The lanthanide complexes have been studied with various aims and objects. Most of the complexes were synthesised and characterized with a view to adding to our knowledge of these comparatively unfamiliar elements. Since the isolation of individual lanthanides was cumbersome, attempts were made to prepare lanthanide complexes so as to use them for the separation of the individual members. Recently a number of complexes have been prepared and an attempt has been made to scan them for their use as pseudo-contact n.m.r. shift reagents in the simplification of n.m.r. spectra of complex organic molecules.

Eisentraut and Sievers \(^1\) synthesised and characterized volatile chelates of trivalent rare-earths and separated mixtures of the complexes by gas-chromatography. The ligand employed was 2,2,6,6-tetramethyl 3,5-heptane dione also called dipivaloyl methane and abbreviated as dpm. The chelates are thermally stable, anhydrous, unsolvated and monomeric. One of the objectives of this study was to separate rare-earth complexes by gas chromatography. Gas chromatography of each complex in benzene solution at 200\(^{\circ}\)C showed a single peak well
separated from the effluent carrier gas stream and were shown to have been eluted without decomposition by comparison of melting points, u.v., and visible spectra with those of each complex before injection. There appear to be appreciable and significant differences in the volatilities of the rare-earth complexes as indicated by sublimation and retention data. The volatility of the complexes appears to decrease as the size of the metal ion increases. In view of the success of these studies Berg and Acosta² reinvestigated the volatile character of the β-diketone chelates of the lanthanides and a few closely related elements. They synthesised the complexes of acetyl acetone, trifluoroacetylacetone, hexafluoroacetylacetone and dipivaloylmethane. They found that the chelate stability and volatility increased with an increase in the degree of fluorination of the ligand and an increase in the spherical nature of the chelate. The studies reported here have extended the knowledge of the lanthanides and related elements and suggested possible new approaches for separating the mixtures of the elements.

Springer, Meek and Sievers³ also prepared the lanthanide chelates of 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl 4,6-octane dione (H(fod)) as tris(fod)monohydrates. The trend of lower
retention time with decreasing ionic radius, first reported by Eisentraut and Sievers\textsuperscript{1} was reaffirmed with the (fod) complexes chromatographically. The retention data could not be correlated with the mass of the complex. The(fod) rare-earth complexes are the most volatile complexes. The fluoro-carbon substitution in the ligand shell markedly increases the volatilities of the complexes over those of compounds containing a similar non-fluorinated ligands. An interesting effect is the correlation between lanthanide contraction and the volatilities of the tris(fod) chelates as evidenced by the retention data. One possible explanation may be to assume that the position of the possible monomer polymer equilibria would vary with ionic radius and cause the observed trend in volatility.

A few years back, it was found that tris/β-diketone complexes of lanthanides are the best shift reagents as they are air stable, soluble in organic solvents and are known to expand their coordination number by acquiring ligands with lone pairs.

Hinckley\textsuperscript{4} observed the pmr spectra of cholesterol and the Eu(dpm)\textsubscript{3}-2py-cholesterol in carbon tetrachloride as solvent. In the spectra he observed that there is very little brodening and there are substantial shifts of resonance peaks. Narrow pmr lines may be expected for solutions containing complexes
of all the rare earths with the exception of gadolinium having a high electron relaxation time, which causes broadening at normal temperatures. The observed paramagnetic shifts are the direct consequence of bonding between the metal complex and cholesterol. There are no pmr absorptions in the cholesterol region of the spectrum due to the metal complex or free pyridine. In the spectrum of cholesterol Eu(dpm)$_3$2py sizable shifts are observed for the vinyl proton and proton nearest the hydroxyl group, which indicate association through the hydroxyl group. Shifts for protons close to the point of association are larger than those for protons further removed. Sanders and Williams$^5$ reported that Eu(dpm)$_3$ is also a good shift reagent and actually better than Eu(dpm)$_3$2py. Briggs$^6$ et al reported that praseodymium complex of dpm shows shifts, which compared with the corresponding europium compounds are usually reversed in direction and about triple in magnitude. They found that Pr(dpm)$_3$ added to a carbon tetrachloride solution of n-pentanol induces a high field shift in the peaks of n-pentanol. The capacity of producing shifts in either direction at will, by the use of Pr$^{3+}$ or Eu$^{3+}$ complex, must greatly increase the utility of the method.

Various workers showed the use of the lanthanide induced shift reagents in the simplification of nmr spectra of different
Ahmad, Bhacca, Selbin and Wander showed the temperature dependence of shift reagents. During the investigation of this phenomenon, it was noted that these samples displayed substantial shifts of field position (of the order of several ppm, reversible on cooling) as the probe temperature was increased gradually to about 75°C. They suggested possible utility of reduced temperature determinations in cases where the limited solubility of the lanthanide complex is inadequate, or of variable temperature studies in lieu of measurements at a number of different relative concentrations.

Titanowski et al reported the properties of rare earth and actinide dpm chelates in order to find the most suitable shift reagent for nitrogen-14 n.m.r. resonance i.e. one which causes maximum chemical shift with minimum signal broadening. They made comparative studies of lanthanide and actinide dpm chelates on 14N n.m.r. spectrum of pyridine to show that Dy(dpm)₃ is by far the best high field shift reagent whilst Yb(dpm)₃ is the best low field shift reagent.

Recently Selbin, Ahmad and Bhacca have reported 47 compounds of rare earth dipivaloylmethane with pyridine, 1,10-phenanthroline, and 2,2′-dipyridyl of the types M(dpm)₃ where M=Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu,
$M(dpm)_3\text{py}$ ($M = \text{same 12 metals}$), $M(dpm)_3\text{dipy}$ ($M = \text{same first 11 metals except Lu}$), $M(dpm)_3\text{ophen}$ ($M = \text{same first 11 metals except Lu}$) and $\text{Ce(dpm)}_4$. These mixed ligand compounds are the first to contain the latter bidentate nitrogen donors complexed to tris(dipivaloyl-methanates).

The work described in this thesis involves the formation of the chelates of trivalent lanthanides (except Pr and Lu) with trifluoroacetylacetone (TFAA), dipivaloylmethane (dpm), and 1,1,1,2,2,3,3-heptafluoro, 7,7-dimethyl, 4,6-octane dione (HFOD), and the mixed ligand complexes of $\text{Ln(TFAA)}_3$ with dipyridyl and o-phenanthroline, $\text{Ln(dpm)}_3$ with pyrazole and imidazole and $\text{Ln(HFOD)}_3$ with o-phenanthroline.

The lanthanide(III) chlorides react with trifluoroacetylacetone ammonium salt forming tris-trifluoroacetylacetionates which are inner complex non-electrolytes, soluble in common organic solvents and produce mixed ligand complexes with 2,2'-dipyridyl and 1,10-phenanthroline enhancing the coordination number of the lanthanide ion from six to eight. This tendency to attain higher coordination number in the presence of a small ligand trifluoroacetylacetone is quite understandable. These mixed ligand complexes on the basis of the elemental analyses for carbon, hydrogen, and nitrogen have been assigned
the general formulae: \( \text{Ln(TFAA)}_3\text{dipy.}2\text{H}_2\text{O} \) and \( \text{Ln(TFAA)}_3\text{ophen} \) where \( \text{Ln} \) stands for a trivalent lanthanide ion (except \( \text{Pm} \) and \( \text{Lu} \)). In the preparation of these complexes it was observed that the synthesis of the complexes with heavier lanthanides was comparatively more laborious than those of the lighter ones. In the case of mixed ligand complexes, an explanation may be found in the fact that the chelates\(^{10}\) of the larger lanthanides ions are more highly associated than those of the smaller ions under the same conditions. The \( \text{tris(trifluoroacetylacetonates)} \) of lanthanides and their mixed ligand complexes with dipyridyl and \( \alpha \)-phenanthroline are quite stable and can be handled in air without any effect of air or moisture. They are insoluble in water and soluble in almost all organic solvents. Their molar conductances at \( 10^{-3}\text{M} \) dilution in dimethylsulphoxide are in the range of 19.5-39.25 ohm\(^{-1}\text{cm}^2\text{mole}^{-1} \), which indicates that these mixed ligand complexes are definitely non-electrolytes as is also apparent from their solubility in organic solvents, insolubility in water, and absence of any trace of a chloride ion in the fused mass of these complexes. The ranges of molar conductance at \( 10^{-3}\text{M} \) concentration in dimethylsulphoxide for 1:1, 2:1 and 3:1 electrolytes have been reported.\(^{11}\) The melting points of the \( \text{Ln(TFAA)}_3\cdot2\text{H}_2\text{O} \) are lower than those of their mixed ligand complexes with dipyridyl or \( \alpha \)-phenanthroline.
The Ln(TFAA)$_3$ being dihydrate must exist as discrete molecules and must not be polymeric. Hence they have melting points lower than those of the mixed chelates with bidentate dipyrildyl or o-phenanthroline. The corresponding chelates with o-phenanthroline show higher melting points than the chelates with dipyrildyl. This may be due to the presence of a rigidly planar, heavy and bulky molecule, the o-phenanthroline. In tris(trifluoroacetylacetone) o-phenanthroline the melting points increase from cerium to dysprosium (185°C to 214°C) and then decreases to ytterbium (200°C). In view of the good solubility of these mixed ligand complexes in organic solvents, not very high melting points and attainment of eight or higher coordination number, it may be assumed that they are not polymeric. The magnetic moments of the o-phenanthroline mixed ligand complexes show the usual unequal double hump when plotted versus the atomic numbers of the elements. The value of 2.20 B.M. for the Ce(TFAA)$_3$ophen shows that the cerium is still existing in the trivalent state and has not been oxidised as happens in the interaction of cerous chloride with the sodium salt of 2,2,6,6-tetramethyl, 3,5-heptane dione. The Ce(dpm)$_4$ was found to be diamagnetic. The Sm(TFAA)$_3$ophen is diamagnetic whereas the Sm(dpm)$_3$, Sm(dpm)$_3$py, Sm(dpm)$_3$dipy and Sm(dpm)$_3$ophen are paramagnetic with quite low values of 2.1, 2.4, 2.4 and 2.2 B.M.
respectively. Samarium has been shown to be diamagnetic by Farrel and Wallace\textsuperscript{12} in SmNi\textsubscript{2}. They found the moments of complexes lower than those of the free metal ions and observed that it might be due to partial quenching of the orbital angular momentum by crystalline field in the case of SmNi\textsubscript{2} and CeNi\textsubscript{2}. The maximum in this series (Ln(TFAA)\textsubscript{3}ophen) occurs at Dy, Ho and the minimum lies at Sm. Hodgson, Marks, Starks and Streitweiser\textsuperscript{13} have reported magnetic moments of 2.46, 3.47, 3.52, 1.58, 9.6 B.M. for the trivalent Ce, Pr, Nd, Sm, and Tb free ions and values of 1.88, 2.84, 2.98, 1.42 and 9.86 B.M. for KLn(C\textsubscript{8}H\textsubscript{8})\textsubscript{2} complexes respectively. The observed values reported are substantially lower than those usually encountered for Ln\textsuperscript{3+} species. Tsutsui and Ely\textsuperscript{14} using the values of their own complexes and comparing them with the theoretical values given by Vleck and Frank\textsuperscript{15} found a good agreement and repeated the explanation given by Friedman and others\textsuperscript{16} that there should not be much deviation from the theoretical values as the 4f orbitals seem to be quite well shielded and should be perturbed only slightly by ligand fields. We would say that a better theoretical understanding is needed before the magnetic moment discrepancies may be explained. The infra red spectra of the complexes have been discussed in detail. The Ln(TFAA)\textsubscript{3}2H\textsubscript{2}O complexes show absorptions at 1695, 1650, 1645, 1648, 1648, \textellipsis
1650, 1648, 1650, 1652 cm$^{-1}$ in Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Tm and Yb and also at 739, 739, 735, 740, 740, 740, 740, 740, 745, 750 and 750 cm$^{-1}$ in Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm and Yb respectively, which are due to coordinated water. Thus the Ln(TFAA)$_3$ dipy.2H$_2$O are ten coordinate complexes.

The tris(dipivaloylmethanates) of lanthanide(III) form 1:1 adducts with pyrazole and imidazole as indicated by their elemental analyses for carbon, hydrogen and nitrogen. The general formulae of the complexes are Ln(dpm)$_3$pyrazole where Ln=Y, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb and Ln(dpm)$_3$imidazole where Ln=Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb. The melting points of the series Ln(dpm)$_3$pyrazole are lower than those of the corresponding Ln(TFAA)$_3$dipy or Ln(TFAA)$_3$ophen or even Ln(dpm)$_3$imidazole.

In tris(dipivaloylmethanato) imidazole lanthanide(III), the melting points increase from lanthanum to terbium and then decrease up to ytterbium, an observation also noted in tris(tri-fluoroacetylacetonato) o-phenanthrol ine. The melting points of the corresponding Ln(dpm)$_3$imidazole or Ln(dpm)$_3$pyrazole are lower than those of Ln(dpm)$_3$ophen. The planar bidentate o-phenanthrol ine brings in more stability than the monodentate imidazole or pyrazole. The molar conductances of $10^{-3}$M solutions of Ln(dpm)$_3$imidazole range between 8.5 and 20.4 mhos cm$^2$ mole$^{-1}$ and those of Ln(dpm)$_3$pyrazole in the range of 11.0-20.0 mhos cm$^2$ mole$^{-1}$ The complexes of the two series are thus
seven coordinate and non-electrolytes. It is interesting that even in the presence of three molecules of such a bulky coordinating agent as 2,2,6,6-tetramethyl, 3,5-heptane dione, an imidazole molecule coordinates with the lanthanide ions. The magnetic moments of the tris(dipivaloylmethanato) imidazole lanthanide(III) show magnetic moments which give the usual unequal double humped curves when plotted against their atomic numbers. The lanthanum and yttrium compounds are diamagnetic. The infrared spectra of these complexes have been discussed.

The 1,1,1,2,2,3,3-heptafluoro, 7,7-dimethyl,4,6-octane dione forms complexes with Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb of the general formula Ln(FOD)₃ where FOD stands for the enolic form of this ligand (HFOD) from which an H⁺ has been eliminated. Such complexes have already been reported. These complexes form adducts with 1,10-phenanthroline with the general formula Ln(FOD)₃ophen. Very well defined solids are obtained. It is very interesting and also striking that even in the presence of three bulky ligands, the heptafluoroctane dione, the lanthanide ions show marvellous avidity for the chelating o-phenanthroline. The molar conductances of the complexes in methanol at 10⁻³ M dilution are in the range of 4.4-13.6 mhos cm² mole⁻¹, which shows their non-electrolytic nature. The molar conductances in methanol are in the ranges
of 8C=115, 160-220 and 29-350 ohm$^{-1}$ cm$^2$ mole$^{-1}$ for 1:1, 1:2 and 1:3 electrolytes respectively. These complexes are non-electrolytes and thus eight coordinate. The melting points. The melting points of Ln(FCO)$_3$ophen show increase in melting point with increase in the atomic number of the lanthanide ion. Thus Pr(FCO)$_3$ophen shows a melting point of 103$^\circ$C and the last lanthanide ion complex, Yb(FCO)$_3$ophen melts at 118-119$^\circ$C. This is in contrast to the melting point trend observed among the tris-heptafluorooctanates of the lanthanide ions. The melting point of La(FCO)$_3$ is 215-230 whereas that of Ln(FCO)$_3$ is 118-125. The same trend is seen in their monohydrates, La(FCO)$_3$H$_2$O, m.p. 215-230, Lu(FCO)$_3$H$_2$O, m.p. 111-115. The Ln(FCO)$_3$ophen complexes have considerably low melting points than those of the simple Ln(FCO)$_3$ or Ln(FCO)$_3$H$_2$O. This trend is specially marked in the case of the lighter lanthanide ions. Further the difference in the melting points of the lightest and the heaviest rare-earth chelate is very little. The lighter rare-earths because of their greater ionic size do not seem to form thermodynamically more stable complexes with the bulky molecule of o-phenanthroline and hence the thermodynamic stability of the larger rare-earth ions is affected more and hence the melting point of Pr(FCO)$_3$ophen becomes 103$^\circ$ whereas that of Pr(FCO)$_3$ is 215-230$^\circ$C. Even the
planarity of the molecule of o-phenanthroline which would have brought more compactness in the solid state, does not compensate the destabilization brought about by the bulk of the ophenanthroline ligand. The magnetic moments of these mixed ligand complexes show the same unequal double humped curve. Sm(FL)3ophen is diamagnetic like the Sm(TFA)3ophen. The infrared spectra of the complexes have been discussed.

The praseodymium and europium β-diketonates have been used as pseudo contact H' n.m.r. shift reagents and the work on the relative merits of trifluoroacetylacetonates, dipivaloylmethanates and heptafluorooctanedicarbonates of lanthanides and their seven coordinate adducts, as pseudocontact H' n.m.r. shift reagents is still in progress.