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METAL CHELATES OF FLUORINATED 1,3-DIKETONES AND RELATED COMPOUNDS

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CONTENTS

ABBREVIATIONS

H(acac)	2,4-Pentanedione (acetylacetone)
H(bza)	1-Phenyl-2,4-butanedione (benzoylacetone)
H(dbm)	1,3-Diphenyl-1,3-propanedione (dibenzoylmethane)
H(tfac)	1,1,1-Trifluoro-2,4-pentanedione (trifluoroacetylacetone)
H(hfac)	1,1,1,5,5,5-Hexafluoro-2,4-pentanedione (hexafluoroacetylacetone)
H(fod) or H(hpm)	1,1,1,2,2,3,3-Heptafluoro-7,7-dimethyl-4,6-octanedione (heptafluorobutanoylpivalylmethane)

H(btfa)	1,1,1-Trifluoro-4-phenyl-2,4-butanedione (benzoyltrifluoroacetone)
H(tta)	1,1,1-Trifluoro-4-(2-thienyl)-2,4-butanedione (thenoyltrifluoroacetone)
H(fta)	1,1,1-Trifluoro-4-(2-furyl)-2,4-butanedione (furoyltrifluoroacetone)
H(dfhd)	1,1,1,5,5,6,6,7,7,7-Decafluoro-2,4-heptanedione
H(dodefod)	1,1,1,2,2,6,6,7,7,8,8,8-Dodecafluoro-3,5-octanedione
H(fhd)	1,1,1,2,2,6,6,7,7,7-Decafluoro-3,5-heptanedione
H(tpm)	1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione (trifluoroacetylpivalylmethane)
H(ppm)	1,1,1,2,2-Pentafluoro-6,6-dimethyl-3,5-heptanedione (pentafluoropropanoylpivalylmethane)
H(tibm)	1,1,1-Trifluoro-5-methyl-2,4-hexanedione (trifluoroacetylisobutyrylmethane)
H(tprm)	1,1,1-Trifluoro-2,4-hexanedione (trifluoroacetylpropionylmethane)
H(tivm)	1,1,1-Trifluoro-6-methyl-2,4-heptanedione (trifluoroacetylisovalerylmethane)
H(tmbm)	1,1,1-Trifluoro-5-methyl-2,4-heptanedione (trifluoroacetyl-α-methylbutyrylmethane)
H(tfacam)	d-3-Trifluoroacetylcamphor
H(stta) or H(ttmbs)	1,1,1-Trifluoro-4-(2-thienyl)-4-mercapto-3-buten-2-one
H(hfac)	1,1,1,5,5,5-Hexafluoro-2-mercapto-2-penten-4-one (monothiohexafluoroacetylacetone)
H(sthd)	2,2,6,6-Tetramethyl-3-mercapto-3-hepten-5-one (monothiodipivalylmethane)
H(stfac) or H(ttfa)	1,1,1-Trifluoro-2-hydroxypent-2-en-4-thione (monothiotrifluoroacetylacetone)
H(tppm)	1,1,1,2,2-Pentafluoro-3-hydroxy-6,6-dimethylhept-3-en-5-thione (monothiopentafluoropropanoylpivalylmethane)
H(thpm)	1,1,1,2,2,3,3-Heptafluoro-4-hydroxy-7,7-dimethyl-4-en-6-thione (monothioheptafluorobutanoylpivalylmethane)
H(ttpm)	1,1,1-Trifluoro-2-hydroxy-5,5-dimethylhex-2-en-4-thione (monothiotrifluoroacetylpivalylmethane)
H(ntfa)	1,1,1-Trifluoro-4-naphthyl-2,4-butanedione (naphthoyltrifluoroacetone)
H(bzdtf)	Benzylidienetrifluoroacetylacetone
H(pta) or H(hpta)	1,1,1-Trifluoro-5,5-dimethyl-3,5-hexanedione (pivalyltrifluoroacetone)
H(tapm)	2,2-Dimethyl-5-mercaptohex-4-en-3-one (monothioacetylpivalylmethane)
H(thd) or H(dpm)	2,2,6,6-Tetramethyl-3,5-heptanedione (dipivalylmethane)

H(pva)	2,2-Dimethyl-3,5-hexanedione (pivalylacetone)
H(dprm)	3,5-Heptanedione (dipropionylacetone)
H(dibm)	2,6-Dimethyl-3,5-heptanedione (diisobutyrylmethane)
H(nta)	1-Naphthyl-1,3-butanedione (naphthoylacetone)
H(sacac)	2-Mercapto-2-penten-4-one (monothioacetylacetone)
H(sbza)	1-Phenyl-1-mercapto-1-buten-3-one (monothiobenzoylacetone)
H(hmcar)	Hydroxymethylene carvone
H(hmpul)	Hydroxymethylene pullgone
H(atc)	(+)-3-Acetylcamphor
H(ibm)	2-Methyl-6,6-dimethyl-3,5-heptanedione (isobutyrylpivalylmethane)
H(nebas)	1-(4-Nitrophenyl)-3-ethoxy-1-mercapto-4-penten-2-one
en	Ethylenediamino
bn	2,3-Butylenediamino
pn	Propylenediamino
TOPO	Tri-*n*-octylphosphine oxide
TBP	Tri-*n*-butylphosphate
DBSO	Di-*n*-butylsulphoxide
MBDPO	Methylenebis(diphenylphosphine oxide)
EBDPO	Ethylenebis(diphenylphosphine oxide)
TPAsO	Triphenylarsine oxide
TPPO	Triphenylphosphine oxide
TFEP	Tris(2,2,2-trifluoroethyl)phosphate
PFPP	Tris(3,3,3,2,2-pentafluoropropyl)phosphate
DMF	*N*,*N*-Dimethylformamide
NBS	*N*-Bromosuccinimide
NCS	*N*-Chlorosuccinimide
NIS	*N*-Iodosuccinimide
H_2(BTAT)	Bis(trifluoroacetylacetone)triethylenetetramine
H_2(BHAT)	Bis(hexafluoroacetylacetone)triethylenetetramine
THF	Tetrahydrofuran
Ph_4As	Tetraphenylarsonium
n-BuOH	*n*-Butanol
n-Hex	*n*-Hexanol
2E-Hex	2-Ethylhexanol
S-Hex	*sec*-Hexanol
Cy-Hex	Cyclohexanol
BG	Butylglycol
4-Me-py	4-Methylpyridine
4-Cl-py	4-Chloropyridine
py	Pyridine
bipy	Bipyridine
dmp	2,2-Dimethoxypropane
asym-dmed	*N*,*N*-Dimethylethylenediamine

ted	1,4-Diazabicyclo(2.2.2)octane (triethylenediamine)
pyz	Pyrazine

A. INTRODUCTION

Since the pioneering work of Urbain [1] and Werner [2] on β-diketone complexes almost four decades back, the study of metal 1,3-diketonates has been actively pursued. The chemistry of such compounds has aroused much recent interest in such diverse areas as spectral studies, gas chromatography, solvent extractions, column and thin-layer chromatography, NMR shift reagents, laser technology and in polymer industry [3—6]. The quasi-aromatic character of such compounds has also received considerable attention. In recent years, significant developments have taken place in the field of chemistry of fluorinated 1,3-diketones and their metal chelates.

Several reviews have appeared on metal 1,3-diketonate complexes [7—9] and one on fluorinated 1,3-diketonates [10]. The present review specifically concerns the metal derivatives of fluorinated 1,3-diketones and non-fluorinated analogues have been included only where comparative studies have been made. In case of laser chelates, there is no comprehensive review to date except for a preliminary section in refs. 8 and 10 and the laser chelates, therefore, have been reviewed comprehensively. This review covers the literature pertaining to metal chelates of fluorinated 1,3-diketones, through December, 1974, (but see Addendum for literature up to July 1976).

B. PREPARATION OF METAL 1,3-DIKETONATES

Under appropriate conditions, the enolic proton of a 1,3-diketone can be replaced by different metals or their salts, forming a metal derivative (Fig. 1), which is a characteristic of 1,3-diketones.

Recent synthetic work in the field of fluorinated 1,3-diketonate chelates is summarized below.

(a) Reaction of fluorinated 1,3-diketones with different metal ions [11]. The addition of a concentrated metal salt solution to the aqueous methanolic or aqueous ethanolic solution of fluorinated 1,3-diketones, results in precipitation of metal chelates. Recrystallization of the product produces high yields

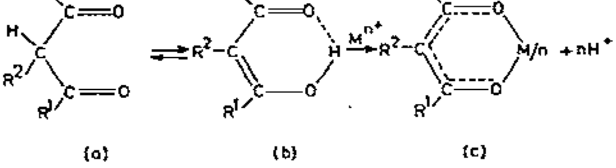


Fig. 1. Tautomers of 1,3-diketone: (a) and (b); metal-1,3-diketonate: (c).

of pure chelates. Be(II), Al(III), Sc(III), Y(III), La(III), Ce(III), Pm(III), Nd(III), Sm(III), Eu(III), Gd(III), U(IV) and Cu(II) chelates of fluorinated 1,3-diketones have been prepared by this method. (eqn. 1).

$$M^{n+} + n\ CF_3COCH_2COCH_3 \xrightarrow{EtOH\ (95\%)} M(CF_3COCHCOCH_3)_n + n\ H^+ \qquad (1)$$

The metal salts, usually used are: acetate, nitrate, oxalate, oxychloride and chloride.

(b) Reactions of fluorinated 1,3-diketones with anhydrous metal chloride. The fluorinated 1,3-diketone is directly added to an anhydrous suspension of metal chloride in carbon tetrachloride. The reaction mixture is usually refluxed till evolution of hydrogen chloride ceases [12,13]. (eqn. 2).

$$ZrCl_4 + 4\ CF_3COCH_2COCF_3 \xrightarrow[reflux]{CCl_4} Zr(CF_3COCHCOCF_3)_4 + 4\ HCl \qquad (2)$$

Mehrotra and coworkers [14—16] and other workers [17—20] have reported the reactions of anhydrous zirconium(IV) halides with excess of 1,3-diketone, yielding dihalobis(1,3-diketonato)zirconium(IV) and/or halotris(1,3-diketonato)zirconium(IV). The solvents used are chloroform [21—23], benzene [17,22], ether [17] or THF [24]. (eqn. 3).

$$ZrX_4 + n\ C_5H_8O_2 \xrightarrow{solvent} Zr(C_5H_7O_2)_n\ X_{4-n} + n\ HX \qquad (3)$$

$(X = Cl, Br; n = 2 \text{ and } 3)$

Iodotris(2,4-pentanediono)zirconium(IV) was prepared [19,25] by treating anhydrous zirconium iodide with tetrakis(2,4-pentanediono)zirconium(IV) in tetrahydrofuran, followed by heating the solvate under vacuum at 80°C (eqn. 4).

$$ZrI_4 + 3\ Zr(C_5H_7O_2)_4 + 4\ C_4H_8O \rightarrow 4\ Zr(C_5H_7O_2)_3I \cdot C_4H_8O$$

$$Zr(C_5H_7O_2)_3I \cdot C_4H_8O \xrightarrow[Vacuum]{80^\circ C} Zr(C_5H_7O_2)_3I + C_4H_8O \qquad (4)$$

(c) Reactions of metal carbonyls with fluorinated 1,3-diketones. The metal hexacarbonyl is refluxed for 2—4 days with a fluorinated 1,3-diketone [26] (eqn. 5).

$$M(CO)_6 + 3\ RCOCH_2COR' \rightarrow M(RCOCHCOR')_3 + \tfrac{3}{2}\ H_2 + 6\ CO \qquad (5)$$

$(M = Co, Mo; R = Me \text{ or } CF_3; R' = Me \text{ or } CF_3)$

Tetracarbonyldi-μ-chloro-dirhodium(I) reacts with β-diketones in presence of barium carbonate to give compounds such as $Rh(CO)_2(acac)$ [27]. Similarly, chloro(pentacarbonyl)manganese(I) and H(hfac) afford the complex

$Mn(CO)_4$(hfac) in low yield (14%) [28] (eqn. 6).

$$Tl_2CO_3 + 3\ C_5H_2F_6O_2 \rightarrow 2\ Tl(C_5HF_6O_2) + C_5H_2F_6O_2 \cdot H_2O + CO_2$$

$$Mn(CO)_5Br + Tl(C_5HF_6O_2) \rightarrow Mn(CO)_4\ (C_5HF_6O_2) + TlBr + CO \qquad (6)$$

The method can be readily adapted for the synthesis of a number of metal chelates (Metal = Mn(I), Tl(I), Rh(I) with H(tfac) and/or H(hfac) ligands) [28].

(d) Direct combination of elemental metals with fluorinated 1,3-diketones. An iron(III) chelate of H(fod) was prepared [29,30] by mixing and refluxing powdered iron and H(fod) under a nitrogen atmosphere. This type of reaction is catalyzed by trace amounts of water. Subsequently this method was employed to prepare chelates of some other metals. The general reaction (eqn. 7) may be represented as follows:

$$M + n\ H(fod) \xrightarrow[\text{(ii) } N_2 \text{ Atmosphere}]{\text{(i) } H_2O} M(fod)_n + \tfrac{1}{2}n\ H_2 \qquad (7)$$

(M = Fe(III), In(III), Ga(III), Cr(III), Mn(III), Pb(II), V(III) and Sc(III). n = 3 or 2.)

This type of reaction is also catalyzed by nitric acid (35%; 0.01 ml) [31].

(e) Air oxidation of tris chelates. Tetrakis(1,1,1-trifluoro-2,4-pentanedionato)-cerium(IV) has been prepared by air oxidation of tris(1,1,1-trifluoro-2,4-pentanedionato)cerium(III) in hot benzene solution [32,33] (eqn. 8).

$$Ce(NO_3)_3 \cdot 6\ H_2O + 3\ C_5H_5F_3O_2 + 3\ NH_3 \rightarrow Ce(C_5H_4F_3O_2)_3 + 3\ NH_4NO_3 + 6\ H_2O$$

$$4\ Ce(C_5H_4F_3O_2)_3 \xrightarrow[\text{benzene}]{O_2} 3\ Ce(C_5H_4F_3O_2)_4 + \text{Insoluble impurity} \qquad (8)$$

In some cases, a modified procedure has been used by adding H(acac) before the air oxidation, to give better yields (eqn. 9).

$$2\ Ce(C_5H_7O_2)_3 + 2\ C_5H_8O_2 + \tfrac{1}{2}\ O_2 \rightarrow 2\ Ce(C_5H_7O_2)_4 + H_2O \qquad (9)$$

However, this modification is not of general application [33].

Tetrakis(1,1,1-trifluoro-2,4-pentanedionato)cerium(IV) has also been prepared by reaction of hydrous cerium(IV) oxide with excess of H(tfac) in water [34].

(f) Metal exchange reaction. Recently, Schurig [35] prepared europium-tris-d-3-trifluoroacetyl camphorate by quantitative homogeneous exchange reaction of lanthanide nitrate with the barium salt of d-3-trifluoroacetyl camphor in ethanol (eqn. 10).

$$2\ Ln(NO_3)_3 \cdot n\ H_2O + 3\ Ba(tfacam)_2 \rightarrow 2\ Ln(tfacam)_3 + 3\ Ba(NO_3)_2 + 2n\ H_2O \qquad (10)$$

(Ln = trivalent lanthanide ion.)

(g) Preparation of mixed chelates. Tetrakis rare earth chelates were prepared [36] by treating the appropriate fluorinated 1,3-diketone in ethanol (95%) with a Lewis base, Q (1.53 g.), followed by appropriate lanthanide halide dissolved in water. On refluxing and cooling at room temperature overnight, the chelates were isolated and recrystallized from suitable solvents. A number of workers cited by Charles and Riedel [37] have followed this procedure, which was modified [18] by using ammonium hydroxide, alkali hydroxide and quartemary salts, in place of a Lewis base (eqns. 11 and 12).

$$\mathrm{LnX_3 + 4\ RCOCH_2COR'} \xrightarrow[\substack{\text{(i) Lewis base or} \\ \text{(ii) NH}_4\text{OH or} \\ \text{(iii) Quaternary salt}}]{\text{Ethanol (95\%) and}} \mathrm{[Ln(RCOCHCOR')_4]^- \cdot H^+Q + 3\,HX} \qquad (11)$$

or

$$\underset{\text{(1 mol)}}{\mathrm{LnX_3}} + \underset{\text{(4 mol)}}{\mathrm{4\ RCOCH_2COR'}} \xrightarrow[\text{(i) MOH (4 mol)}]{\text{Ethanol (95\%) and}} \mathrm{[Ln(RCOCHCOR')_4]^- \cdot M^+ + 3\ MX + 4\ H_2O} \qquad (12)$$

(Ln = La—Lu; Q = piperidine, morpholine, dimethylamine, diethylamine, pyridine, pyrrole, triethylamine, trimethylamine, *t*-butylamine, 2,4,6-trimethylpyridine, NH_3 and Ph_4As; M = Na, K and Cs.)

The mixed complex, $NaMg(acac)_3$ was prepared by the reaction of magnesium acetate and sodium acetylacetonate, $Na^+(acac)^-$ in methanol. The reaction of $K^+(hfac)^-$ with $M(hfac)_2 \cdot H_2O$ gave $KM(hfac)_3$ [M = Cu(II) or Mg(II)]. Similarly the mixed alkali metal chelates have also been prepared by treating alkali metal hexafluoroacetylacetonate, $M^+(hfac)^-$ and sodium hexafluoroacetylacetonate in 2 : 1 or 1 : 1 stoichiometric ratio in ethanol. The crystals of mixed chelates are obtained by slow evaporation of ethanol [38a] (eqns. 13 and 14).

$$2\ \mathrm{M^+(hfac)^- + Na^+(hfac)^-} \xrightarrow{\text{Ethanol}} \mathrm{M_2Na(hfac)_3} \qquad (13)$$

(M = K, Rb or Cs)

or

$$\mathrm{M^+(hfac)^- + M^{1+}(hfac)^- \rightarrow MM^1(hfac)_2} \qquad (14)$$

(M = K, Rb or Cs; M^1 = Li, Na, K and Rb)

1,1,1-Trifluoro-2,4-pentanedionatobis(ethylenediamino)cobalt(III) bromide was prepared [39] with H(tfac) at 40° C.

(h) Preparation of mono- and dithio-β-diketone chelates. A large number of monothio-β-diketones and their metal chelates have been reported [40—44]. The successful preparation of metal chelates of dithio-β-diketone has been reported [45,46] by treating an ethanolic solution of dithio-β-diketone containing the appropriate metal ion with hydrogen chloride.

C. X-RAY STRUCTURAL ANALYSES OF METAL 1,3-DIKETONATES

The important data available from the X-ray structure determinations are: range of bond lengths for the M—O (1,3-diketone), C—C and C—X (halogen or hydrogen), angles within the complex molecule, and its geometry.

For example, the first chelate of a fluorinated β-diketone examined is Cs[Y(hfac)$_4$], containing two d^0 cations Cs$^+$ and Y^{3+} and a β-diketonate with two donor oxygens for each negative charge [47,48]. The X-ray analysis reveals that the crystal structure contains discrete monomeric [Y(hfac)$_4$]$^-$ anions. As shown in Fig. 2 "eight essentially equidistant [average Y—O, 2.323(4) Å] oxygen atoms surround the central yttrium atom in a slightly distorted dodecahedral configuration" [48] resulting in overall D_2 symmetry. The monomeric anions are linked together in infinite columns parallel to the crystallographic a axis by a close Cs—F association (3.2—3.7 Å). Eight fluorine atoms, from two neighbouring [Y(hfac)]$^-$ moieties, surround each cesium cation (three pairs at 3.21, 3.27, 3.31 and one pair at 3.75 Å) [48].

A preliminary X-ray examination of a series of lanthanide and americium 1,3-diketonates has been reported [49] and is in agreement with previous observations [48]. Detailed crystal structure determinations of three compounds, viz., Cs[Y(hfac)$_4$], Cs[Eu(hfac)$_4$] and Cs[Am(hfac)$_4$], indicate that the compounds are isomorphous [50]. Significant differences between the corresponding parameters of all three compounds have been noted. For example, the differences in the trivalent metal radii are reflected in the bond lengths (average); 2.41 Å for Am—O, compared to 2.38 Å for Eu—O and 2.32 Å for Y—O. All compounds exhibit the same qualitative features of symmetry and packing, namely, "the chelate ligands are essentially planar but folded along the O ··· O line about 8° with respect to the O—M—O plane, and the type of span by the ligands and the dodecahedron of O atoms results in approximately D_2 symmetry for the anions" [50]. A comparison of the bond distances and angles among the three complexes is given in Fig. 3a.

In the crystal structure [48] of Cs[Y(hfac)$_4$], eight fluorine atoms from two neighbouring [Y(hfac)$_4$]$^-$ moieties are coordinated to cesium ion at pair dis-

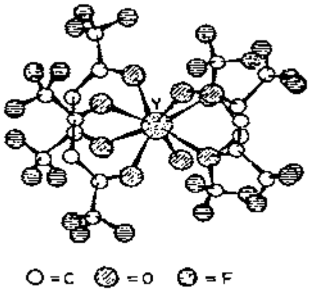


Fig. 2. The anion in Cs$^+$[Y(CF$_3$COCHCOCF$_3$)$_4$]$^-$

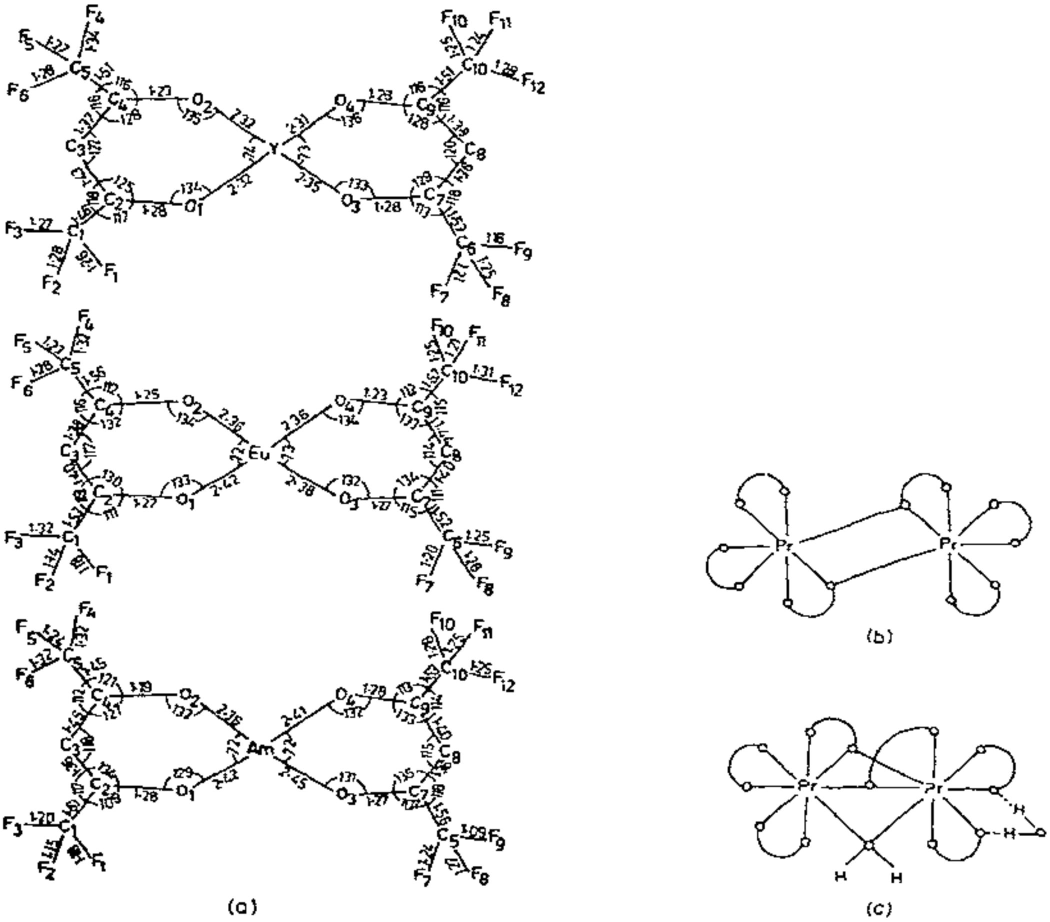


Fig. 3. (a) Comparison of bond lengths and angles in Cs[Y(hfac)$_4$], Cs[Eu(hfac)$_4$] and Cs[Am(hfac)$_4$]. (b) Schematic dimeric structure of Pr(thd)$_3${Pr$_2$(thd)$_6$}. (c) Schematic dimeric structure of Pr(fod)$_3$ · H_2O, [(fod)$_3$Pr(OH$_2$)Pr(fod)$_3$] · H_2O.

tances of 3.21, 3.27, 3.31 and 3.75 Å. However, Burns and Danford [50] rule out the last pair as being too long and instead, include six oxygen atoms in pair distances at 3.29, 3.40 and 3.50 Å. This gives the Cs^+ cation in Cs[Y(hfac)$_4$ a 12-fold coordination. Similarly, Cs^+ cation also exhibits a 12-fold coordination in Cs[Eu(hfac)$_4$] and in Cs[Am(hfac)$_4$]. Both groups of workers [48,50] agree that there are only F ··· F contacts between chains.

The X-ray powder diffraction patterns for the following series of chelates, viz: Ln(hfac)$_3$ · n H_2O, (NH_4)Ln(hfac)$_3$ · n H_2O, pyH Ln(hfac)$_4$ · n H_2O and Ln(hfac)$_2$ · CF_3CO_2 · 2 H_2O (where Ln = La—Lu and Y) have been studied [51]. The number of crystal forms seems to depend markedly on the extent of hydration of the compound: a maximum of two isomorphous series is observed for each of the hydrated chelates, but as many as four isomorphous series have been found for some of the anhydrous compounds (Table 1).

Crystal structure of $Eu(tta)_3 \cdot (H_2O)_2$ shows [52] square-antiprismatic symmetry (Eu—OH_2, 2.55 Å; Eu—O chelate, 2.4 Å), whereas $(NH_4)Pr(tta)_4 \cdot H_2O$ reveals dodecahedral symmetry Pr—O, 2.45 (r_a Å), Pr—O, 2.45 (r_b Å), respectively [52,53].

The crystal structure of $Th(tfac)_4$ indicates that the thorium atom is coordinated by eight oxygen atoms of the four ligand anions, tfac in form of a 1111(D_4-422) square-antiprism [54]. The mean of Th—O distance is 2.39 Å with standard deviation of ±0.04 Å. The trifluoroacetylacetonate rings are approximately planar, except for the CH_3 and CF_3 groups, which show significant deviations. The Th—O bonds form angles of approximately 72° and 50° with theoretical 8-axis of the square-antiprism.

Cunningham et al. [55] studied the crystal structure of $Y(acac)_3 \cdot 3\ H_2O$ and noticed that each yttrium ion is surrounded by eight oxygen atoms, contributed by three bidentate acac groups (average $Y—O_{acac} = 2.366$ Å) and two water molecules (average $Y—O_{H_2O} = 2.409$ Å). Thus, the polyhedron formed about the yttrium ion by the eight coordinated oxygen atoms is a distorted square-antiprism. The third water molecule, associated with each β-diketonate unit, links the β-diketonates, in pairs, by hydrogen bonding. Similarly, crystal structure of $Y(bza)_3 \cdot H_2O$ indicates [56] that the molecules are monomeric with the yttrium ion being at the centre of a distorted monocapped octahedron of chelate oxygen atoms (average $Y—O_{bza} = 2.28(1)$ Å) capped on one face by the water molecule [$Y—O_{H_2O} = 2.341(3)$ Å].

A comparison of $Y—O_{chelate}$ distances in $Y(acac)_3 \cdot 3\ H_2O$, $Cs[Y(hfac)_4]$ and $Y(bza)_3 \cdot H_2O$, indicates a shortening of Y—O distances due to change in the coordination polyhedron about yttrium cation [56].

Coetzer and Boeyens [57] studied the crystal structure of $Ni(sthd)_2$ by X-ray diffraction. The geometry of the chelate, $Ni(sthd)_2$ is almost square-planar with slight distortion towards a tetrahedron, in which Ni(II) is surrounded by a *cis* arrangement of two oxygen and two sulphur atoms. The crystallographic evidence supports extensive delocalization in the chelate rings and the molecule has an *S—S cis* configuration.

The X-ray analysis of $Er(thd)_3$ indicates that the Er^{3+} ion is coordinated by

TABLE 1

Number of structural transformations which occur as the rare earth series is traversed in several series of chelates

S. No.	Chelate	Number of crystal forms
1	$Ln(hfac)_3 \cdot 2\ H_2O$	1 (Nd—Lu)
2	$Ln(hfac)_2 \cdot CF_3CO_2 \cdot 2\ H_2O$	2 (Pr—Sm; Gd—Yb)
3	pyH $Ln(hfac)_4$	1 (Pr—Yb)
4	$NH_4Ln(hfac)_4$	4 (La—Nd; Nd; Sm—Ho; Er—Lu)

six oxygen atoms and the coordination geometry is almost trigonal prismatic [58]. The crystal structure of $Pr(thd)_3$ has been investigated and each asymmetric unit is found to consist of a dimer, $Pr_2(thd)_6$ (Fig. 3b), in which each of the Pr atoms is surrounded by seven oxygen atoms (average Pr—O distance is 2.446 Å) in position consistent with maximum repulsion (3.05 Å apart). Two of the oxygen atoms are shared equally between Pr atoms [59].

The crystal structure of the praseodymium β-diketonate monohydrate, "$Pr(fod)_3 \cdot H_2O$", exists in a dimeric form (Fig. 3c) [60] in the solid state. "The dimer is formed through bridging across two carbonyl oxygen atoms as well as a molecule of water." The other water molecule is situated between two perfluoro side chains (hydrogen bonded; H ··· F) and/or hydrogen bonded to the chelate oxygens (H ··· O) as shown in Fig. 3c.

Both Pr atoms are eight-coordinated, but the coordination geometries are different and related to a dodecahedron and a bicapped trigonal prism, respectively. The parent octahedra are also different being *trans* and *cis* respectively [60].

The crystal structure of $Dy(thd)_3 \cdot H_2O$ has revealed that the oxygen polyhedron around the Dy has pure 7-coordination geometry, the seventh ligand being the water molecule [61]. Similarly, $Lu(fod)_3 \cdot H_2O$ crystals indicate a dimerized structure through water molecule with hydrogen bonds across centres of symmetry. The coordination is seven-fold with a monocapped trigonal prismatic geometry [62].

A comparison of the variable parameters; such as bite, d(M—O) and O—M—O angle with those obtained for the lanthanide chelates, $Pr_2(thd)_6$, $Nd_2(thd)_6$, $Dy(thd)_3 \cdot H_2O$, $Er(thd)_3$ and $Lu(fod)_3 \cdot H_2O$, are given in Table 2 [58].

Crystal structure of the basic erbium tetramethylheptanedionate, $Er_8O(thd)_{10}(OH)_{12}$, has been studied in detail recently by the same workers [63] and the structure is reported to be noteworthy for two characteristic features, viz; a unique arrangement around the central oxygen atom and the high coordination number of the inner sphere erbium atoms (8 coordination number).

Recently, the crystal structure of $Ni(stafac)_2$ has also been studied and a *cis*-square-planar geometry for the molecule reported [64].

Three dimensional X-ray crystal analyses have been carried out on the tris(hexafluoroacetylacetonato)copper(II) and tris(hexafluoroacetylacetonato)magnesium salts of monoprotonated 1,8-bis(dimethylamino)naphthalene

TABLE 2

Comparison of some variable parameters of some lanthanide chelates

Parameters	$Pr_2(thd)_6$	$Nd_2(thd)_6$	$Dy(thd)_3 \cdot H_2O$	$Er(thd)_3$	$Lu(fod)_3 \cdot H_2O$
Bite (Å)	2.83	2.77	2.74	2.67	2.63
O—M—O (°)	70.4	71.6	73.6	74.4	75.8
M—O (Å)	2.41	2.38	2.30	2.21	2.17

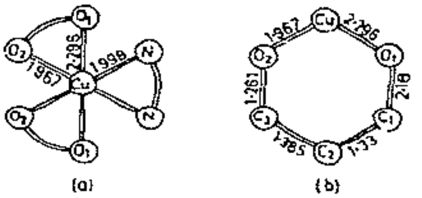
[65,66], $C_{14}H_{19}N_2^+$ $[(hfac)_3M]^-$ (M = Mg or Cu), with particular reference to the location of protonic hydrogen atoms, a comparison of the M^{2+}—O bond lengths for a d^9 and d^0 electronic configuration [65]. In the anions all six chelate rings show delocalisation. The magnesium ion is octahedrally coordinated by oxygen atoms, while for copper, there appears to be tetragonal distortion. In the cation, the proton lies in the plane of the naphthalene ring between the two nitrogen atoms and appears closer to one nitrogen in the magnesium and the other nitrogen in the copper complex.

The X-ray structure of tris(hexafluoroacetylacetonato)-π-cyclopentadienylzirconium [67], $(\pi\text{-}C_5H_5)Zr(hfac)_3$, has been elucidated, and the molecular complex exhibits pentagonal bipyramidal geometry. Of the six coordinated oxygen atoms, five lie in an equatorial plane about the zirconium while the sixth oxygen and the π-cyclopentadienyl group occupy the two axial positions. A folding of 4.5 and 8.4°, respectively is exhibited by two chelate rings about the O ··· O line while the third ring is planar.

An examination of the crystal structure of $Cu(hfac)_2(asym\text{-}dmed)_2$ [68, 69] has revealed that the copper atom occupies the centre of an octahedron, centrosymmetrically 6-coordinated by four nitrogen atoms from two chelating amine (asym-dmed) lignads. The latter are arranged in a square plane, in the *gauche* conformation, with the Cu—NMe_2 distance [2.064(3) Å] significantly greater than the Cu—NH_2 distance [1.989(3) Å]. The remaining fifth and sixth positions of an octahedron are coordinated by one oxygen from each hfac anion in a novel monodentate form, in the axial positions with a long Cu—O distance [2.793(2) Å]. The remaining uncoordinated oxygen atoms of hfac anions form a hydrogen-bond with the —NH_2 group of the amine.

The crystal structure of dirubidium tris(hexafluoroacetylacetonato)sodate, $Rb_2Na(hfac)_3$ has been studied [70]; the compound is an anionic complex of sodium, $Na(hfac)_3^{2-}$; where "the sodium is surrounded by a trigonal prism of oxygen atoms from the three β-diketonates". The rubidium ions are located below and above the triangular faces of the prism, and are also in contact with fluorine atoms.

Palenik and co-workers [71] reported X-ray diffraction and electron spin resonance studies of the bipy adduct of bis(hexafluoroacetylacetonato)copper(II), $Cu(hfac)_2 \cdot bipy$ illustrated in Fig. 4. Two of the three symmetrical chelating ligands are distorted owing to the Jahn—Teller effect in the copper-



(a) (b)

Fig. 4. (a) Over-all geometry of the $Cu(hfac)_2$ adduct together with the Cu—O and Cu—N bond lengths. (b) Shows the Jahn—Teller distortion.

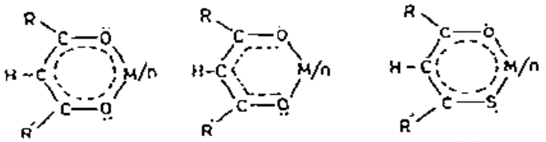
(II) ion and the orbital degeneracy present in octahedral d^9 configuration removed. The two fold axis passes through the bipy ligand and requires the two Cu—N bonds to be identical (both Cu—N bond lengths observed are 1.998 ± 0.004 Å).

The crystal structure [72] of Cu(hfac)$_2$(ted) reveals the crystals to be orthorhombic. An interesting feature of this molecule is that Cu^{2+} ion has tetragonally distorted octahedral geometry with a pair of long axial Cu—N bonds [2.566(7) Å] and two pairs of short equatorial Cu—O bonds [Cu—O bond lengths are 1.921 and 1.908 Å; mean 1.956(7) Å]. Each Cu^{2+} is coordinated by four oxygen atoms, two from each hfac molecule and by two nitrogen atoms from different ted molecules (axial) and each ted molecule bridges two Cu^{2+} ions. A possible explanation for the very long Cu—N bond in Cu(hfac)$_2$(ted), is the interaction of ted hydrogen with hfac ring. To support the above view, the crystal structure [73] of Cu(hfac)$_2$(pyz) shows the species to form a linear coordination polymer with Cu(hfac)$_2$ moieties bridged by pyz rings. The crystals are triclinic. The Cu^{2+} ion contains three different pairs of bonds, in the equatorial plane the Cu—O bonds are; 1.924(7) (one pair) and 2.004(7) Å (one pair), and in the axial direction the Cu—N distance is 2.529(9) Å (one pair). In this case also, the Jahn—Teller effect can explain the appearance of four short equatorial and two long axial bonds [74].

Recently, X-ray diffraction techniques [75] have been used to differentiate the *cis* and *trans* isomers of Ru(tfac)$_3$.

D. REACTIONS OF METAL 1,3-DIKETONATES

According to Collman et al. [76] and other workers [77], each chelate ring in metal 1,3-diketonates, has a cyclic π-orbital, formed by overlap of vacant d-orbital of the central metal atom with the 6π-electron orbital of the ligand (fig. 5a), whereas Lloyd and Marshall [78] suggested an acyclic conjugated π-electron system (Fig. 5b) as there does not appear to be much delocalization through the M—O bonds. However, Holm and Cotton [79] expressed doubts over such aromaticity in these compounds. These systems have been found to undergo typical electrophilic substitution reactions of the hydrogen atom attached to sp^2 hybridized carbon atom, and the metal 1,3-diketonates have, therefore, been termed quasi-aromatic [80]. When the oxygen atom of metal 1,3-diketonate (Fig. 5c) is replaced by sulphur, π-bonding between metal and sulphur increases and consequently the quasi-aromaticity of metal monothio-

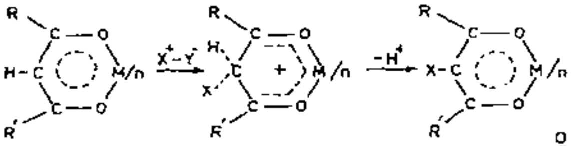


(a) (b) (c)

Fig. 5. Quasi-aromatic structures of metal 1,3-diketonates.

β-diketonate also increases in comparison to β-diketonate analogues [81]. In the present section we have followed Collman's notations [76].

As early as 1925, the first electrophilic substitution reactions of metal 1,3-diketonates were reported [82] and tris(3-bromo-2,4-pentane-dianato)chromium(III) isolated by treating chromium(III) acetylacetonate with bromine in chloroform. However, this sytem went unnoticed until 1958 when the nitration of copper(II) acetylacetonate with N_2O_4 was reported by Nyholm and co-workers [83]. Since then, numerous reports have appeared concerning halogenation [84—87], nitration [88—93], thiocyanogenation [94—96], formylation [89,97,98], chloromethylation [80,99], aminomethylation [80, 99], diazotization [90] and several Friedel—Crafts reactions [88,89,95,98] having been effected in this system without rupture of the chelate rings (eqn. 15).



(15)

Where: X = Cl, Br, I, SCN, SAr, NO_2, $CH_2N(CH_3)_2$, $-\overset{O}{\overset{\|}{C}}-H$ and $\overset{O}{\overset{\|}{C}}-R$

M = Cr(III), Co(III), Rh(III), Be(II), Cu(II), Al(III), Fe(III) and Eu(III)

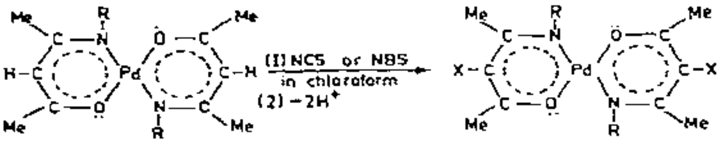
n = 3 or 2.

Generally, the metal 1,3-diketonate systems are acid labile. Selective conditions are therefore required to carry out these electrophilic reactions without degrading the chelate rings. The widely studied metal 1,3-diketonate systems are of Cr(III), Co(III) and Rh(III), which are kinetically stable. Chelates of Be(II), Cu(II), Fe(III), Al(III), Pd(II), Mn(III), Ni(II), Zn(II), VO(II), Th(IV) and Zr(IV) however, undergo only some of these reactions [86,91,93,97].

The *N*-halosuccinimides (NCS, NBS and NIS) are the best reagents for halogenation of metal 1,3-diketonates [84—86,87]. The rate of bromination is much faster than that of iodination and chlorination [97]. Two reaction mechanisms may be put forward to explain the halogenation: (a) Ionic mechanism: which is operative only in polar solvents like chloroform, methanol and acetic acid [84—86]. (b) Free radical: which is operative in non-polar solvent like carbon tetrachloride [100].

Yokoyama et al. [101] reported the successful bromination of Co(III) chelates of monothio-β-diketones, Co(sacac)$_3$ and Co(sbza)$_3$, with NBS or bromine in chloroform, acetone and in acetic acid. The brominated Co(III) chelates have been characterized by IR spectra and remarkable differences have been observed between brominated and non-brominated chelates in the region of 1560—1540 cm^{-1}. In NMR spectra, disappearance of the methine proton signal at τ 3.76 takes place. Recently (1973) [102], mono-, di- and tribrominated chelates were isolated from the bromination products of Co-(sacac)$_3$ and characterized spectroscopically. The NMR spectra indicate that these chelates exist exclusively as *cis* (*facial*) isomer.

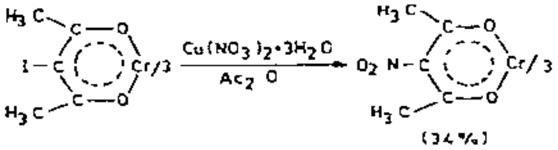
Kasahara and Izumi [103] reported the halogenation of palladium(II) chelates of β-oxo-amines with NBS and NCS in chloroform, (eqn. 16) characterized by IR, UV and NMR spectra.



(16)

R = Ph, p − MeC$_6$H$_4$ or α-naphthyl. X = Cl or Br

The substituted halogen in such halogenated chelates, is chemically inert toward nucleophilic substitution reactions [85]. However, under certain conditions, halogens have been displaced in some cases from chelate rings by electrophilic reagents [97] (eqn. 17).



(17)

The usual nitrating mixture (nitric acid and sulphuric acid) is not a good reagent to nitrate the chelate rings as the latter undergo rapid degradation. Dinitrogen tetroxide nitrates in low yields [88], but metal 1,3-diketonates have been nitrated in good yields by copper(II) nitrate trihydrate in acetic acid [89,104]. Similarly, ferric nitrate nonahydrate, cobaltous nitrate hexahydrate, aluminium nitrate nonahydrate, nickel nitrate hexahydrate and manganese nitrate hexahydrate have also been used as nitrating agents [91]. Some characteristic features of the nitration reaction are summarized as follows:

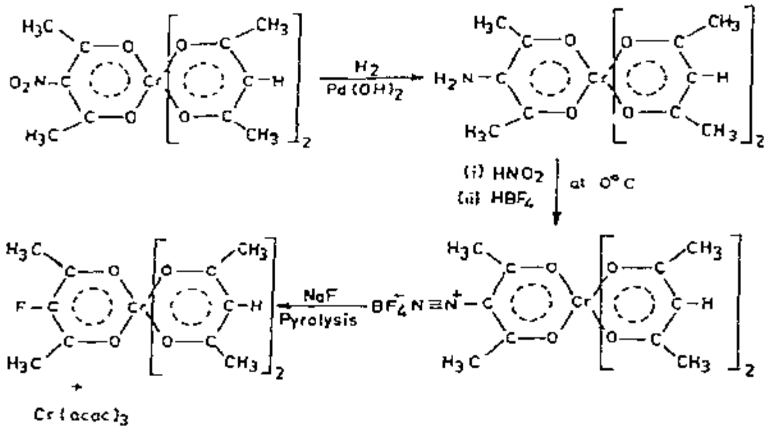
(a) While copper(II) nitrate trihydrate can nitrate the chelate rings, dehydrated copper(II) nitrate does not nitrate under similar conditions. This has been ascribed to the covalent nature of dehydrated copper(II) nitrate [93].

(b) During nitration of chelate rings of metal 1,3-diketonates, the ring metal atom may be replaced simultaneously by another metal (cation of the metal nitrate) [91].

(c) Metal nitrates, in acetic anhydride medium, may react with 1,3-diketone for preparation and synchronous nitration of chelate rings [91].

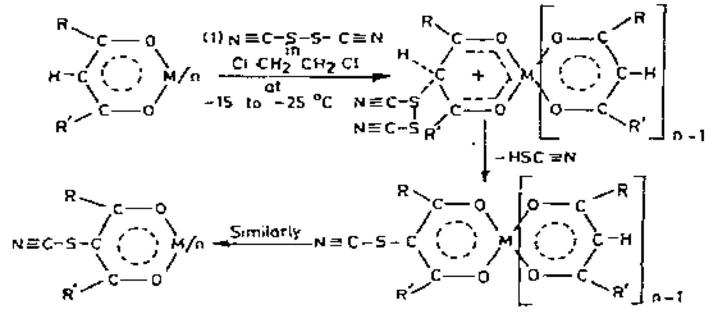
(d) Oxidation of cobalt(II) chelates to cobalt(III) chelates [93] may take place under nitration reaction conditions [91], and this has been ascribed to NO_3^- ions [93].

Generally, chemical reactions of metal 2-nitro-1,3-diketonates are sluggish [90]. However, on catalytic reduction [H_2/Pd(OH)$_2$], chromium(III) 2-amino-1,3-diketonates have been obtained but corresponding amine chelates from rhodium(III) and cobalt(III) nitro chelates could not be obtained due to decomposition of chelates. The amino chromium(III) chelate behaves as a typical aromatic amine forming a hydrochloride ($pK_a = 5.24$) [97] and has also been diazotized [90]. In fact, the aromatic character of metal 1,3-diketonates has been best shown by preparing a diazonium fluoborate which is thermally stable, decomposition temperature being, 165—167° C (a sharp peak at 2200 cm^{-1} in IR spectrum due to diazonium ion, $-\overset{+}{N}\equiv N$). A mixture of diazonium fluoborate and sodium fluoride, has afforded a fluoro chelate (C—F stretching vibration peaks at 1490, 1320 and 1152 cm^{-1}) on pyrolysis [90,97] (eqn. 18).



(18)

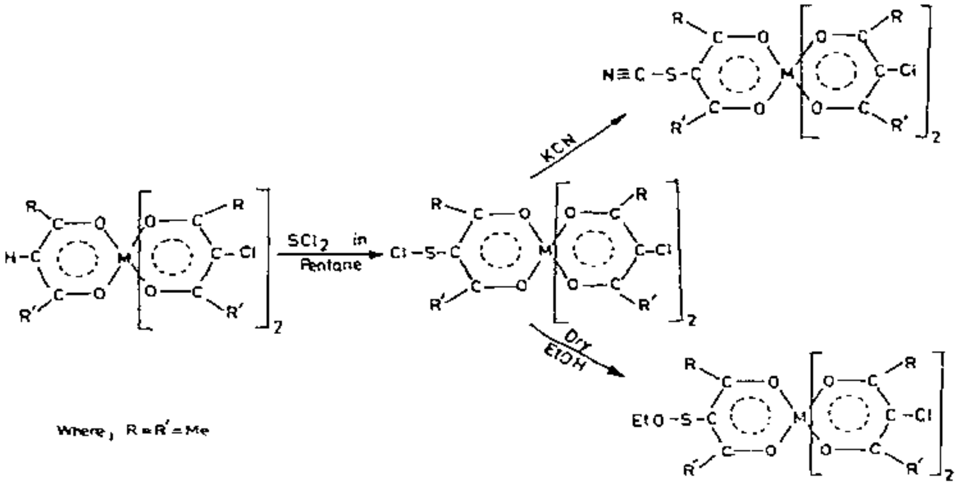
The electrophilic substitution reactions of metal 1,3-diketonates with sulphur electrophiles have also been successful. Treatment of metal 1,3-diketonates with thiocyanogen yields tris-thiocyanato chelates [94—96] (eqn. 19). The tris-thiocyanato chelates have been characterized by IR spectra, an additional nitrile group, (—C≡N) peak in the region 2165—2150 cm^{-1} [95,96].



(19)

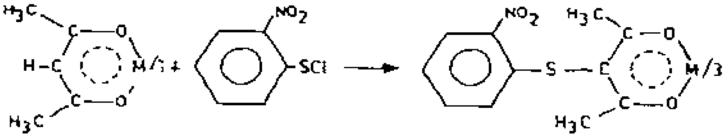
Where; M = Cr(III), Co(III), Rh(III), Al(III), Sc(III), Fe(III), Cu(II) and Pd(II)
R = Me or Ph; R′ = Me or Ph; n = 3 or 2

Similarly, aryl sulphides and chloro-sulphur groups can replace the hydrogen of chelate rings by aryl sulphenyl chloride and sulphur dichloride (eqn. 20), respectively, without any catalyst [95,97].

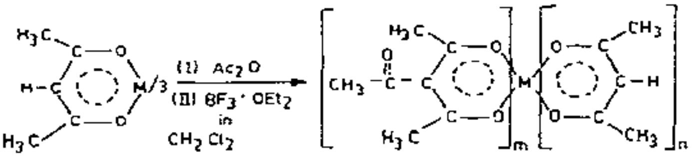


Where, $R = R' = Me$

(20)

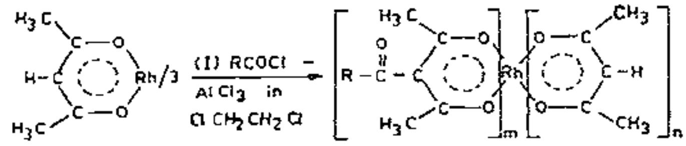


Successful acetylation of chromium(III) 1,3-diketonate with aluminium chloride—acetyl chloride mixture could not be effected due to decomposition of chelate rings [95]. Other acetylating mixtures like py-Ac$_2$O and py-AcCl also failed to react. Zinc chloride and stannic chloride were ineffective for catalysing the acetylation reaction. However, a mixture of boron trifluoride etherate and acetic anhydride acetylated both Co(III) [95] and Cr(III) 1,3-diketonates [95,98] but not Rh(III) 1,3-diketonate. A successful acetylation of the latter with aluminium chloride and acetyl chloride has been reported [95]. In case of Cr(III) and Co(III) 1,3-diketonates, mono-, di- and tri-acetylated chelates have been isolated. Rh(III) 1,3-diketonates, however, yield only mono- and di-acetylated products [95] (eqn. 21). All acetylated



Where ; $m = 1, 2$ or 3 ; $n = 2, 1$ or 0 and $M = Co(III)$ and $Cr(III)$

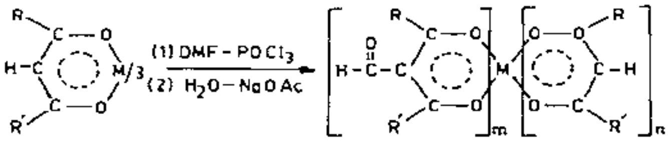
(21)



Where ; $m = 1, 2$ or 3 ; $n = 2, 1$ or 0 ; $R = Me, Ph$ or *n*-Pr.

metal chelates have been characterized by IR spectra (an additional uncoordinated $>C=O$ band appears at 1680 cm^{-1}) [95,98]. Additional confirmation has been provided by NMR spectra of mono-, di- and tri-acetylated Co-(III) 1,3-diketonates, which exhibit additional signals due to uncoordinated acetyl group at 8.02, 8.03 and 8.04 τ, respectively, as compared to uncoordinated chelates [95].

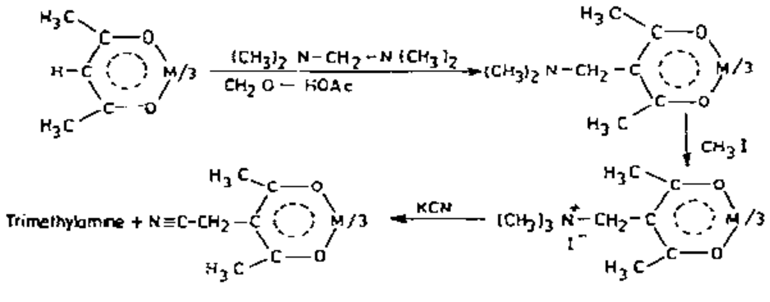
Vilsmeirer reaction has been used to introduce the formyl group into metal 1,3-diketonates of Cr(III), Co(III) and Rh(III) [89,97,98]. As in acetylation [95], formylation of single chelate ring of metal 1,3-diketonates, deactivates the remaining unsubstituted rings [89,98]. Again, mono-, di- and tri-formylated Co(III) 1,3-diketonates have been isolated while only mono-formylated Cr(III) and Rh(III) 1,3-diketonates (eqn. 22), result. All formylated metal 1,3-diketonates have been characterized by IR spectra (an additional conjugated $>C=O$ absorption band at 1670 cm^{-1}) [97,98]. It has also been noticed that uncoordinated aldehyde groups are inert to chemical reactions of the carbonyl group [97].



(22)

Where, (a) M = Co(III)^{97} [m = 1, 2 or 3, n = 2, 1 or 0]; (b) m = Rh (III) and Cr (III)^{98} (m = 1; n = 2)
R = R′ = Me

A modified Mannich reaction of metal 1,3-diketonates has been reported [99]. Mannich bases have been characterized by IR spectra; additional confirmation being obtained by the NMR spectral studies of Mannich bases of Co(III) analogue. These basic chelates quaternize on treatment with methyl iodide. The quaternized metal 1,3-diketonates, on further treatment with potassium cyanide, yield neutral trinitrile chelates (eqn. 23) which are easily purified and characterized [99].



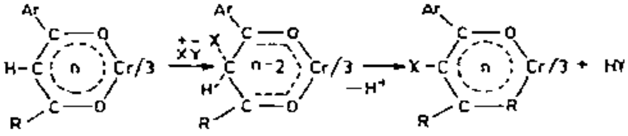
(23)

Where; M = Cr (III), Co (III) and Rh (III)

Attempts to effect chloromethylation of metal 1,3-diketonates have yielded methylene bridged, cross linked chelates of polymeric nature [99].

It may be noticed that the rate of electrophilic substitution is faster in methyl-substituted metal 1,3-diketonates compared to their phenyl substituted analogues. The steric effects of coplanar phenyl groups play an important role in these reactions. Such steric effect of a bulky group can also be illustrated by chlorination and nitration reactions of $Cr(dpm)_3$ in which chelates undergo substitution very slowly under forcing conditions [97]. The rate of the electrophilic substitution reactions also falls sharply when methyl groups of metal 1,3-diketonates are replaced by CF_3 groups and in some instances the reactions have not taken place at all [80,97].

Joshi and Pathak [105] reported the first electrophilic substitution reactions of chromium(III) chelates of fluorinated 1,3-diketonates. Under controlled conditions, electrophilic substitution reactions have been effected even on metal 1,3-diketonates containing a $—CF_3$ group (eqn. 24).



(24)

Where: $X^+ = Cl^+$, Br^+ or NO_2^+ ; $Ar = 4-F \cdot C_6H_4$ or a derivative
$R = Me$, Et, Pr^n, CF_3 or Ph.
n = number of electrons in the π-system of the metal 1,3-diketonates

The IR spectral studies reveal disappearance of the band in the region of 1225—1180 cm^{-1} (C—H in-plane-bending vibration), providing strong evidence for substitution at the central carbon (γ-carbon) atom of the chelate ring. This is supported by marked differences in the region of 1610—1540 cm^{-1} also.

The electrophilic substitutions of metal 1,3-diketonates are very slow [105] when flanked by a substituted phenyl group at C-1 and a CF_3 group at C-3. This type of deactivation of γ-hydrogen of the chelate ring is due to pronounced inductive effect of the CF_3 group.

Generally speaking, the rates of such reactions are faster in polar solvents (e.g. methanol, chloroform and ether) owing to their high dielectric constant and consequent increased production of electrophiles [100,105] as compared to non-polar solvents (e.g. carbon tetrachloride).

E. SPECTRAL STUDIES OF METAL 1,3-DIKETONATES

(i) Infrared spectra

The IR spectra of metal 1,3-diketonates have received considerable attention. Bands at 1380 and 1520 cm^{-1} were initially assigned [106] to the C=O and C=C stretching modes. These values were subsequently inverted by Nakamoto et al. [107] on the basis of their calculations. However, as a result of the study of IR spectra of ^{18}O-labelled acetylacetonates of Cr(III) and Mn(III), the position of the C=C and C=O stretching modes were again inverted [108] the earlier assignments being correct. Later on, similar observations were noted with various deuterated complexes of Pt(II) acetylacetonate [109] and ^{13}C and ^{18}O labelled chelates of Cu(II) acetylacetonate [110] and related complexes. The IR and Raman spectra of some tris- and tetrakis-europium(III) 1,3-diketonates using trifluoroacetylacetone, benzoyltrifluoroacetone and halogen (F, Cl and Br) substituted benzoyltrifluoroacetone were studied [111] in detail. It was concluded that the tetrakis ligand complexes belong to the symmetry group S_4 or C_1, instead of belonging to any one of the symmetry groups C_{1h}, D_{4h}, D_{2d}, C_{4v} and C_{2v}. Deuteration effects on the IR spectra of these metal 1,3-diketonates were also examined [111].

Similarly, a number of metal chelates, M(tfac)$_{2(\mathrm{or}\ 3\ \mathrm{or}\ 4)}$ and M(hfac)$_{2(\mathrm{or}\ 3\ \mathrm{or}\ 4)}$ (where M = Cu(II), Pd(II), Co(II), Ni(II), Rh(III), Cr(III), Fe(III), Al(III), Zr(IV), Tl(IV), Nd(III), Zn(II), Mn(II) and Fe(II)) have been subjected to examination by IR spectroscopic method [112—114]. For charge-to-radius $(q/r) > 3.6$, the carbonyl bands occur in the 1625—1650 cm^{-1} region; for q/r ratios < 3.6, in the 1590—1615 cm^{-1} region [65].

The fluorinated monothio-1,3-diketonates [M(RC($\overline{\mathrm{S}}$)=CHCOCF$_3$)$_n$; M = Ni, Pd, Cr, Co; $n = 2, 3$] have been examined by Livingstone and co-workers [40,42,115]. The characteristic bands in the region of 1590—1535, 1542—1477, 1261—1220, 817—800 and 499—451 cm^{-1} have been noted and assigned to C$\overset{\cdots}{-}$C stretching; C$\overset{\cdots}{-}$O stretching, C$\overset{\cdots}{-}$S stretching, C$\overset{\cdots}{-}$S stretching coupled with C—H in-plane-bending, and M—O stretching frequencies respectively. In contrast, some recent data [108—110] show that the first band between 1590—1535 cm^{-1} may be attributed to C$\overset{\cdots}{-}$O stretching and the second band between 1542—1477 cm^{-1} to C$\overset{\cdots}{-}$C stretching frequencies, respectively.

Rao and Li [116] studied the IR spectra of (i) M(btfa)$_2 \cdot 2\,H_2O$ and (ii) M(btfa)$_2 \cdot$ B (where M = Cd, Zn, Mn, VO$_2$ and B = TOPO, TBP, TPPO). The (i) chelates show a broad peak in the 3350—3500 cm^{-1} region, which is assigned to the OH-stretching frequency of coordinated water. This region is free of absorption, in case of chelates (ii), indicating the absence of coordinated water in these adducts. They also noted the order of C=O stretching frequency for the chelates (i), which is Cd=Zn=Pb, 1613; Mn, 1610; Cu, 1597 cm^{-1}. The order of stability constants (as log of formation constants) is: Zn, 7.30; Cd, 7.60; Mn, 8.20; Cu, 13.2. These data indicate a qualitative relation between the strength of metal—oxygen bond, and the frequency of the perturbed carbonyl absorptions.

Similarly, the IR spectra of neodymium benzoyltrifluoroacetonate adducts with n-butyl alcohol, pyridine and n-butylamine have been examined [117].

The IR spectra [118] of the tris-chelates Ln(dfhd)$_3 \cdot 2\,H_2O$, Ln(dfhd)$_3 \cdot$ 2 DMF and Lu(hfac)$_3 \cdot$ dmp have a broad peak at 3510 cm^{-1} (OH stretching; due to H$_2$O). The IR spectra of DMF adducts are interesting because they throw some light on the coordination number of the rare earths in these chelates. There is no absorption peak in the region 1650—1730 cm^{-1} of DMF adducts of the hfac and dfhd chelates. The C=O frequencies of Ln(dfhd)$_3 \cdot 2\,H_2O$ and Ln(hfac)$_3 \cdot n\,H_2O$ are found at 1640—1650 cm^{-1} and apparently the C=O absorption of DMF in the adduct is hidden by these strong peaks. The DMF coordination through the C=O group [119,120] is indicated by a shift of

C=O stretching frequency from 1685 cm^{-1} to $\leqslant$ 1650 cm^{-1}. This further indicates seven- and eight-coordination rare earths in the mono- and bis-adducts respectively and has been confirmed by molecular weight determination [118]. Similarly, IR spectral studies of tris-hexafluoroacetylacetonates, $Ln(hfac)_3 \cdot n\ H_2O$ have been reported [51].

The IR spectra of fluorinated 1,3-diketonates of type, $M(RCOCHCOCF_3)_2$ (R = Me, Et, Pr, *tert*-butyl, Ph, $C_6H_4CH_2$ and CF_3), have been examined [121]. The carbonyl stretching frequencies are not affected by the mass of the substituent, but are dependent on the nature of substituents. They [121] have also tried to establish the correlation between the electronegativities of transition elements and the carbonyl frequencies of the chelates.

The IR spectra of a number of tris [122] and tetrakis [123] metal chelates of fluorinated 1,3-diketones have been examined. The strong negative inductive effect of the CF_3 groups strengthens the C$\doteq$O and C$\doteq$C bonds, causing marked shifts of the C$\doteq$O and C$\doteq$C stretching bands to higher frequencies.

Recently (1975), Nakamura and Nakamoto [124] reported detailed IR spectral studies of $K[PtCl(acac)_2]$ and its metal complexes, $M[PtCl(acac)_2]_n$ (M = VO(II), Co(II), Ni(II), Cu(II), Zn(II), Pd(II) and Fe(III); n = 2 or 3) and $NiBr(Hacac)_2$. A comparison of IR spectra of $Ni[(PtCl(acac)_2]_2$, $[PtCl(acac)_2]^-$ and $NiBr_2(Hacac)_2$ reveals that the C=O groups of $Ni[PtCl(acac)_2]_2$ retain the keto character even after coordination to the Ni atom and that its Ni—O (keto—acac) bonds are much weaker than those of enol—acac complexes. The assignment of the M—O (keto—acac) stretching bonds are made on the basis of metal isotope technique.

(ii) Electronic spectra

Since Irving's [125] statement that "on chelation to a metal, there is generally a bathochromic shift in the wavelength of maximum absorption of the ligand", substantial progress has been made toward understanding the electronic absorption spectra of metal 1,3-diketonate chelates. Extensive studies of the electronic spectra of metal 1,3-diketonate chelates, with particular reference to Hückel semi-empirical calculations [126] and self consistent field (SCF) calculations, have been reviewed [8].

The beryllium chelate, $Be(tta)_2$ exhibits two different solution spectra [127]. One spectrum resembles the enol form of the 1,3-diketone and has a maximum at 350 mμ while the other exhibits an additional band at 365 mμ.

The molar absorptivity of the fluorinated 1,3-diketonates of uranyl(VI) has been found to be maximal (31,200) with the H(fta) [128]. Spectrometric studies of uranyl(VI) complexes with H(tta) in dilute solution point to a 2 : 3 complex, while in concentrated solution, a 1 : 2 complex is indicated [129].

The absorption spectra of cobalt(II) complexes of various fluorinated 1,3-diketonates which appear to be spin-free planar quadricoordinated complexes have been studied [130].

Walker and Li [131] described the effect of 4-methyl pyridine on the visible spectra of benzene solutions of some fluorinated 1,3-diketonates of Cu(II). The nature of the spectra gives strong evidence for the formation of both 1 : 1 and 1 : 2 adducts of the type $Cu(chelate)_2 \cdot 4\text{-Me-py}$ and $Cu(chelate)_2 \cdot (4\text{-Me-py})_2$, for all chelates with the exception of $Cu(acac)_2$. From examination of the adducts of $Cu(chelate)_2$ (chelate = hfac, tta, tfac and acac) with phosphorus esters, S (S = TOPO, TPPO, TBP and TPP) spectrophotometrically [132] it is apparent that when CH_3 group is replaced by the electron withdrawing CF_3 group, the stability of the binary $Cu(chelate)_2$ complex decreases. At the same time, however, this decrease of electron density around the central Cu^{2+} ion, enhances its ability to take on a further monodentate ligand. The results also show that with a given $Cu(chelate)_2$, the stability of $Cu(chelate)_2 \cdot S$ increases with increase in basicity of S.

Casey and Walker [133] also studied the absorption spectra of Cu(chelate) N-base adducts in the visible region

$$Cu(chelate)_2 + {}_xB \rightleftharpoons Cu(chelate)_2 \cdot B_x \tag{25}$$

(x = 1 and or 2; B = quinoline and isoquinoline)

and support the formation of both 1 : 1 and 1 : 2 adducts. At higher concentration of N-base, the bis-(1 : 2) adducts are formed.

The visible spectra of $Cu(btfa)_2$, in presence of increasing amount of TOPO, have also been studied [116] and do not reveal any single isosbestic point in contrast to the $Cu(btfa)_2 \cdot TBP$ system. Based on the values of K for $Cu(btfa)_2 \cdot TBP$, $Cu(btfa)_2 \cdot TPPO$, and $Cu(btfa)_2 \cdot TOPO$, the order for the electron donating ability of the compound is TBP < TPPO < TOPO. This order agrees with the stability constants observed for $Cu(tta)_2 \cdot TBP$, $Cu(tta)_2 \cdot TPPO$ and $Cu(tta)_2 \cdot TOPO$.

Ho and Livingstone [43] studied the visible—ultraviolet spectra of a number of iron(III) chelates, $Fe(R^1C(S) = CHCOR^2)_3$ which are quite similar. All have a main band at 315—380 mμ with very high extinction coefficients, and one or two shoulders appear at longer wavelengths. No conclusive information has been drawn from the spectra, as these are probably dominated by the intense charge-transfer band at short wavelengths.

The ultraviolet spectra of $Ni(tta)_2$ in various solvents [134], reveal that the potential analytical applications of $Ni(tta)_2$ are superior to many of the standard spectrophotometric methods for the determination of trace amounts of nickel.

Shigematsu et al. [135] recorded the absorption spectra of the uranium btfa chelates in butyl acetate and of H(stta) and its metal chelates in cyclohexane. Each chelate showed its own specific colour, had an absorption maximum and was stable for at least 7 days. The compounds could be identified by observing the individual specific colour on the chromato plates.

The intercombination spectra of chromium 1,3-diketonates and several derivatives have been recorded at 77 and 4 K. In the 12000—15000 cm^{-1} region vibronic components of $^2E \leftarrow {}^4A_2$ and the 2 T state were located. The effect of ligand halogenation on the trigonal field splitting is small [136]. Similarly, $^2E \leftarrow {}^4A_2$ transition in chromium 1,3-diketonates has been detected in absorption [137] and emission [138] at 12900 cm^{-1} and effect of substitution on the ligand upon the transition energy assessed.

In addition, ligand field spectra of manganese(III) chelates show that $3d^4$ complexes are not centrosymmetric at ambient temperatures, but undergo oscillations from one potential minimum to the other [139]. The effect of axial ligation with pyridine on ligand field spectrum of Cu(hfac)$_2$ has been studied, and four-band gaussian analyses presented [10].

The charge transfer spectra [140] of a series of tris(1,3-diketonato)iron(III) chelates having CH_3, CF_3 and C_6H_5 substituents, in the 20—38 kK region, exhibit three electronic transitions. Using a single one-electron molecular orbital scheme the following assignments were proposed

(a) $\pi \rightarrow \pi^*$ Intra ligand transition — the most intense absorption band being between 30—37 kK (log ϵ = 4.5—4.1).

(b) $t_{2g} \rightarrow \pi^*$ Metal-to-ligand charge transfer — the absorption band being between 24—29 kK region.

(c) $\pi \rightarrow e_g$ Ligand-to-metal charge transfer — the absorption band being between 20—23 kK region.

These assignments are justified on the basis of the relative energy separations in the simplified molecular orbital diagram (Fig. 6).

The octahedral splitting parameters, Δ, for the Fe(III) chelate were calculated using the relationship: $\Delta = g(\text{metal ion})f(\text{ligand})$. The energy separations $(\pi - t_{2g})$ and $(e_g - \pi^*)$ have been determined from the charge transfer spectra and the sum $(\pi - t_{2g}) + \Delta + (e_g - \pi^*)$ agrees with the observed $\pi \rightarrow \pi^*$ transition energy. The CF_3 substituents on the chelate ring destabilize all the metal levels relative to CH_3 while the phenyl substituents stabilize them.

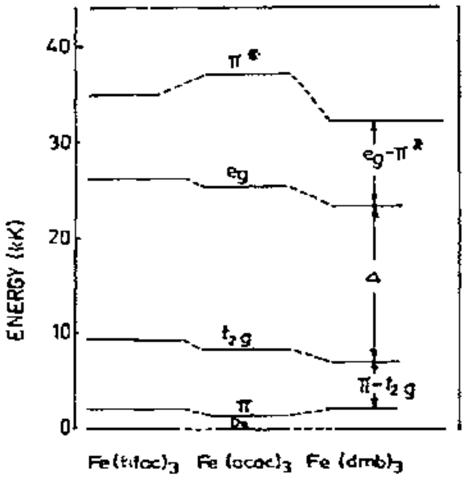


Fig. 6. Molecular orbital diagram of the symmetrically substituted chelates.

The electronic spectra of a series of 1,3-diketonate chelates of Cr(III) with CF_3, *tert*-C_4H_9 and C_6H_5 substituents have been studied and assignments made of d—d, charge transfer and intra-ligand transitions. The ligand field parameters, B_{35} and B_{55} have been calculated and used to determine spectrochemical and nephelauxetic series for the ligands. The values of B_{55} indicate a strong π-type back-bonding mechanism for delocalization of the metal t_{2g} electrons. Trends in B_{35} and B_{55} have been interpreted in terms of the inductive and resonance effects of the chelate ring and its 1,3-substituents [141].

Fatta and Lintvedt [142] also recorded the spin-forbidden transitions ${}^4T_{1g} \leftarrow {}^6A_{1g}$ and ${}^4T_{2g} \leftarrow {}^6A_{1g}$ for a series of tris(1,3-diketonato)iron(III) chelates with CH_3, *tert*-C_4H_9, CF_3 and C_6H_5 substituents and the transition energies calculated. The ratio of C/B for diketonates is not constant, but varies from 5.4 to 7.4 depending upon the substituent groups on the chelate rings. There are systematic and opposite changes in the interelectronic repulsion parameters F^2 and F^4 throughout the series of Fe(III) chelates. A suitable mechanism for the trends in F^2 and F^4 has been suggested involving the concept of orbital electronegativity.

(iii) Mass spectra

The pioneering mass spectral studies of McDonald and Shannon (1966) [143] on transition metal complexes, containing 1,3-diketone ligands, opened a new era in the chemistry of metal 1,3-diketonates. Later on, many workers [144—147] reported mass spectroscopic studies of acetylacetonates, 1,3-diketonates of first transition metals, metal complexes of dibenzoylmethane and lanthanide complexes of hexamethylacetylacetone. The mass spectral studies of metal complexes of fluorinated 1,3-diketones were initiated by Westmore and co-workers [148,149], who studied the mass spectra of hexafluoroacetylacetonates and trifluoroacetylacetonates of Al(III), Cr(III), Fe(III), Fe(II), Cu(II) and Zn(II), with particular reference to their relative intensities and appearance potentials of major ions. The main features of the spectra are:

(a) Substitution of CF_3 for CH_3 in these complexes leads to more extensive fragmentation of the molecule owing to the relative instability of molecular ion due to weak $C—CF_3$ bonds.

(b) There is a tendency towards formation of even-electron ions, accompanied by metal valence change where necessary. The initial molecular ion is formed as a result of electron removal from the ligand π-system. Fragmentation proceeds with loss of neutral odd-electron species (e.g. $\cdot F$, $\cdot CH_3$, $\cdot CF_3$, ·acac, ·tfac and ·hfac) and retention of metal charge on the resulting even-electron ion; the latter then suffering loss of a second even-electron neutral species (e.g. CF_2, CH_2CO, L—F) with a one-electron reduction of the central metal ion. Alternative pathways, in which metal reduction could occur, are loss of an α or γ substituent as an odd-electron neutral fragment. Fluorine substitution appears to favour loss of an α-substituent to a complete neutral fragment.

(c) A number of metastable peaks of considerable interest are due to the following metastable transitions in which a neutral, metal containing species is eliminated.

$$[FM(hfac){-}CF_2]^+ \rightarrow MF_3 + CF_2COCHCO^+$$

(M = Al, Cr)

$$[Fe(hfac){-}CF_2]^+ \rightarrow FeF_2 + CF_2COCHCO^+$$

$$[Al(hfac){-}CF_2]^+ \rightarrow [Al(hfac)_2{-}CF_2{-}CF_3] + CF_3^+$$

$$[(tfac)Cu \cdot CH_3]^+ \rightarrow CuCH_3 + tfac^+ \qquad (26)$$

(d) A number of transitions, involving loss of CF_2 or (L—F), are observed in the spectra. It may be noted that corresponding loss of CH_2 was not observed in the spectra of acetylacetonates. The mechanism of elimination of CF_2 and the factors which favour the CF_2 elimination have been discussed, and it may be pointed out that the CF_3 substituents are preferentially eliminated from the molecular ions as radical, rather than as negative ions.

(e) In case of metal 1,3-diketonates, ionisation causes the removal of electron from the ligand-dominated molecular orbital and the fragmentation involves homolytic fission of the C—R or C—H bonds which assumes the transfer of one electron from the bond to the half-filled bonding ligand π-orbital giving even electron species. The extent of fragmentation of the molecular ions depends upon the nature of the substituents on the chelate ring; being larger for electron-withdrawing and smaller for electron-releasing substituents.

(f) Spectra of compounds, containing aromatic substituents exhibit, $LCuH^+$ and $(LCu{-}H)^+$ species in addition to the LCu^+ species. Migration of a hydrogen atom is confirmed by deuteration studies [150]. Similar rearrangement of C_6H_5 radical has also been observed by Bonati and Distefaro [151].

(g) Doubly charged ions viz., $(L_3Cr(III){-}F)^{2+}$, $(L_3Cr(III){-}\alpha)^{2+}$ and $(L_3Cr(III){-}2\,\alpha)^{2+}$ have been observed in the mass spectrum of $Cr(hfac)_3$. A possible mechanism suggested for their formation is that two electrons are lost from different chelate rings [148].

In earlier studies, the role of the metal was generally considered to be important and it was mentioned that the divalent and trivalent derivatives of a given 1,3-diketone show ionisation potentials (I.P.) falling in a limited range, irrespective of the electronic configuration of the central metal atom. Keeping in view the earlier studies in paramagnetic NMR spectra pointing out the substantial influence of the metal atom on certain properties of the chelate ring and its substituents, Bonati et al. [151,152] examined the ionization energies of rhodium and iridium-1,3-diketonates with special reference to the nature of the last occupied orbital. They measured the first ionization energies of a number of $(CO)_2M(1,3\text{-diketonate})$ complexes by electron impact and proposed that the M.O. is not localized on the π-system of the chelate ring, but delocalized as a whole and has a significant participation of metal atomic orbitals. The important feature of the mass spectra is that the nature of both the chelate ring as well as central metal influences the fragmentation pattern of the metal 1,3-diketonate relative intensities.

Recently, the mass spectral studies of a series of fluorinated monothio-1,3-diketonates, $M[RC(S) = CHCOCF_3]_n$ (where, R = Me, Ph, p-MeC_6H_4, p-BrC_6H_4, p-$NO_2C_6H_4$, p-FC_6H_4 and 2-thienyl; $n = 2$ or 3; M = Zn(II), Ni(II), Pd(II), Pt(II), Co(III), Rh(III), Fe(III) and Ru(III)) were reported [153—156].

The important features are:

(a) A comparison of the mass spectra of Ni(II), Zn(II), Pt(II), Pd(II), Co(III) and Rh(III) chelates indicates that while the spectra of Ni(II), Pt(II) and Co(III) chelates have more peaks due to metal containing species, the reverse holds good, in the spectra of Zn(II), Pd(II) and Rh(III) chelates, for the metal free fragments [153—155].

(b) Molecular ion peak has been observed in all metal chelates of fluorinated monothio-β-diketones [153—156] except for Co(III) [155] and Fe(III) [156] chelates due to thermal degradation of ML_3 to ML_2 ($L = RC(S) = CHCOCF_3$). Similarly, a molecular ion peak was not observed in the case of metal chelates of β-diketone [145] ($M(acac)_3$; M = Cr(III), Fe(III) and Co(III)) and of dithio-β-diketone [157], $[M(CH_3C(S) = CHC(S)CH_3]_3$ (M = Fe(III) and Co(III)). In contrast, the Fe(III) chelates of fluorinated β-diketones [158], $Fe(RCOCHCOCF_3)_3$ (R = Me, Ph and C_4H_3S) do exhibit the molecular ion peak, which is however, less intense as compared to the peak for M—L [158].

A comparison between cobalt(III) chelates of fluorinated β-diketones [158] and their monothio analogues reveals that the thermal stability of the latter decreases by the replacement of one oxygen atom of fluorinated β-diketone by sulphur atom [155].

(c) Fragmentation pathways have been confirmed on the basis of a number of metastable peaks, which have been noticed for metal chelates of fluorinated monothio-β-diketone $[M(RC(S) = CHCOCF_3)_n$; M = Ni(II), Zn(II), Pd(II), Pt(II), Co(III) and Ru(III)], except for Fe(III) [156] and Rh(III) chelates [155]. The metal containing fragments of the latter do not show metastable peaks.

(d) All the chelates of both Zn(II) and Ni(II) exhibit a strong peak due to L^+. The formation of the latter may be attributed to a valence change of the metal ion from bivalent to the univalent state and has a resonance stabilized cyclic structure [153].

$$[ML_2] \rightarrow L^+ + ML \; [M = Ni(II), Zn(II)] \qquad (27)$$

(e) Valency changes in case of cobalt chelates are from Co(III) to Co(II) and Co(I) complexes while Rh(III), Fe(III) and Ru(III) change to Rh(II), Fe(II) and Ru(II) states, respectively [155,156].

(f) Fluorine migration has been observed in Co(III) (R = Me, Ph, p-MeC_6H_4, p-BrC_6H_4, p-FC_6H_4 and C_4H_3S) [155] and Fe(III) (R = Ph and C_4H_3S) [156]

chelates but not in Rh(III) and Ru(III) chelates. In the reaction

$$M{-}2L \rightarrow M{-}2L{-}CF_2$$

a metastable peak has been noticed only for Co(III) chelates and not for Fe(III) chelates. Similarly, fluorine migration has been reported in the case of Zn(II) [153] and Pt(II) [154] chelates but not with Ni(II) [153] and Pd(II) [154] chelates.

(g) Zn(II), Ni(II), Pd(II), Pt(II) and Cu(II) chelates of H(stta) exhibit a strong peak corresponding to L—S besides a metastable peak due to the transition L → L—S. These peaks do not appear in the spectra of the metal chelates of the other monothio 1,3-diketones. In cases of thienyl ligand [$M(RCOCHCOCF_3)_n$; R = C_4H_3S], the product (L—S) is stabilized by resonance, as shown below (Fig. 7a) but this is not possible in other monothio-1,3-diketones.

(h) A comparison of mass spectra of Zn(II), Ni(II), Pd(II), Pt(II), Co(III), Fe(III), Ru(III) and Rh(III) chelates of fluorinated monothio-1,3-diketones reveals that the fragmentation pattern is determined by the metal ion.

Das and Livingstone [153—156] also proposed a mechanism for metal containing fragments of all types of metal chelates (Fig. 7b [153]). The role of the metal ion has also been emphasised recently [159].

The mass spectrum [52,160] of the eight coordinated chelate, $Cs[Y(hfac)_4]$ exhibits peaks having mass values (m/e) 1050 ± 5, 917 ± 2, 843, 807, 738, 710, 641, 503, 434, 340, 296, 208, 133, 69 and 39; and assigned to $Cs[Y(hfac)_4]^+$, $[Y(hfac)_4]^+$, $Cs[Y(hfac)_3]^+$, $(CF_3CO)\,Y(hfac)_3^+$, $(CO)Y(hfac)_3^+$, $[Y(hfac)_3]^+$, $(COCHCOCF_3)Y(hfac)_2^+$, $Y(hfac)_2^+$, $(COCHCOCF_3)Y(hfac)^+$, $Cs(hfac)^+$, $Y(hfac)^+$, $H(hfac)^+$ (?), Cs^+, CF_3 and HF_2^+ ions respectively. The intense peak at mass 843, assigned to the $Cs[Y(hfac)_3]^+$ ion, shows that the cesium ion is held strongly and loss of the ligand molecule precedes that of Cs^+. The reasons ascribed are: (i) strong ion pairing between the cesium ion and the fluorine atoms of the chelate ligands surrounding the yttrium atom,

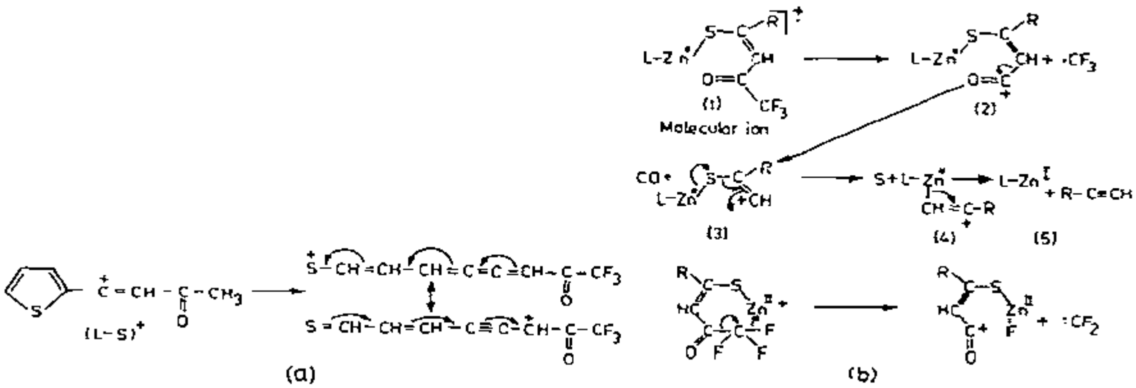


Fig. 7. (a) Resonance stabilization of the (L—S)$^+$ species formed by chelate of 2-thienyl ligand in the mass spectrometer. (b) Reaction of zinc chelate in the mass spectrometer.

or (ii) possible direct bonding of cesium ion to the methylene (=CH—) carbon atom of one of the ligands.

Mass spectra of alkaline earth chelates, ML_2 [M = Ca(II), Sr(II), Ba(II), Mg(II); L = tpm, ppm, hpm] have been examined by Belcher et al. [161]. In the case of magnesium chelates the fragmentation pattern revealed that no metal valency change is possible. The first step is the loss of odd electron fragments from the molecular ion $Mg(tpm)_2^+$ to form $Mg(tpm)^+$ ion, followed by loss of even electron, CF_2 fragment. Only one peak with an *m/e* value, higher than that of the molecular ion, is observed and corresponds to $Mg_2(tpm)_3^+$ ion.

The mass spectra of calcium, strontium, and barium chelates are complex exhibiting a larger number of peaks due to polymeric ion which extend to *m/e* values above 1500. The main features are a small molecular ion peak, ML_2^+ (which is sometimes absent), and more abundant peaks due to ions $(M_2L_3)^+$ and $(M_3L_5)^+$. The latter predominate over the ions of polymeric structure $(M_2L_4)^+$ and $(M_3L_6)^+$ from which they are derived. The $(M_2L_3)^+$ ion is the most predominant in the spectra and is probably derived from $(M_2L_4)^+$ ion. In both cases of $(M_2L_3)^+$ and $(M_3L_5)^+$ ions, a series of other transitions can be postulated. The fragmentation pattern of the $(M_3L_6)^+$ ion can, for example be represented as follows

$$[M_3L_6]^+ \rightarrow [M_3L_5]^+ \rightarrow [FM_3L_4]^+ \rightarrow [F_2M_3L_3]^+ \rightarrow [F_3M_3L_2]^+ \rightarrow [F_4M_3L]^+ \qquad (28)$$

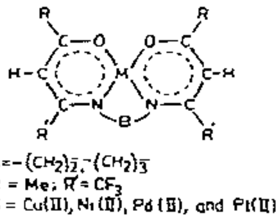
The basic features of the mass spectrum of lead chelate, $Pb(hpm)_2$ are similar [162]. The highest intensity peak is attributed to a chelate fragment produced by loss of one ligand from the molecular ion. There is no evidence for a peak of high intensity produced by the loss of a CH_3 group from molecular ion.

Belcher et al. [163] also examined the mass spectra of monothiotrifluoroacetylacetonates of Ni(II), Pd(II), Pt(II), Zn(II) and Co(III). The spectra show close similarities and the most prominent ions are $[M(ttfa)_2]^+$, $[M(ttfa)_2{-}CF_3]^+$, $[M(ttfa)]^+$ and $[M(ttfa){-}CF_2]^+$. The molecular ion peak shows highest intensity in all spectra except for $Co(ttfa)_3$, where the ion $[Co(ttfa)_2]^+$ (and not the ion $[Co(ttfa)_3]^+$) is the most intense.

The mass spectral studies of $Zr(hfac)_4$ and $Hf(hfac)_4$ have also been reported [164].

Bayer et al. [164a,164b] characterized the volatile metal chelates having d^8 electronic configuration, e.g. $M(shfac)_2$ (M = Ni(II) [164a], Pd(II) and Pt(II) [164b]) and $Ni(stfac)_2$ [164a], by mass spectral studies and noted their monomeric nature. The molecular ion peaks are at 504, 552, 641, and 396 *m/e* values, respectively. They also noted an isotopic (^{60}Ni) molecular ion peak in case of $Ni(shfac)_2$ and $Ni(stfac)_2$ at *m/e* values of 506 and 398, respectively.

Mass spectral studies of chelates of Cu(II), Ni(II), Pd(II) and Pt(II) with bisacetylacetone ethylenediimine and its fluorinated analogues (Fig. 8) have been described in detail.



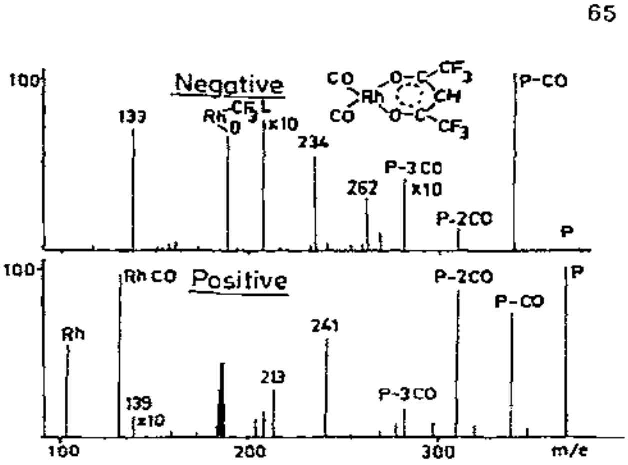


Fig. 8. Metal chelates of bis 1,3-diketone-ethylenedi-imine and its fluorinated analogues.

Fig. 9. Negative ion spectrum of $Rh(CO)_2(hfac)$.

For fluorinated analogues, the major features of fragmentation patterns are given in Table 3.

The cleavage of the carbon—carbon bond in the bridging group of the liggand molecule is the first major breakdown but the principal fragments still retain the metal atom. This is due to the inherent stability of such complexes, particularly with respect to the nitrogen—metal coordination. Other fragments arising out of the free ligand, or due to the removal of the bridge are not observed for the 2-carbon bridge compounds [165].

The mass spectra of the negative ions from several metal 1,3-diketonates have been examined and the negative ion spectra are found to be complementary to the positive ion spectra (Fig. 9) [166]. An ion present in positive spectrum with low relative abundance, gives an intense peak in the corresponding negative spectrum and vice versa. This has been explained on energetic grounds by an extension of Stevenson's rule [167].

The mass spectral studies have also been used in analysis of rocks and ores containing zirconium, by treating these with fluorinated β-diketones like H(tfac), H(btfa) and H(fod), yielding volatile metal chelates. In most metal chelates, the base peak is $^{90}ZrL_3^+$ and the parent peak is $^{90}ZrL_4^+$ (which is two orders less intense than the base peak). The presence of hafnium in zirconium ores is also indicated by a base peak for $^{180}HfL_3$ at 90 mass units above the zirconium base peak [167a] (the intensity being one hundredth of the zirconium base peak).

(iv) NMR spectra

The position of the C—H (at the central carbon atom of the chelate ring) resonance is not positive evidence for aromatic character [79]. Collman [80] examined the NMR spectra of a series of metal-1,3-diketonates and noted a

TABLE 3

Major features of metal chelate mass spectral fragmentation patterns (*m/e* value given for Cu^{63}, Ni^{58}, Pd^{104} and Pt^{194})

Chelate	
m/e	Fragments [a]
Cu[en(tfac)$_2$]	
392vs	M.I.
374m	M.I.—F
324m	M.I.—CF$_3$
228vs	Cu L/2
Cu[pn(tfac)$_2$]	
407vs	M.I.
392m	M.I.—CH$_3$
388m	M.I.—F
338m	M.I.—CF$_3$
242s	Cu L$'$/2
228s	CuL$''$/2
Pt[pn(tfac)$_2$]	
538s	M.I.
523m	M.I.—CH$_3$
519m	M.I.—F
469m	M.I.—CF$_3$
373s	PtL$'$/2
359s	PtL$''$/2
Ni[en(tfac)$_2$]	
388vs	M.I.
319m	M.I.—CF$_3$
223vs	Ni L/2
Ni[pn(tfac)$_2$]	
402vs	M.I.
387s	M.I.—CH$_3$
383m	M.I.—F
333m	M.I.—CF$_3$
237s	NiL$'$/2
223s	NiL$''$/2
Pd[en(tfac)$_2$]	
434vs	M.I.
415m	M.I.—F
365m	M.I.—CF$_3$
269vs	Pd L/2
Pd[pn(tfac)$_2$]	
448vs	M.I.
433m	M.I.—CH$_3$
429m	M.I.—F
379m	M.I.—CF$_3$
283s	PdL$'$/2
269s	PdL$''$/2

[a] M.I. = Molecular ion.

very interesting splitting phenomenon which can be "plausibly explained by a 'long range ring current' anisotropy".

The proton and fluorine ^{19}F NMR spectra of the H(hfac) chelates of Zr(IV) and Hf(IV) have been studied [164] and are listed in Table 4.

The proton peaks are well-defined and are noticed in the neighbourhood of =CH— proton peaks of the free ligand, H(hfac) [168—170] and its metal chelates [171—173]. The fluorine peaks for H(hfac) and for Zr(IV) and Hf(IV) chelates occur upfield from the peaks (—5.46, —5.42, —5.27 ppm) observed for $Rh(hfac)_3$ [171].

The NMR spectral studies of metal 1,3-diketonates have been applied in diverse fields, viz:

(A) Isomerism. Tris-chelate complexes, containing symmetrical chelate rings, possess ideal D_3 symmetry with ring substituents of the same type and same location, in each ring, being equivalent. However, if the chelate rings are asymmetrical, there are possibilities of both *cis* and *trans* isomers (Fig. 10a), each of which is enantiomeric. The *cis* isomer has a three-fold symmetry axis, whereas the *trans* isomer possesses no symmetry at all.

The detection of *cis* and *trans* isomers of metal chelates by NMR was first studied by Fay and Piper [174—176]. They studied a series of metal 1,3-diketonates of the type: $M(RCOCHCOR')_3$ (where, R = Me or Ph; R' = Me or CF_3, and M = Cr(III), Co(III), Rh(III), Mn(III), Fe(III), Al(III), Ga(III) and In(III)), and observed that in the case of Cr(III), Co(III) and Rh(III) chelates, the *cis* isomers are the more soluble, less easily eluted (more polar) and give single signals for each ring substituent, while the *trans* isomers are less soluble, more easily eluted (less polar), give broadened split signals. In the case of Al(III), Mn(III), Fe(III), Ga(III) and In(III) chelates, only *trans* isomers have been isolated in solid phase. Some more labile complexes exist as equilibrium mixtures of *cis* and *trans* forms in solution (Fig. 10b).

TABLE 4

Proton and fluorine magnetic resonance chemical shifts

Compound	=CH—proton chemical shift δ(p.p.m.)	Fluorine chemical shift δ(p.p.m.)	Relative fluorine peak area
$Zr(hfac)_4$	—6.56	—1.96	25
		—1.56	1
$Hf(hfac)_4$	—6.54	—1.83	40
		—1.41	1
H(hfac)	—6.43 [a]	—1.87 [c]	
	—6.36 [b]		

[a] Ref. 168 (10% by weight in CCl_4); ref. 169 (pure liquid). [b] ref. 170 (0.3 M in CCl_4).
[c] ref. 170 (0.35 M in CCl_4).

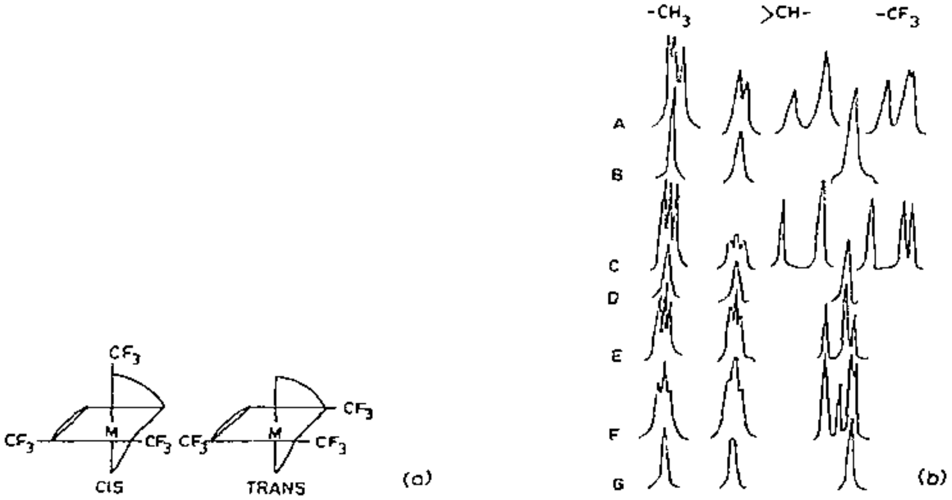


Fig. 10. (a) Geometrical isomers of $M(tfac)_3$ where the ligand is the anion of 1,1,1-trifluoro-2,4-pentanedione and M = chromium. (b) Proton and fluorine spectra of $M(tfac)_3$ A = *trans*-$Co(tfac)_3$; B = *cis*-$Co(tfac)_3$; C = *trans*-$Rh(tfac)_3$; D = *cis*-$Rh(tfac)_3$; E = *cis*- and *trans*-$Al(tfac)_3$; F = *cis*- and *trans*-$Ga(tfac)_3$; G = $In(tfac)_3$.

The difference between *cis* and *trans* isomers of Co(III) and Rh(III) complexes becomes clear from Fig. 10b. In the *trans* isomer of $M(tfac)_3$, the chemical shift differences between non-equivalent CH_3, CH and CF_3 groups at 60 MHz is approximately 3.3 and 9—13 Hz respectively. Some characteristics of proton and fluorine resonance spectra are given in Table 5.

The rates of isomerization were estimated by determining the temperature at which the fluorine resonance spectra of chloroform solutions of the com-

TABLE 5

Proton and fluorine chemical shifts in metal trifluoroacetylacetonates [a]

Compound	$-CH_3$	$=CH-$	$-CF_3$
cis-$Co(tfac)_3$	−144.0	−362.7	40.9
trans-$Co(tfac)_3$	−145.1	−362.9	40.7, 49.3 [b]
cis-$Rh(tfac)_3$	−141.8	−359.3	±0.0
trans-$Rh(tfac)_3$	−142.4	−360.3	4.5, 14.0 [b]
cis-$Al(tfac)_3$	—	—	182.8
trans-$Al(tfac)_3$	−133.9	−359.0	181.5
cis-$Ga(tfac)_3$	—	—	168.9
trans-$Ga(tfac)_3$	−134.8	−355.2	170.0
$In(tfac)_3$	−135.3	−353.2	162.0 [c]

[a] Proton shifts are in c.p.s. relative to T.M.S. Fluorine shifts are in c.p.s. relative to $Rh(tfac)_3$. Temperature 25°C. [b] 11 g/100 ml of chlorobenzene. [c] Time averaged chemical shifts.

pounds coalesced to give single sharp resonance lines (Fig. 11). The coalescence of these resonance lines is attributed to all the three trifluoromethyl groups becoming equivalent because of the rapid interchange of positions. This exchange may be viewed as a very rapid isomerization, and its rate is estimated from the temperature of coalescence [176—178].

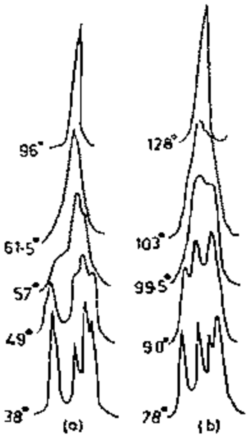
Of the two possible mechanisms, viz., (i) intermolecular and (ii) intramolecular for stereochemical rearrangements, the intermolecular mechanism has been ruled out on the grounds of fluorine ^{19}F NMR studies [176,179].

The results obtained for Al(III) and In(III) chelate systems support an intramolecular mechanism and several possibilities have been suggested.

(a) Bond rupture mechanism [179,180]. This mechanism was first proposed by Werner [180] in 1912 for the isomerization of bidentate chelate complexes. The possible trigonal—bipyramidal transition state is shown in Fig. 12 for the tris-chelate complexes. A tetragonal pyramidal transition state has also been proposed.

(b) Ray and Dutt mechanism [181]. The mechanism is pictured as simultaneous translation of two of the chelate rings in their respective planes, one moving up with respect to the plane of the third chelate ring and the other moving down (both rings are moving through an angle of 90° in opposite directions). During this the donor—metal—donor (D—M—D) intra-ring angles would be maintained at 90°, and the D—M—D angles between any two rings are reduced in the transition state. During the transition state, the plane of one ligand is perpendicular to the planes of the other two (Fig. 13a).

(c) Bailar twist mechanism (I) (about C_3 or pseudo-C_3 axis). Bailar [182] and others [183] separately suggested, that in this mechanism, racemization is achieved by twisting three of the ligands through an angle of 120° about



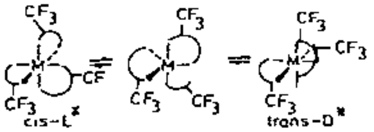
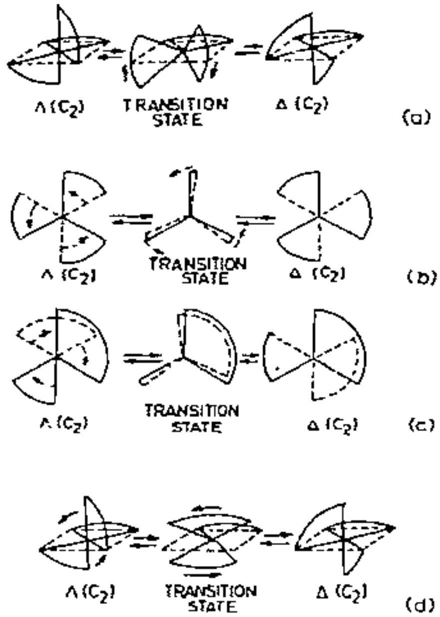


Fig. 11. Fluorine resonance spectra of (a) Ga(tfac)$_3$ and (b) Al(tfac)$_3$ at several temperatures near the coalescence region.

Fig. 12. The bond rupture mechanism.



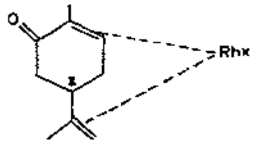


Fig. 13 (a) The Ray and Dutt twist mechanism for intramolecular isomerization of complexes of three bidentate ligands without bond breaking. (b) The Bailar twist mechanism about a real or pseudo C_3 axis. (c) The Bailar twist mechanism about one of the imaginary C_3 axes. (d) The Sievers and Springer mechanism which is the rigid ring equivalent to a Bailar twist about a real or pseudo C_3 axis.

Fig. 14. Diastereoisomeric (±) carvonerhodium(I)-3-trifluoroacetyl (1R) camphorate. X = 3-trifluoroacetyl (1R) camphorate.

the C_3 axes of the octahedron in counter clockwise direction, but this does not permit *cis—trans* isomerization in the system. The transition state is sometimes referred to as the trigonal prismatic intermediate and has D_{3v} symmetry (Fig. 13b).

(d) Bailar twist mechanism (II) (about an imaginary C_3 axis). In this, the motion may be imagined as the rotation of the three metal—donor bonds extended down from the plane of the paper, through 120° about one of the imaginary C_3 axes. The transition state is rhombic with C_{2v} symmetry, as depicted in Fig. 13c.

(e) Sievers and Springer mechanism [184]. The mechanism is illustrated in Fig. 13d. During twist, one ring is imagined to be fixed in space as in the Ray and Dutt mechanism while the other two rings move in an unlike fashion and rather revolve past each other, in the direction indicated, while continually changing planes. The chelate ring internal angles remain constant during the transformation and consequently, the D—M—D angles between the bonds in different rings are compressed to 90° in the transition state. However, in the case of heavy steric crowding between chelate rings, the ring D—M—D bond

angles may have even smaller values than 81° 48′.

Studies of the paramagnetic $V(tfac)_3$ complex have shown that NMR spectra of the terminal groups of the *cis* and *trans* isomers are considerably different by virtue of their greatly different contact shifts [185].

Novel octahedral tin complexes of the type $R_2Sn(L)_2$ (R = Me, Ph; L = hfac) are shown by NMR spectra to consist of the *trans* configuration with ring proton shifts similar to those seen in most metal 1,3-diketonates [186].

Recently (1974), Schurig [187] prepared novel stable diastereoisomers, containing two chiral bidentate terpenoid ligands bonded to rhodium(I). The diastereoisomers (Fig. 14) exhibit the expected differences in their physical properties. Spectral differences have been observed in the proton nuclear magnetic resonance of the methyl group (about 2.5 Hz).

A new series of pseudo-octahedral complexes, Ni(BTAT), Ni(BHAT), Cd(BTAT), Co(BTAT)X, and $[Co(BTAT)_2]CoY_4$ ($X = Br^-, I^-, NO_3^-$ and ClO_4^-; $Y = Cl^-$ and SCN^-), have been prepared [188] from the linear Schiff base ligands, bis(tfac) triethylenetetramine, H_2BTAT and bis(hfac) triethylenetetramine, H_2BHAT. Out of three possible structures (I), (II) and (III) of H_2BTAT ligand, structure (I) has been confirmed by NMR spectral studies (Fig. 15a). The NMR spectrum of Co(BTAT)Br in methanol-d_4 is shown in Fig. 15b. Four geometrical isomers are possible for the octahedral BTAT complexes (Fig. 16 I—IV). However, formation of complex (I), s-*cis*-Co(BTAT)Br (Fig. 16) proceeds preferentially, stereospecifically as indicated by these studies [188].

^{19}F NMR spectrum of $(\pi\text{-}C_5H_5)Ti(hfac)_2Cl$ has been found [189] to exhibit two sets of four equal intensity lines, with one set relatively weak. Each set was assigned to a different isomer. Both the proton and ^{19}F NMR spectra of $(\pi\text{-}C_5H_5)Zr(tfac)_3$ at room temperature show that two isomers are present in a ratio of 3 : 2. These isomers differ in the orientation of the tfac ligand bridging the axial and equatorial positions; i.e., the $—CF_3$ can be equatorial or axial, leading to two ^{19}F resonances [189]. X-ray and NMR studies on (π-

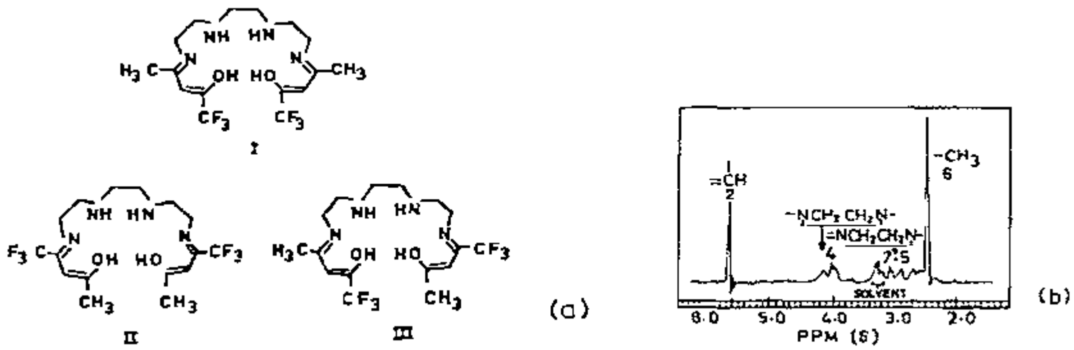
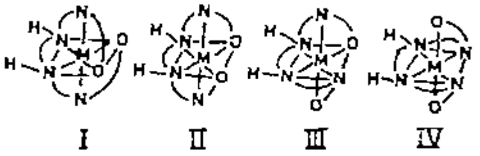


Fig. 15. (a) Possible structures of H_2BTAT. (b) NMR spectrum of Co(BTAT)Br in methanol-d_4.



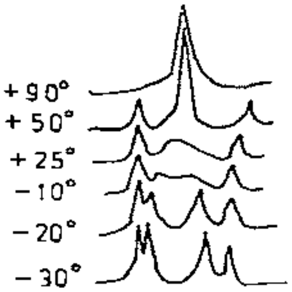


Fig. 16. Geometrical isomers of Co(BTAT)Br. Form (I) and (II) are *s-cis* (differing in the N—N—O angles); form (III) is uns-*cis*, and (IV) is *trans* form.

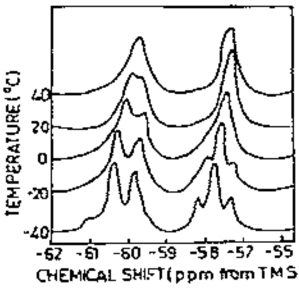
Fig. 17. The coalescence of the fluorine resonance of (π-C_5H_5)Zr(hfac)$_3$ in methylcyclohexane at 50°—90°C in acetone at the lower temperatures. The spectra of the complex have been aligned vertically although the chemical shifts differ appreciably in the two solvents.

C_5H_5)Zr(hfac)$_3$ have suggested a pentagonal bipyramidal geometry for the molecule [189]. There are four lines of intensity ratio 2 : 2 : 1 : 1 in the fluorine spectra. The observations of Elder et al. [189] are in harmony with the suggested line intensity at —30° C in acetone (Fig. 17).

(B) Equilibrium. Tris- and tetrakis-1,3-diketone complexes undergo ligand exchanges which have been detected by NMR. The species Al(tfac)$_n$ (acac)$_{3-n}$ (n = 1, 2) are produced by reaction of Al(tfac)$_3$—acac in solution [190]. The kinetics and mechanism of exchange reactions of Zr(tfac)$_4$, Hf(tfac)$_4$, Zr(acac)$_4$ and Hf(acac)$_4$ with their free ligands have been reported [191]. Particularly interesting are ligand exchange reactions between tetrakis complexes in the absence of added free ligand. Reactions of M(tfac)$_4$ and M(acac)$_4$ (M = Zr, Hf, Ce, Th) produced M(tfac)$_n$ · (acac)$_{4-n}$. The individual complexes with n = 0, 1, 2, 3, 4 are detectable in equilibrium mixtures by PMR and ^{19}F resonance [192, 193].

Similar studies have been made [52,173] on chelate complexes of yttrium(III). As with the group IVb metals [192,194] ligand exchange occurs and five different complexes are formed: [Y(hfac)$_4$]$^-$, [Y(hfac)$_3$(tfac)]$^-$, [Y(hfac)$_2$(tfac)$_2$]$^-$, [Y(hfac)(tfac)$_3$]$^-$ and [Y(tfac)$_4$]$^-$; the equilibrium concentrations of each one in a given mixture are dependent upon the particular ratio of starting materials. At —40° C, eight separate resonances are observed (one for the —CH= protons of hfac, and one for the —CH= proton of tfac, in each of the molecules in which they occur).

At temperatures above —40° C, the resonances for the individual molecules, [Y(hfac)$_4$]$^-$, [Y(hfac)$_3$(tfac)]$^-$, etc., merge until at +40° C, only one hfac and one tfac peak are observed (Fig. 18). The most reasonable explanation is that ligand-exchange processes become sufficiently rapid to average the environments intermolecularly. This demonstrates that, whatever the mechanism,



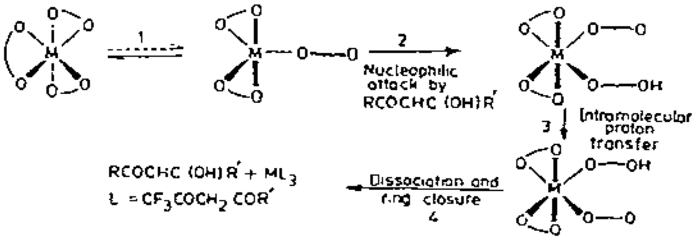


Fig. 18. Effect of temperature on the —CH=proton NMR spectrum of a mixture of Y-$(hfac)_4^-$ and $Y(tfac)_4^-$, mole fraction $Y(hfac)_4^-/(Y(hfac)_4^- + Y(tfac)_4^-) = 0.55$.

Fig. 19. The mechanism of the ligand exchange reactions between $In(CF_3COCHCOR)_3$ complexes and excess free ligand CF_3COCH_2COR.

the two different ligands are exchanging at the same rate. This conclusion is also arrived at for the Zr(IV) and Hf(IV) systems [194]. The NMR technique has also been used to obtain kinetic information for the above systems.

Phosphorus NMR data for complexes of the type $M(tta)_2 \cdot TOPO$ (M = divalent metal ion), have been compiled [195]. Spectral data is used to determine the equilibrium constant of the following reaction which occurs in carbon tetrachloride: $Zn(tfa)_2 \cdot 2\ H_2O + 2\ TOPO \rightarrow Zn(tta)_2 \cdot 2\ TOPO + 2\ H_2O$.

Tanner et al. [196] studied the ligand exchange reactions between $In(CF_3COCHCOR)_3$ complexes (R = Me; *i*-Bu, Ph, 2-naphthyl and 2-thienyl) and excess free ligand, CF_3COCH_2COR in solvents like diisopropyl ketone, acetonitrile, benzene and dimethyl sulfoxide. Studies of the life times of the reactants, as obtained from their ^{19}F NMR line-widths, show that the exchange is first order in $In(CF_3COCHCOR)_3$ concentration, but zero order in free ligand concentration. The rate controlling process in the exchange is identified as the rotation of one monodentate ligand about a partial double bond prior to intramolecular proton transfer to a second monodentate ligand. The reaction mechanism is illustrated in Fig. 19.

(C) Miscellaneous. The NMR spectra of the following types of metal 1,3-diketonate chelates have been studied [197]: (a), $V(RCOCHCOR')_3$; and (b), $V[RCOCHC(NR'')R']_3$ (where; (a) R = Me, R' = CF_3; (b), R = R'' = Me, R' = Ph). From considerations of the signs of the contact shifts of protons and methyl groups of the chelate rings and by comparison of these shifts with calculated spin-density distribution for the ligand treated as a π-radical, it is concluded that metal to ligand parallel spin transfer is the principal mode of spin delocalization.

The ^1H NMR spectra of the dicarbonyl derivatives of the metal 1,3-diketonate chelates [198], $(CO)_2M(RCOCHCOR')$, (where; M = Ir, and Rh; R = Me or CF_3; R' = CF_3 or Ph), are in accordance with their diamagnetic character. ^{19}F NMR spectra for compounds a, b and c have also been examined in detail, $(CO)_2M(RCOCHCOR')$ (where M = Ir for a, R = Me, R' = CF_3; for b, R = R' = CF_3; for c, R = R' = Me). In the case of compound b, the equivalence of the fluorines is apparent and only one peak is observed. It may be pointed out that there is a notable difference in the chemical shifts (ca. 0.5) of both signals of compound c, in deuterochloroform and in deuterobenzene, and this has been attritubted to the presence of a delocalized electronic environment on the chelate ring. The latter can also act as a pathway by which the effect of one substituent can also influence another one on the same ring. For example, the position of the CH_3 signal is lowered when another CH_3 is replaced by C_6H_5; and is further lowered when replaced by CF_3 group. Both effects are greater with iridium than with rhodium derivatives. The signal due to the methylene proton (=CH—) of the chelate ring is particularly sensitive to the nature of the other substituents. The position of the signal is lowered by electronegative substituents on the ring (Table 6) [198].

Richardson and Sievers [118] studied the NMR spectra of a series of tris- and tetrakis-rare earth chelates of H(dfhd) and H(hfac). In the case of dmp adducts, $Lu(hfac)_3 \cdot$ dmp, the NMR spectra indicate that dmp is chelated to give a four-member ring and an eight coordinated rare earth ion (the peaks at δ 1.31 and 3.19 ppm in dmp are shifted downfield to δ 1.41 and 3.43 ppm in $Lu(hfac)_3 \cdot$ dmp). The examination of NMR spectra of $Lu(hfac)_3 \cdot 2$ DMF, in carbon tetrachloride, clearly indicates that the DMF is coordinated to $Lu(hfac)_3$ (the peaks at δ 2.84, 2.97 and 7.93 ppm in DMF are shifted downfield to δ 2.90, 3.03 and 7.95 ppm), whereas in benzene the DMF peaks in the adduct, $Lu(hfac)_3 \cdot 2$ DMF, are shifted upfield (the peaks at δ 2.02, 2.43 ppm in DMF are shifted to δ 1.97 and 2.29 ppm respectively). The peaks at δ 6.47 and 6.57 ppm in $NH_4Y(dfhd)_4$ and $Lu(dfhd)_3 \cdot 2\ H_2O$, respectively, can be assigned to =CH— resonance. Richardson and Sievers [118] also remarked that "the single =CH— resonance is undoubtedly due to rapid ligand exchange and/or intramolecular rearrangement of the ligands, which would average the non-equivalent protons".

The carbon-bonded platinum(II) complexes of the type $K[Pt(tfac)_2X]$ (where X = halogen) have been identified by NMR spectra with both oxygen- and carbon-bonded 1,3-diketone groups present [199].

TABLE 6

The lowering ($\Delta\tau$) in the position of the methylene proton (=CH—) of the chelate ring

R	R'	M = H [a]	M = $(CO)_2Rh$ [b]	M = $(CO)_2Ir$ [b]	Average
Me	Me	0.44	0.50	0.48	0.47 ± 0.03
Ph	Me	0.29	0.66	0.66	—
CF_3	CF_3	0.87	0.96	0.90	0.92 ± 0.05
Ph	Ph	0.80	—	⩾1.34	—

[a] The chemical shift of H(acac)(enol) was taken as zero. [b] The chemical shift of $M(acac)_3$ was taken as zero.

Solvent-effects on the NMR spectrum of Al(III) 1,3-diketonates have been investigated. When applied to aromatic solvents with large diamagnetic anisotropies, it is postulated, that in solvents having donor groups, e.g., nitrobenzene solvation exists along the C_3 axes of the metal chelates [200].

Bonati and co-workers [201] reported the synthesis of a series of diamagnetic compounds of formula, $Rh(CH_3COO)(1,3\text{-diketonato})(H_2O)_2$ (where, 1,3-diketonato = tfac and hfac). On the basis of NMR spectral studies, they proposed one structure (Fig. 20) out of six possible structures.

Pannetier et al. [202] prepared a series of iridium 1,3-diketonates (Fig. 21) and reported NMR spectral studies which show a regular variation of the chemical shifts of the olefinic protons of 1,5-cyclooctadiene (Cod) with the electronic properties of the 1,3-diketones. These displacements correlate well with Hammett's constants of radicals R and R′. Better results are obtained using separate field and resonance terms. Analogous results are obtained for the IR frequency ν(Ir—Cod).

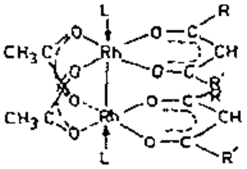
(v) Mössbauer spectra

Very little work has been done in the field of Mössbauer spectral studies. Bancroft et al. [203] recorded the Mössbauer spectra of only seven Fe(III)-1,3-diketonates two fluorinated viz.; $Fe(hfac)_3$ and $Fe(tfac)_3$ and five non-fluorinated, at liquid nitrogen temperature (78 K). In many cases, asymmetric peaks are obtained. All chemical shifts are close to 0.62 mm s^{-1}. A computer analysis showed quadrupole splitting ranging up to 0.75 mm s^{-1}. The asymmetry of the two lines has been interpreted in terms of electronic relaxation processes in the solid. From the Mössbauer spectral studies, the following important conclusions have been drawn.

(a) The quadrupole splitting changes considerably even though the chemical shift is little affected by the immediate atomic environment of a high-spin Fe(III) complex.

(b) "The changes in quadrupole splitting are related to changes in π-donation from the iron atom to the chelate rings" [203].

(c) The asymmetry of the spectra may be ascribed to differential narrowing of the two quadrupole lines. This may mean that the electronic field gradient at the nucleus is positive, with relaxation time of about 10^{-10} s.



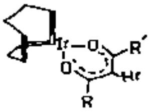


Fig. 20. Structure of $[Rh(CH_3COO)(1,3\text{-Diketonato})]$-$L_2$. L = H_2O, py, 2-Cl-py, 2-Me-py.

Fig. 21. Iridium 1,3-diketonates. R = CF_3, Me, $(Me)_3C$or Ph. R′ = CF_3, Me, $(Me)_3C$ or Ph.

Takashima et al. [204] studied the Mössbauer spectra of a series of dibenzoylmethane complexes with general formula, $Fe(dbm)_2X_2$ or $Fe(dbm)_2Y$ (where X and Y represent a variety of ligands, e.g., py, nicotine, piperidine and ethylenediamine). All these metal 1,3-diketonates have octahedral symmetry, "the iron(III) being coordinated to four planar oxygen atoms from two dibenzoylmethanes and two nitrogen atoms at axial positions" [204]. It is also remarkable that the extent of deviation from octahedral symmetry about the iron atom, depends on the nature of axial ligands, which in turn, correspond to changes in Mössbauer parameters.

de Vries et al. [205] also examined the Mössbauer spectra of iron(II)-1,3-diketonates, $Fe(RCOCHCOR')_2L_2$ (where (a) R = R′ = Me; (b) R = Me, R′ = Ph; (c) R = R′ = Ph; L = H_2O, NH_3, py or piperidine) and concluded that Fe(II) ion in these chelates is six coordinated. The isomer shifts depend only on the nature of the ligands, directly attached with Fe(II) ion. A linear relationship between isomer shifts and quadrupole splittings has been established. A large axial distortion has been confirmed by the analysis of the quadrupole splitting; and is supported by relatively narrow range (2.0—2.9 mm s^{-1}) of quadrupole splitting observed.

F. METAL 1,3-DIKETONATES AS NMR SHIFT REAGENTS

The role of paramagnetic ions in NMR spectroscopy is well known and has been discussed by Bloembergen et al. [206] in the studies of some nickel(II) compounds. In 1969, Hinckley [207] noticed that on adding the pyridine adduct of $Eu(dpm)_3$ to a carbon tetrachloride solution of cholesterol, characteristic selective downfield shifts in the spectrum of the steroid took place; the europium complex was called a "shift reagent".

The discovery at once suggested that it could lead to simplification of spectra by removal of signal coincidence and also characterization of the nucleus in terms of its geometrical relationship with respect to one or more distant functional groups [208,209]. Potential uses of shift reagents in the assignments of ^{13}C NMR spectra [210] have now been made. For example, lanthanide chelates of optically active camphor derivatives produce different shifts in racemic solutions of optically active compounds, thereby allowing measurements of optical purity by NMR. Tris(3-pivaloyl-*d*-camphorato)-europium(III) has been used in the studies of optical purity of organic bases [211]. Tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium-(III) * (Fig. 22a) and tris[3-(heptafluoropropyl hydroxymethylene)-4-camphorato]europium(III) (Fig. 22b) have been shown to induce pseudocontact shifts of different magnitudes in corresponding protons of enantiomeric alcohols and amines [212,213] and also used for determining the optical purity of amino alcohols [214].

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* This is also commonly known by the simpler name, tris[3-trifluoroacetyl-d-camphorato]-europium(III).

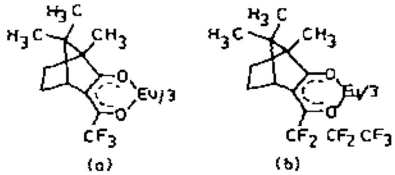


Fig. 22. Europium 1,3-diketonates.

The paramagnetic tris-lanthanide(III) chelates of H(fod), $Ln(fod)_3$, have been increasingly used as NMR shift reagents since the first report [215]. The chemical property which permits this application is the Lewis acidity, which the chelates possess, as a consequence of their coordinative unsaturation. The neutral tris-chelates dissolve in organic solvents and form labile adducts with a large variety of nucleophilic substrates. Lewis acidity of these chelates also causes two side interactions which may interfere with their usage as NMR shift reagents. The sources of interference are formation of hydrates [216—218] and formation of self-associated oligomers [219—222]. Springer and coworkers [222] also studied in detail the self-association of these acidic chelates, $Pr(fod)_3$ and $Eu(fod)_3$ as well as the adduct formation of $Eu(fod)_3$ with methyldimethyl carbamate (TMC).

It has also been noticed that the paramagnetic lanthanide ions cause isotropic hyperfine shifts in the resonance frequencies of substrate nuclei [223].

It has been confirmed (Fig. 23) [215,224] by performing a series of experiments on NMR spectra that the anhydrous shift reagent $Eu(fod)_3$ is about twice as effective as the hydrated $Eu(fod)_3 \cdot H_2O$ reagent in shifting ability.

Er(III) chelates of fluorinated 1,3-diketones [e.g., H(fod) and H(tfacam)] undergo [219] much stronger interactions with nucleophiles (ethers, ketones, alcohols, esters and olefins) than similar non-fluorinated Er(III) chelates. This is most likely due to the increased acidity of the fluorinated chelates due to a decrease in the basicity of the fluorinated β-diketones [219]. Thus it could be

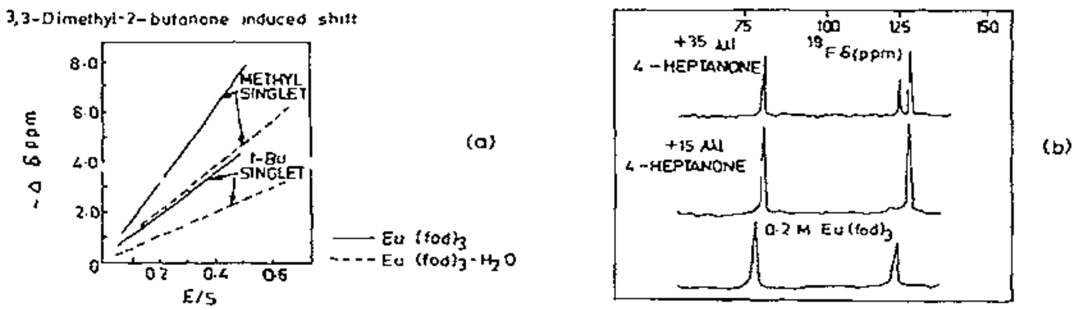


Fig. 23. (a) $\Delta\delta$ vs. E/S for pinacolone with $Eu(fod)_3$ and with $Eu(fod)_3 \cdot (H_2O)$. (b) Anhydrous shift reagent before and after addition of 4-heptanone.

predicted from GC data that Eu(fod)$_3$ would form stronger complexes and be a superior shift reagent, compared with Eu(thd)$_3$ [215,219]. Eu(fod)$_3$ is probably the best overall shift reagent for spectral clarification presently available. Its ability to form more stable complexes than Eu(thd)$_3$ with nucleophiles makes it more useful for weak donors. For example, a comparison of the NMR spectra of isomeric mixture 4(4′)-methoxy-4′(4)-butylazoxybenzene (Fig. 24) in the presence of Eu(fod)$_3$ or Eu(thd)$_3$, clearly indicates that the europium chelate of fluorinated β-diketone, Eu(fod)$_3$ is capable of separating the methyl signal of these isomeric compounds, while the europium chelate of non-fluorinated β-diketone, Eu(thd)$_3$, has failed to separate these methyl signals [225]. The fod chelates are also useful in the studies of peptides [224]. This, coupled with its superior solubility (about 10 times more soluble than Eu(thd)$_3$ in common NMR solvents), makes it a likely reagent for NMR applications. The fod lanthanide chelates, apart from having improved solubility, have also a more acidic metal ion due to the presence of fluorine. This greater Lewis acidity causes a stronger association with the substrate and thus extends its range to less basic groups; although the bound chemical shift is smaller for these fluorinated LSRs, the observed LIS is larger because of the stronger binding in the complex. However, an alternative method for comparing the shifting power of LSRs, by measuring their vinylic proton shifts, allows a comparison of the shifting power of various fluorinated LSRs with the non-fluorinated analogues [219,224,226].

$\text{Eu(fod)}_3 > \text{Eu(ppm)}_3 > \text{Eu(tpm)}_3 > \text{Eu(dpm)}_3$

Many other chelates produce greater shifts (e.g., Ho(fod)$_3$ which shifts upfield) but produce considerably broader peaks. Sometimes, it may be advan-

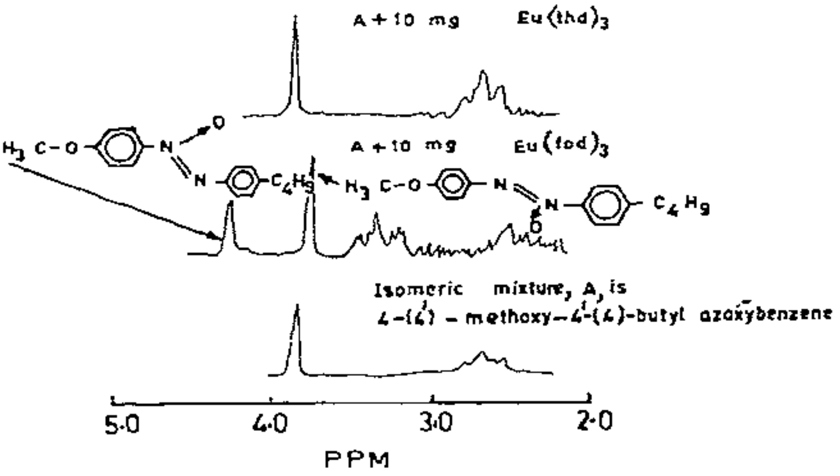


Fig. 24. The partial proton spectra (60 MHz) of an isomeric mixture in CCl$_4$ (0.2 M) before and after the addition of 10 mg of Eu(thd)$_3$ or Eu(fod)$_3$.

tageous to use Ho(fod)$_3$ if one is not interested in fine structure. For extremely weak nucleophiles, Yb(fod)$_3$ could possibly be used more effectively. Pr(fod)$_3$ is probably the best shift reagent available for producing an upfield shift [224].

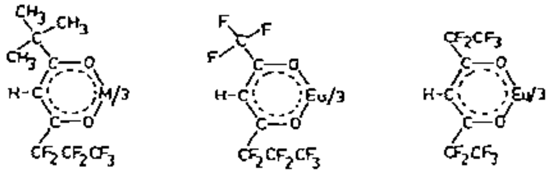
The shifting ability of nine trivalent lanthanide chelates of H(fod), having the structure Ln(fod)$_3$ (Ln = Eu(III), Yb(III), Tm(III), Sm(III), Pr(III), Dy(III), Er(III) and Ho(III)) have been tested [225] with furan and THF (Fig. 25a). Furan, as a representative weak base, was used primarily to test the ability of these new LSRs to interact with an extremely weak donor and none of the observed shifts was very large. On the other hand, all LSRs induced appreciably large shifts with THF, providing a more suitable basis for comparison. For the first attempt at spectral clarification Eu(fod)$_3$ is usually the best shift reagent.

Still more acidic and more soluble lanthanide chelates of H(dfhd), (Fig. 25b) may be used with very weak nucleophiles [119,224]. The dfhd chelate of Eu(III) induces greater shifts than the fod or thd chelates on an equimolar basis with *N,N*-dimethylaniline.

The H(fhd) chelates (Fig. 25c) of La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb and Lu have also been examined [227] for shift reagent capability, using (n-Bu)$_2$C=O as the substrate. La and Lu complexes do not induce paramagnetic shift but complexes of Pr, Nd, Sm, Gd, Dy and Ho gave upfield shifts. Complexes of Eu, Er and Yb produced downfield shifts as expected. All spectra, except that of Eu(fhd)$_3$ showed considerable broadening of the peaks and only Dy(fhd)$_3$ and Yb(fhd)$_3$ exhibited fine structure. Similar results have been reported by Horrocks and Sipe [228]. Burgett and Warner [227] reported that Ho(fhd)$_3$ shifts are greater than Dy(fhd)$_3$ shifts while Er(fhd)$_3$ shifts are greater than those of Yb(fhd)$_3$; Horrocks and Sipe [228] report reverse order for the thd chelates.

Table 7 gives the Δ's for the more remote protons, as a function of innermost protons and concludes that while the latter are approximately equally shifted by Eu(fod)$_3$ and Eu(fhd)$_3$, Eu(fhd)$_3$ shifts the former to a greater extent. This is due to smaller steric interactions between the substrate and the side chains of Eu(fhd)$_3$ as compared to Eu(fod)$_3$.

Very recently (1974), a novel and efficient NMR shift reagent, tetrakis-(1,1,1-trifluoro-4-phenylbutane-2,4-dionato)uranium, U(btfa)$_4$, has been pre-



(a) M=Eu,Yb,Tm,Nd,Sm,Pr Dy,Er, and Ho (b) (c)

Fig. 25. (a) The nine trivalent lanthanide chelates of H(fod). (b) The dfhd chelate of Eu(III). (c) The H(fhd) chelate of Eu(III).

TABLE 7

Shift attenuation in some straight-chain compounds

No. of intervening carbons	ROH [a] [229]	$(n\text{-Bu})_2O$ [b] [215]	$(n\text{-Bu})_2O$ [c] [227]	$(n\text{-Bu})_2C{=}O$ [c] [227]
1	1	1	1	—
2	0.60	0.60	0.91	1
3	0.42	0.19	0.45	0.69
4	0.20	0.12	0.22	0.29
5	0.14	—	—	0.13

[a] Using $Eu(dpm)_3$ as shift reagent. [b] Using $Eu(fod)_3$ as shift reagent. [c] Using $Eu(fhd)_3$ as shift reagent.

pared [230]. Since it is capable of forming adducts with Lewis bases (e.g. py and n-BuOH) and inducing proton shifts of a magnitude similar to those obtained with $Eu(dpm)_3$, $U(btfa)_4$ may be useful as a chemical shift reagent.

Springer and co-workers [231] developed a method for increasing the time resolution of dynamic NMR spectroscopy. A lanthanide shift reagent is used to cause a continuous change of the NMR time scale through the exchange of the sensitive region, but at the same time the rate of the observed processes remains constant.

When H(fod) is added to a solution of $Eu(fod)_3$, a tetrakis complex may be formed [224]. This is indicated by the observation that only one *t*-butyl resonance exists in the proton spectra of deuterochloroform solution containing both $Eu(fod)_3$ and H(fod). The addition of H(fod) to deuterochloroform solutions of $Eu(fod)_3$ produces small changes in shifting ability of the latter. This may be ascribed to either (a) H(fod) as a base cannot compete with ethanol effectively and is displaced, or, (b) an $H[Eu(fod)_4]$ species is generated which functions as a shift reagent by forming a species with coordination number 8 or 9. It is further confirmed by dissolving equimolar amounts of $Eu(fod)_3$ and $Pr(fod)_3$ in CCl_4 and studying the NMR (^1H and ^{19}F) (Fig. 26a). Rapid inter-complex exchange of fod ligands is likely to occur by means of dimer or oligomer association in $Pr(fod)_3$—$Eu(fod)_3$ mixture (Figs. 26b and 26c).

Recently some comparisons of coordinating ability of different functional groups with LSRs have been made. The coordinating powers of thiols, thioethers and aryl phosphines are generally much less than that of their oxygen and nitrogen analogues [232]. The following are some series of functional groups, in order of their ability, to coordinate and cause an LIS

(a) phosphoryl > carbonyl > thiocarbonyl > thiophosphoryl [233]

(b) ethers > thioethers > ketones > esters [234]

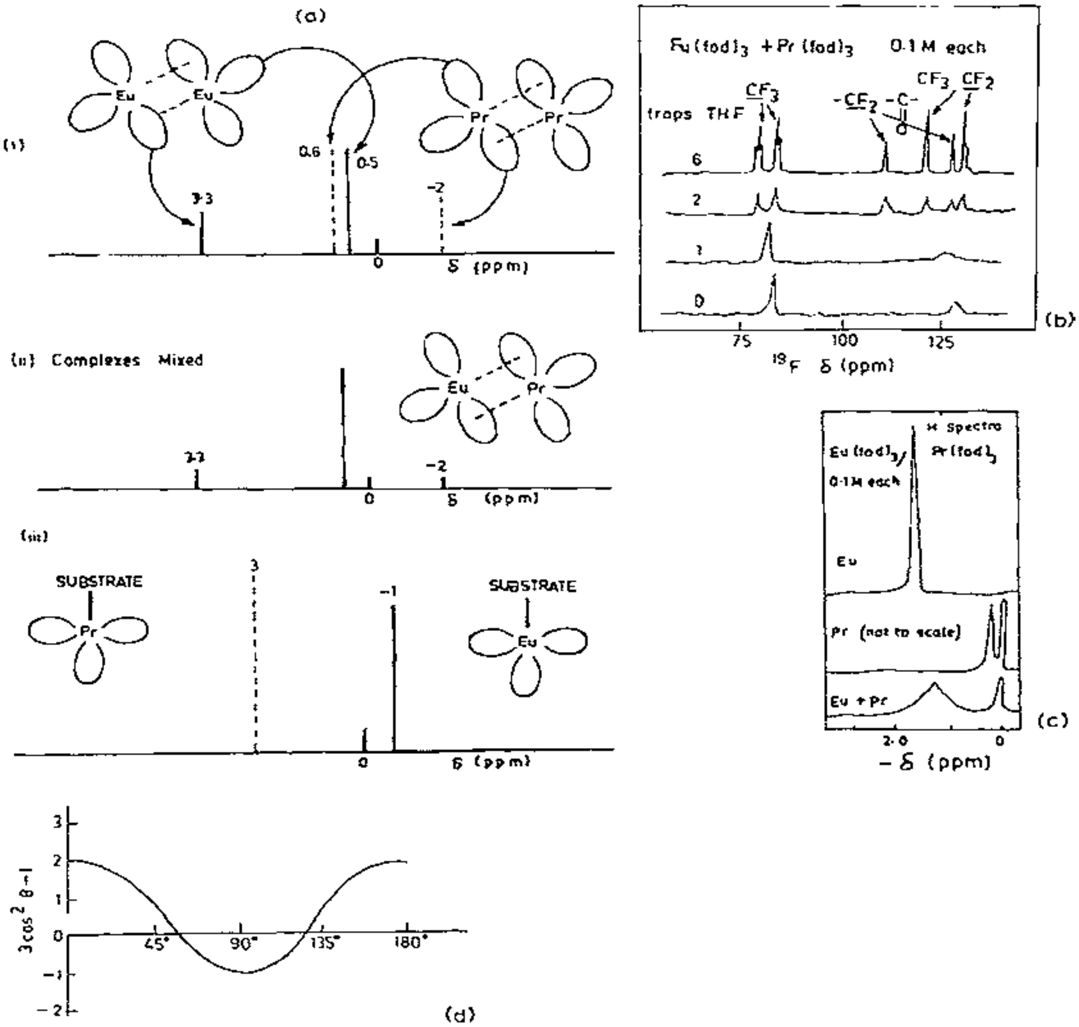


Fig. 26. (a) Schematic representation of (i) separate solution of Eu(fod)$_3$ and Pr(fod)$_3$ in dry CCl$_4$ solution, (ii) the mixed solution, and (iii) the solution in the presence of excess of substrate. (b) ^{19}F Spectra obtained by incremental addition of THF to a Pr(fod)$_3$—Eu(fod)$_3$ mixture. (c) ^{1}H spectra of Eu(fod)$_3$ (above), Pr(fod)$_3$ (middle), and Eu(fod)$_3$—Pr(fod)$_3$ mixture (below). (d) The variation of 3 cos$^2\theta$ − 1 with the angle θ.

(c) amines > hydroxyls > ketones > aldehydes [226]

(d) ethers > esters > nitriles [229]

Mechanism of the shifts. The mechanism of the induced shifts caused by the lanthanide shift reagents has been discussed in the recent literature. In lanthanide—substrate complex, interaction between the paramagnetic metal ion and the nuclei of the substrate causes changes in the chemical shift of the nuclei. Interaction between metal cation and ligands gives rise to contact and pseudo-contact interactions resulting in contact and pseudo-contact shifts.

The pseudo-contact interaction may be defined as a magnetic field effect acting through space rather than an effect through bonds [226,235] (e.g., the observed shifts ($\delta\Delta$) are dominated in case of σ framework by pseudo-contact interaction), and in turn, pseudo-contact shift can be defined as a dipolar interaction between nucleus and the electron spin magnetization of the paramagnetic metal ion [236]. Theories have been developed for expression of the magnitude of the pseudo-contact shift, which can be expressed by the equation of McConnell and Robertson [237], as follows

$$\delta\Delta = \frac{X(3\cos^2\theta - 1)}{r^3} \tag{29}$$

Equation 29 is valid for axially symmetric molecule; r is the nucleus—metal distance vector; and θ is the angle between this vector and the principal symmetry axis. This axis is usually taken to be the line connecting the metal ion and the coordination atom so that θ is the H—Ln—O angle for the protons in the nucleophile. X, a constant for a given metal adduct at a given temperature, is dependent on the magnetic anisotropy of the ion and is the same for all nuclei in a molecule.

Now

$$X = \frac{-\beta S(S+1)}{27\,kT} f(g) \tag{30}$$

According to the theory of McConnell and Robertson [237] and from later theory of Bleaney [238]

$$X = \frac{\beta^2 J(J+1)(2\,J-1)(2\,J+3)\,\langle \| \alpha \| J\rangle}{60\,k^2 T^2}\; 2\,A_2^0\langle r^2\rangle\, g^2 \tag{31}$$

where, β = Bohr magneton; S = electron spin; k = Boltzmann's constant; $A_2^0\langle r^2\rangle$ = the crystal field coefficient and g = the g tensors.

The value of X is different for each complex as it involves the g tensor, which is split into $g_\perp$ and $g_\parallel$, the tensor perpendicular and parallel to the molecular axis. According to McConnell and Robertson's [237] theory, "the pseudo-contact shift arises from a failure of the dipolar interaction to average to zero owing to the metal possessing an anisotropic g tensor". The fact that the pseudo-contact shift is the one which is observed is supported by various correlations noticed between ^{13}C or ^{1}H shifts and chemically reasonable coordination and substrate geometries [235,239]. The only exception noticed is when carbon is bonded to the coordinating atom. The shifts are then not always as predicted, and may be due to contact interaction.

The shifts in ^{14}N spectra are almost exclusively contact in nature and aquolanthanide ions induce large contact shifts in case of ^{31}P and ^{13}C in phosphates and carboxylates, respectively [235]. The transmissions of contact shifts from Eu(fod)$_3$, via the π-system of pyridine-*N*-oxide, have also been observed.

Contact shifts occur by direct electron—nucleus magnetic interaction and consequently result from movement of unpaired electron spin density from the metal cation to the ligand by covalent bond formation [226]. Hence, "this mechanism operates through the metal cation coordinating bond and depends upon the degree of covalency in this bond" [236]. This interaction is dependent on $g_{av}J(J+1)$ (where J represents the Russell—Saunders state and g_{av} the average magnetic moment). The size of the anisotropy, $g_{\parallel} - g_{\perp}$, is considerably dependent on geometry but g_{av} is virtually geometry independent at room temperature. The relative contact shifts at room temperature should be the same for all lanthanide systems unless the nature of the bonding changes in the series [209]. With aromatic substrates, various LSRs have been reported to exhibit different degrees of contact interaction and a series with an increasing degree of contact interaction is as follows [226]

$$\underset{\text{increasing contact interaction}}{\underrightarrow{\mathrm{Pr(fod)_3} < \mathrm{Yb(fod)_3} < \mathrm{Eu(dpm)_3} < \mathrm{Er(dpm)_3} < \mathrm{Eu(fod)_3}}} \qquad (32)$$

Apart from these exceptions, the pseudo-contact nature of the shifts is now well established. However, it should be used carefully because the sign of $3\cos^2\theta - 1$ changes when $\theta > 54.7°$, and upfield shifts will be noticed [226,235]. For example, europium upfield shifts have been reported in connection with structural problems [240—247]. But if θ is sufficiently large, the reversal of the direction of "normal shift" has been observed [226, 235]. Figure 26d shows how the LIS varies from positive to negative as the angle is altered. Therefore, it is remarked, "care should be used in the interpretation of future results obtained with these shift reagents especially in cases where bridged or folded molecules are involved" [245]. By changing solvent or ligand of the LSR, the direction of shifts is also altered [240,241,248,249].

G. CHROMATOGRAPHIC STUDIES OF METAL 1,3-DIKETONATES

(i) Thin layer chromatography

Honjo and Kiba [250] examined chromatographically the chelates of stta with Co(II), Ni(II), Cu(II), Zn(II), Hg(II), Pb(II) and Cd(II) on a thin layer of silica gel with various organic solvents. An excellent separation was achieved and the R_f value generally increased in the following order: Cd(II), Zn(II), Pb(II), H(stta) < Hg(II), Co(II), (III) < Cu(II) < Ni(II) (with carbon tetrachloride); Cd(II), Zn(II), Pb(II), H(stta) < Co(III) < Hg(II) < Cu(II) < Ni(II) (with carbon disulphide); Cd(II), H(stta) < Zn(II) < Pb(II) < Hg(II), Co(III), Cu(II), Ni(II) (with ethyl acetate); and Cd(II), Zn(II), Pb(II), H(stta) < Hg(II) <Co(III) < Cu(II) < Ni(II) (with cyclohexane—chloroform, chloroform—carbon disulphide and carbon tetrachloride—carbon disulphide mixtures). A few μg of $Ni(stta)_2$ chelates could be determined quantitatively. Some aspects of the behaviour of the stta chelates on the thin-layer of silica gel have also been discussed.

Recently, the *cis* and *trans* forms of $Ru(tfac)_3$ have been separated by tlc [75]. Everett and Chen [251] separated diastereomers (A—D) of $Co[(-)hmcar]_3$ by tlc with silica gel as the sorbent, using *n*-pentane-diethylether (3 : 1 v/v) solvent mixture; the isomers (in order of increasing R_f values) and yields are as follows: A, Δ-*cis* (18%); B, Λ-*trans* (48%); C, Δ-*trans* (26%); D, Λ-*cis* (8%).

Similarly, four diastereomers of $Co[(+)hmpul]_3$ have also been separated by tlc.

Thin layer chromatography has also been applied to detect the disproportionation and linkage isomerization products of metal 1,3-diketonates [252]; e.g. the disproportionation and linkage isomerization products of (3-formyl-acac)$Co(acac)_2$ have revealed six components by tlc, out of which four components (A—D); viz., (A), $(acac)_3Co$; (B), (2-acetyl-1,3-butanediono)Co-$(acac)_2$; (C), (3-formyl-acac)$Co(acac)_2$ and (D), $(3\text{-formyl-acac})_2Co(acac)$ have been isolated by column chromatography and characterized by spectroscopic methods. Similarly, tlc has been used to detect the disproportionation and linkage isomerization products of (2-acetyl-1,3-butanediono)$Co(acac)_2$, $(3\text{-formyl-acac})_2Co(acac)$, $[(3\text{-formyl-acac})_3Co + (acac)_3Co]$ and $(3\text{-chloro-acac})_2Co(acac)$ in different solvents [252].

(ii) Column chromatography

Column chromatographic studies of metal 1,3-diketonates have been made. Fay and Piper [174,175] prepared a series of metal 1,3-diketonates, $M(RCOCHCOR')_3$ (where, M = Cr(III), Co(III), Rh(III), Al(III), Mn(III), Fe(III), In(III), Ga(III); R = Me or Ph; R′ = Me or CF_3), and *cis—trans* isomers of the inert complexes (M = Cr(III), Co(III), Rh(III)) have been separated by column chromatography on acid washed alumina using ethanol/benzene—hexane mixture as the eluting solvent. Since the *cis* isomers are more soluble in solvents than the *trans* isomers, the *cis* isomers are first concentrated by extraction with benzene—hexane or ethanol. Only the *trans* isomer is isolated in the solid state in case of labile metal 1,3-diketonates (M = Al(III), Ga(III), In(III), Mn(III), Fe(III)). The geometrical configuration of the isomers has been established by proton and fluorine NMR spectra and X-ray powder patterns. The yield of *cis* isomers may be increased by isomerization of the *trans* isomers at elevated temperature. For $Co(tfac)_3$ equilibrium (ca 20% *cis*) is achieved by refluxing in benzene for 6—10 h.

Collman et al. [90,95,99] used column chromatography for separation of different products of metal 1,3-diketonates in reactions such as nitration, chlorination, acetylation, benzoylation, butyrylation, reduction, pyrolysis of diazonium salt and disproportionation and linkage isomerization [252]. The most commonly used adsorbents are florisil and alumina with benzene, chloroform, methanol and dichloromethane as eluents. Similarly, Kawanishi et al. [102] isolated mono-, di- and tri-brominated products of cobalt chelate of monothio-1,3-pentanedione, $Co(sacac)_3$, on silica gel column using benzene as eluent. Four diastereomers of $Co[(+)atc]_3$, viz., α-isomer (Δ-*trans*), β-isomer (Λ-*trans*), γ-isomer (Λ-*cis*) and δ-isomer (Δ-*cis*) have been isolated also [253] on alumina using benzene as eluent.

H(tta) has been used in conjuction with column chromatography for the separation of rare earths [254].

(iii) Gas chromatography

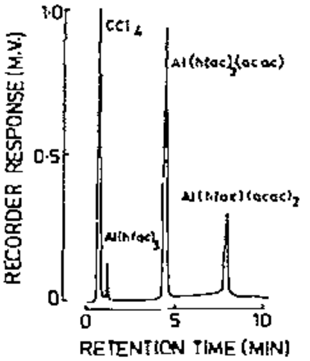
Gas chromatography has been usefully employed in the study of metal 1,3-diketonate chelates, with particular reference to investigations of stereochemistry, ligand exchange, isomerization, metal ligand stoichiometry, interactions of complexes with weak donors, separation of geometrical and optical isomers and ultratrace metal analysis. For most purposes, the metal chelates must exhibit a vapour pressure of the order 0.1—1 mm in order to have gas-phase migration through the column at a reasonable rate. The 1,3-diketones which have been most thoroughly examined and satisfy the above criteria are [255] H(acac), H(tfac), H(hfac), H(thd), H(fod), H(dfhd), H(fhd) and H(tfacam). The factors which govern the gas-chromatographic studies are (1) volatility, (2) solvolytic and thermal stability.

(1) Volatility of the metal 1,3-diketonates. It is affected by the following factors.

(a) Substitution of fluorine for hydrogen in the "ligand shell". It is now well established that the volatility of metal 1,3-diketonates and the ease with which they can be eluted is greatly increased by substitution of fluorine for hydrogen in the "ligand shell" [118,256,257]. With non-polar liquid stationary phases, the ease with which the complexes can be eluted roughly parallels their saturation vapour pressures. The column temperatures required for $Cr(acac)_3$, $Cr(tfac)_3$ and $Cr(hfac)_3$ are between 150—220, 100—150 and 30—80°C respectively [255]. It has also led to the development of an empirical rule from a knowledge of their chromatographic retention behaviour. *For complexes of a given metal ion, increasing substitution of fluorine for hydrogen reduces the retention time.*

Sievers et al. [29,255] observed more than fifty examples of this phenomenon. As shown in Fig. 27, the chelate with 18 fluorine atoms is eluted more easily than the one with 12 fluorine atoms, which in turn has a shorter retention time than the chelate with 6-fluorine atoms. Non-fluorinated $Al(acac)_3$ has a much longer retention time.

Fluorinated substituents in the ligand shell markedly increase the volatility of the complexes as compared to compounds containing a non-fluorinated ligand. With Cr(III) and with Al(III), the tris-fod complexes have been shown to have volatilities greater than those of the analogous tris-acac and tris-thd



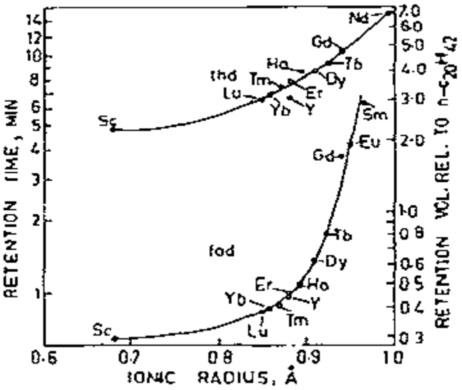


Fig. 27. Gas chromatography of metal 1,3-diketonates with degrees of substitution of hydrogen by fluorine in the ligand shell.

Fig. 28. Gas chromatographic retention data as a function of the ionic radius of the metal column temp 171°C liquid phase polydimethyl siloxane. Sample: Ln(thd)$_3$ or Ln(fod)$_3$.

compounds and only slightly less than those of the analogous tris-tfac compounds [29]. The increased volatility of chelates containing the highly electronegative fluorine substituted ligands implies that these groups produce a shell with rather lower attractive tendencies around the complex molecule as compared to a similar hydrogen chelate. The fod chelates are the most volatile rare earth compounds yet reported [29,256].

In a GC study of a series of compounds the retention time of fluorinated 1,3-diketonates increases in the order [258] M(hfac)$_3$ $<<$ M(tfac)$_3$ $<$ M(tprm)$_3$ $<$ M(tibm)$_3$ $<$ M(tpm)$_3$ $<$ M(tmbm)$_3$ $<$ M(tivm)$_3$ $<<$ M(fta)$_3$ $<$ M(btfa)$_3$ $<$ M(tta)$_3$ in contrast with the alkyl-substituted metal 1,3-diketonate series. The retention time, evidently, depends upon the volatility of the chelates.

(b) Lanthanide contraction (decreasing ionic radius). An interesting correlation exists between the lanthanide contraction and the volatility of the tris-chelates as evidenced by retention data (Fig. 28). For a given metal ion, the ease of elution of chelates, with common ligand as an inverse function of the ionic radius, is confirmed for both the non-fluorinated H(thd) and the fluorinated H(fod) systems [29].

Shigematsu et al. [259—261] reaffirmed this correlation by GC studies of rare earth chelates with H(pta). The trifluoroacetylacetonates of Al(III), Ga(III) and In(III) also show a similar effect [258].

Similar observations have also been noted, in the cases of tetrakis and tris-adduct chelates of fluorinated 1,3-diketones with rare earths [118]. Several possible explanations for the phenomenon have been recently advanced [29,256].

(2) Solvolytic stability of metal 1,3-diketonates. The GC behaviour of the Nd(III), Gd(III) and Er(III) chelates of twenty non-fluorinated and fluorin-

ated 1,3-diketones has been studied [262]; chelates, containing a tertiary carbon atom in the α-position to the carboxyl group can be more advantageously studied (e.g., chelates of H(dpm), H(ibpm), H(dibm)). In such cases, the shielding by the sterically crowded group stabilizes the chelate.

Applications.

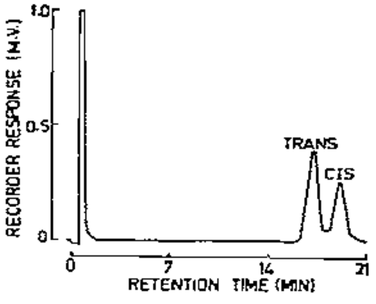
(1) Stereochemical studies. An illustration is the separation of geometrical isomers of Cr(tfac)$_3$ as shown in Fig. 29. In the *cis* (or *facial*) isomer the CF$_3$ groups are mutually adjacent and lie above the upper front face to the octahedron (Fig. 10a). In the *trans* (*meridianal*) isomer, one of the CF$_3$ groups is interchanged with a CH$_3$ group. *Cis—trans* isomers of Rh(tfac)$_3$ have also been separated by GC in 79.8% (*trans*) and 20.2% (*cis*) respectively [255]. Tanikawa et al. [263] were able to achieve a partial separation of *cis—trans*-Ga-(tfac)$_3$ at a column temperature of 140° C.

Mixed ligand complexes can also be easily separated and analysed by gas chromatography. If mixture of H(hfac) and H(tfac) are mixed with Cr(NO$_3$)$_3$ · 9 H$_2$O in ethanol, seven compounds with the formulae Cr(tfac)$_x$(hfac)$_{3-x}$, are formed. Under various conditions, all seven compounds have been separated by gas chromatography [257].

A partial resolution of dextro- and levo-Cr(hfac)$_3$ was achieved [264] by gas solid chromatography using a column filled with powdered quartz prepared by pulverizing a large single crystal of dextro quartz [255,265].

Recently, *N,N'*-2,3-butylene-bis(trifluoroacetylacetoniminato) chelates of copper(II), nickel(II) and palladium(II) were prepared [266]. Each exhibit two isomeric forms (Fig. 30(I) and (II)) and were readily resolved by GLC. The chelates and their analogues are sufficiently volatile and thermally stable for quantitative elution.

(2) Metal analysis. Although several types of ligands have been examined, the fluorinated 1,3-diketone, H(tfac), is more often used in quantitative analysis. The electron capture detector is especially sensitive to volatile fluorinated



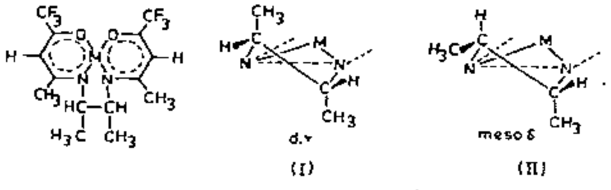


Fig. 29. Separation of geometric isomers of Cr(tfac)$_3$ by gas chromatography.

Fig. 30. Isomeric forms of copper(II) and nickel(II) *N,N'*-2,3-butylene-bis(trifluoroacetylacetoniminato) chelates.

metal chelates. Quantitative gas chromatographic schemes now exist for the determination of Be in blood, urine and tissue; chromium in serum; aluminium in uranium; aluminium, gallium and indium in aqueous solution; iron in ore; chromium in steel; titanium in bauxite; aluminium, iron and copper in alloys; uranium, tungsten and molybdenum in alloys and ores, etc. [255].

Morie and Sweet in 1965 described the analysis of mixtures of Al, Ga and In. These metals were extracted from an aqueous medium by shaking for 4 h. at room temperature with a solution of H(tfac) in benzene [267]. Gas-chromatographic measurements were carried out using a stationary phase of silicone DC-550 oil and a thermal conductivity detector. Similarly, Morie and Sweet also measured aluminium and iron in a nickel—copper alloy [268].

Electron capture gas chromatography has been used to analyse ultratrace quantities of metal as metal 1,3-diketonates, $M(RCOCH\ COR')_n$ (where, M = Be(II), Cr(III), Fe(III), Ni(II), Cu(II), Y(III), Al(III); R = R′ = Me or CF_3; $n = 2$ or 3) in aqueous solutions [30,269—272] in biological fluids [10,273] and Be(II) in polluted air [274]. A rapid and sensitive method for the ultratrace analysis for Be(II) and Cr(III) in terrestrial, meteoritic and in lunar rock and dust samples returned from the Apollo,11, 12, 14 and 15 sites have been developed [275—277] using electron capture gas chromatography. The detection limit is approximately 4×10^{-14} g.

Sievers and co-workers [278] also developed an advantageous gas chromatography—mass spectrometry (GC—MS) method for trace metal analysis which holds great potential. Its one important advantage is the capability of monitoring a peak which can be uniquely identified with a single metal, and the freedom from the interferences in larger volumes of sample.

Chromium has been analysed in biological systems as $Cr(tfac)_3$ [278], and beryllium measured in air as $Be(tfac)_2$ [278]. The identity of eluted $Cr(tfac)_3$ or $Be(tfac)_2$ is confirmed by GC—MS. The lower limit of detectability is of the order of 1×10^{-12} g of beryllium [278].

The elution of nickel(II) and copper(II) chelates of H(fod) have been reported [279] as has the chromatography of copper(II), zinc(II), cobalt(II) and lead(II), 1,3-diketonates [263] and cobalt(II), nickel(II) and copper(II) tta complexes [280]. Thermal decomposition of some of these complexes was evident and separations were not achieved. Thermal degradation of metal complexes, which have coordination numbers greater than twice the ionic charge of the metal, is observed frequently, and is probably a result of the coordination of water. To avoid the formation of hydrated chelates, Stephen et al. [281] prepared low field complexes of cobalt(II) and nickel(II) using monothioacetylacetone. These complexes are thermally stable and good chromatographic performance was reported. Karoyannis and Corwin [282] recently reported the chromatography of 39 different metal 1,3-diketonates by hyperpressure chromatography, but only limited separation was achieved.

Chromatographic studies on mixed ligand complexes, prepared with a view to obtaining stable complexes of uranium and thorium [283], have been made; particularly on mixed ligand systems of cobalt(II) and nickel(II) [284], but have met with only limited success, and no separations have been reported.

Burgett [285] prepared volatile complexes of iron(II), cobalt(II) and nickel(II) by solvent extraction, using the mixed ligand system H(fhd)—DBSO. The composition of the extracted species is reported to be $M(fhd)_2 \cdot 2$ DBSO. The complexes were eluted from the gas chromatographic column without decomposition as determined by mass spectrometric detection. Separation of iron(II) and cobalt(II) from nickel(II) was readily achieved; however, iron(II) and cobalt(II) were not separated.

Burgett and Fritz [286] used the gas—liquid chromatogrphic method for the separation and subsequent quantitative determination of yttrium group lanthanides, synergistically extracted from aqueous solution with polyfluorinated 1,3-diketone H(fhd) as ligand and DBSO as neutral donor. The composition of the extracted species is reported to be $RE(fhd)_3 \cdot 2$ DBSO. The solvent extraction enables prior separation of lanthanides from interfering metals with subsequent separation and quantitative analysis of the lanthanides. Individual lanthanides were determined with 97.5% recovery with a relative mean deviation of ±1.5 pph and a relative standard deviation of ±1.9 pph. Mixtures of lanthanides were determined with 97.1% recovery with a relative mean deviation of ±2.3 pph and a relative standard deviation of ±3.1 pph. They have also developed an efficient GLC method for the separation and subsequent quantitative determination of cerium group lanthanides as the mixed-ligand complexes with H(fhd) and DBSO [287].

Individual lanthanides were determined (Table 8) with 99.0% recovery with a relative mean deviation of ±2.0%. Mixtures of lanthanides were analyzed with 101.2% recovery with a mean deviation of ±2.2%.

Schwarzberg et al. [288] separated the three metals, viz., Al(III), Ga(III) and In(III), whose separation is somewhat more difficult, with H(tfac). This

TABLE 8

Determination of the individual lanthanides as H(fhd)—DBSO mixed ligand complexes

RE	Taken (μg)	Found (μg)	Relative error (%)
Eu	6.38	6.35	−0.5
	3.41	3.44	+0.9
Sm	5.87	5.80	−1.2
	4.44	4.35	−2.0
Pr	4.97	5.04	+1.4
	1.26	1.31	+4.0
Nd	3.24	3.20	−1.2
	5.72	5.66	−1.0
Ce	5.18	5.04	−2.7
	3.16	3.16	−1.9
La	4.46	4.08	−4.9
	6.47	6.30	−2.6

was followed by the work of Uden and co-workers [289] who examined, for the first time, metal monothiotrifluoroacetylacetonates of Ni(II), Pd(II) and Pt(II) by the gas chromatographic technique. A new ligand [164b], H(shfac), forms extremely volatile and thermally stable metal chelates of Zn(II), Fe(III), Ni(II), Pt(II), Pd(II), Cd(II) and Pb(II). The successful GC application of H-(shfac) has been demonstrated by separation of d^8 metals (Ni(II), Pd(II) and Pt(II)). These separations have confirmed the great potential of monothio-1,3-diketonates as suitable chelates for gas chromatographic study.

The analytical GC of a range of fluorinated and non-fluorinated 1,3-diketonates of Al(III), Cr(III) and Fe(III) has been studied in detail and conditions have been established for their complete separation; the chelates of H-(tpm) show the best characteristics for this purpose. Apiezon substrate has been shown to give optimal resolution. The efficiency of the process is demonstrated by the removal of 2% proportions of two metal chelates from a sample of the third [290].

The gas chromatographic separation of Cu(II), Ni(II), Pd(II) and Pt(II) metals as ttfa chelates, is reported for the first time [163,291,292]. Also reported are the first gas chromatographic separations of volatile quadridentate metal chelates of Cu(II), Co(II), Ni(II), Pd(II) and Pt(II) with bisacetylacetone-ethylenediimine and its fluorinated analogues [164,292,293]. In the GC study of Pb(II) chelates of H(hpm), H(ppm) and H(tpm), it has been noted that these chelates are highly thermally stable, but strong column interaction makes successful quantitative GC difficult [162]. The results of preliminary gas chromatographic studies of Mg(II), Ca(II), Sr(II) and Ba(II) chelates of H(hpm) and H(tpm) are also discussed; elution appears to occur without decomposition but no separation of the Ca(II), Sr(II) and Ba(II) chelates is achieved [161].

Ross et al. [31] quantitatively extracted cobalt from aqueous solution with the aid of radioactive ^{60}Co. The lower limit of detectability for Co as Co-$(\mathrm{fod})_3$ is about 4.4×10^{-11} g. They also described methods for extraction of cobalt from the natural cobalt complex of cyanocobalamin (Vitamin B_{12}) to form the volatile metal fluorinated 1,3-diketonate, $\mathrm{Co(fod)_3}$.

(3) Interaction between selected organic nucleophiles and NMR shift reagents. Gas chromatography offers an independent method of examining the interactions between nucleophiles and lanthanide shift reagents. The success of this method depends upon the ability to incorporate the lanthanide shift reagent into the stationary phase of a GC column and therefore, solubility in organic solvents is an important factor. The experimental details are generally similar to those described by Feibush et al. [219].

A theory for the study of interactions of this nature has been developed with an assumption that the following equilibrium exists in the liquid phase of the GC column [294].

$$\mathrm{D(solution)} + \mathrm{chelate} \overset{K}{\rightleftharpoons} \mathrm{chelate.D}$$

$$K = \frac{[\mathrm{chelate.D}]}{[\mathrm{D(solution)}].[\mathrm{Chelate}]} \tag{33}$$

where D(solution) represents donor molecules in solution but not complexed with chelate, and chelate.D represents the adduct formed between the chelate and the donor. If extremely small donor sample injections are made, the concentration of chelate in solution is in such great excess that it is essentially constant. Then, a pseudo-equilibrium constant K' can be obtained which is related to K by the expression:

$$K' = K[\text{chelate}] = \frac{[\text{chelate.D}]}{[\text{D(solution)}]} = \frac{[\text{complexed}]}{[\text{free}]} \tag{34}$$

Therefore, the physical significance of K' is that it provides a means for determining the percentage of time when a donor molecule is complexed while in solution. The relative values of K' provide valuable information about the strength (stability) of the adducts of chelate—nucleophile interactions and it has been shown that K' is directly related to retention data as follows [294]:

$$K' = (t_{\text{chelate}}/t_{\text{squalane}}) - 1 \tag{35}$$

where, t_{chelate} = corrected normalized retention time of a particular donor on a GC column in which a solution of Eu(fod)_3 in squalane functions as the liquid phase, and t_{squalane} = corrected normalized retention time of that donor on a GC column using squalane alone as the liquid phase.

Applications. Feibush et al. [219] and other workers [224,294] reported the retention of many different ethers, ketones, alcohols, esters, olefines and alkanes by gas-chromatographic columns with liquid phases composed of solutions of tris-1,3-diketonate rare earth chelates. Ln(tfacam)_3 or Ln(fod)_3 (where, Ln = La, Pr, Sm, Tb, Er, Lu, Sc, Dy, Ho etc.).

Extensive GC studies have been conducted to examine the interactions of selected ketones and alcohols with the NMR shift reagent, Eu(fod)_3. In general, alcohols form more stable complexes than ketones with Eu(fod)_3. This is indicated by generally higher K' values obtained for alcohols (e.g., the K' values for 2-butanone and 2-butanol, are 14.6 and 20.8 respectively). The more nucleophilic organic compounds, for example (THF), are found to undergo much stronger interaction with rare earth chelates than the less basic solutes. The Er(III) chelates of fluorinated 1,3-diketones (e.g., Er(tfacam)_3] undergo a much greater interaction with nucleophiles than similar non-fluorinated Er(III) chelates. Several trends appearing in the data may be explained on the basis of relative nucleophilicities and steric constraints of the interactions [224,294].

(a) As a general rule, increasing the length of alkyl chains in a series of similar compounds increases the stability of the complexes formed. For example, a comparison of the values of K' of compound nos. 1—3 in the alkanone series and compound nos. 9—12 in the alkanol series (Table 9a), indicates that the stability of complexes increases with increasing chain length, and is ascribed to increased electron donating ability due to the inductive effect of longer alkyl chain. In compound nos. 4—6 in the alkanone series and compound no. 13 in the alkanol series, the stability decreases, in cases where steric

TABLE 9a

K' values for different types of donors

S. No.	Compound	K'	S. No.	Compound	K'
1	2-Butanone	14.6	8	4-Heptanone	13.5
2	2-Pentanone	15.6	9	2-Butanol	20.8
3	3-Hexanone	16.9	10	2-Pentanol	22.1
4	2-Heptanone	16.4	11	2-Hexanol	22.7
5	2-Octanone	16.3	12	2-Heptanol	23.2
6	3-Pentanone	13.2	13	3-Methyl-3-pentanol	10.6
7	3-Heptanone	14.2			

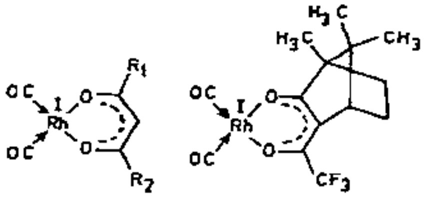
effects predominate over the inductive effects. The position of the functional group within the molecule is also an important factor [220] (Table 9a). The K' values of 4, 7 and 8, indicate that the most stable complexes are formed with donor molecules in which the functional group involved in the interaction is close to one end of the molecule [294].

(b) It is observed from Table 9b that branching in case of alcohols results in formation of less stable complexes as compared to non-branched isomers (independent of degree and location of hydroxyl group). In these cases, inductive effects are strong enough to overshadow the steric effects. In contrast to this, in case of ketones, both the inductive and steric effects are considered and both the degree and location of branching affect the stability of complexes formed. As shown in Table 9b the branching at α (compound nos. 2, 4 and 7) or at γ (compound no. 10) to the keto function, increases the stability of complexes formed as compared to the non-branched isomer due to stronger inductive effect, which more than compensates for the steric effect. While branching at β to the keto function (compound nos. 5 and 9), decreases the stability of complexes formed due to stronger steric effect.

TABLE 9b

K' values for different type of branching in different types of donors

S. No.	Compound	K'	S. No.	Compound	K'
1	2-Pentanone	15.6	10	5-Methyl-2-hexanone	17.2
2	3-Methyl-2-butanone	17.3	11	2-Pentanol	22.1
3	2-Hexanone	16.9	12	2-Methyl-2-butanol	13.3
4	3,3-Dimethyl-2-butanone	18.7	13	2-Butanol	20.8
5	4-Methyl-2-pentanone	15.1	14	2-Methyl-2-propanol	14.8
6	2-Octanone	16.3	15	3-Hexanol	18.5
7	3-Methyl-2-heptanone	19.0	16	2-Methyl-3-pentanol	15.0
8	2-Heptanone	16.4	17	3-Methyl-3-pentanol	10.6
9	4-Methyl-2-hexanone	15.8	18	2-Hexanol	22.7
			19	3,3-Dimethyl-2-butanol	16.1



I $R_1=CH_3$ $R_2=CH_3$
II $R_1=CH_3$ $R_2=CF_3$
III $R_1=CF_3$ $R_2=CF_3$

IV

Fig. 31. A series of 1,3-diketonates of $Rh(I)(CO)_2$.

(c) The chelates of fluorinated 1,3-diketones display greater interaction with nucleophiles as compared to non-fluorinated chelate analogues [219].

(d) In a series of $Ln(tfacam)_3$ chelates, it was found that for strong donors, such as THF, the retention time increased exponentially with the inverse of the ionic radius of the metal. This is due to a decrease in the extent of polymerization of the chelates with decreasing radius [219].

(e) Alcohols, which are deuterated geminally to the hydroxy group, have longer retention times than their non-deuterated isomers on the column using $Eu(fod)_3$ in squalane as the liquid phase. This indicates that the deuterated species form more stable complexes with $Eu(fod)_3$ [294].

(4) Miscellaneous. In a search for new complex forming reagents suitable for chromatography, Gil-Av and co-workers [295—297] prepared a series of $Rh(I)(CO)_2$ 1,3-diketonates (Fig. 31) and studied the separation of 27 C_2—C_6 *n*-alkenes. All the four Rn 1,3-diketonates (compounds I to IV, Fig. 31) are capable of separating alkenes; compound IV being superior to the rest because of its high interaction with alkenes and its stability.

Uden and Jenkins [298] studied in detail the absorption and displacement effects in the gas chromatography of Al(III), Cr(III) and Fe(III) 1,3-diketonates, $M(RCOCHCOR')_n$ (where, RCOCHCOR′ anion = acac, tfac, dpm, tpm, ppm and hpm), and showed that their elution and separation characteristics arise from a number of adsorptive effects.

H. PHYSICAL MEASUREMENTS OF METAL 1,3-DIKETONATES

(i) Vapour pressure

Considering [299] the vapour pressures of a series of lanthanide chelates, $Ln(thd)_3$, the chelates of the lanthanides with higher atomic number are much more volatile than those of lower atomic number, e.g. $Lu(thd)_3$ chelate exhibits a vapour pressure of 1 mm at 170°C whereas $La(thd)_3$ chelate exhibits the same vapour pressure at 225°C.

Similarly, vapour pressures of seven $Ln(fod)_3$ chelates (Ln = La, Nd, Sm, Gd, Dy, Er and Yb) have been measured by the Knudsen effusion method

TABLE 10

Vapour pressure results

Compounds	No. of modes	Temperature measurements		$\ln P(\text{mm}) = \frac{-A}{T} + B$		ΔH_{sub} (Kcal mole^{-1})	ΔS_{sub} Cal mole^{-1} (degree)
		T_{max} (°C)	T_{min} (°C)	A	B		
La(fod)_3	4	130.3	114.0	17479 ± 341	35.329 ± 0.865	34.7 ± 0.7	57.0 ± 1.72
Nd(fod)_3	4	128.5	113.6	18670 ± 335	38.852 ± 0.848	37.1 ± 0.7	64.0 ± 1.68
Sm(fod)_3	5	120.7	105.7	19068 ± 224	40.820 ± 0.577	37.9 ± 0.4	67.9 ± 1.15
Gd(fod)_3	4	111.6	88.9	18613 ± 101	40.246 ± 0.269	37.0 ± 0.2	66.8 ± 0.53
Dy(fod)_3	5	111.9	97.4	18828 ± 348	40.798 ± 0.917	37.4 ± 0.7	67.0 ± 1.82
Er(fod)_3	4	88.9	75.5	18625 ± 514	42.994 ± 1.445	37.0 ± 1.0	72.3 ± 2.87
Yb(fod)_3	7	82.4	66.2	18608 ± 424	44.497 ± 1.224	37.0 ± 0.8	75.2 ± 2.43
Er(thd)_3	7	108.4	84.9	17964 ± 189	39.937 ± 0.511	35.7 ± 0.4	66.2 ± 1.02

adapted for continuous recording of weight loss. The sensitivity of the diffusion method permits vapour pressure measurements at low temperatures, when decomposition of chelates is minimized. It has also been noted that vapour pressure increases as the atomic number of the lanthanide ion increases; a typical pressure is 10^{-4} mm at 100°C for Gd(fod)$_3$. These workers also determined the ΔH_{sub} values, which are constant at 37 kcal mole^{-1} for all Ln(fod)$_3$ compounds except La(fod)$_3$ [300] (Table 10).

(ii) Magnetic moments

The iron(III) chelates of fluorinated monothio 1,3-diketonates [43], Fe-[RC(S)=CHCOCF$_3$]$_3$ (R = Ph, 4-BrC$_6$H$_4$, 4-MeOC$_6$H$_4$, 2-thienyl, 2-furyl), display magnetic behaviour; their room temperature moments varying between 2.3 and 5.8 B.M. The moments of complexes are temperature-dependent, due to a thermal equilibrium between the nearly equi-energetic spin-paired (t^5_{2g}) and spin-free ($t^3_{2g}e_g{}^2$) configurations of the iron atoms, resulting from approximately equal magnitudes of the ligand field (Δ) and the pairing energy (π) in these complexes. The ligand field, and consequently the magnetic behaviour, are sensitive to the nature of substituents; electron withdrawing groups appear to be the most effective in increasing the population of the spin-paired configuration [301].

The copper(II) complexes of fluorinated monothio-1,3-diketones, Cu[RC-(S)=CHCOCF$_3$]$_2$ (R = 4 MeOC$_6$H$_4$, 4-MeC$_6$H$_4$, 4-BrC$_6$H$_4$, 2-furyl) [42], have room temperature magnetic moments of about 1.90 B.M., corresponding to one unpaired electron, while the cuprous complexes, Cu[RC(S)=CHCOCF$_3$] (R = 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-BrC$_6$H$_4$), are diamagnetic. Similarly, the nickel complexes of fluorinated monothio-1,3-diketones, NiL$_2$py$_2$ [L = RC(S)=CHCOCF$_3$], have magnetic moments between 3.06—3.29 B.M.

Casey and Walker studied the room temperature magnetic moments of N-base adducts of Cu(II)-1,3-diketone chelates in the range 1.9—2.1 B.M. [133].

The magnetic behaviour of the Co(BTAT)X (X = Br$^-$, I$^-$, NO$_3{}^-$ and ClO$_4{}^-$) complexes depends upon the nature of the non-coordinated anion. The anion X derivatives are diamagnetic, with magnetic moments of 0.55 B.M., which indicates a spin-paired Co(III) configuration. The [CoCl$_4$]$^{2-}$ and [Co(SCN)$_4$]$^{2-}$ derivatives display magnetic moments of 4.43 and 4.74 B.M. owing to tetrahedral Co(II) in the complex anions [183].

The magnetic moments of VO(nebas)$_2$ and VO(ttmbs)$_2$ have also been determined [302] (1.70 and 1.78 B.M., respectively).

I. THERMOGRAVIMETRIC STUDIES OF METAL 1,3-DIKETONATES

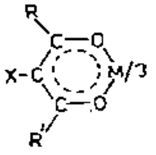
Thermogravimetric analysis (TGA) is a useful tool in comparing the relative volatilities and thermal stabilities of different metal 1,3-diketonate chelates. In general, metal chelates, which show greater volatility, are eluted from gas chromatographic columns containing non-polar liquid partitioning phases, in preference to those chelates whose thermograms indicate lesser volatility.

A wide class of volatile metal 1,3-diketonate chelates, M[RCOC(X)COR′]$_n$ have been examined [303]; (where, M = La(III), Pr(III), Nd(III), Sm(III), Eu(III), Tb(III), Er(III), Y(III), Lu(III), Sc(III), Dy(III), Tm(III), Na(I), Zr(IV), Cr(III), Al(III), Rh(III), Fe(III); n = 1,3 or 4; R = $(Me)_3C$, CF_3, CF_3CF_2, $CF_3CF_2CF_2$, Ph; R′ = $(Me)_3C$, CF_3, CF_3CF_2, 2-thienyl; X = H, Me, Ph, Br). The effects of different moieties in the 1,3 and 5 positions were reported with special reference to the influence of fluorine substitution on the volatility (Fig. 32).

The tris rare earth chelates of H(thd) have been of considerable interest as these chelates are volatile at moderately low temperatures (100—200°C) [304]. The correlation reported earlier, relating gas chromatographic data (Fig. 28) [304,305] with ionic radius of trivalent rare earth ion agrees with thermogravimetric data. The analytical data exhibited in Figs. 33 and 34 show "that the trend in volatility arising from the lanthanide contraction is real and not a specific solution effect" [29]. The chelates of the larger metal ions are volatilized at higher temperatures than their smaller analogues [29]. Similarly, the fluorinated compounds show increased volatility as compared to their equivalent non-fluorinated analogues (Figs. 33—35).

Volatility and thermal stability. The prevalence of hydration in metal 1,3-diketonates seems to produce undesirable effects on the thermal stability in many cases [306—308]. Attempts to elute neodymium(III) trifluoroacetylacetonate dihydrate, $Nd(tfac)_3 \cdot 2\ H_2O$, were unsuccessful [309]. The possible explanation is that hydration leads to hydrolytic instability at the temperature required for sublimation.

Some chelates of acac are thermally unstable and not volatile, while those of hfac sublime, albeit in some instances, with considerable decomposition [118]. Larger ligands or ligands containing fluorine [H(pta), H(fod), H(thd)



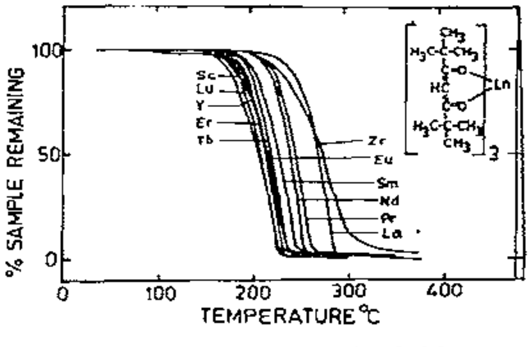
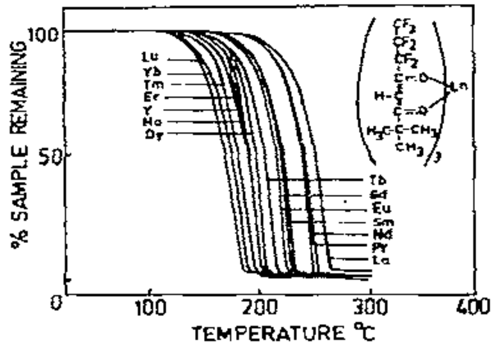


Fig. 32. General formula of substituted volatile metal 1,3-diketonate chelates M[RCOC(X)COR′]$_n$.

Fig. 33. T.G. curves of rare earth thd complexes.



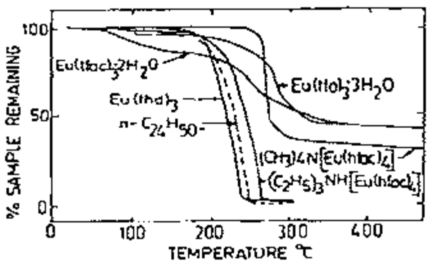


Fig. 34. T.G. curves of rare earth fod complexes.

Fig. 35. T.G. curves of europium(III)β-diketonates.

and H(dfhd)) are sufficiently thermally stable to permit volatilization, without decomposition of chelates. Water hydration may not necessarily have a deleterious effect on the thermal stability of chelates. In cases when water is not coordinated to the metal or the metal—water bond is much more easily broken than the metal—diketonate bonds, (e.g. Ln(dfhd)$_3$ · 2 H_2O and Ln(fod)$_3$ · H_2O), hydrolysis causes negligible decomposition [118].

Figure 36 shows the thermograms of some Cr(III)-1,3-diketonate chelates, where R and R′ groups have been substituted as indicated. The fluorine substituted chelates show greater volatility than the non-fluorine substituted species. Also, the effect of bromine in the 3-position of Cr(acac)$_3$ (curve I); tends to reduce the volatility of the volatile chelate, and at about 200°C Cr(Br-acac)$_3$ decomposes instead of subliming. An important observation is that substitution of a group, other than H, in the 3-position of the 1,3-diketone ligands tends to reduce thermal stability or substantially decrease the volatility of the resulting metal chelate [303].

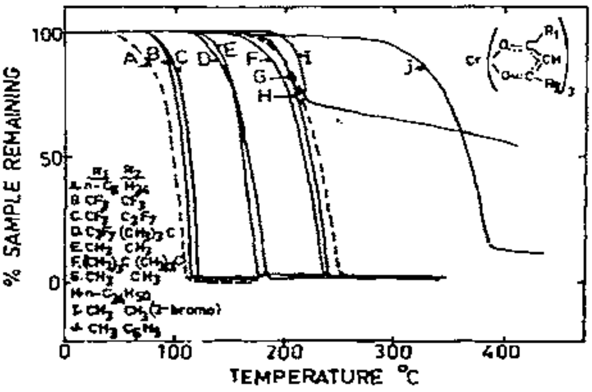


Fig. 36. Thermogravimetric curves of Cr(III)β-diketonates.

Figure 37 shows the thermograms of a series of tris-aluminium chelates of a variety of 1,3-diketone ligands. It is again important to notice the increased volatility of the tris-aluminium chelates with increased fluorine substitution in the chelate ligand. The order of volatility seems to be $Al(hfac)_3 > Al(hfac)_2(acac) > Al(hfac)(acac)_2 > Al(tfac)_3 > Al(fod)_3 >> Al(acac)_3 > Al(thd)_3$. This is in general agreement with the empirical rule that increasing the extent of fluorine substitution in the ligand shell increases the volatility of the metal complex. Eisentraut and Sievers [303] reported that the Fe(III) chelates are more volatile than the corresponding Rh(III) chelates containing the same fluorinated ligand.

With respect to the thermograms of fod complexes of $Al(fod)_3$, $Pd(fod)_2$, $Cu(fod)_2$, $Fe(fod)_3$ and $Ni(fod)_2 \cdot 2\,H_2O$ the complexes of Al(III), Pd(II), Fe(III) and Cu(II) are vaporized quantitatively, at relatively low temperature, in helium stream and only $Ni(fod)_2 \cdot 2\,H_2O$, left any residue [30].

The monothiotrifluoroacetylacetonates [163] display greater volatility and thermal stability than the analogous monothioacetylacetonates [310]. It has been observed that $Zn(ttfa)_2$, $Co(ttfa)_2$ and $Ni(ttfa)_2$ are completely volatile, while $Pd(ttfa)_2$ and $Pt(ttfa)_2$ show volatility up to 85 and 65%, respectively (Fig. 38). Similarly, the examination of the thermograms of nickel(II)bis-monothiofluorinated 1,3-diketonates show complete volatilisation of all chelates, with $Ni(ttfa)_2$ displaying the greatest volatility, while $Ni(tamp)_2$ the least volatility [163].

Examination by differential scanning colorimetry (DSC) showed decomposition exotherms for $Pr(ttfa)_2$, $Pd(ttfa)_2$, $Zn(ttfa)_2$ and $Co(ttfa)_3$ at 205, 212, 195 and 208°C, respectively. In contrast DSC examination of $Ni(ttfa)_2$, $Ni(ttpm)_2$, $Ni(tapm)_2$, $Ni(ta)_2$, $Zn(ttfa)_2$, $Co(ttfa)_3$, $Pd(ttfa)_2$ and $Pd(ttfa)_2$, gave endothermic peaks, corresponding to the melting points of the chelates [163].

The thermograms of $Pb(hpm)_2$, $Pb(tpm)_2$ and $Pb(ppm)_2$ at various heating rates have been recorded by Belcher et al. [162] and noted that $Pb(hpm)_2$ is the most volatile chelate of the series. They also studied the thermograms of

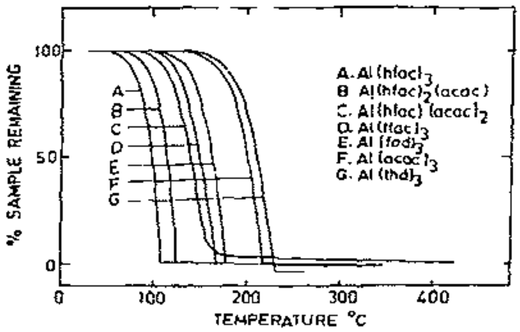


Fig. 37. Thermogravimetric curves of some volatile Al(III)β-diketonates.

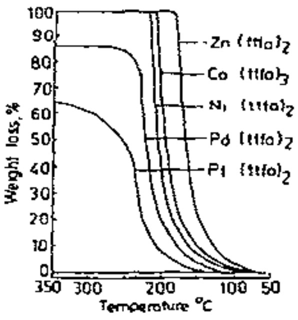


Fig. 38. Thermograms of monothiotrifluoroacetylacetonates.

alkaline earth chelates and concluded that for each ligand, there is a significant difference in volatility.

Considering [259,260] the thermograms of H(pta) complexes of the rare earths (e.g., Nd, Sm, Eu, Tb, Dy, Er, Yb and Lu, and Sc and Y) chelates of smaller metal ions, which show a shorter retention time, are volatilized at lower temperatures. The weight losses of all the chelates, except the neodymium chelate, approach 100%.

Utsunomiya [258] examined the thermograms of aluminium, gallium and indium fluorinated 1,3-diketonates (Fig. 39). The aluminium-1,3-diketonates are volatile and are thermally stable, The volatility increases in the following order: for fluorinated 1,3-diketone chelates, $Al(tta)_3 \leqslant Al(btfa)_3 < Al(fta)_3 << Al(tivm)_3 < Al(tmbm)_3 < Al(tpm)_3 < Al(tibm)_3 \leqslant Al(tprm)_3 \leqslant Al(tfac)_3 << Al(hfac)_3$. Gallium(III)-1,3-diketonates do not completely sublime. The volatility increases in the order: $Ga(tta)_3 < Ga(btfa)_3 < Ga(tfa)_3 << Ga(tivm)_3 < Ga(tmbm)_3 < Ga(tprm)_3 < Ga(tpm)_3 < Ga(tibm)_3 < Ga(tfac)_3 << Ga(hfac)_3$. Many of the indium(III) chelates do not quantitatively sublime, and the increasing order of the volatility is as follows: $In(tta)_3 < In(btfa)_3 < In(fta)_3 << In(tivm)_3 < In(tmbm)_3 < In(tprm)_3 < In(tfac)_3 < In(tpm)_3 < In(tibm)_3$.

The substitution of the fluoromethyl group increases the volatility of the chelates, while an aryl group, such as a furyl, phenyl or thienyl group, tends to decrease the volatility. In case of alkyl substitution, there is no good correlation but the volatility of some of the indium chelates does seem to increase in the following order:

$CH_3{-} < (CH_3)_2CH{-} < (CH_3)_3C{-}$

Recently, Burgett and Fritz [286,287] examined the mixed ligand complexes $RE(fhd)_3 \cdot 2$ DBSO of the yttrium and cerium group lanthanides (Fig. 40) and results indicate complete volatilization without decomposition. Exam-

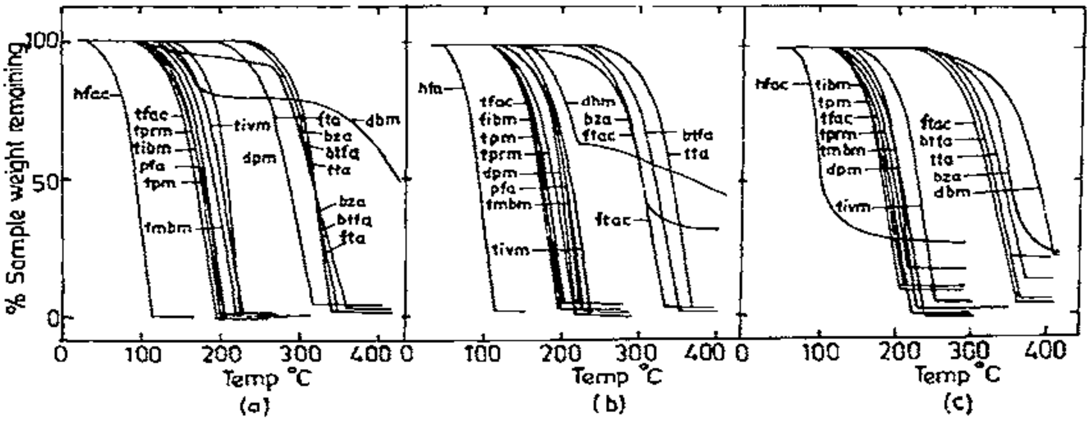


Fig. 39. Thermogravimetric curves of (a) aluminium 1,3-diketonates; (b) gallium 1,3-diketonates; (c) indium 1,3-diketonates.

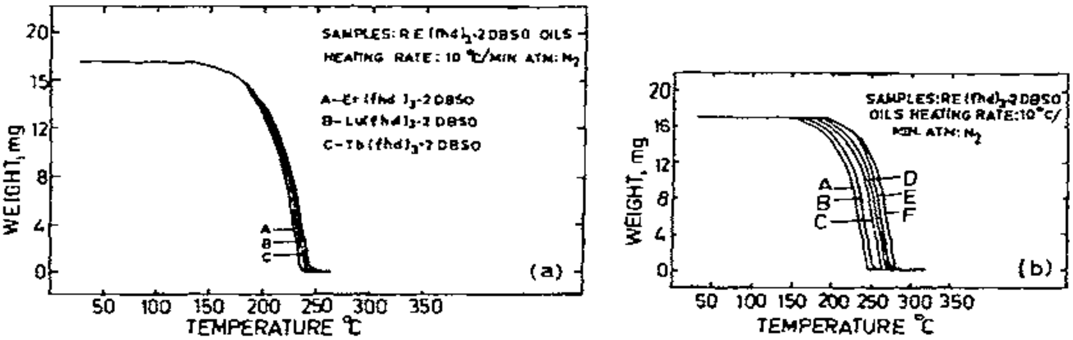


Fig. 40. (a) Thermograms of mixed ligand complexes of the lanthanides with the H(fhd)-DBSO system. (b) TG curves for mixed ligand complexes of the lanthanides with H(fhd) and DBSO. A, Eu(fhd)$_3$ · 2 DBSO; B, Sm(fhd)$_3$ · 2 DBSO; C, Nd(fhd)$_3$ · 2 DBSO; D, Pr-(fhd)$_3$ · 2 DBSO; E, Ce(fhd)$_3$ · 2 DBSO; F, La(fhd)$_3$ · 2 DBSO.

ination of the temperature at the mid-point of weight loss shows significant differences in volatility for the mixed-ligand complexes with DBSO. The heavier rare earths were found to be volatilized at lower temperature than their lighter neighbours. They have also reported TGA of Fe(II), Co(II) and Ni(II) chelates having composition, M(fhd)$_2$ · 2 DBSO [285].

Belcher et al. [292] examined the thermograms of Cu(II)-1,3-diketonates, bidentate and tetradentate 1,3-ketoamine chelates, and Ni(II) monothio-1,3-diketonates, bidentate and tetradentate 1,3-ketoamine chelates and concluded that all chelates sublime completely, including even hydrates and polymers. For Cu(II) chelates, in the case of bis-dentate species, fluorinated complexes exhibit higher volatility than their non-fluorinated analogues. In contrast, this trend is somewhat surprisingly reversed, for the tetradentate chelates. For the nickel(II) complexes, fluorinated monothio-1,3-diketonates and 1,3-ketoamine chelates, are the most volatile, followed by their non-fluorinated analogues, respectively; the tetradentate chelates are less volatile and exhibit the same volatility reversal as the copper species. From thermal data, it is predicted that Cu(hpm)$_2$ (also known as Cu(fod)$_2$), is the preferred complex for Cu determination. Similarly, Ni(ttfa)$_2$ is preferred for nickel.

Richardson and Sievers [118] studied the thermal stability and volatility of tris and tetrakis chelates of fluorinated 1,3-diketones. The TGA data show that the rare earth tris-dfhd chelates are quite volatile. Only the lighter rare earth chelates (La, Pr, Nd) decompose to any considerable extent. The small degree of decomposition for the dfhd chelates contrasts greatly with that for the hfac chelates Ln(hfac) · 2 H_2O, where decomposition is extensive even at the heavy end of the series. An expected phenomenon observed by many workers is the generally high volatility and thermal stability of rare earth tetrakis chelates. The hfac and dfhd chelates are no exception. *Particularly striking* is the complete lack of decomposition of $(NH_4)Ln(hfac)_4$, (Ln = Sm—Lu) and $(pyH)Ln(hfac)_4$, (Ln = Pr—Lu) as compared to the high thermal instability of

Ln(hfac)$_3$ · 2 H_2O. None of the tetrakis-dfhd chelates showed decomposition.

Recently, Uden and Blessel [266] examined the thermograms of isomeric mixtures, meso (green) and racemic (purple) forms of Cu[bn(tfac)$_2$]. The purple isomer is more volatile than the green.

J. SOLVENT EXTRACTION STUDIES OF METAL 1,3-DIKETONATES

A number of authors have reported solvent extraction of the metals with fluorinated β-diketones [311—313]. In some cases, pure β-diketones alone are used as both the chelating ligand and the non-aqueous solvent [314—316]. The earlier extensive work of Freiser [314], on extraction of several elements with H(acac), has indicated optimum pH for the complete extraction of each element. Stary [311] reported a wide-ranging survey of solvent extraction of metals with H(acac). Substitution of CF_3 group increases the volatility of metal chelates and also permits extraction even from considerably acidic medium [317—319]. Recently, De et al. [320] exhaustively reviewed the solvent extraction of metals with β-diketones.

An efficient extraction of Cu, Fe and Al with H(tfac) from aqueous medium (pH, 4.5—5.5; acetate buffered) into chloroform has been reported by Scribner et al. [321]. Fe is also extracted at lower pH value, but the efficiency of extraction is a function of pH and equilibrium time. Mn, Ni, Zn and Mg are poorly extracted with H(tfac) and chloroform (1—3%; acetate buffered solution). The practical application of solvent extractions has been established by analysing the metals in National Bureau of Standards Samples (nickel—copper alloy; NBS 162a).

Morie and Sweet [267] studied the solvent extraction of Al, Gd and In with H(tfac) into benzene. The stability of metal chelates usually varies inversely with the acidity constant of the ligand [322], while the reagent anion concentration, at a given pH, is higher for the more acidic reagent. Extraction occurs at a lower pH with H(tfac) as compared to H(acac) [323]. Similarly, H(tfac) has also been used for the solvent extraction of plutonium(IV) and zirconium(IV) [324].

Sweet and Parlett [325] examined the solvent extraction of some lanthanides with H(thd) and observed 100% extraction from a pH of about 7.0—12.5. The stability of the lanthanide chelates of H(thd) is greater than those of corresponding acetylacetonates and benzoylacetonates [312]. This extra stability of the thd chelates is ascribed to steric hindrance of bulky *t*-butyl groups, which prevents hydrate formation by blocking the coordination sites [326]. In contrast to this, Brown et al. [327] observed poor extraction of lanthanides (28% Nd, 49% Tb and 84% Yb) with H(acac), due to hydrate formation of lanthanide chelates.

Ni, Co, Cu, Zn, Cd and Pd have been extracted (99.9%) with chloroform containing H(tfac) and isobutylamine (IBA) at pH $\simeq$9. It has also been noticed that in the absence of IBA, Ni, Zn, Cd and Co are not efficiently extracted with chloroform H(tfac), due to the presence of coordinated water.

Addition of IBA to the system results in preferential formation of IBA adducts (confirmed by IR spectra) which are more readily extracted with chloroform [328].

It has also been observed that "the metal ions, with a coordination number greater than twice the charge, will on reaction with bidentate agents (such as 1,3-diketones) satisfy the coordination requirement via hydrate formation, solvate formation or adduct formation" [328,329]. Hydrate formation decreases the efficiency of solvent extraction (with halohydrocarbon), while solvate formation, or adduct formation enhance solvent extraction [329].

The separation of ^{95}Zr and ^{95}Nb has been achieved [318] by solvent extraction using H(tfac) and H(btfa) as a chelating agent. The synergistic effect of many kinds of oxygen- and nitrogen-containing solvents on the extraction of europium ions with H(btfa) in *n*-hexane has also been studied [319]. The addition of alcohols, esters, ketones, amines and heterocyclic compounds enhances the extraction, and in general, the solvents with longer carbon chain, especially alcohols and amines, have larger synergistic effects. The coordination of nitrogen-containing Lewis bases to the chelates is stronger than that of oxygen-containing bases. Since the solvent extraction of neodymium and lutetium ions with fluorinated 1,3-diketones is as good as that of europium ions, it is a favourable procedure for the extraction of rare earth ions.

The synergistic effects of *n*-Hex, TBP and TOPO on the extraction of rare earth ions with H(btfa) in benzene have been studied by Shigematsu et al. [330,331]. As the ionic radius increases, the stability of rare earth benzoyltrifluoroacetonates decreases and that of the adducts increases. Although the overall stability constant of the adduct increases in the following order; lutetium < terbium < europium < lanthanum, as mentioned above, the first stability constant does not show such a distinct sequence. Therefore, the contribution of the second stability constant seems to be an important factor. The extraction constant of the chelates increases with a rise in the temperature. The extraction constant is expressed as [332]

$$K = \frac{[\mathrm{MR_3}]_{(\mathrm{org})}[\mathrm{H^+}]^3_{(\mathrm{aqu})}}{[\mathrm{M^{3+}}]_{(\mathrm{aqu})}[\mathrm{HR}]^3_{(\mathrm{org})}} \qquad (36)$$

In case of an extraction equilibrium of the type

$$\mathrm{M^{3+}}_{(\mathrm{aqu})} + 3\ \mathrm{HR}_{(\mathrm{org})} \rightleftharpoons \mathrm{MR}_{3(\mathrm{org})} + 3\ \mathrm{H^+}_{(\mathrm{aqu})} \qquad (37)$$

where M^{3+} is a trivalent metal ion, HR is a β-diketone and MR_3 is the neutral chelate extracted.

The influence of the terminals of fluorinated and non-fluorinated 1,3-diketones on the synergistic effect has been studied for the metal 1,3-diketone-TOPO system [333,334] and the following increasing sequence observed.

alkyl < aryl < fluorine containing group. (38)

The CF_3 group strongly enhanced the ability to interact with a further ligand such as TOPO [334,335]. The extractions have also been enhanced by adduct formation with carboxylic acids [336].

The influence of organic Lewis bases on the solvent extraction of Eu(III), Zn(II) and Co(II) by H(btfa) into benzene has been studied in great detail [337,338], and the stability of adducts with oxygen containing bases noted as follows [337]

$$n\text{-Hex} < \text{TBP} < \text{TBPO} \simeq \text{TOPO} \tag{39}$$

The stability of nitrogen compounds is as follows [337]

$$\text{quinaldine} < \text{acridine} < \text{quinoline} < \text{lepidine} < \text{isoquinoline} \tag{40}$$

The stability constant of the monooxide adducts increases in the following order [338]

$$\text{TPPO} < \text{TPAsO} \simeq \text{TOPO} \tag{41}$$

and the synergistic effect of neutral ligand on the zinc chelate system increases in following order [338]

$$\text{TPPO} < \text{EBDPO} < \text{MBDPO} < \text{TOPO} \tag{42}$$

A striking synergistic effect has been observed in the presence of α,α'-dipyridyl and *o*-phenanthroline, on the extraction of zinc with H(pta) [339].

New analytical applications of H(stta) have been developed [340–343]. A sensitive and selective method has been developed for the determination of minute amounts of cobalt [340]. The separation of Hg(III), Co(II) and Zn(II) has been effected by extraction chromatography [341] and of Ni(II) and Co(II) by the back-extraction process [342]. Extraction of trace amounts of various metal ions has been done in the presence or absence of TOPO [343].

Recently, the synergic solvent extraction of Fe(II), Co(II), Ni(II), Cu(II) and Pb(II) with H(fhd) and DBSO has been described by Burgett [344]. The synergistic effect of H(acac), in the extraction of rare earth chelates, $M(ttfa)_3$, is attributed to the formation of $M(ttfa)_3 \cdot H(acac)$ [345].

The solvent extraction of Co(II) with H(tta) into benzene (from acetate buffer) in the presence of alcohol (*n*-Hex, 2-E-Hex, *S*-Hex, Cy-Hex and BG) has been reported. The compositions of extracted species are $Co(tta)_2 \cdot S$ and $Co(tta)_2 \cdot S_2$ (S = alcohol) [346].

Tomazic and O'Laughlin [347] studied the partition of H(hfac) in the system: water–TBP–organic solvent and the extraction of sodium by fluorinated β-diketones e.g., H(hfac), H(fod), H(dodefod). They noticed a strong interaction between fluorinated β-diketone and TBP (confirmed by IR spectral studies). The extraction of sodium with these fluorinated β-diketones is greater than with H(acac) or H(tfac) [348].

The fluorometric determination of europium and samarium in the *o*-phenanthroline H(tta) system [349] and that of europium in the H(tta)-TOPO system were investigated [350].

Similar observations have been noted in the determination of europium as the H(btfa)-TOPO system [351]. The use of low concentrations of H(ntfa) for determination of Eu(III) and Sm(III) [352] has also been examined (pH = 5.5—6.5).

Methods for extraction, separation and photometric determination of uranium have been developed [317,353—355] using H(acac) [353], H(dbm) [354], H(tfac) [355] and H(btfa) [317,320]. Quantitative extraction with H(btfa) has been achieved at a lower pH range [356]. The solvent extraction—spectrophotometric determination of Pb(II) [357], Cu(II) [358], Pd(II) [359], Hg(II) [360] and V(IV) [361] with H(stta) has also been described. Recently Uhlemann et al. [362—365] demonstrated the application of thiodibenzoylmethane in extraction and photometric determination of traces of Cu(II) [362], Cd(II) [365], Ni(II) [363], Co(II) [363], Hg(II) [364] and Tl(II) [364].

Generally, the chelates of the rare earths form hydrates which are poorly extracted. Ferrano and Healy [366] found that an organic base such as TBP would displace the hydrated water and act as a synergist for extraction of rare earths. The successful extraction of lanthanide by using synergistic extraction systems of fluorinated 1,3-diketones (H(tfac), H(hfac), H(fod), H(fhd), H(dodefod) and H(dfhd)) and various neutral donors (TBM, TFEB and PEPP has been reported [367]. Butts and Banks [368] initially reported the use of these mixed-ligand systems for gas chromatography, and a detailed study demonstrating the chromatographic behaviour of several mixed ligand systems has been completed [369].

K. LASER CHELATES

Since Urbain's work [1] on the rare earth 1,3-diketonates, the chemistry of such compounds has assumed considerable importance because of their practical use as potential laser materials. The first laser action from europium benzoylacetonate at 6130 Å was reported by Lempicki and Samelson [370] and Schimitschek [371].

Halverson et al. [372] prepared tris-europium hexafluoroacetylacetonate and obtained luminescence spectra in ethanol—methanol (3 : 1) solution. They noted that the presence of moisture has a marked effect on the spectral appearance of luminescence near 6100 Å; it does not appear to influence the long-lived phosphorescence near 4500 Å.

Bhaumik et al. [373] prepared the dihydrate of europium benzoylacetonate by the aqueous method [374,375]. This material, however, showed no evidence for laser oscillation. But when Bhaumik et al. [373] prepared europium benzoylacetonate by Crosby and Whan's non-aqueous method [374] (or piperidinium method), the products obtained were of varying melting points and of stoichiometric composition and yielded laser emission from alcohol solution. An empirical formula for this crystalline compound has been proposed, $Eu(bza)_4 \cdot HP$ (where P = piperidine), which indicates a new chemical adduct of europium tris-benzoylacetonate with one molecule of benzylacetone and one molecule of piperidine. Laser activity of this compound in methanol—ethanol (3 : 1) has been demonstrated and a characteristic intense Eu^{3+} red luminescence (consisting of two strong lines in the 6130 and 6140 Å region) has also been observed. As is well known, these arise from the transition $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+}. There has also been prepared [273] a series of europium tetrakis-benzoylacetonate $Eu(bza)_4 \cdot HP$, $Eu(bza)_4 \cdot HM$ and $Eu(bza)_4 \cdot HD$; (where P = piperidine, M = morpholine and D = dimethylamine); the emitting chelate species in alcohol solution is the same in all three cases. This was explained by postulating that the ionization of the chelate in alcohol solution produced an emitting chelate ion $[Eu(bza)_4]^-$, and the species HP^+, HM^+ or HD^+ respectively. Subsequently, this work [373,376] has been supported by a number of workers [377—380], and all of them are agreed that laser emission arises only from the tetrakis-europium 1,3-diketonates while tris-europium 1,3-diketonates do not lase. It may be noted that earlier workers [370,371, 381,382] have not characterized their rare earth 1,3-diketonates, either by chemical and/or by spectroscopic methods.

Schimitschek et al. [383] prepared a series of europium tetrakis-1,3-diketonates, e.g., $Eu(tta)_4 \cdot HD$, $Eu(tfac)_4 \cdot HNR_3$ and $Eu(btfa)_4 \cdot HI$ (I = imidazole) and presented data on laser action in acetonitrile. They demonstrated stable laser liquid operation at about —150°C.

A series of europium tetrakis 1,3-diketonates has been prepared [324]. UV radiation, absorbed by the europium ion in europium 1,3-diketonate, is efficiently converted via intramolecular energy transfer to fluorescence characteristic of Eu^{3+}. The effect of various substituents (R') on the chelate laser emission has also been discussed, and maximum laser yields are obtained when (R) is a trifluoromethyl (CF_3) group [384]. Riedel and Charles [37,385] also prepared a series of europium-1,3-diketonates (Fig. 41) and examined the following changes on the fluorescence: (i) R is varied and Q is maintained constant [37] and (ii) Q is varied and R is maintained constant [385]. All the chelates, both as solid and in acetonitrile solution, showed strong room temperature orange-red fluorescence characteristic of Eu^{3+} when irradiated with UV light. The room temperature fluorosecence intensity of the solid varied appreciably from compound to compound.

Blance et al. [386] and Melby et al. [36] prepared rare earth 1,3-diketonates complexed with 1,10-phenanthroline and α,α'-dipyridyl. Rao et al. [387—389] prepared a series of lanthanide-1,3-diketonates (Ln = Eu^{3+}, Sm^{3+}, Tb^{3+}), viz: (i) mixed ligand complexes containing 1,3-diketone and the acetate

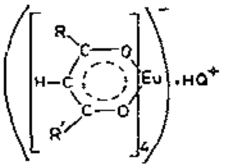


Fig. 41. R = CF_3; R' = ph, 1-naphthyl, 2-naphthyl, 4-MeO · C_6H_4, 2-MeO · C_6H_4, 2,5-$(MeO)_2$ · C_6H_4, 4-biphenyl 2-fluorenyl, 3-phenanthryl and 4-F · C_6H_4.

anion, (ii) 1,3-diketonate complexed with nitrogen donors such as 1,10-phenanthroline and α,α'-dipyridyl, (iii) 1,3-diketonate complexed with Lewis bases. The absorption and fluorescence emission spectra have also been examined. The most intense fluorescence band in Tb^{3+} chelate corresponds to $^5D_4 \rightarrow {}^7F_5$ transition. Weaker transitions from $^5D_3 \rightarrow {}^7F_J$ levels ($J = 6$, 5 and 4) have also been noted. The emission spectra of all the Sm^{3+} complexes consist of 9 groups of lines arising from transition from any one of the three resonance levels, $^4G_{7/2}$, $^4F_{3/2}$ or $^4G_{5/2}$ to the various J levels of the ground state, the three levels being excited by energy transfer.

A series of α-active actinide (An^{3+}) 1,3-diketonates has been prepared [390], namely, the hexafluoroacetylacetonate chelates, $CsAn(hfac)_4 \cdot H_2O$ (with the An^{3+} ions = $^{241}Am^{3+}$, $^{243}Am^{3+}$, $^{244}Cm^{3+}$, $^{249}Bk^{3+}$, $^{247}Cf^{3+}$ and $^{253}Es^{3+}$), and the UV excited and the α-activity-self excited optical emission at room temperature examined. It has been concluded that UV excited sharp-line sensitized luminescence (SLSL) studies are feasible on Cm^{3+}-1,3-diketonate chelates and that these spectra resemble those of Eu^{3+}-1,3-diketonate chelates in emission wavelength and efficiency. An important difference between the emission characteristics of the Cm^{3+} and Eu^{3+} chelates is the simplicity of the SLSL spectra of the former. The simplicity arises because the position and spacing of the $5f^7$ electronic energy levels of Cm^{3+} are such that only one set of transitions ($J = \frac{7}{2} \rightarrow J = \frac{7}{2}$) occur in the SLSL process, while on the other hand, in the case of Eu^{3+}, transitions occur from both the $^5D_1$ and $^5D_2$ states to all six states of the ^7F multiplet. A comparison of the important parameters for a liquid laser are given in Table 11.

TABLE 11

Parameters for liquid laser evaluation [a]

Parameter	10^{-3} M $CmCl_3$ and 10^{-3}M $CsTb(hfac)_4$ in anhydrous ethanol	10^{-3} M $CsEu(hfac)_4$ in anhydrous ethanol.	5×10^{-3} M $Eu(btfa)_4 \cdot H^+$ Pyrr. in acetonitrile
Emission wavelength λ (A)	6040	6140	6118
Line width at half-maximum intensity Δλ (Å)	80	40	≃40
Quantum efficiency ϕ (%)	7	15(19 for 10^2 M)	≃50
(1/*e*) decay time (*T*)(s)	120	400	≃600

[a] $H.^+$ Pyrr = pyrrolidinium ion

Measurements [391] of the relative fluorescence output of mixed crystals of the type, (Eu, Gd)(btfa)$_4$(pipH), indicate the occurrence of efficient intermolecular energy transfer. Experimental data suggest energy migration occurs via the ligand exciton band with the Eu^{3+} ion acting as a trap. Investigations of crystals of type (Eu, Nd, Gd)(btfa)$_4$(pipH) have given results consistent with this interpretation. In these crystals the Nd^{3+} acts as a second exciton trap and, in addition, evidence of direct transfer of energy from excited Eu^{3+} to Nd^{3+} ion has been obtained.

Brown and Shepherd [38] prepared two series of terbium(III) complexes, e.g. Tb(hfac)$_2$ · 2 H$_2$O, Tb(hfac)$_4$ · Q (Q = pipH$^+$, NH$_4^+$, Ph$_4$As$^+$, Me$_2$NH$^+$, *t*-BuNH$_3$$^+$, (pipH)(pic)), Tb(tfac)$_3$ · 2 H$_2$O, Tb(tfac)$_4$Q (Q = pipH$^+$, NH$_4^+$, Ph$_4$As$^+$, Na$^+$, K$^+$, Cs$^+$), and examined the factors affecting the quantum efficiencies of fluorescence of the above chelates in the solid state. They established that the temperature-dependence of the $^5D_4$ life time is caused by thermal depopulation of the ion level to a ligand triplet state.

Thirty-three new tetrakis rare earth chelate salts of the type: piperidinium$^+$-[(ArCOCHCOR)$_4$M]$^-$ (where, Ar = fluorophenyl or substituted fluorophenyl, R = alkyl, aryl or perfluoromethyl and M = La^{3+}, Pr^{3+}, Nd^{3+} and Eu^{3+}) have been prepared [123]. Some of these complexes have been examined for their fluorescence in the solid state at 77K. In case of europium chelates, $^5D_0 \to {}^7F_0$, $^5D_0 \to {}^7F_1$, $^5D_0 \to {}^7F_2$, $^5D_0 \to {}^7F_3$, $^5D_0 \to {}^7F_4$, $^5D_1 \to {}^7F_1$, $^5D_1 \to {}^7F_2$, $^5D_1 \to {}^7F_3$, $^5D_2 \to {}^7F_4$, $^5D_2 \to {}^7F_5$ and $^5D_2 \to {}^7F_6$ transitions have been observed. The $^5D_0 \to {}^7F_2$ (at 6170 Å) group is by far the most intense, accounting for approximately 95% of the total emission in all europium chelates. It may be noted that this is the first case of piperidinium tetrakis-europium-1,3-diketonates in which the $^5D_2$ level has been observed to fluoresce. The results confirmed that fluorine substitution increases fluorescence intensity due to decreased vibration energy. The enhanced fluorescence intensity may be partly due to the strong negative inductive effect of the trifluoromethyl group increasing the covalent nature of the europium—oxygen bond, which in turn increases the efficiency of the intramolecular energy transfer from the triplet state to the Eu^{3+} ion [123,392,393].

Mechanism. The earlier work of Weissman [394] supported by Sevchenko and Trofirmov [395] indicated that excitation of a metal complex in the region of light absorption, associated primarily with the ligands of the complex, resulted in a high yield of line emission characteristic of the metal ion. Crosby et al. [396,397] studied the path of energy migration in rare earth chelates and categorized the luminescence of the rare earth chelates involved in five groups [398].

1. Luminescence of rare earth chelates due to total molecular band emission and to not having low lying ^4F energy levels, e.g., chelates of La^{3+}, Gd^{3+} and Lu^{3+}.
2. Luminescence of rare earth chelates consisting of strong line emission, e.g. Eu^{3+}, Tb^{3+} and Dy^{3+} chelates.

3. Combination of band and line emission with line predominating, e.g. Sm^{3+} chelates.

4. Combination of both band and line emission of comparable intensity, e.g. chelates of Tb^{3+}.

5. Combination of band and line emission with band predominating, e.g. Yb^{3+} chelates.

The following steps sum up the basic mechanism of the IMET process as involved in rare earth complexes (Fig. 42).

(i) $(S_{\mathrm{lig}} \to S^*_{\mathrm{lig}})$: Absorption of the UV radiation by the organic moiety of the rare earth 1,3-diketonate excites the singlet (S_{lig}) state to the first excited singlet (S^*_{lig}).

(ii) $(S^*_{\mathrm{lig}} \rightsquigarrow T)$: This radiationless inter-system crossing of energy from S^*_{lig} to the triplet (T) is the most important factor for the IMET mechanism and is markedly influenced by the nature of the ligand.

(iii) $(T \rightsquigarrow {}^4f)$: By transferring energy from the donor triplet state (T) to the ${}^4f$ acceptor level (resonance level) via a radiationless process, the organic moiety (ligand) goes back to the ground state while indirectly exciting the coordinated metal ion. It has been noted that line emission requirements for a given chelate are the lowest triplet state energy level of the chelate being nearly equal to or lying just above the resonance level of the rare earth ion.

(iv) $(f \to f)$: At this final stage, a radiative transition, if occurring, within the rare earth ion states gives rise to characteristic line emission.

Kleinerman [399] proposed a second intramolecular mechanism involving the direct transfer of energy from S_1 to RE ion ($S_1 \longrightarrow$ RE level → emission).

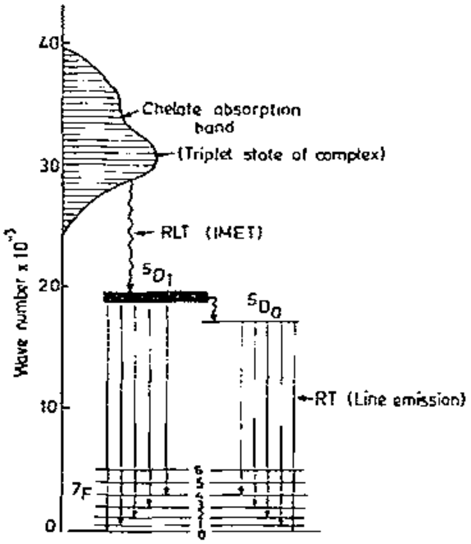


Fig. 42. A schematic representation of the intramolecular energy transfer (IMET) process in Eu^{3+} complex. RLT = Radiationless transition; RT = Radiative transition.

Later on a third intramolecular mechanism was proposed [400]. In this, the energy is transferred from S_1 to an upper intermediate RE level and is then transferred back to T_1 and returns to a lower RE level ($S_1 \rightarrow$ RE level higher than $T_1 \rightsquigarrow T_1 \rightsquigarrow$ RE level lower than T_1 emission).

In 1970, Tanaka et al. [401] prepared tetrakis-europium, terbium chelates of fluorinated β-diketones (H(btfa), H(tta), H(ntfa), and H(bzdtf)) and examined the detailed fluorescence mechanism. They concluded, on the basis of experimental data, that the intramolecular energy transfer occurs by means of the mechanism I, proposed by Crosby et al. [396,397].

Very recently, it was shown [391] that efficient intermolecular energy transfer also occurs in the crystals of (Eu, Gd)(btfa)$_4$ complexes with cations such as Et_3NH^+, $BuNH_3^+$ and $C_6H_{10}NH_3^+$.

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ADDENDUM

Since this review was submitted, a number of significant papers have appeared and the following references are listed, so as to make the review as current as possible.

1 Dipole-moment measurements of metal chelates Part II: dipole-moment of nickel(II), palladium(II), platinum(II) and cobalt(III) complexes of six fluorinated mercapto-β-diketonates. M. Das and S.E. Livingstone, J.C.S. Dalton, (1975) 452.

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3 Derivatives of divalent germanium, tin and lead part V: bis(pentane-2,4-dionato)-bis-(1,1,1-trifluoropentane-2,4-dionato)-, and bis(1,1,1,5,5,5-hexafluoro-pentane-2,4-dionato)tin(II), P.F.R. Ewings, P.G. Harrison and D.E. Fenton, J. Dalton, (1975) 821.

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