium have been exploited for synthesizing novel derivatives of the first type and also for throwing light on their structural features. A brief mention has been made of a new class of metalla-derivatives of β-diketones.

INTRODUCTION

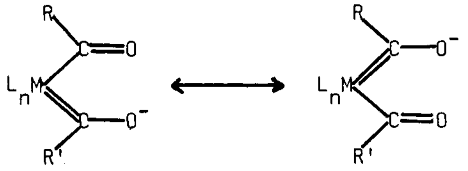
The chemistry of metal β-diketonates broadly follows the pattern of development of inorganic chemistry as a whole (ref. 1). Beginning with the synthesis of these derivatives for the first time in 1887 (centenniel ?), the nature of bonding and chelation was elucidated (ref. 1-9) in several prominent schools beginning with those of Werner and Morgan. The suggestion of aromaticity in the β-diketonate ring by Calvin and Wilson (ref. 10) in 1945 aroused a novel interest in these derivatives.

The strong chelating tendency of these monovalent bifunctional ligands led to the synthesis of a number of neutral complexes, $[M(A)_n]$ (where M = central element and A = a β-diketone ligand) with predominant covalent characteristics, i.e., solubility in organic solvents and volatility (cf., adding 'wings' to the metals) at a time when such examples of covalent derivatives of electropositive metals were much less known. These characteristics have been extensively exploited in solvent extraction and chromatographic techniques. Current interest in metal β-diketonates also arises from their applications as contact shift reagents (ref. 11) in n.m.r. spectroscopy and as laser materials.

With increasing applications of sophisticated structural determination techniques since 1950's, the classical work of Cotton and Holm (ref. 12) in 1958 on trimeric nickel acetylacetonates opened a new chapter in this direction. The work of Lewis, et al. (ref. 13) has confirmed a bonding mode through 3-C atom in the complex, $K[Pt(acac)_2Cl]$, which was initially described by Werner in 1901.

A new chapter in the field of a closely allied metal thio-β-diketonate derivatives was introduced by Chaston and Livingstone (ref. 14) in 1969, followed by extensive work including a few publications (ref. 15-21) from our laboratories also.

Since the first report on metalla-derivatives of β-diketones by Lukehart in 1975, these novel compounds have attracted considerable attention (ref. 22). These can be represented by the general formula, $L_nM(RCO)(R'CO)^-$ in which two acyl groups occupy adjacent coordination sites on a metal atom. Resonance of the derivatives as indicated below:



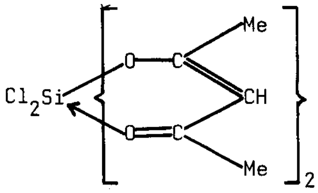
(L_nM is a moiety of the type <u>cis</u>-$(OC)_4Re$ or $(\eta$-$C_5H_5)(OC)Fe]$, confers an acyl/carbene hybrid electronic structure on the molecule. These can be formally compared to the conventional organic B-diketonate anions, in which the sp^2 CH methine group has been replaced by the 'isolobal' (ref.23) metal fragment. Following earlier publications on the same lines, work has now been initiated on the reactions of these metalla-β-diketones with mono- and bi-metallic alkoxides for synthesis of derivatives of the types $(RO)_2TiA_2$, ZrA_4, $(RO)_2NbA_3$, $A_2Cr(\mu\text{-}OPr^i)_2CrA_2$, where 'A' is cis-$(OC)_4Re(MeCO)_2^-$.

CLASSIFICATION

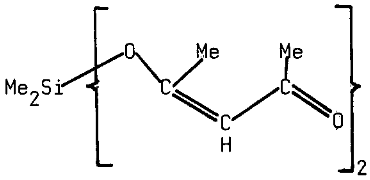
Metal β-diketonate derivatives may be classified into the following three broad categories depending upon the mode of bonding of β-diketonate moieties with metal atom:

(i) Oxygen bonded β-diketonate complexes

This is the most common mode of bonding with β-diketonato ligand acting as (a) bidentate chelating which is by far the most common form (1), (b) unidentate (2) and (c) neutral ligand (3 ; ref. 24) :

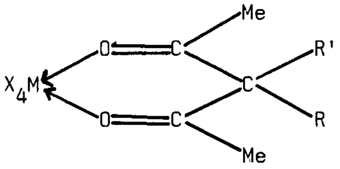


1



and

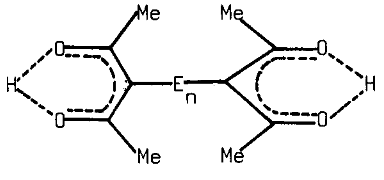
2



3

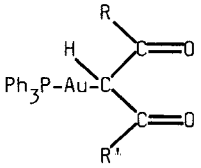
(ii) Carbon bonded β-diketonate derivatives

In a number of their β-diketonate derivatives, elements like sulphur, selenium, tellurium, mercury and gold prefer a bonding through the central carbon atom of the ligand rather than the carbonyl oxygen atoms (4 and 5):



4

[E = S ; n=1 or 2 (ref.25); E=Se ; n = 2 (ref. 26)]

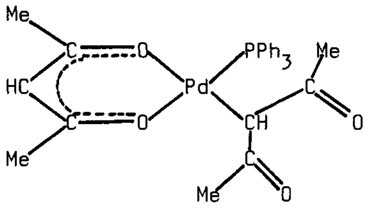


5 (ref. 27)

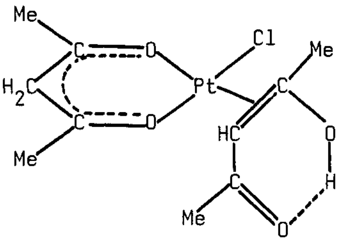
(iii) Both oxygen and carbon bonded complexes

Since 1962, a large number of carbon bonded β-diketonate complexes of later transition metals like silver, maganese, nickel and platinum also have been characterized, although in some of these along with a carbon bonded β-diketonate ligand, another β-diketonate ligand chelates the metal through carbonyl oxygens.

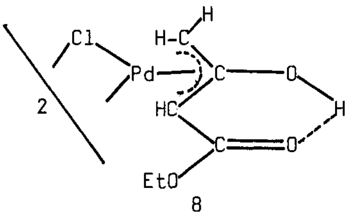
The first C-3 bonded platinum complex was identified as $Me_3Pt(acac\text{-}C\text{-}3)(bpy)$ by Swallow and Truter (ref. 28) in 1962. Later the complex $K[Pt(acac)_2Cl]^-$ (assumed to involve an O-unidentate acac ligand by Werner in 1901) was shown by IR and NMR (ref. 29) as well as X-ray (ref. 30) studies to be a C-3 bonded derivatives. Some other types of C-bonded complexes have since been identified and are illustrated below: (a) C-3, bonded (6 ; ref. 6 & 31) ; (b)η^2-(C,C') bonded (7 ; ref. 32) ; (c)η^3-allylic coordination (8 ; ref. 33) and (d) terminal carbon bonded (9 ; ref. 34):



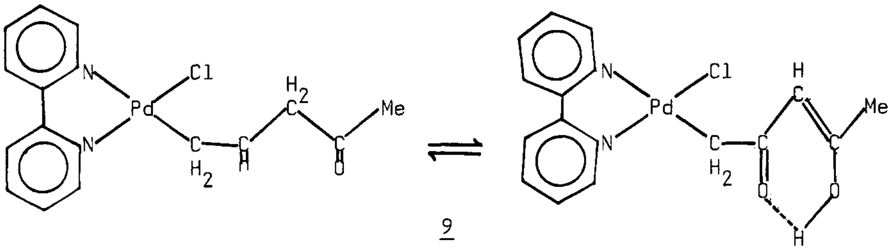
6



7



8



9

A BRIEF RESUMÉ OF WORK CARRIED OUT IN OUR LABORATORIES

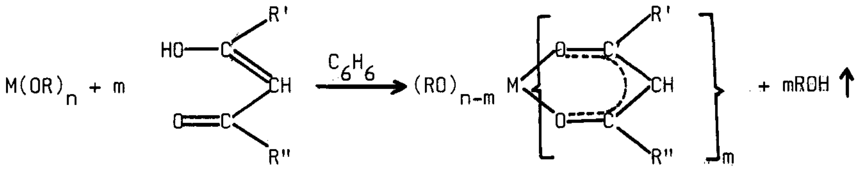
1. Reactions of metal alkoxides with β-diketonates and β-ketoesters

The marked reactivity of metal alkoxides towards hydroxy compounds led us to look into the reactions of metal alkoxides with β-diketones, β-ketoesters and allied reagents. A large number of novel derivatives with metals sometimes depicting uncommon coordination numbers have been synthesised during the course of this work, elucidation of the structural features of which by more sophisticated physico-chemical investigations should provide a rich field of research for coordination chemists in the coming years.

The β-diketones in general depict a facile reactivity towards metal alkoxides, in which the alkoxy groups undergo facile replacements by the enolate forms of the β-diketones or β-ketoesters. Following the pioneering work of Schmidt (ref. 35), Reeves and Mazzeno (ref. 36) as well as of Yamamoto and Kambara (ref. 37), Mehrotra and coworkers (ref. 38-41) made a detailed study of the reactions of titanium alkoxides with β-diketones, fluoro-β-diketones and β-ketoesters in different molar ratios. The reactions in 1:1 and 1:2 molar ratios were facile resulting in mono- and bis-chelates respectively. Further reaction was slow and although the third alkoxy group was replaced, yet the final product decomposed immediately to yield titanyl bis(β-diketonate). Out of the above, the fluoro-β-diketonates were comparatively volatile and can be distilled in vacuo.

Contrary to the conclusions of Fay et al. (ref. 42 & 43), Bradley and Holloway (ref. 44 & 45) characterized the above derivatives as cis products. Compounds like $TiX_2(acac)_2$ exist only in cis (optically active) forms over a wide temperature range. Although steric hindrance of the alkoxy groups did raise the activation energy for intramolecular exchange of ligands in these fluxional molecules, yet the formation of trans form was not enhanced.

In the reactions of metal alkoxides with β-diketones the alkoxide is mixed with a stoichiometric amount of the desired ligand in benzene medium and after fractionation of the benzene-alcohol azeotrope, the corresponding β-diketone or β-ketoester derivative can be isolated by removal of excess benzene by evaporation (ref. 46). The advantage of this method is the possibility to prepare complexes with different coordination numbers using the desired stoichiometric ratio of the ligand. A few of such reactions are represented by the following equations:



(i) M=Al,n=3 ; R=Et,Pr^i; R'=Me,R"=Me,Ph,OEt; m=1-3(ref. 47-50)

(ii) M=Ga,n=3 ; R=Pr^i ; R'=Me,R="Me,OMe,OEt ; m=1-3 (ref. 51)

(iii) M=Ti,n=4 ; R=Et,Pr^i ; R'=Me,R"=Me,Ph , OMe,OEt ;R'=CF_3,R"=CF_3,C_6H_5; m=1,2 (ref. 38-41)

(iv) M=Zr,n=4 ; R'=Me,R"=Me,Ph,OMe; R'=R"=CF_3; m=1-4 (ref.52 & 53)

(v) M=Cr,n=3; R=Me,Et ; R'=Me,R"=Me,Ph ; R'=CF_3,R"=C_4H_3S ;m = 1-3 (ref. 54)

(vi) M=Nb,Ta; n=5 ; R'=Me,R"=Me,Ph,OMe,OEt; R'=R"=Ph ; m=1-3 (ref. 55-58)

(vii) M=Ni,n=2; R=Me,Pr^i ; R'=Me,R"=Me,Ph ; R'=CF_3,R"=C_4H_3S ; m=1,2 (ref. 59)

(viii)M=Sn, n=4 ; R=Pr^i ; R'=Me,R"=Me,Ph ; R'=R"=Ph ; m=1,2 (ref. 60)

(ix) M=La (ref. 61) ; Pr (ref. 62); Nd,Sm (ref. 63) ; Gd,Er,Y,Yb (ref.64) ; n=3 ; R=Pr^i ; R'=Me, R"=Me,Ph,OMe,OEt ; R'=R"=Ph ; m = 1-3.

(x) M=EtSn, BuSn, n=3; R=Pr^i ; R'=Me, R"=Ph ; R'=R"=Ph, m=1,2 ; R'=R"=Me,m=1-3 (ref. 65)

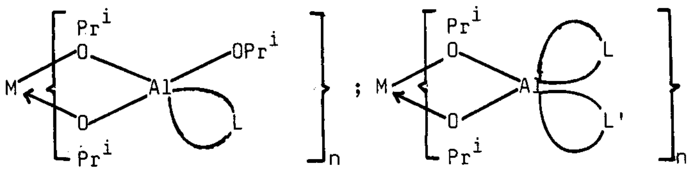
(xi) M=Et_2Sn,Bu_2Sn, n=2 ; R=Et ; R'=Me,R"=Me,Ph, OMe; m=1,2 (ref. 66)

(xii) M=Et_3Sn,Bu_3Sn, n=1 ; R=Et ; R'=Me, R"=Me,Ph,OMe ; m=1 (ref.66)

(xiii) M=Ph_3Sb, n=2 ; R=Me ; R'=Me, R"=Me,Ph ; R'=R"=Ph ; m=1 (ref. 67)

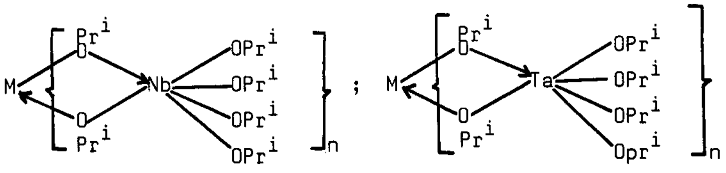
(b) $[(COD)Rh(OMe)]_2$ + 2HOCR'C=CHC(O)R" ⟶ 2(COD)RhOCR'C(CH)(O)R" + 2MeOH ↑
$[(COD\text{-}Me)Pt(OMe)]_2$ + 2HOCR'C=CHC(O)R" ⟶ 2(COD-Me)PtOCR'C(CH)(O)R" + 2MeOH ↑
R' = Me, R" = Me,Ph ; R'=R"=Ph (ref. 68)

In addition to the reactions of simple (mono-metallic) alkoxides, those of bi-metallic and ter-metallic alkoxides have been investigated extensively yielding a wide variety of novel (and in many cases volatile) derivatives, a few of which are illustrated below:



[HL or HL'= a β-diketone or β-ketoester ligand ; when n = 2, M=Be,Zn,Cd (ref. 70), Mg,Ca,Sr,Ba (ref.46), Mn(II), Fe(II) (ref. 69 & 71), Co(II) (ref. 72a), Ni(II) (ref. 72b), Cu(II) (ref. 72c), Sn(II) (ref. 73) etc. when n=3, M=Al,Ga,In (ref. 46), Cr(III) (ref. 72d), etc. ; when n=4, M = Sm(IV), Th(IV), U(IV) (ref. 73b) etc.].

Similar products have been obtained by gradual replacements of the terminal isopropoxy groups by the same or different β-diketonate ligands in derivatives like:



In all these, a maximum of two terminal isopropoxide groups can be replaced by β-diketonate moiety as in the bis-β-diketonate products, the metal niobium/tantalum attains coordination number eight (M=Ni (ref. 74) ; M=Cr (ref. 75).

Similar, monomeric volatile products are obtained (ref. 76) by gradual replacement of terminal isopropoxy groups by β-diketonate ligands in derivatives with the general formula $M(Zr_2(OPr^i)_9)_n$.

In these reactions also, the zirconium atom appears to attain the maximum coordination number eight. Forcing the replacement reaction further brings about disproportionation of the bimetallic isopropoxide in the terminal metal β-diketonate and central metal isopropoxide ; the latter can then undergo further replacement reactions by β-diketone ligands as a simple monometallic isopropoxide.

2. Some salient contributions from our laboratories

The synthesis of titanium dialkoxide bis-β-diketonates and their distinctly monomeric nature (ref. 77) in a number of organic solvents and convertibility into titanium dichloride bis-β-diketonates by facile reactions with hydrogen chloride led to serious doubts about the well-established notions about the trimeric nature of $[TiX_2(acac)_2]_3$, reported in the beginning of of this century independently by Rosenheim (ref. 78) and Dilthey (ref. 79). This product had been assigned an ionic structure of the type $[Ti(acac)_3]_2^+ [TiCl_6]^{2-}$, which is the trimeric form of $TiCl_2(acac)_2$, merely on the basis of analogy with the products, $SiCl(acac)_3HCl$ and $ZrCl(acac)_3$, obtained earlier in the corresponding reactions of acetylacetone with silicon or zirconium tetrachlorides. The only evidence adduced in support of the above structure was that the product on treatment with ferric chloride readily gives a product of the composition $[Ti(acac)_3][FeCl_4]$, the formation of which could be easily explained on the basis of the following plausible reaction:

$$[Ti(acac)_3]_2^+ [TiCl_6]^{2-} + 2FeCl_3 \longrightarrow 2[Ti(acac)_3][FeCl_4] + TiCl_4$$

On repeating the experimental work of Rosenheim and Dilthey, the analytical results of the products obtained did correspond to $TiCl_2(acac)_2$ and $[Ti(acac)_3][FeCl_4]$. However, on actual measurement of molecular weights of the derivative $TiCl_2(acac)_2$ in a number of common organic solvents, the observed experimental value was found to correspond to the simple monomeric $TiCl_2(acac)_2$. Further, the derivative was found to be non-electrolyte in these solvents, thereby ruling out the possibility of the above trimeric ionic form $[Ti(acac)_3]_2^+[TiCl_6]^{2-}$, as suggested by earlier workers and quoted even in undergraduate text-books.

The product of the reaction between titanium tetrachloride and excess of acetylacetone was, thus shown to be a simple hexa-coordinated derivative $TiCl_2(acac)_2$. This was also in conformity with a considerable amount of work on the reactions of titanium tetrachloride with reagents having active hydroxy groups like alcohols (ref. 80) and carboxylic acids (ref. 81), in which two of the four chlorine atoms on titanium tetrachloride were shown to be much more reactive. The convertibility of $TiCl_2(acac)_2$ into monomeric $Ti(OEt)_2(acac)_2$ by the reaction with ethanol in the presence of a base further lent support to the similarity in the monomeric nature of the two allied derivatives.

The formation of the product $[Ti(acac)_3][FeCl_4]$ from the reaction of $TiCl_2(acac)_2$ and $FeCl_3$ has been shown to be much more complicated. Efforts have been made to elucidate it in a number of publications (ref. 82 & 83) dealing with synthesis and isolation of the products, $TiCl_3(acac)$ in addition to $TiCl_2(acac)_2$ as well as $FeCl_2(acac)$, $FeCl(acac)_2$ and $Fe(acac)_3$ and the observations of formation of the products with the composition, $[Ti(acac)_3][FeCl_4]$ by their mutual interactions.

In the reaction of stannic chloride with acetylacetone in chloroform at room temperature, the product isolated corresponds in composition to $SnCl_4.Hacac$ which was found to be stable even upto 60-70° under 0.1 mm pressure but decomposed above 90-100° to give stannic dichloride bis(acetylacetonate) as follows (ref. 84):

$$2SnCl_4.Hacac \longrightarrow SnCl_2(acac)_2 + SnCl_4 + 2HCl$$

Stannic dichloride bis(acetylacetonate) has been prepared alternatively by refluxing stannic chloride and acetylacetone in benzene or chloroform and it has also been shown to be a monomeric covalent compound (ref. 85).

In still another field, the simple technique of the reactions of metal alkoxides with β-diketones and β-ketoesters appears to have provided a very convenient route for the preparation of anhydrous lanthanide derivatives for the first time in 1965. Earlier methods used for the preparation of lanthanide tris-β-diketonates were examined critically by Pope et al. (ref. 86) and by Moeller et al.(ref. 87), who have conclusively established that the products from aqueous solutions were invariably hydrates, from which generally hydroxy derivatives were obtained on dehydration even under mild conditions. Attempts were also made to synthesize these derivatives in non-aqueous media also by (i) the reaction of lanthanon metal with excess acetylacetone using metal evaporation technique (ref. 88) or (ii) by the reaction of lanthanide hydrides (ref. 89 & 90) with excess acetylacetone in the presence of acetic acid. Liss and Bos (ref. 91) have recently claimed to have isolated a crystalline tris-chelate by the former method, yet according to their own description, unusual properties like large number of extra peaks in infrared spectra, the observed low m.p. (94°) and loss in weight when the derivatives are exposed to air, probably indicate the presence of some volatile fractions in their products which might have been formed in the side decomposition reactions earlier.

As indicated earlier, the reactions of lanthanon isopropoxides with β-diketones (ref. 61-64) are straightforward and yield not only the pure ahhydrous tris-β-diketonates, but also the mixed isopropoxide β-diketonates. These lanthanide isopropoxide β-diketonates interchange their isopropoxy groups with β-diketones and β-ketoesters in different molar ratios to yield a variety of mixed as well as tris-chelates.

These tris-β-diketonates have been found to be dimeric products, which are not as highly hygroscopic as the anhydrous derivatives claimed to have been obtained earlier by dehydration of hydrated products, $Ln(acac)_3.2H_2O$ from aqueous medium. A plausible explanation for this difference has been suggested (ref. 64) by the author. $Y(acac)_3(OH_2)_2$, $La(acac)_3(OH_2$ and $Ho(TTA)_3(OH_2)_2$ have been shown (ref. 92-94) to depict the two water molecules on octa-coordination positions of the square face of an antiprism (Fig. 1). Mere removal of the two water molecules under the mildest conditions possible (to avoid side-hydrolysis of the products), would leave an open unaltered structure with two coordination sites vacant, rendering it extremely susceptible to atmospheric moisture. By contrast, the anhydrous dimeric products synthesized through the alkoxide route are fairly stable towards atmospheric moisture and could possibly have a structure of type (ref. 90) shown in Fig. 2 in which two square antiprisms share one square face:

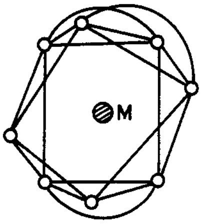


Fig. 1 Structure of $Ln(acac)_3(OH_2)_2$ unit.

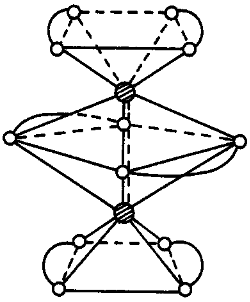


Fig. 2 Structure of anhydrous $[Ln(acac)_3]_2$.

Detailed physico-chemical investigations have been initiated recently on the structural features of other alkoxide B-diketonate systems. For example, it has been shown (ref. 95) by IR and NMR(^{27}Al, ^{1}H and ^{13}C) studies that the volatile products obtained by the reactions of B-diketonates and B-ketoesters(HL) with $ZrAl(OPr^i)_7$ can be represented by $(Pr^iO)_3Zr(\mu\text{-}OPr^i)_2Al(\overset{\frown}{L})_2$, indicating that the isopropoxy groups at the aluminium are preferably replaced in these reactions. Following the earlier studies (ref. 52 & 53) on $(Pr^iO_2Al(\mu\text{-}OPr^i)_2Zr(OPr^i)_2(\mu\text{-}OPr^i)_2Al(OPr^i)_2$ an attempt (ref. 96) has been made to throw light on the different isomeric species formed by its reactions with β-diketones and β-ketoesters.

In addition to the β-diketone, thio-β-diketone and allied β-ketoester derivatives, work is being extended to a number of other similar ligands in the author's laboratories, e.g., β-aminothionates (ref. 97), β-ketoaminates (ref. 98) and alkylacetopyruvates (ref. 99).

Special reference may be made to a series of publications by Rai and coworkers on the pyrazolone complexes of titanium (ref. 100), boron (ref. 101), zirconium (ref. 102) and tin (ref. 103) and two recent reviews (ref. 104 & 105) with relevant references by the author.

The author is grateful to a large number of colleagues, especially Drs. K.C.Pande, D.M.Puri, G.Srivastava, A.K.Rai, R.K.Mehrotra, B.C.Pant, V.D.Gupta, T.N.Misra, S.N.Misra, P.N.Kapoor, S.Jain, U.B.Saxena, J.M.Batwara, S.R.Bindal, B.P.Bachlas, U.D.Tripathi, A.Singh, D.P.Gaur, P.C.Bharara, R.Bohra, B.S.Saraswat, P.Rupani, B.P.Baranwal, K.N.Mahendra , J.Singh, V.K.Jain, S.K.Saini, M.Aggarwal, R.Jain for their dedicated research efforts in our research schools at the University of Lucknow, Gorakhpur, Rajasthan and Delhi.

REFERENCES

1. R.C.Mehrotra, R.Bohra and D.P.Gaur, Metal β-Diketonates and Allied Derivatives, Academic Press, London (1978).
2. J.P.Fackler, Jr., Prog. Inorg. Chem. 7, 361-425 (1966).
3. F.Bonati, Organomet. Chem. Rev. 1, 379-389 (1966).
4. R.M.Pike, Coord. Chem. Rev. 2, 163-172 (1967).
5. D.P.Graddon, Coord. Chem. Rev. 4, 1-28 (1969).

6. D.P.Gibson, Coord. Chem. Rev. 4, 225-240 (1969).

7. D.W.Thompson, Structure and Bonding (Berlin) 9, 27-47 (1971).

8. K.C.Joshi and V.N.Pathak, Coord. Chem. Rev. 22, 37-122 (1977).

9. S.Kowaguchi, Coord. Chem. Rev. 70, 51-84 (1986).

10. M.Calvin and K.W.Wilson, J.Am.Chem.Soc. 67, 2003-2007 (1945).

11. R.E.Sievers, Nuclear Shift Reagents, Academic Press, New York (1973).

12. R.H.Holm and F.A.Cotton, J.Am.Chem.Soc. 80, 5658-5663 (1958).

13. G.Allen, J.Lewis, R.F.Long and C.Oldham, Nature, Lond. 202, 589-590 (1964).

14. S.H.H.Chaston and S.E.Livingstone, Proc.Chem.Soc. 111 (1964).

15. V.K.Jain, R.Bohra and R.C.Mehrotra, Inorg. Chim. Acta Lett. 44, L265-L267 (1980).

16. S.K.Saini, R.R.Tripathi, V.D.Gupta and R.C.Mehrotra, Aust.J.Chem. 33, 1137-1141 (1980).

17. S.K.Saini, V.D.Gupta and R.C.Mehrotra, Aust. J.Chem. 35, 2215-2219 (1982).

18. S.K.Saini, V.D.Gupta and R.C.Mehrotra, J.Ind.Chem.Soc. 59, 1424-1426 (1982).

19. R.K.Gupta, A.K.Rai and R.C.Mehrotra, Inorg.Chim.Acta 82, 145-147 (1984).

20. R.C.Mehrotra, Silicon, Germanium, Tin and Lead Compounds 10, 185-210 (1987).

21. R.C.Mehrotra and S.K.Saini, Silicon, Germanium, Tin and Lead Compounds 10, (1987).

22. C.M.Lukehart, Adv.Organomet.Chem. 25, 45-72 (1986).

23. R.Hoffmann, Angew.Chem.Int.Ed.Engl. 21, 711-724 (1982).

24.A.L.Allred and D.W.Thompson, Inorg.Chem. 7, 1196-1201 (1968).

25. M.V.Vaillant and M. Troost, Compt. Rend. 119, 647 (1894).

26. D.H.Dewar, J.E.Fergusson, P.R.Hentschel, C.J.Wilkins and P.P.Williams, J.Chem.Soc. 688-691 (1964).

27. D.Gibson, B.F.G.Johnson and J.Lewis, J.Chem.Soc.(A) 367-369 (1970).

28. A.G.Swallow and M.R.Truter, Proc.Roy.Soc.,Lond. 266, 527-546 (1962).

29. J.Lewis, R.F.Long and C.Oldham, J.Chem.Soc. 6740-6747 (1965).

30. R.Mason, G.B.Robertson and P.J.Pauling, J.Chem.Soc.(A) 485-492 (1969).

31. S.Baba, T.Ogura and S.Kawaguchi, Inorg.Nucl.Chem.Lett. 7, 1195-1198 (1971).

32. J.Hillis, J.Francis, M.Ori and M.Tsutsui, J.Am.Chem.Soc. 96, 4800-4804 (1974).

33. N.Yanase, Y.Nakamura and S.Kawaguchi, Inorg.Chem. 19, 1575-1581 (1980).

34. Z.Kanda, Y.Nakamura and S.Kawaguchi, Inorg.Chem. 17, 910-914 (1978).

35. F.Schmidt, Angew.Chem. 24, 536-538 (1952).

36. R.E.Reeves and L.W.Mazzeno,Jr., J.Am.Chem.Soc. 76, 2533-2536 (1954).

37. A.Yamamoto and S.Kambara, J.Am.Chem.Soc. 79, 4344-4348 (1957).

38. D.M.Puri and R.C.Mehrotra, J.Less-Common Met. 3, 253-258 (1961).

39. D.M.Puri, K.C.Pande and R.C.Mehrotra, J.Less-Common Met. 4, 393-398 (1962).

40. D.M.Puri and R.C.Mehrotra, J.Ind.Chem.Soc. 39, 499-506 (1962).

41. P.C.Bharara, V.D.Gupta and R.C.Mehrotra, Synth.React.Inorg.Met.-Org.Chem. 5, 59-67 (1975).

42. R.C.Fay and R.N.Lowry, Inorg.Chem. 6, 1512-1519 (1967).

43. N.Serpone and R.C.Fay, Inorg.Chem. 6, 1835-1843 (1967).

44. D.C.Bradley and C.E.Holloway, J.Chem.Soc.,Chem.Commun. 284 (1965).

45. D.C.Bradley and C.E.Holloway, J.Chem.Soc.(A) 282-285 (1969).

46. D.C.Bradley,D.P.Gaur and R.C.Mehrotra, Metal Alkoxides, Academic Press, London (1977).

47. R.K.Mehrotra and R.C.Mehrotra, Can.J.Chem. 39, 795-798 (1961).

48. S.R.Bindal, Organic Derivatives of Metals of Group IIIB with Special Reference to Gallium Ph.D.Thesis, University of Rajasthan, Jaipur, India (1970).

49. B.S.Saraswat, private communication.

50. J.H.Wengrovins,M.F.Garbauskas,E.A.Williams,R.C.Going,P.E.Donahue and J.F.Smith, J.Am.Chem.Soc. 108, 982-989 (1986).

51. R.C.Mehrotra and S.R.Bindal, Can.J.Chem. 47, 2661-2663 (1969).

52. U.B.Saxena, A.K.Rai,V.K.Mathur,R.C.Mehrotra and D.Radford,J.Chem.Soc.(A)904-907 (1970).

53. P.C.Bharara, V.D.Gupta and R.C.Mehrotra, Ind.J.Chem. 13, 725-727 (1975).
54. K.N.Mahendra, G.K.Parashar and R.C.Mehrotra, Trans.Metal Chem. 3, 130-133 (1978); Synth. React.Inorg.Met.-Org.Chem. 9, 213-222 (1979).
55. R.C.Mehrotra and P.N.Kapoor, J.Less-Common Met. 7, 453-457 (1964).
56. R.C.Mehrotra and P.N.Kapoor, J.Less-Common Met. 7, 176-179 (1964).
57. P.N.Kapoor and R.C.Mehrotra, J.Less-Common Met. 8, 339-346 (1965).
58. R.C.Mehrotra, P.N.Kapoor, S.Prakash and R.N.Kapoor, Aust.J.Chem. 19, 2079-2081 (1966).
59. B.P.Baranwal and R.C.Mehrotra, Trans.Metal Chem. 3, 220-224 (1978) ; Ind.J.Chem. 17A, 77-78 (1979).
60. V.D.Gupta, The University of Rajasthan Studies in Science, Jaipur, p.41 (1968).
61. R.C.Mehrotra, T.N.Misra and S.N.Misra, Ind.J.Chem. 3, 525-527 (1965).
62. S.N.Misra, T.N.Misra and R.C.Mehrotra, Ind.J.Chem. 5, 372-374 (1967).
63. B.P.Gupta, B.P.Bachlas and R.C.Mehrotra, Ind.J.Chem. 18A, 370-372 (1974).
64. R.C.Mehrotra, Coordination Chemistry of Lanthanides with emphasis on derivatives with Ln-O-C bonds - a special lecture delivered at XVIIth International Conference on Coordination Chemistry held at Sao Paulo, Brazil in July 1977.
65. D.P.Gaur, G.Srivastava and R.C.Mehrotra, Ind.J.Chem. 12, 399-401 (1974).
66. R.C.Mehrotra and V.D.Gupta, J.Organomet.Chem. 4, 237-240 (1965).
67. V.K.Jain, R.Bohra and R.C.Mehrotra, Synth.React.Inorg.Met.-Org.Chem. 9, 491-502 (1979); J.Organomet.Chem. 184, 57-62 (1980).
68. R.C.Mehrotra and S.K.Agarwal, J.Ind.Chem.Soc. 62, 805-808 (1985).
69. R.C.Mehrotra and S.K.Agarwal, Synth.React.Inorg.Met.-Org.Chem. 16,213-228 (1986).
70. M.Aggarwal and R.C.Mehrotra, Synth.React.Inorg.Met.-Org.Chem. 13,571-583 ; 14, 139-150 (1984).
71. R.C.Mehrotra, J.Ind.Chem.Soc. 59, 715-722 (1982).
72. (a) J.V.Singh and R.C.Mehrotra, J.Coord.Chem. 13, 273-279(1984);(b) Can.J.Chem. 62, 1003-1007 (1984);(c) Z.Anorg.Allgem.Chem. 512,221-230 (1984);(d) Inorg.Chem. 23,1046-1048 (1984).
73. (a) R.R.Goel, N.C.Jain and R.C.Mehrotra, Synth.React.Inorg.Met.-Org.Chem. 11, 345-359 (1981) ; (b) R.C.Mehrotra, (unpublished work).
74. R.Jain, A.K.Rai and R.C.Mehrotra, Z.Naturforsch. 40b, 1371-1376 (1985).
75. R.C.Mehrotra and S.K.Agarwal, Inorg.Chim.Acta 112, 177-181 (1986).
76. R.K.Dubey, A.Singh and R.C.Mehrotra, Inorg.Chim.Acta 118,151-156 (1986).
77. K.C.Pande and R.C.Mehrotra, Chemistry and Industry 1198-1199 (1958).
78. A.Rosenheim, L.Lowenstamm and L.Singer, Chem.Ber. 36, 1833- (1903).
79. W.Dilthey, Chem.Ber. 37, 589- (1904).
80. J.S.Jennings, W.Wardlaw and W.J.R.Way, J.Chem.Soc. 637-640 (1936).
81. R.C.Mehrotra and R.Bohra, Metal Carboxylates, Academic Press,London (1983).
82. D.M.Puri and R.C.Mehrotra, J.Less-Common Met. 3, 247-252 (1961).
83. D.M.Puri, K.C.Pande and R.C.Mehrotra, J.Less-Common Met. 4, 481-486 (1962).
84. R.C.Mehrotra and V.D.Gupta, J.Ind.Chem.Soc. 40, 911-916 (1963).
85. G.T.Morgan and H.D.K.Drew, J.Chem.Soc. 125, 372-381 (1924).
86. G.W.Pope, J.F.Steinbach and W.F.Wagner, J.Inorg.Nucl.Chem. 20, 304-313 (1961).
87. T.Moeller, D.F.Martin, L.C.Thompson, R.Ferrus, G.R.Feistel and W.J.Randall, Chem.Rev. 65, 1-50 (1965).
88. J.R.Blackborow, C.R.Eady, E.A.K.Von Gustorf,A.Scrivante and O.Wolfbeis, J.Organomet. Chem. 108, C32-C34 (1976).
89. J.M.Koehler and W.G.Bos, Inorg.Nucl.Chem.Lett. 3,545-548 (1967).
90. J.K.Przystal, W.G.Bos and J.B.Liss, J.Inorg.Nucl.Chem. 33, 679-689 (1971).
91. J.B.Liss and W.G.Bos, J.Inorg.Nucl.Chem. 39, 443-447 (1977).
92. J.A.Cunningham, D.E.Sands and W.F.Wagner, Inorg.Chem. 6, 499-503 (1967).
93. T.Phillips,II, D.E.Sands and W.F.Wagner, Inorg.Chem. 7, 2295-2299 (1968).
94. N.Shi, J.Wu,G.Xu, J.Qian, J.Yao,H.Fan,M.Kusunoki, N.Yasuoka and M.Kakudo, Fenzi Kexue Yu Huaxue Yanjiu 4 , 11-18 (1984).
95. R.Jain, A.K.Rai and R.C.Mehrotra, Polyhedron 5, 1017-1021 (1986).
96. R.Jain, A.K.Rai and R.C.Mehrotra, Inorg.Chim.Acta 126, 99-106 (1987).
97. D.D.S.Yadav and R.C.Mehrotra, Inorg.Chim.Acta 96, 39-42 (1985).
98. Y.P.Singh, P.Rupani,A.Singh,A.K.Rai,R.C.Mehrotra,R.D.Rogers and J.L.Atwood, Inorg.Chem. 25, 3076-3080 (1986).
99. P.Pardarsani,A.K.Rai and R.C.Mehrotra, Ind.J.Chem. 26A (1987).
100. S.Saxena,Y.P.Singh and A.K.Rai, J.Organomet.Chem. 270, 301-309 (1984).
101. Y.P.Singh, S.Saxena and A.K.Rai, Ind.J.Chem. 22A, 298-300 (1983).
102. S.Saxena, Y.P.Singh and A.K.Rai, Synth.React.Inorg.Met.-Org.Chem.13,855-866 (1983).
103. S.Saxena, Y.P.Singh and A.K.Rai, Ind.J.Chem. 23A, 878-880 (1984).
104. R.C.Mehrotra, Proc.Ind.Nat.Sc.Acad. 52A, 954-972 (1986).
105. R.C.Mehrotra, J.Non-Crystalline Solids (1987).