Coordination Chemistry Reviews, 31 (1980) 67—91

COORDINATION CHEMISTRY OF LANTHANIDES WITH EMPHASIS ON DERIVATIVES WITH Ln—O—C BONDS

R.C. MEHROTRA *, P.N. KAPOOR and J.M. BATWARA **
University of Delhi, Delhi-110007 (India)

(Received 15 August 1977; in revised form 26 June 1979)

CONTENTS

A. INTRODUCTION

Coordination chemistry of lanthanides has developed rapidly during the last few years. Besides the isolation of a large number of new complexes sometimes involving novel methods of synthesis, varied applications of these species have been recently suggested. In spite of rapid progress in the field, no review dealing with the general chemistry of lanthanide complexes has appeared since Moeller et al. [1] and Sinha [2] covered the subject about 13—14 years ago. A few reviews covering specific aspects of lanthanide chemistry, such as solution chemistry of lanthanide complexes [1—3], laser active lanthanide chelates [4,5], lanthanide shift reagents [6—9], the organometallic com-

---

* To whom correspondence should be sent.

** Chemistry Department, R.R. College, Alwar, Rajasthan, India.

pounds [10—12], structures of highly coordinated lanthanide complexes [13,14] and nitrogen donor lanthanide complexes [15] have appeared recently. These aspects are, therefore, not included in the present review. A very large number of adduct complexes have also been reported, but these are also excluded in general from the present article, except those with polyethers which have some special characteristics.

In the present review, our main focus of attention has been to discuss some novel methods employed during the last 1—2 decades for the synthesis of a few selected classes of lanthanide complexes with Ln—O—C bonds, which can not be easily synthesised in aqueous media due to their high reactivity with water. The advantages of non-aqueous media, particularly utilising metal alkoxides as starting materials for the synthesis of derivatives which could not be prepared in aqueous solutions have been emphasised in the appropriate places.

The essential features of the lanthanide ions, which determine their coordination behaviour, have been discussed in detail elsewhere [16] and only some aspects pertinent to the present review are summarised below:

1. For the tripositive lanthanide ions possessing a general electronic configuration of $[\mathrm{Xe}]\,4f^n \cdot 5s^2 \cdot p^6 \cdot d^0$, it has been suggested [13,16] that involvement of deep seated $4f$ orbitals during complexation with ligand orbital systems is almost negligible and the nephelauxetic effect (i.e., the slight red shift in the absorption bands) is a second order phenomenon.
2. In view of their large sizes, the mode of bonding between lanthanide ions and the ligands may be considered mainly electrostatic in nature. In a given series, increasing covalency is expected with decrease in the sizes (La—Lu) of the central metal ions. A gradual increase in volatilities of some lanthanide β-diketonates is probably indicative of this effect [17—20]. These and other classes of volatile compounds of lanthanides will be discussed later in the present review.
3. Recent X-ray studies have radically altered our views regarding the coordination number of complexed lanthanide ions [13,16]. Coordination number six with a preferred 'octahedral geometry' has been assumed for a long time on the basis of computing only the main donor atoms of the chelated ligands and ignoring the potentiality of: (a) subsidiary coordination with adduct molecules like water [21], e.g. $\mathrm{Y(C_6H_5COCHCOCH_3)_3 \cdot H_2O}$; benzene [22], e.g., $\mathrm{Yb(CH_3COCHCOCH_3)_3 \cdot H_2O \cdot 0.5\,C_6H_6}$, and amine [23], e.g., $\mathrm{Yb(CH_3COCHCOCH_3)_3 \cdot CH_3COCH{=}C(NH_2)CH_3}$ and (b) intermolecular coordination [24], e.g., $\mathrm{Pr_2[(CH_3)_3CCOCHCOC(CH_3)_3]_6}$. Coordination numbers as high as 12 have been now established for lanthanide ions [25], e.g., in $\mathrm{K_3M_2(NO_3)_9}$ (where M = Pr, Nd and Sm). This tendency to saturate the metal coordination sphere would, as expected, be largely determined by steric geometry of the ligand. Whereas lanthanide atoms show a surprisingly low coordination number of three in air-sensitive monomeric tris-N-bis(trimethylsilyl) lanthanides [26,27], $\mathrm{Ln[N(SiMe_3)_2]_3}$ and coordination number six in tris-(diisopropoxo aluminium di-μ-isopropoxo) lanthanides [28] $\mathrm{Ln[(OPr^i)_2Al(OPr^i)_2]_3}$, the apparently nine-coordinated tris-(methylcyclopentadienyl) neodymium tetra-

merises in its tendency to saturate the tenth coordination site [29].

4. Lanthanide ions behave as hard acids [30] and are expected to form stronger bonds with ligands having O or N as donor atoms. The preponderance of lanthanide complexes with oxygen donor ligands arouses some misconception regarding stability of Ln—N bonds. Although many nitrogen containing complexes have been prepared during recent years [15,26,27] many of these are hydrolytically unstable in spite of their thermal stability. As suggested by Sinha [2], this hydrolytic instability might arise from the basicity behaviour of lanthanide ions in aqueous solutions containing nitrogen containing ligands. It may be of interest to emphasize that under anhydrous conditions even ammonia forms volatile adducts with lanthanides [31,32].

5. In view of the lack of any directional bonding between lanthanide ions and the ligands, a kind of flexibility in accommodating the latter around the metal ions results in non-rigid (distorted) patterns for the structures of their complexes. This aspect has been discussed quite recently [13]. A further consideration worthy of mention is the lability of the ligands attached to lanthanides in the solution state [33]; consequences of this effect will also be discussed later in this review.

6. Water of hydration plays a significant role in the formation and stabilities of coordination compounds of lanthanides. The tenaciously held water molecule (tendency increases with decrease in size) which cannot be removed without decomposition, also inhibits further coordination by other potential donors to the metal ions. The strong coordination tendency of oxy- or hydroxy- ion is probably the main driving force in such decomposition. One of the clearer examples of this tendency is the attempted dehydration of lanthanide tris-acetylacetonate hydrates discussed later in this review.

7. In view of the above special characteristics of lanthanide ions, the synthetic chemistry of complex formation is rather complicated, particularly in aqueous solutions. Some of the factors governing these complexation reactions are: (i) molar ratio of ligand to cation; (ii) nature and concentration of starting materials and the solvent used; (iii) decomposition or hydrolysis of the ligand and/or of the product formed; (iv) pH and temperature and (v) presence of more than one competitive reaction and resultant equilibria. In view of the above, conditions of preparation have to be carefully controlled to avoid formation of unsuspected or undesired side-products and contaminants; a few illustrative cases are discussed later.

In view of the complications arising in synthetic methods in aqueous medium, reactions in non-aqueous media like alcohols and hydrocarbons have been attempted utilising lanthanide metals [34—37], their hydrides [38,39], anhydrous chlorides [40] and alkoxides [41—46] as starting materials. The reactions in the first two cases are generally slow and are accompanied with the formation of side products. Hydrogen chloride produced in the reactions of lanthanide chlorides often causes side reactions.

Amongst the lanthanide alkoxides, the isopropoxides have emerged as the most suitable starting materials [41—46]. The isopropoxides are soluble in benzene and undergo very facile interchange reactions in different stoichiometric ratios with a variety of organic reagents containing hydroxyl groups (e.g., higher alcohols, polyhydroxy alcohols, amino alcohols, carboxylic acids, hydroxy carboxylic acids, β-diketones and β-ketoesters)

$$\mathrm{Ln(OPr^i)_3} + n\,\mathrm{LOH} \xrightarrow{\mathrm{Benzene}} \mathrm{Ln(OPr^i)}_{3-n}\mathrm{(OL)}_n + n\,\mathrm{Pr^iOH}$$

(n = 1, 2 or 3)

The isopropanol produced in these reactions can be fractionated out in the form of an azeotrope (b.p. 71.8°C) from the solvent benzene (b.p. 80°C). A convenient oxidimetric method has been developed [47] for estimation of isopropanol in the azeotrope and thus, the progress of replacement reactions can be easily followed. Lanthanide isopropoxides thus provide convenient synthetic routes for lanthanide complexes with Ln—O—C bonds.

B. COMPOUNDS CONTAINING Ln—O—C BONDS

This class covers a variety of compounds ranging from the simplest metal alkoxides to the numerous chelates of β-diketones. The compounds vary remarkably in their hydrolytic and thermal stability, solubility in organic solvents, associative nature and volatilisation behaviour.

(i) Alkoxides

Although keen interest has recently been evinced in metal alkoxides [48,49] in general, the corresponding lanthanide derivatives have received scant attention and the earliest reference to their preparation, when Bradley and Faktor [50] synthesised some alkoxides of lanthanum, is barely twenty years old. With the exception of some synthetic efforts of Mazdiyasni and coworkers [32,34,35], most of the studies undertaken in this field to date have been carried out in our laboratories [51—58].

The following general methods have been used for the preparation of lanthanide alkoxides

$$\mathrm{Ln} + 3\,\mathrm{ROH} \xrightarrow{\mathrm{ROH}} \mathrm{Ln(OR)_3} + 3/2\,\mathrm{H_2}\uparrow \qquad (1)$$

$$\mathrm{LnCl_3} + 3\,\mathrm{ROH} \xrightarrow{\mathrm{NH_3}} \mathrm{Ln(OR)_3} + 3\,\mathrm{NH_4Cl} \qquad (2)$$

$$\mathrm{LnCl_3} + 3\,\mathrm{MOR} \xrightarrow{\mathrm{C_6H_6}} \mathrm{Ln(OR)_3} + 3\,\mathrm{MCl} \qquad (3)$$

$$\mathrm{Ln(OR)_3} + 3\,\mathrm{R'OH} \xrightarrow{\mathrm{C_6H_6}} \mathrm{Ln(OR')_3} + 3\,\mathrm{ROH} \qquad (4)$$

$$\mathrm{Ln(OR)_3} + 3\,\mathrm{CH_3COOR'} \xrightarrow{\mathrm{C_6H_{12}}} \mathrm{Ln(OR')_3} + 3\,\mathrm{CH_3COOR} \qquad (5)$$

Ln = La, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Yb and Lu; R or R′ = CH_3, C_2H_5, C_3H_7, $C_3H^i_7$, C_4H_9, $C_4H^s_9$, $C_4H^t_9$, C_5H_{11}, $C_5H^t_{11}$ and C_6H_5; M = Li (for insoluble alkoxides) and M = Na or K (for soluble alkoxides).

Method 1 has been used for the preparation of isopropoxides of a few lanthanides [34,45] by treating metal shavings with isopropanol in the presence of catalyst mercuric chloride. Some side dehydrogenation reactions resulting in unsaturated moieties have been observed in these reactions. Method 2, tried in our laboratory, did not yield pure lanthanide alkoxides as the products could not be freed from ammonium chloride contamination [57]. Recently, Mazdiyasni and Schaper [32] have been able to prepare lanthanide hexafluoroisopropoxide diammoniate by this method, whereas Merbach and Carrard [59] could isolate only unspecified products from such reactions. Method 3 is now considered to be the most appropriate for the synthesis of pure alkoxides both insoluble as well as benzene soluble using M as Li or Na(K), respectively [51—58]. The yields are almost quantitative. In a recent publication, however, Andersen et al. [60] have reported the isolation of a partially chlorinated product $Nd_6(OPr^i)_{17}Cl$ in a reaction between neodymium chloride and three moles of sodium isopropoxide in isopropanol—benzene mixture. The derivative has been shown by X-ray crystallography to have an interesting structure involving six neodymium atoms on the corners of a trigonal prism with a chlorine atom in the centre. Methods 4 and 5 have been extensively employed to prepare higher alkoxides by using alcohol interchange or *trans*-esterification reactions [51—53,56,57].

Methoxides, ethoxides and phenoxides of lanthanides have been found to be sparingly soluble in benzene [50—58] and are non-volatile. These properties indicate their polymeric nature involving intermolecular bonds through oxygen atoms. Lanthanide isopropoxides [51—58] in general are highly soluble in benzene and other inert solvents and sublime in poor yields (10—20%) in the temperature range 180—280°/0.1 mm. These and higher alkoxides have been found to be oligomers (molecular association ~4) in boiling benzene. All these alkoxides are extremely sensitive to moisture. Quite interestingly, similar fluorinated derivatives such as lanthanide hexafluoroisopropoxide diammoniate, $Ln[OCH(CF_3)_2]_3 \cdot 2\ NH_3$, have been found to distil in the temperature range of 120—140°/0.08 mm, but these are insoluble in benzene and n-hexane [32]. In view of the generally higher volatility of the fluorinated alkoxides, the report of Merbach and Carrard [59] about the non-volatility of similar products prepared by them appears to be in error, which might arise from the side formation of methoxides from methanol produced in the systems employed.

Method 5 has also been used to prepare [61] mono-, bis- and tris-trimethylsiloxide derivatives of gadolinium and erbium by the following reaction

$$Ln(OPr^i)_3 + x\ Me_3SiOCOCH_3 \xrightarrow{C_6H_{12}} Ln(OPr^i)_{3-x}(OSiMe_3)_x + x\ CH_3COOPr^i$$

(x = 1, 2 or 3; Ln = Gd or Er)

These compounds are soluble in benzene in which the tris-derivative $Ln(OSiMe_3)_3$ depicts a molecular association of 3.5, which is slightly higher than that of the corresponding trimeric tertiary butoxides $Ln(OCMe_3)_3$. These observations indicate that the Me_3SiO group provides less effective shielding of lanthanide ions compared to Me_3CO groups, in spite of the larger covalent radius of Si than that of the C atoms.

(ii) Halide alkoxides

Halide alkoxides, $Ln(OR)_n(X)_{3-n}$ (where R = $C_3H_7^i$ and $C_4H_9^t$; X = Cl and Br and $n = 1$ or 2) have been synthesised for a number of lanthanides by a number of workers [54,62—64]. These can be prepared by treatment of the alkoxides with the corresponding acetyl halides in the appropriate molar ratio. Thus the reactions of gadolinium and erbium isopropoxides with acetyl chloride in 1 : 1, 1 : 2 and 1 : 3 molar ratios yield, $Ln(OPr^i)_2Cl \cdot 0.5\ CH_3COOPr^i$, $Ln(OPr^i)Cl_2 \cdot CH_3COOPr^i$ and $LnCl_3 \cdot 2\ CH_3COOPr^i$ respectively [64]. With the gradual replacement of alkoxy by halide groups, coordination tendency for ester molecules appears to increase as could be expected from a higher positive charge induced on the lanthanide ions. The ester molecules can, however, be removed under vacuum at temperatures of 60—80°C.

An interesting variation for the ester adducted halide isopropoxides has been observed with regard to their solubility differences in benzene. Whereas all products from lanthanum through gadolinium are sparingly soluble, the corresponding products of erbium, ytterbium and yttrium show much higher solubility in benzene [54,62—64]. In this context it may be recalled that many properties of lanthanide derivatives show a discontinuity at gadolinium [65—71]. This so-called 'gadolinium break' is also discerned in the properties of trihalides. It has been shown [72] that the bonding in trichlorides of lanthanum to gadolinium is predominantly ionic and these show similarity in structure to hexagonal uranium trichloride, whereas the trichlorides of heavier lanthanides show structures similar to monoclinic aluminium chloride. The above observed differences in halide alkoxides may also arise from a similar origin, i.e. due to the changes in structures and nature of bonding at gadolinium.

The reactions of lanthanide t-butoxides with acetyl chloride, however, resulted in products containing acetoxy groups as well; the latter have been shown [64] to be formed by further reactions of the halide butoxide products formed initially with the liberated tertiary butylacetate

$$Ln(OBu^t)_3 + CH_3COCl \rightarrow LnCl(OBu^t)_2 + CH_3COOBu^t$$

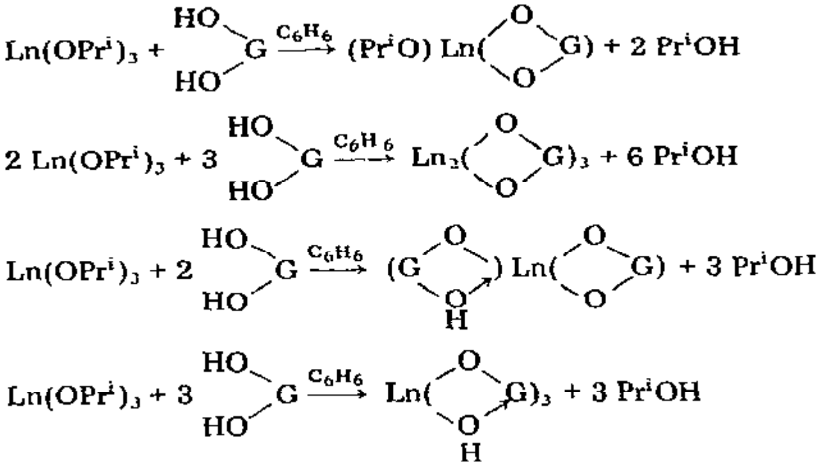
$$LnCl(OBu^t)_2 + CH_3COCl \rightarrow LnCl_2(OBu^t) + CH_3COOBu^t$$

$$LnCl_2(OBu^t) + CH_3COOBu^t \rightarrow LnCl(OOC \cdot CH_3)(OBu^t) + Bu^tCl$$

$$LnCl(OOC \cdot CH_3)(OBu^t) + CH_3COOBu^t \rightarrow Ln(OOC \cdot CH_3)_2(OBu^t) + Bu^tCl$$

(iii) Glycoxides

Although an aqueous solution study [73] indicated the coordination of glycols to lanthanide ions, the compounds could not be isolated due to strong competition with water molecules. Mehrotra and coworkers [74,75] synthesised the glycoxide derivatives of lanthanides by reaction of the corresponding isopropoxides in different molar ratios with a number of glycols, e.g. ethane-1,2-diol, butane-2,3-diol, 2,3-dimethyl butane-2,3-diol (pinacol) and 2-methyl pentanediol (hexylene glycol). The reactions may be shown as follows



All these glycoxide products have been found to be sparingly soluble in benzene and infusible up to 250°C. These observations as well as IR spectra of these compounds suggest polynuclear structures for these derivatives [75].

(iv) Carboxylates

Various methods have been described for the preparation of carboxylate derivatives of lanthanides. Reactions of lanthanide oxides, hydroxides, chlorides or nitrates with acetic acid and/or acetic anhydride have been reported to yield triacetates, oxyacetates and their acetic acid adducts [40,76—80]. Similar methods have also been used to prepare substituted carboxylates [81,82]. The higher acylates and benzoates of lanthanides could also be obtained by precipitation in aqueous solutions using sodium salts of the corresponding fatty acids [83,84]. Both lower and higher acylates can be conveniently prepared by reactions of lanthanide isopropoxides with the respective carboxylic acid in appropriate molar ratios [75,85].

$$\mathrm{Ln(OPr^i)_3} + n\ \mathrm{RCOOH} \rightarrow \mathrm{Ln(OPr^i)_{3-\mathit{n}}(OOCR)_{\mathit{n}}} + n\ \mathrm{Pr^iOH}$$

(where R = CH_3, C_3H_7, C_4H_9, $C_{11}H_{23}$, $C_{15}H_{31}$ and $C_{17}H_{35}$; Ln = Sm, Gd or Er and n = 1, 2 or 3)

It has been noted that whereas lower acylates are generally insoluble in benzene, higher acylates including benzoates are soluble in this solvent. IR studies for these compounds indicate [75] different modes of bonding. Whereas lower acylates appear to prefer polynuclear structures, bidentate coordination has been suggested for the higher acylates and benzoate derivatives [84]. Thermal studies show decomposition of these carboxylates to oxides via oxycarboxylates [82].

A number of hydroxy carboxylic acid derivatives, e.g. glycolates [85], lactates [86], malonates [87], citrates [88], tartrates [89] and gluconates [90] of lanthanides have been synthesised from aqueous solutions. Most of these derivatives except glycolates of lower lanthanides are isolated in the form of hydrates. Successful preparation of anhydrous complexes of lactic ($CH_3CHOHCOOH$), mandelic ($C_6H_5CHOHCOOH$) and salicylic ($C_6H_4OHCOOH$) acids could be achieved by reactions of lanthanide isopropoxide with the corresponding acids in the required molar ratios [91,92]. The reactions in case of mandelic acid can be represented as

$$Ln(OPr^i)_3 + C_6H_5CHOHCOOH \xrightarrow{C_6H_6} Ln(OOC \cdot OCHC_6H_5)(OPr^i) + 2\ Pr^iOH$$

$$Ln(OPr^i)_3 + 2\ C_6H_5CHOHCOOH \xrightarrow{C_6H_6} Ln(OOC \cdot OCHC_6H_5)(OOC \cdot HOCHC_6H_5) + 3\ Pr^iOH$$

$$Ln(OPr^i)_3 + 3\ C_6H_5CHOHCOOH \xrightarrow{C_6H_6} Ln(OOC \cdot HOCHC_6H_5)_3 + 3\ Pr^iOH$$

(Ln = La, Pr, Nd, Yb or Y)

It has been perceived in the reaction of lanthanide isopropoxides with mandelic acid in 1 : 3 ratio that the hydroxy groups do not react in preference to the carboxylic groups. However, in similar reactions in 1 : 1 and 1 : 2 molar ratios, hydroxy groups also take part in replacement reactions. Similar reactions have been observed [92] with salicylic acid.

The sparingly soluble nature of all the products in solvents like benzene may be due to either their associated or chelated character [92]. In a more recent crystal structure determination for aquo-tris-salicylatosamarium, Burns and Baldwin [93] have found that there are no discrete molecules and instead, each metal is linked to 6 different salicylato ions through a variety of donation modes in which both the carboxylic and phenolic oxygen atoms participate.

(v) Salicylaldehyde derivatives

Attempts to prepare salicylaldehyde derivatives of lanthanides in aqueous solutions [94] usually result in isolation of hydroxy derivatives of the type $Ln(Sal)_2(OH)$, ($Sal = C_6H_4O \cdot CHO$). Although careful control of reaction conditions yields the tris-derivatives $Ln(Sal)_3$ for lighter lanthanides, heavier lanthanides again form hydroxy compounds [95,96]. The anhydrous tris-derivatives of ytterbium and yttrium could be successfully prepared [92] by the reactions of the corresponding isopropoxides with salicylaldehyde in the required molar ratios

$$Ln(OPr^i)_3 + n\ C_6H_4OH \cdot CHO \rightarrow Ln(OPr^i)_{3-n}(C_6H_4O \cdot CHO)_n + n\ Pr^iOH$$

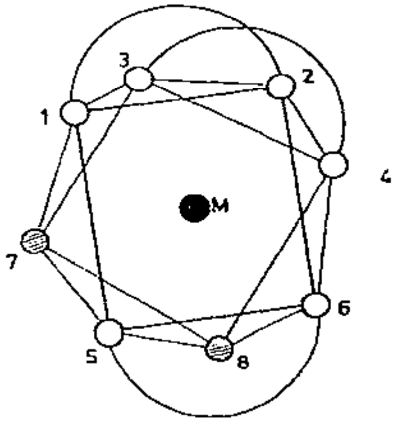
These compounds are soluble in benzene. In contrast to phenoxide compounds which are insoluble in this solvent, the solubility of these products indicates that the carbonyl of the aldehyde group also participates in chelate formation. IR spectra confirm this observation as the C=O stretching frequency of the aldehyde is lowered to ca. 1620 cm^{-1} in these complexes from ca. 1650 cm^{-1} in the free ligand [97]. It may also be pointed out that the so called tris-chelates of salicylaldehyde prepared from aqueous solutions exhibit the carbonyl stretching band at ca. 1650 cm^{-1} [96].

(vi) β-Diketonates and β-ketoester derivatives

A general upsurge of interest in metal β-diketonates during the last two decades [98] is also reflected in the chemistry of lanthanides. This has resulted in detailed investigations unfolding some lesser known facets of general lanthanide coordination chemistry. Particular mention may be made of different stereochemical aspects of lanthanide complexes which could be unveiled by the extensive physicochemical studies of a number of tris-chelates, their adducts and the tetrakis-chelates. As regards the preparative aspects, investigation has revealed the inherent weaknesses of some of the synthetic routes generally employed for these derivatives. For example, the method using an organic base to prepare tris-β-diketonates [99] was later found to yield tetrakis-derivatives [100—105]. Use of sodium acetate for a similar purpose was found to result in the formation of mixed acetate derivatives [106,107].

Early methods used for the preparation of lanthanide tris-β-diketonates have been critically examined by Moeller et al. [1] and by Pope et al. [108] who conclusively established that the products from aqueous solutions are almost invariably hydrates; sometimes hydroxy derivatives are also formed. Recently, Dutt and co-workers [109—119] prepared a large number of β-diketonates of lanthanides using the modified method of Stites et al. [120] which involves taking the water soluble lanthanide salt (e.g. chloride, nitrate, acetate) and the ligand in a molar ratio of 1 : 3 in water-alcohol mixture, followed by addition of ammonia until precipitation or turbidity appears. Most of the β-diketonates thus formed have a composition of the type $LnL_2(OH) \cdot H_2O$, where HL stands for various β-diketones. More recently, Lyle and Witts [121] have examined various methods employed for the synthesis of lanthanide β-diketonates and they have also pointed towards the need for some methodical modifications.

In view of the possibilities of using anhydrous tris-β-diketonates of lanthanides as laser materials, NMR shift reagents or in vapour phase chromatography, interest in such derivatives has been aroused in the last few years. It may be pertinent to point out that recent studies have shown [21,24,122—130] the possibility of quite distinct structural characteristics for hydrated and anhydrous products. For example, $Y(acac)_3 \cdot (OH_2)_2$ and $La(acac)_3 \cdot (OH_2)_2$ have been shown [122,123] to depict the octacoordinated structure (Fig. 1) with water molecules occupying adjacent positions in the square face of the anti-



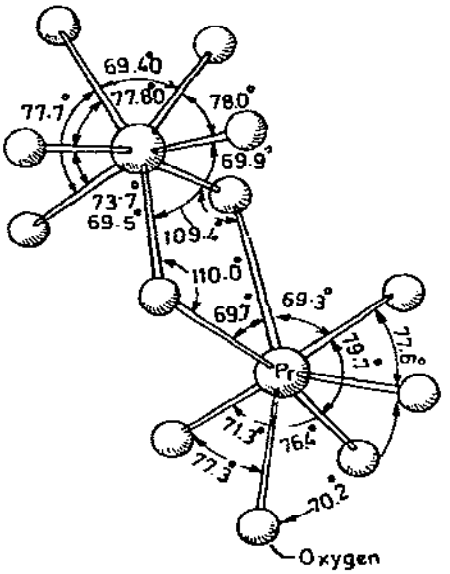


Fig. 1. Structure of $[Ln(acac)_3(H_2O)_2]$ unit showing ▨ H_2O molecules and ○ oxygen.

Fig. 2. Structure of dimeric anhydrous $[Pr_2(dpm)_6]$ complex (dpm = Dipivaloylmethane).

prism. The anhydrous lanthanide tris-acetylacetonates, benzoylacetonates and dibenzoylmethanates synthesised in our laboratories [131] have been found to be essentially dimeric in nature.

In fact, Erasmus and Boeymens [24] have found anhydrous $Pr(dpm)_3$ to be dimeric $Pr_2(dpm)_6$, in which each praseodymium atom is surrounded by seven oxygen atoms forming a distorted trigonal prism (see Fig. 2). One of the chelating oxygens of the β-diketonate ligand forms a bridge with another molecule of $Pr(dpm)_3$, thus serving as the seventh ligand atom in the coordination sphere of the other praseodymium ion.

The hydrated tris-β-diketonates of lanthanides are in general thermally unstable [132,133] and some of these undergo slow decomposition even at room temperature [130]. In some special cases, however, the metal-to-water bond appears to become sufficiently weak, e.g. (a) in highly fluorinated β-diketonates in which water molecules tend to form hydrogen bonds with the electronegative fluorine atoms of the ligand; (b) in compounds like tris-dipivaloylmethanates, $Ln(dpm)_3$, which have sterically bulky groups, and (c) in derivatives like tris-dibenzoylmethanates, $Ln(dbm)_3$, in which ligand oxygen atoms form strong intermolecular coordination bonds. In such compounds, therefore, dehydration can be effected without decomposition [18,20,134].

Another notable property of lanthanide β-diketonates is the tendency of self association. In solid as well as in solution states monomeric, dimeric and trimeric structures have been known for anhydrous, hydrated or adducted tris-chelates of lanthanides [135—143] and equilibria of the following types have been detected [139] in solution

$$\mathrm{LnL_3} \rightleftharpoons \tfrac{1}{2}(\mathrm{LnL_3})_2 \rightleftharpoons \tfrac{1}{3}(\mathrm{LnL_3})_3$$

Even the same complex can be prepared in monomeric, dimeric or in the form of a mixture of the two, depending on conditions of treatment. Thus Calton et al. [143] have demonstrated that anhydrous tris-tetramethylheptanedionate holmium, $\mathrm{Ho(dpm)_3}$ may be prepared as (i) a monomer by crystallisation from light petroleum (b.p. 60—80°) or by sublimation at 0.1 mm along a glass tube, (ii) a mixture of monomer and dimer by crystallization from aqueous alcohol followed by drying over P_4O_{10} and (iii) a dimer by sublimation of the compound on to a probe at —196°C under 0.1 mm pressure.

In view of the special flexibility of lanthanide ions in accommodating the ligand ions, the following factors governing associative tendencies of lanthanide β-diketonates may be mentioned:

(1) The state of hydration or adduct formation, which may check oligomerisation.

(2) The size of the lanthanide ion, as greater association may be expected for larger ions under identical conditions.

(3) The nature of the ligand, particularly the presence of groups inhibiting closer approach of the chelate moieties.

(4) *S*-electron or acceptor groups in the ligand which determine the extent and strength of intermolecular coordination leading to association.

(5) Thermodynamic conditions of compound crystal formation.

As a matter of synthetic interest, repeated efforts have been reported in the literature on methods to prepare anhydrous acetylacetonates of lanthanides. The dehydration of hydrated chelates $\mathrm{Ln(acac)_3 \cdot}\, n\, \mathrm{H_2O}$ obtained from aqueous media by different methods, e.g., azeotropic removal of water [108]; heating the hydrate in air, inert atmosphere or vacuum [108,144,145]; storage over dehydrants [19,133], yields generally hydrolysed products. The so-called anhydrous products obtained under the mildest conditions of dehydration also appear to be extremely hygroscopic [145]. In view of the above difficulties, attempts have been made to carry out the reaction of the metals [36,37] or their hydrides [38,39] with excess acetylacetone, but products appear to be contaminated [38,75] due to side reactions. The reactions of lanthanide isopropoxide with β-diketones and even β-ketoesters [75,131,146—150] have been shown to proceed with facility to completion in benzene as the isopropanol formed in the reaction is fractionated out azeotropically

$$\mathrm{Ln(OPr^i)_3} + n\ \mathrm{Hacac} \xrightarrow{\mathrm{C_6H_6}} \mathrm{Ln(acac)}_n\mathrm{(OPr^i)}_{3-n} + \mathrm{Pr^iOH}$$

(where $n = 1, 2$ or 3)

It is interesting to mention that the anhydrous tris-derivatives prepared by this method do not appear to exhibit as much moisture sensitivity as derivatives isolated by the dehydration of the hydrated sample obtained in aqueous medium. This may be due to structural differences, as the anhydrous product obtained by dehydration under extremely moderate conditions of a dihydrate like that shown in Fig. 1, could leave vacant sites to which a donor water molecule from atmospheric moisture could be easily attracted.

The β-diketone ligands containing groups like hexa, hepta, octa and decafluoroalkyl groups and isobutyl or tetramethyl butyl(dipivaloyl) groups produce volatile lanthanide tris-chelates [17—20]. Although water of hydration in the tris-chelate endows undesirable effects on thermal stability in many cases, e.g. hydrated lanthanide tris-hexafluoroacetylacetonate, $Ln(hfa)_3 \cdot n\ H_2O$, decomposes on heating, yet with increase in the number of fluorine atoms in the ligand, even this drawback seems to disappear, as the dihydrated lanthanide tris-decafluoroheptapentanedionate, $Ln(dfhd)_3 \cdot 2\ H_2O$ can sublime unchanged in low temperature ranges of 165—200°C [20]. The increased volatility in these cases has been attributed to (i) reduction in van der Waals forces, (ii) decrease in intermolecular hydrogen bonding, (iii) prevention of the close packing in the crystal lattice, (iv) shell-like structure of the fluorinated chelates and (v) check on intramolecular bonds through oxygen by sufficiently bulky substituents, etc. The adducts obtained by the replacement of water molecules by dimethyl formamide (DMF) e.g. in $Ln(hfac)_3 \cdot DMF$, $Ln(hfac)_3 \cdot 2\ DMF$, and $Ln(dfhd)_3 \cdot 2\ DMF$, have been reported to volatilise without decomposition [20] in few cases. Sievers [151] has observed that the volatility of lanthanide β-diketonates increases with decreasing ionic radius. It has been suggested by this author that with decrease in the size of lanthanide ions, the permanent local dipole of the β-diketonate chelate as well as its polarisability decreases. Hence, with reduction in dipole—dipole (molecular or local) interactions and dipole induced dipole interaction, the volatility of the complexes increases. The author, however, observed that the volatility of the chelates does not appear to be correlated with either mass differences or with monomer—polymer equilibria brought about by change in the radius of the central lanthanide ions.

The tetrakis-chelates of lanthanides generally show higher volatility and thermal stability than the hydrated tris-chelates. It is interesting to note that in contrast to high thermal instability of $Ln(hfac)_3 \cdot 2\ H_2O$, the tetrakis-chelate with pyridine, $PyHLn(hfac)_4$, shows higher volatility without any noticeable decomposition [20].

(vii) 8-Hydroxyquinolinolates

Several authors [152—155] have pointed out that it is exceedingly difficult to achieve the simple 3 : 1 stoichiometry in the 8-hydroxyquinoline derivatives of lanthanides; some occlusion of the ligand occurs even under the most careful preparation, together with basic or acetoxy products obtained from buffered aqueous solutions. Charles and Perrotto [152] reported a C_9H_6NO/Ln ratio as low as 2.18 in samples which were considered apparently as tris complexes. Batwara and Mehrotra [131] have recently synthesised the tris-derivatives of gadolinium and erbium by reactions of their isopropoxides with the ligand in the required molar ratios in dry benzene solvent. IR and UV studies supported the stoichiometry and absence of occluded 8-hydroxyquinolinol in these derivatives. These compounds are non-volatile and sparingly soluble in benzene, but they dissolve in chloroform.

(viii) Aminoalkoxides

In view of the non-isolation of aminoalcohol complexes of lanthanides through aqueous medium, Mehrotra and co-workers [75] attempted the preparation of these through lanthanide isopropoxide reactions with various alkanolamines, viz. $H_2NCH_2CH_2OH$, $HN(CH_2CH_2OH)_2$ and $N(CH_2CH_2OH)_3$ in appropriate molar ratios. The products obtained are only sparingly soluble in benzene and probably form polynuclear structures. IR studies showed evidence for intermolecular bonding through oxygen and coordination of nitrogen to the lanthanide atoms. The reactions can be represented as follows

$$Ln(OPr^i)_3 + 3\,(HOCH_2CH_2NH_2) \xrightarrow{C_6H_6} Ln(OCH_2CH_2NH_2)_3 + 3\,Pr^iOH$$

$$2\,Ln(OPr^i)_3 + 3\,(HOCH_2CH_2)_2NH \xrightarrow{C_6H_6} Ln_2[(OCH_2CH_2)_2NH]_3 + 6\,Pr^iOH$$

$$Ln(OPr^i)_3 + (HOCH_2CH_2)_3N \xrightarrow{C_6H_6} Ln(OCH_2CH_2)_3N + 3\,Pr^iOH$$

(ix) Schiff base and allied derivatives

In attempts to prepare tris β-ketoaminates of lanthanides by the reactions of the lanthanide isopropoxides with β-ketoamines, Sahai [46] observed that the mono-isopropoxide bis-β-ketoaminates were obtained as final products

$$Ln(OPr^i)_3 + 2\,CH_3COCH_2C(NR)CH_3 \rightarrow (Pr^iO)\,Ln(CH_3COCHC(NR)CH_3)_2$$
$$+ 2\,Pr^iOH$$

($Ln = Pr$ and Er, $R = Et$ and Pr^n)

Yamada et al. [156] claimed to have obtained lanthanide tris-salicylaldiminate by grinding $LnCl_3 \cdot 6\,H_2O$ with salicyldiamine. However, Sahai [46] found that the above reaction yields instead lanthanide tris-salicylaldehyde derivatives. Agrawal and Tandon [157] have recently isolated the tris-derivatives by the reactions of lanthanum, praseodymium and neodymium isopropoxides with a number of monofunctional bidentate ligands like 2-hydroxy-1-naphthylidine-n-butylamine, 2-hydroxy-1-naphthylidene aniline, 1,1,1-trifluoro-2,4-pentadione-n-propylamine, and 1,1,1-trifluoro-2,4-pentanedione-n-butylamine.

In hydrated tris-hydroxybenzoylhydrazine complexes of lanthanides also, it has been found that the ligand is coordinated via both the O as well as the primary-N atoms [158]. Lanthanide complexes of the composition $LnL_2(OH)_2$, with LH = acetoacetatoluidide, have also been recently reported by Dutt and De [159].

C. MIXED LIGAND COMPLEXES

Some mixed ligand derivatives were isolated by Charles [106] in 1964 during attempts to prepare tris- and tetrakis-complexes of lanthanides employing conventional synthetic methods. For example, Charles reported formation of Eu(dbm)$_2$(RCO$_2$), where dbm is the dibenzoylmethanate moiety and R is CH$_3$-, C$_2$H$_5$- or C$_6$H$_5$ when the sodium salt of the carboxylic acid was used as a base to precipitate the europium dibenzoylmethanate complex. Janardhanarao and Sinha [107] have also similarly obtained Eu(ba)$_2$(CH$_3$CO$_2$) and Eu(pn)$_2$(CH$_3$CO$_2$) where Hba and Hpn represent benzoylacetone and pongamol respectively. The preparations of monohydroxy-bis-chelate lanthanide hydrates LnL$_2$ · (OH)H$_2$O for a number of β-diketonates and β-ketoesters, e.g. HL = acetylacetone, dipivaloylmethane, ethylacetoncetate etc. by Dutt and co-workers have already been described [109—119,160]. These authors [160] used these complexes as starting materials for reactions with a variety of ligands such as HL and/or HL^i = acetylacetone, benzoylacetone, dibenzoylmethane, 8-hydroxyquinoline, picolinic acid, quinaldic acid, etc. to synthesise a series of mixed ligand derivatives of the type LnL$_2$L^i · H$_2$O.

$$\mathrm{LnL_2OH \cdot H_2O + HL^{\mathit{i}} \rightarrow LnL_2L^{\mathit{i}} \cdot H_2O + H_2O}$$

Dutt and Sur [161] have also reported mixed tetrakis-compounds, Na[Ln(acac)$_3$L], derived from the reactions of hydrated tris-acetylacetonates of lanthanides with other β-diketones, HL = propinoylacetone, benzoylacetone and dibenzoylmethane under alkaline conditions. Addition of acetylacetone to lanthanide tristhienyl trifluoroacetylacetone, Ln(tta)$_3$, afforded mixed tetrakis Ln(tta)$_3$(Hacac), derivatives [162]. Horocks and Wong [163] have also more recently reported the synthesis of mixed β-diketonato porphyrine lanthanide complexes which have an 8-coordination sphere around the metal ion. Mixed ligand complexes containing 8-hydroxyquinoline and alizarin [164] have also been obtained, which are soluble in isobutanol and n- and isopentanol.

The preparation of a number of mixed alkoxy-complexes has already been described [54,62—64,74,75,131,146—150]. In view of the stepwise lability of the isopropoxy groups in these reactions, Batwara and Mehrotra [131] have studied the reactions of the mixed isopropoxide chelates, viz. Ln(OPr^i)L$_2$ or Ln(OPr^i)$_2$L with various other ligands to prepare a large number of mixed ligand complexes of the type LnL$_2$L^i, LnLL$^i_2$, LnLL^{i}L^{ii}, etc. where HL, HL^i and HL^{ii} stand for acetylacetone, benzoylacetone, dibenzoylmethane, 8-hydroxyquinoline (8 HQ), hexylene glycol, acetic acid, etc. Most of these compounds have been characterised by IR and UV spectra and molecular weight determinations. An interesting observation has been made that whereas the tris-8-hydroxyquinolinates of lanthanides are insoluble in benzene, the mono-8-hydroxyquinolinate-bis-β-diketonate lanthanide complexes, Ln(8 HQ)L$_2$, have been found to be highly soluble in benzene solvent. This clearly confirms that the mixed ligand species are not mere mixtures of the corresponding tris-chelates.

D. MACROCYCLIC POLYETHER COMPLEXES

Alkali and alkaline earth metal complexes of macrocyclic polyethers [165] and cryptates [166] have received considerable attention during the last decade not only because of their novel coordination chemistry but also as models for biological systems, particularly with respect to ion transportation in living cells. Due to the effective shielding of their 4*f* valency electrons, lanthanides exhibit a close similarity to the alkali and alkaline earth metals, in their capacity to form electrostatic, non-directional bonds.

A number of lanthanide nitrate complexes of macrocyclic polyethers have been reported [167] with the following salient features:

(a) Dibenzo-18-crown-6 forms less stable lanthanide nitrate complexes than benzo-15-crown-5.

(b) The thermal stabilities of the unsolvated macrocyclic polyether complexes of the lanthanide nitrate decrease upon increasing atomic number of the lanthanide.

(c) The tendencies of the metal ions in the macrocyclic polyether complexes of the lanthanide nitrate to complex with other ligands such as H_2O and acetone increase upon increasing atomic number of the lanthanides.

(d) The nature of these complexes appears to be quite dependent on the reaction conditions employed, e.g. Cassol et al. [168] have reported the synthesis of two complete series of unsolvated 1 : 1 complexes $Ln(NO_3)_3$ (polyether) (Ln = all lanthanides except Pm; polyether = benzo-15-crown-5 or dibenzo-18-crown-6) by slow crystallisation from concentrated acetonitrile solution. However, King and Heckley [167] obtained unsolvated 1 : 1 complexes only for lighter (i.e. larger) lanthanides (La, Ce, Pr and Nd) with both macrocyclic polyethers whereas smaller polyether benzo-15-crown-5 yielded only solvated complexes, $Ln(NO_3)_3$ (polyether) $\cdot$ 3 $H_2O \cdot (CH_3)_2CO$ with heavier (i.e. smaller) lanthanides (Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu).

The single crystal X-ray study [169] of *syn*-di(*cis*-cyclohexyl) 18-crown-6 lanthanum nitrate shows the metal ion to be coordinated to six polyether oxygen atoms and one bidentate nitrate ion on the more sterically hindered side of the ring and to two bidentate nitrate ions on the less hindered side. The six ether oxygen atoms are not quite coplanar. This complex is also apparently the first uncharged moleculer twelve coordinated complex of the rare earths.

More recently, a few 1 : 1 lanthanide nitrate complexes of polyoxapolyazamacrocycle have also been reported [170]. Lanthanide nitrate or perchlorate also forms complexes of the type, MX_3(shoth) (where M = lanthanide; X = NO_3 or ClO_4, and shoth = *cis, syn, cis*-2,5,8,15,18,21-hexaoxatricyclo-[20,4,0,0] hexacosane [171]. The ^1H and ^{13}C NMR spectra of complexes of shoth show shifts which are predominantly dipolar and the magnetic susceptibility tensors show that the complexes are not axially symmetric. Similarly, 15-crown-5 and 18-crown-6 form stable 1 : 1 complexes [172] with PrX_3 (where X = Cl, NCS, or ClO_4). However, unsolvated (in the case of La—Eu) and solvated (in the case of Dy—Yb) complexes were obtained with lanthanide perchlorate and dibenzo-30-crown-10 in acetonitrile [173].

E. BIMETALLIC COMPOUNDS CONTAINING Ln—O—C BONDS

A recent development in the synthesis of volatile lanthanide complexes has been the preparation of double metal alkoxides [174—179]. The compounds are formulated as $Ln[M(OPr^i)_4]_3$ where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Yb, Lu, Sc and Y and M = Al, Ga or In. These complexes can be prepared by the following general methods

$$LnCl_3 + 3\ KM(OPr^i)_4 \xrightarrow{C_6H_6} Ln[M(OPr^i)_4]_3 + 3\ KCl \tag{1}$$

$$LnCl_3 + 3\ MCl_3 + 12\ KOPr^i \xrightarrow{Pr^iOH} Ln[M(OPr^i)_4]_3 + 12\ KCl \tag{2}$$

$$Ln(OPr^i)_3 + 3\ M(OPr^i)_3 \xrightarrow{Pr^iOH} Ln[M(OPr^i)_4]_3 \tag{3}$$

All these complexes are soluble in organic solvents, in which their molecular weights correspond to the formula weights based on the composition, $Ln[M(OPr^i)_4]_3$. Another covalent characteristic exhibited by these derivatives is their comparative volatility under reduced pressures; all these complexes distil in the temperature range of 180—200/0.1 mm in almost quantitative yields (see Table 1). In fact, the double isoproposides formed in the reactions (1) and (2) could be distilled out in fairly high yields from the reaction mixtures

TABLE 1

Boiling points and molecular complexities of lanthanide double isopropoxides

Double alkoxide	B.p. (°C/mm)	Molecular complexity
$Sc[Al(OPr^i)_4]_3$	145/0.5	1.0
$Y[Al(OPr^i)_4]_3$	192/0.5	1.1
$La[Al(OPr^i)_4]_3$	208/0.5	1.1
$Ce[Al(OPr^i)_4]_3$	200/0.5	
$La[Ga(OPr^i)_4]_3$	139/0.6	0.92
$Pr[Al(OPr^i)_4]_3$	192/0.3	1.0
$Pr[Ga(OPr^i)_4]_3$	123/0.1	0.84
$Nd[Al(OPr^i)_4]_3$	186/0.1	0.93
$Nd[Ga(OPr^i)_4]_3$	165/0.7	0.93
$Sm[Al(OPr^i)_4]_3$	203/0.7	1.2
$Sm[Ga(OPr^i)_4]_3$	140/0.4	0.97
$Gd[Al(OPr^i)_4]_3$	195/0.5	1.0
$Gd[Ga(OPr^i)_4]_3$	145/0.5	1.0
$Dy[Al(OPr^i)_4]_3$	203/0.5	1.0
$Ho[Al(OPr^i)_4]_3$	180/0.2	1.0
$Er[Al(OPr^i)_4]_3$	187/0.2	1.0
$Yb[Al(OPr^i)_4]_3$	200/0.5	1.1
$Lu[Al(OPr^i)_4]_3$	190/0.3	1.0

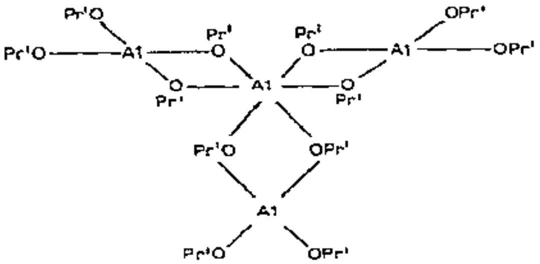


Fig. 3. Structure of tetrameric aluminium triisopropoxide $[Al(OPr^i)_3]_4$.

leaving the alkali chloride behind. This facility has enabled the synthesis of $Ce^{III}[Al(OPr^i)_4]_3$, which could be purified by volatilisation whereas the comparatively less volatile $Ce(OPr^i)_3$ has not yet been isolated in a pure state, as it tends to get oxidised very readily to the yellow ceric(IV) derivatives by contact with atmospheric oxygen. In reaction (3), the double isopropoxide distils out leaving the less volatile lanthanide isopropoxide when it is taken in excess; on the other hand, if aluminium isopropoxide is taken initially in more than 1 : 3 molar ratios, its excess is distilled out first around 100°C/1 mm pressure, followed by the distillation of the double isopropoxide $Ln[Al(OPr^i)_4]_3$ around 200°C/1 mm.

In view of the rather poor volatilities of the tris-isopropoxides of lanthanides, the highly volatile character of the monomeric double metal isopropoxides, e.g. $Ln[Al(OPr^i)_4]_3$, indicates interesting structural characteristics. Mehrotra and Agarwal [174] proposed a chelated structure of the type indicated below (Fig. 4) in analogy with the structure of tetrameric aluminium isopropoxide, $Al_4(OPr^i)_{12}$, (Fig. 3) proposed by Bradley [180] and confirmed by Shiner et al. [181] with the help of NMR spectroscopy. The NMR studies by Shiner et al. [181] find further confirmation in the work of Oliver et al. [182] and of Mehrotra and Mehrotra [183]. All these workers obtained three sets of doublets corresponding to methyl protons. The area of the upfield doublet was equal to the total area of the two low field doublets which were found to

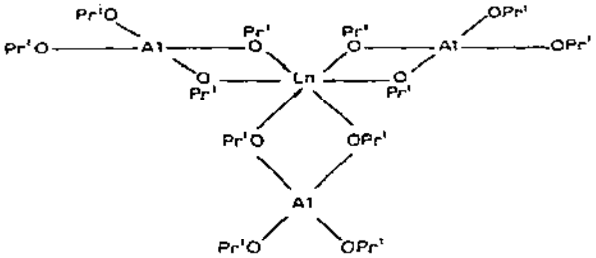


Fig. 4. Structure of monomeric lanthanide aluminium isopropoxide, $Ln[Al(OPr^i)_4]_3$.

be equal in themselves. The upfield doublet has been explained as due to the protons of the six terminal isopropoxy groups and the appearance of low field doublets to the methyl protons of the six bridged isopropoxy groups. The explanation given by Shiner et al. [181] for the presence of two sets of low field doublets was the non-interchangeability of the isopropoxy groups attached to the central aluminium atom. However, later workers have ascribed the appearance of these two equal doublets to the magnetic non-equivalence of the two methyls of each bridging isopropoxy group. This explanation was confirmed by Mehrotra as in an HA 100 spectrum of tetrameric aluminium isopropoxide, only two sets of septets due to methine protons could be obtained; the total area of these two identical septets was 1/6th of the total area of 3 doublets obtained due to methyl protons. These two equal septets can, therefore, be ascribed to the methine protons of the terminal and bridging isopropoxy groups which are equal in number.

The NMR spectra of the lanthanum double isopropoxide $La[Al(OPr^i)_4]_3$ was studied for the first time by Oliver and Worrall [184]. They observed only one doublet, centered at 1.48 downfield from tetramethylsilane (tms), and explained the occurrence of a single doublet in their NMR spectrum as due to the rapid exchange of the terminal and the bridging isopropoxy groups. Resolution of peaks could not be achieved even by cooling the solution to −60°C.

The NMR spectra of $Y[Al(OPr^i)_4]_3$ and $Pr[Al(OPr^i)_4]_3$ studied by Mehrotra and Mehrotra [183] also showed the presence of single doublets. The peak in the yttrium complex was found to be 1.25 ppm downfield from tms and in the praseodymium complex at 3.22 ppm upfield from tms. The shift of the position of the peak in the latter case can be explained as due to the paramagnetic effect of the central praseodymium.

As the above NMR studies could not provide a confirmation of the structures of lanthanide double isopropoxides proposed earlier, Mehrotra and Mehrotra [185] conjectured that the rate of exchange between the terminal and the bridging isopropoxy groups should be considerably reduced with the last members of lanthanide series, as the ionic radii decrease from 1.62 Å for lanthanum to 1.56 Å for ytterbium and lutetium. In their NMR studies of ytterbium aluminium isopropoxide, these workers obtained a very weak peak at 1.19 ppm downfield from tms and two broad peaks centered at 5.56 and 7.10 ppm upfield from tms. The latter peaks had an area ratio of 6 : 1 indicating that these could be assigned to methyl and methine protons, contact shifted considerably due to the paramagnetic nature of ytterbium. On cooling the solution to about −35°C, the peak at 5.56 resolved into two peaks of equal area centered at 5.6 and 7.1 ppm, and the upfield peak contact shifted to 8.8 ppm. However, the total area ratio of methyl and methine proton peaks remained as 6 : 1. This spectrum appears to lend support to the presence of two types of isopropoxy groups, viz. bridging and terminal, in almost equal numbers. The NMR studies of $Lu[Al(OPr^i)_4]_3$ have been all the more interesting as even at room temperature the spectra showed the presence of two doublets downfield from tms assigned to methyl proton.

In the spectrum (HA100) of scandium aluminium isopropoxide $Sc[Al(OPr^i)_4]_3$, it was observed that not only the bridging but the terminal methyl groups also are magnetically non-equivalent.

Some chemical evidence has also been obtained by Mehrotra [45] showing the difference in the behaviour of bridging and terminal isopropoxy groups in these double metal alkoxides of lanthanides. In reactions of $Ho[Al(OPr^i)_4]_3$ with excess of tertiary butanol, Bu^tOH, or tertiary amyl alcohol, Am^tOH only six isopropoxy groups undergo interchange reactions and further reaction was found to be extremely slow. These reactions, which yielded the stable products $Ho[Al(OPr^i)_2(OBu^t)_2]_3$ and $Ho[Al(OPr^i)_2(OAm^t)_2]_3$, show that bridging isopropoxy groups remained intact. A further verification was found by Mehrotra [45] in the reactions of $Ho[Al(OPr^i)_4]_3$ with acetylacetone, Hacac in benzene medium in 1 : 3, 1 : 6 and 1 : 12 molar ratios. Stable species corresponding to $Ho[Al_3(OPr^i)_9(acac)_3]$ and $Ho[Al(OPr^i)_2(acac)_2]_3$ were obtained whereas $Ho[Al(acac)_4]_3$ was found to dissociate in boiling benzene into the corresponding acetylacetonates, $Al(acac)_3$ and $Ho(acac)_3$.

The proposed structures of double lanthanide aluminium isopropoxides have been further supported by the similarity in the fragmentation pattern of $La[Al(OPr^i)_4]_3$, observed by Oliver and Worrall [186] and also of $Ho[Al(OPr^i)_4]_3$ and $Er[Al(OPr^i)_4]_3$ observed by Mehrotra [45] with the fragmentation pattern of $Al[Al(OPr^i)_4]_3$, observed by Fieggen et al. [187].

F. COMPOUNDS CONTAINING Ln—S—C BONDS AND Ln—N—C BONDS

Lanthanide complexes derived from sulphur donor atoms are expected to be weak because of poor interaction between hard acids (lanthanide atoms) and soft bases (sulphur ligands). Dutt et al. [188] were the first to indicate the formation of lanthanide chelates of mono-thiobenzoylacetone in aqueous solution. Following this, the neutral and anionic lanthanide complexes of the types, $M(dtc)_3$ and $[Et_4N][M(dtc)_4]$, (where M = La to Lu inclusive; except Pm; dtc = N,N-diethyldithiocarbamate) have been prepared by reactions between anhydrous tribromide and stoichiometric amount of sodium N,N-diethyldithiocarbamate in anhydrous ethanol [189]. These complexes are readily crystallised from anhydrous acetonitrile or methylene chloride and are insoluble in benzene. Treatment of the tris-N,N-dithiocarbamate complex with Na(dtc) and Et_4NBr in anhydrous alcohol also produces the ionic complex $[Et_4N][M(dtc)_4]$. X-ray powder diffraction results indicate that structural change occurs within the lanthanide series of tris-complexes. Those of La to Nd inclusive are isostructural whilst those of Sm to Lu inclusive form a second isostructural series. The anionic dithiophosphinate complexes of lanthanide, $[Ln\{S_2P(OEt)_2\}_4]^-$, have also been isolated [190]. The crystal structure of tetraphenylphosphonium tetrakis-(dimethyldithiophosphinato)praseodymium has been determined [191]. The Pr ion is coordinated to eight sulphur atoms which have a distorted tetragonal antiprismatic arrangement. The Pr atoms alone form almost perfect hexagonal lattices. The crystal structure of tris-

(dicyclohexyldithiophosphinate) complexes of Pr and Sm have also been determined [192]. In both the cases Pr and Sm atoms are coordinated to six sulphur atoms. The coordination polyhedra are distorted trigonal prisms with different degrees of distortion. In these complexes, the M—S bond lengths are the shortest lanthanide—sulphur bonds which have so far been observed. The mass spectra of Pr and Sm complexes of dithiophosphonic acid, $Ln(S_2PR_2)_3$ where $R = C_6H_{11}$, indicate the stability of Ln—S bond in the vapour phase [193]. In both cases, the parent peak is observed along with peaks due to loss of two cyclohexyl groups. This suggests an appreciable stability of Ln—S bond under electronic impact. ^1H and ^{31}P chemical shifts have also been measured [194] for the derivatives $[Ph_4As]\,[Ln\{S_2P(OEt)_2\}_4]$. This complex reacts with triphenylphosphineoxide in ethanolic solution to displace one (in the case of La—Pr products) or two (in the case of Nd—Lu products) ligands to form neutral complexes [195], $Ln\{S_2P(OEt)_2\}_3 \cdot (OPPh_3)_2$. The neutral lanthanum complex has a square antiprismatic structure and the Ln atom is coordinated to six sulphur and two oxygen atoms; the bulky phosphineoxides are located on opposite sides of the molecule.

Recently, the preparation of tris- and tetrakis-monothiodibenzoylmethanates, monothiobenzoylacetonates and monothiotrifluorothienylacetonates of lanthanides have been reported [196]. The tris-complexes are highly soluble in methanol, ethanol, acetone, chloroform and benzene whereas tetrakis-chelates are soluble in the last three solvents only.

Another interesting class of volatile compounds containing Ln—N bonds [26,27], has been prepared by the following reactions

$$LnCl_3 + 3\ LiN(SiMe_3)_2 \rightarrow Ln\{N(SiMe_3)_2\}_3 + 3\ LiCl$$

(Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Ho, Yb, and Lu)

All these complexes are three coordinate, readily hydrolysable, soluble in organic solvent and crystallise as needles from pentane. They are monomeric in benzene and volatile at 75—100°C and 10^{-4} mm Hg. X-ray studies have shown that Eu and Yb compounds are isomorphous.

Tris-N-bis(trimethyl)silyl lanthanides react [197] with triphenylphosphineoxide to form a 1 : 1 adduct, $La\{N(SiMe_3)_2\}_3 \cdot OPPh_3$, and an unexpected new μ-peroxo complex, $O_2La_2(NSi_2Me_6)_4 \cdot (OPPh_3)_2$. The peroxo group acts as a doubly bidentate bridge between the two lanthanum atoms which are each bonded to two silylamido and one phosphineoxide ligand, giving each La atom a coordination number of five. This is the first lanthanide peroxy compound reported. The four coordinate adducts, $La\{N(SiMe_3)_2\}_3 \cdot OPPh_3$, are monomeric and have pseudotetrahedral geometry around the La atom.

Lanthanide porphyrin complexes which also contain Ln—N bonds are interesting due to their possible use as paramagnetic and fluorescence probes of biomolecules [198—201]. The highly electropositive trivalent lanthanide porphyrin complexes [202] are expected to depict behaviour intermediate between that of the highly electropositive Mg—porphyrin complex and the first transition series Fe—porphyrin complex. The preparation of virtually all the lanthanide octaethylporphyrin complexes [203], Ln(oep)OH, was achieved by heating the appropriate anhydrous lanthanide halide and octaethylporphyrin in imidazole melt at 210°C. This method was also used to prepare tetraphenylporphyrin, mesoporphyrin and protoporphyrin lanthanide complexes. The lighter lanthanide porphyrin complexes are very susceptible to hydrolysis, but middle lanthanide porphyrin complexes are moderately stable, and the heavier lanthanide porphyrin complexes are relatively more stable to hydrolysis. A dimeric structure of these lanthanide porphyrin complexes has been proposed on the basis of geometrical considerations.

ACKNOWLEDGEMENTS

One of the co-authors (J.M.B.) expresses gratitude to University Grants Commission, New Delhi, for the award of National Associateship and to the Government of Rajasthan for grant of duty leave.

REFERENCES

1 T. Moeller, D.F. Martin, L.C. Thompson, R. Ferrus, G.R. Feistal and W.J. Randall, Chem. Rev., 65 (1965) 1.
2 S.P. Sinha, Complexes of Rare Earths, Pergamon, Oxford, 1966.
3 T. Moeller, E.R. Birnbaum, J.H. Forsberg and R.B. Gayhart, Progress in the Science and Technology of the Rare Earths, Vol. 3, 1968, p. 61.
4 G.A. Crosby, Mol. Cryst., 1 (1966) 37.
5 A. Lempicki and H. Samelson in A.K. Levine (Ed.), Laser, Vol. 1, Marcel Dekker, New York, 1966, p. 181.
6 B.D. Flockhart, Crit. Rev. Anal. Chem., 6 (1976) 69.
7 O. Fofer, Top. Stereochem., 9 (1976) 111.
8 A.N. Cokerill, G.L.O. Davies, R.C. Harden and D.M. Rackhan, Chem. Rev., 73 (1973) 55.
9 B.C. Mayo, Chem. Soc. Rev., (1973) 49; J.A. Glasel, Prog. Inorg. Chem., 18 (1973) 383.
10 M. Tsutsui, C. Hyde, A. Gebala and N. Ely, in Organometallic Chemistry, Plenum, New York, 1975, p. 93; H. Gysling and M. Tsutsui, Adv. Organometal. Chem., 9 (1970) 461.
11 E.C. Baker, G.W. Halstead and K.N. Raymond, Struct. Bonding, 25 (1976) 23.
12 T.J. Marks, Progr. Inorg. Chem., 24 (1978) 51.
13 S.P. Sinha, Struct. Bonding, 25 (1976) 69.
14 M.G.B. Drew, Progr. Inorg. Chem., 23 (1977) 67; M.G.B. Drew, Coord. Chem. Rev., 24 (1977) 179.
15 J.H. Forsberg, Coord. Chem. Rev., 10 (1973) 195.
16 T. Moeller, in H.J. Emeleus (Ed.), MTP International Reviews of Science Vol. 1, Butterworths, London, 1972, p. 275.
17 C.S. Springer, Jr., D.W. Meek and R.E. Sievers, Inorg. Chem., 6 (1967) 1105.
18 K.J. Eisentraut and R.E. Sievers, J. Inorg. Nucl. Chem., 29, (1967) 1931.
19 M.F. Richardson, W.F. Wagner and D.E. Sands, J. Inorg. Nucl. Chem., 30, (1968) 1275.
20 M.F. Richardson and R.E. Sievers, Inorg. Chem., 10 (1971) 498.
21 F.A. Cotton and P. Legzdins, Inorg. Chem., 7 (1968) 1777.
22 E.D. Watkins, J.A. Cunningham, T. Philips, D.E. Sands and W.F. Wagner, Inorg. Chem., 8 (1969) 29.
23 M.F. Richardson, C.W.R. Corfield, D.E. Sands and R.E. Sievers, Inorg. Chem., 9 (1970) 1632.
24 C.S. Erasmus and J.C.A. Boeymens, Acta Crystallogr., Sect. B, 26 (1970) 1843.

25 W.T. Carnall, S. Siegel, J.R. Farraro, B. Tani and E. Gebert, Inorg. Chem., 12 (1970) 560.
26 J.S. Ghotra, M.B. Hursthouse and A.J. Welch, J. Chem. Soc. Chem. Commun., (1973) 669.
27 D.C. Bradley, J.S. Ghotra and F.A. Hart, J. Chem. Soc. Dalton Trans., (1973) 1021.
28 R.C. Mehrotra, M.M. Agarwal and A. Mehrotra, Synth. Inorg. Met.-Org. Chem., 3 (1973) 181, 407.
29 J.H. Burns, W.H. Baldwin and F.H. Fink, Inorg. Chem., 13 (1974) 1916.
30 R.G. Pearson (Ed.), Hard and Soft Acids and Bases, Dowden Hutchinson and Ross, New York, 1973.
31 F. Calderazzo, R. Pappalardo and S. Losi, J. Inorg. Nucl. Chem., 28 (1966) 987.
32 K.S. Mazdiyasni and B.J. Schaper, J. Less-Common Metals, 30 (1973) 105.
33 A.H. Bruder, S.R. Tanny, H.A. Rockefeller and C.S. Springer, Jr., Inorg. Chem., 13 (1974) 880.
34 K.S. Mazdiyasni, C.T. Lynch and J.S. Smith, Inorg. Chem., 5 (1966) 343.
35 L.M. Brown and K.S. Mazdiyasni, Inorg. Chem., 9 (1970) 2783.
36 J.R. Blackborow, C.R. Eady, E.A.K. Von Gustorf, A. Scrvanti and O. Wolfbeis, J. Organometal. Chem., 108 (1976) C32.
37 I.B. Lis and W.G. Bos, J. Inorg. Nucl. Chem., 39 (1977) 443.
38 J.M. Koehler and W.G. Bos, Inorg. Nucl. Chem. Lett., 3 (1967) 545.
39 J.K. Przystal, W.G. Bos and J.B. Lis, J. Inorg. Nucl. Chem., 33 (1971) 679.
40 S.N. Misra, T.N. Misra and R.C. Mehrotra, J. Inorg. Nucl. Chem., 25 (1963) 201.
41 T.N. Misra, Ph.D. Thesis, University of Rajasthan, Jaipur, 1964.
42 S.N. Misra, Ph.D. Thesis, University of Rajasthan, Jaipur, 1965.
43 J.M. Batwara, Ph.D. Thesis, University of Rajasthan, Jaipur, 1969.
44 U.D. Tripathi, Ph.D. Thesis, University of Rajasthan, Jaipur, 1971.
45 A. Mehrotra, Ph.D. Thesis, University of Rajasthan, Jaipur, 1972.
46 J. Sahai, Ph.D. Thesis, University of Rajasthan, Jaipur, 1974.
47 R.C. Mehrotra, J. Indian Chem. Soc., 31 (1954) 304.
48 D.C. Bradley, Adv. Inorg. Chem. Radiochem., 15 (1972) 259.
49 D.C. Bradley, D.P. Gaur and R.C. Mehrotra, Metal Alkoxides, Academic Press, London, 1978.
50 D.C. Bradley and M.M. Faktor, Chem. Ind. (London), (1958) 1332.
51 S.N. Misra, T.N. Misra, R.N. Kapoor and R.C. Mehrotra, Chem. Ind. (London), (1963) 120.
52 B.S. Sankhla, S.N. Misra and R.N. Kapoor, Chem. Ind. (London), (1965) 382.
53 J.M. Batwara, U.D. Tripathi, R.K. Mehrotra and R.C. Mehrotra, Chem. Ind. (London), (1966) 1379.
54 J.M. Batwara, U.D. Tripathi and R.C. Mehrotra, J. Chem. Soc. A, (1967) 991.
55 B.S. Sankhla, S.N. Misra and R.N. Kapoor, Aust. J. Chem., 20 (1967) 2013.
56 S.N. Misra, T.N. Misra and R.C. Mehrotra, Aust. J. Chem., 21 (1968) 797.
57 J.M. Batwara and R.C. Mehrotra, Inorg. Chem., 9 (1970) 2505.
58 A. Mehrotra and R.C. Mehrotra, Indian J. Chem., 10 (1972) 532.
59 A. Merbach and J.P. Carrard, Helv. Chim. Acta, 54 (1971) 2771.
60 R.A. Andersen, D.H. Templeton and A. Zalkin, Inorg. Chem., 17 (1978) 1962.
61 J.M. Batwara and R.C. Mehrotra, J. Inorg. Nucl. Chem., 32 (1970) 411.
62 R.N. Kapoor and B.S. Sankhala, Can. J. Chem., 44 (1966) 2113.
63 S.N. Misra, T.N. Misra and R.C. Mehrotra, Indian J. Chem., 5 (1967) 439.
64 J.M. Batwara and R.C. Mehrotra, unpublished results.
65 J.E. Powell and J.L. Farrell, in E.V. Kleber (Ed.), Rare Earth Research, Macmillan, London, 1961, p. 26.
66 W.R. Stagg and J.E. Powell, Inorg. Chem., 3 (1964) 242.
67 L.A.K. Stavely, D.R. Markham and M.R. Jones, Nature (London), 211 (1966) 1173.
68 N.A. Shorik and V.V. Serebennikov, Zh. Neorg. Khim., 11 (1966) 764.

69 V.A. Korobova and G.A. Prik, Russ. J. Inorg. Chem., 10 (1965) 456.
70 L.A.K. Stavely, D.R. Markham and M.R. Jones, J. Inorg. Nucl. Chem., 30 (1968) 231.
71 S.L. Bertha and G.R. Choppin, Inorg. Chem., 8 (1969) 613.
72 D. Brown, Halides of Lanthanides and Actinides, Wiley, London, 1968, p. 154.
73 G.S. Manku and R.C. Chadha, J. Inorg. Nucl. Chem., 34 (1972) 357.
74 S.N. Misra, T.N. Misra and R.C. Mehrotra, Indian J. Chem., 5 (1967) 372.
75 J.M. Batwara, U.D. Tripathi and R.C. Mehrotra, unpublished results.
76 S. Panda and D. Patnaik, J. Indian Chem. Soc., 33 (1966) 877.
77 T. Moeller, V. Galasyn and J. Xavier, J. Inorg. Nucl. Chem., 15 (1960) 259.
78 V.N. Maksimov, A.V. Novoselova and K.N. Somenkov, Zh. Neorg. Khim., 2 (1957) 997.
79 J.A. Seaton, F.G. Sherif and L.F. Audrieth, J. Inorg. Nucl. Chem., 9 (1959) 222.
80 J.R. Witt and E.J. Onstott, J. Inorg. Nucl. Chem., 24 (1962) 637.
81 T.A. Krasovskaya and S.B. Pirkes, Russ. J. Inorg. Chem., 17 (1972) 780.
82 R.C. Paul, G. Singh and J.S. Ghotra, Indian J. Chem., 11 (1973) 294.
83 S.N. Misra, T.N. Misra and R.C. Mehrotra, J. Inorg. Nucl. Chem., 25 (1963) 195.
84 M.D. Taylor, C.P. Carter and C.I. Wynter, J. Inorg. Nucl. Chem., 30 (1968) 1504.
85 M. Hasan, B.S. Sankhla, S.N. Misra and R.N. Kapoor, J. Prakt. Chem., 38 (1968) 313.
86 M.A. Gouveia and R.G. Decarvalho, J. Inorg. Nucl. Chem., 28 (1966) 913.
87 O.E. Zvyagintsev and V.P. Tikhonev, Russ. J. Inorg. Chem., 9 (1966) 865.
88 Z.M. Babeshkina, L.I. Martynenko and A.I. Grigorev, Zh. Neorg. Khim., 11 (1966) 1282.
89 F. Brezina and J. Rosicky, Monatsh. Chem., 96 (1965) 1025.
90 D.T. Sawyer, Chem. Rev., 64 (1964) 633.
91 S. Dubey, A.M. Bhandari, S.N. Misra and R.N. Kapoor, Indian J. Chem., 7 (1969) 710.
92 U.D. Tripathi and R.C. Mehrotra, unpublished results.
93 J.H. Burns and W.H. Baldwin, Inorg. Chem., 16 (1977) 289.
94 E.O. Brimm, Ph.D. Thesis, University of Illinois, Illinois, U.S.A., 1940; referred to in ref. 1.
95 R.G. Charles, J. Inorg. Nucl. Chem., 26 (1964) 2298.
96 S.S. Krishnamurthy, Ph.D. Thesis, Indian Institute of Sciences, Bangalore, India, 1967.
97 H. Yamada, Bull. Chem. Soc. Jpn., 32 (1959) 1051.
98 R.C. Mehrotra, R. Bohra and D.P. Gaur, Metal β-Diketonates and Allied Derivatives, Academic Press, London, 1978.
99 R.E. Whan and G.A. Crosby, J. Mol. Spectrosc., 8 (1962) 315.
100 M. Metlay, J. Chem. Phys., 39 (1963) 491.
101 M.L. Bhaumik, P.C. Fletcher, L.J. Ougent, S.M. Lee, S. Higa, C.L. Telk and M. Weimberg, J. Phys. Chem., 68 (1964) 1490.
102 L.R. Melby, N.J. Rose, E. Abramson and J.C. Caris, J. Am. Chem. Soc., 86 (1964) 5117.
103 H. Baur, J. Blanc and D.L. Ross, J. Am. Chem. Soc., 86 (1964) 6125.
104 R.G. Charles and E.P. Riedel, J. Inorg. Nucl. Chem., 28 (1966) 3005.
105 N. Fillipescu, G.W. Mushrush, C.R. Hurt and N. McAvoy, Nature (London), 211 (1966) 960.
106 R.G. Charles, J. Inorg. Nucl. Chem., 26 (1964) 2195.
107 V. Janardhanarao and A.P.B. Sinha, Indian J. Chem., 4 (1966) 196.
108 G.W. Pope, J.F. Steinbach and W.F. Wagner, J. Inorg. Nucl. Chem., 20 (1961) 304.
109 N.K. Dutt and P. Bandyopadhyaya, J. Inorg. Nucl. Chem., 26 (1964) 729.
110 N.K. Dutt and P. Bandyopadhyaya, J. Inorg. Nucl. Chem., 26 (1964) 1610.
111 N.K. Dutt and S. Updhyaya, J. Inorg. Nucl. Chem., 28 (1966) 2719.
112 N.K. Dutt and K. Nag, J. Inorg. Nucl. Chem., 30 (1968) 2779.
113 N.K. Dutt and S. Sur, J. Inorg. Nucl. Chem., 31 (1969) 3171.
114 N.K. Dutt and S. Rahut, J. Inorg. Nucl. Chem., 32 (1970) 2905.
115 N.K. Dutt and U.M. Sharma, J. Inorg. Nucl. Chem., 32 (1970) 1035.

116 N.K. Dutt, S. Sur and S. Rahut, J. Inorg. Nucl. Chem., 33 (1971) 121.
117 N.K. Dutt and S. Sur, J. Inorg. Nucl. Chem., 33 (1971) 1717.
118 N.K. Dutt and S. Rahut, J. Inorg. Nucl. Chem., 33 (1971) 1725.
119 N.K. Dutt and S. Sanyal, J. Inorg. Nucl. Chem., 33 (1971) 651.
120 J.G. Stites, C.N. McCarty and L.L. Quill, J. Am. Chem. Soc., 70 (1948) 3142.
121 S.J. Lyle and A.D. Witts, Inorg. Chim. Acta, 5 (1971) 481.
122 J.A. Cunningham, D.E. Sands and W.F. Wagner, Inorg. Chem., 6 (1967) 99.
123 T. Phillips, D.E. Sands and W.F. Wagner, Inorg. Chem., 7 (1968) 2295.
124 J.A. Cunningham, D.E. Sands, W.F. Wagner and M.F. Richardson, Inorg. Chem., 8 (1969) 22.
125 A. Zalkin, D.H. Templeton and D.G. Karraker, Inorg. Chem., 8 (1969) 2280.
126 A.L. Ilinskii, L.A. Aslanov, V.I. Ivanov, A.D. Khalilov and O.M. Pertrukhin, J. Struct. Chem., 10 (1969) 263.
127 J.P.R. DeVilliers and J.C.A. Boeyens, Acta Crystallogr., Sect. B, 27 (1971) 692.
128 R.M. Wing, J.J. Uebel and K.K. Anderson, J. Am. Chem. Soc., 95 (1973) 6046.
129 D.L. Kepert, J. Chem. Soc. Dalton Trans., (1974) 617.
130 J.G. White, Inorg. Chim. Acta, 16 (1976) 159.
131 J.M. Batwara and R.C. Mehrotra, Proc. Rare Earth Research Conf., 1968, p. 771.
132 R.G. Charles and R.C. Ohlman, J. Inorg. Nucl. Chem., 27 (1965) 255.
133 K. Utsunomiya and T. Shigematsu, Anal. Chim. Acta, 58 (1972) 411.
134 R.G. Charles and A. Perrotto, J. Inorg. Nucl. Chem., 26 (1964) 373.
135 K.J. Eisentraut and R.E. Sievers, J. Am. Chem. Soc., 87 (1965) 4254.
136 K.J. Eisentraut and R.E. Sievers, J. Am. Chem. Soc., 91 (1969) 3476.
137 M.K. Archer and R.W. Jotham, Inorg. Nucl. Chem. Lett., 7 (1971) 1135.
138 S. Schwendiman and J.O. Zink, Inorg. Chem., 11 (1972) 3051.
139 A.H. Bruder, S.R. Tanny, H.A. Rockfeller and C.S. Springer, Inorg. Chem., 13 (1974) 880.
140 J.A. Cunningham and R.E. Sievers, J. Am. Chem. Soc., 97 (1975) 1586.
141 D.R. Dakternieks, J. Inorg. Nucl. Chem., 38 (1976) 141.
142 G.D. Ross Napier and T.M. Shepherd, J. Inorg. Nucl. Chem., 38 (1976) 1587.
143 G.A. Calton, F.A. Hart and G.P. Moss, J. Chem. Soc. Dalton Trans., (1975) 221.
144 N.K. Khalmurzaev, I.A. Muraveva, L.I. Martynenko and V.I. Spitsyn, Russ. J. Inorg. Chem., 21 (1976) 894.
145 H. Samelson, C. Brecher and A. Lempicki, J. Chem. Phys., 64 (1967) 165.
146 S.N. Misra, T.N. Misra and R.C. Mehrotra, Indian J. Chem., 3 (1965) 525.
147 B.S. Sankhla and R.N. Kapoor, Aust. J. Chem., 20 (1967) 685.
148 S.N. Misra, T.N. Misra and R.C. Mehrotra, Indian J. Chem., 5 (1967) 372.
149 B.S. Sankhla and R.N. Kapoor, Can. J. Chem., 44 (1966) 1369.
150 M. Hasan, S.N. Misra and R.N. Kapoor, Indian J. Chem., 7 (1969) 519.
151 R.E. Sievers, in S. Kirschner (Ed.), Coordination Chemistry, Plenum, New York, 1969, p. 270.
152 R.G. Charles and A. Perrotto, Anal. Chim. Acta, 30 (1964) 131.
153 P. Feng and Q. Fernando, Anal. Chim. Acta, 24 (1961) 548.
154 T. Moeller and D.E. Jackson, Anal. Chem., 22 (1950) 1393.
155 H.F. Aly, F.M. Abdel Karim and A.T. Kandil, J. Inorg. Nucl. Chem., 33 (1971) 4340.
156 S. Yamada, K. Yamanouchia and H. Huma, Synth. Inorg. Met.-Org. Chem., 1 (1971) 9.
157 S.K. Agrawal and J.P. Tandon, private communication, 1975.
158 J. Mach, Monatsh. Chem., 104 (1973) 564.
159 N.K. Dutt and R. De, Indian J. Chem. A, 14 (1976) 498.
160 N.K. Dutt and S. Upadhyaya, J. Inorg. Nucl. Chem., 29 (1967) 1369.
161 N.K. Dutt and S. Sur, J. Inorg. Nucl. Chem., 33 (1971) 115.
162 C. Woo, W.F. Wagner and D.E. Sands, J. Inorg. Nucl. Chem., 34 (1972) 307.
163 W.D. Horrocks and D.P. Wong, J. Am. Chem. Soc., 98 (1976) 7157.

164 L.S. Serdyuk and S.M. Lazorina, Dopov., Akad. Nauk Ukr. RSR, (1964) 1621; Chem. Abstr. 62 (1965) 8645a.
165 C.J. Pedersen and H.K. Frensdorff, Angew. Chem., Int. Ed. Engl., 11 (1972) 16.
166 B. Dietrich, J.M. Lehn, J.P. Sauvage and J. Blanzat, Tetrahedron, 29 (1973) 1629.
167 R.B. King and P.R. Heckley, J. Am. Chem. Soc., 96 (1974) 3118.
168 A. Cassol, A. Seminaro and G. Depaoli, Inorg. Nucl. Chem. Lett., 9 (1973) 1163.
169 M.E. Harmon, F.A. Hart, M.B. Hursthouse, G.P. Moss and P.R. Raithby, J. Chem. Soc. Chem. Commun., (1976) 396.
170 J.F. Desreux, A. Renard and G. Duyckaerts, J. Inorg. Nucl. Chem., 39 (1977) 1587.
171 G.A. Catton, M.E. Harmon, F.A. Hart, G.E. Hawkes and G.P. Moss, J. Chem. Soc. Dalton Trans. (1978) 181.
172 J.C.G. Bunzli, D. Wessner and H.T.T. Oanh, Inorg. Chim. Acta, 32 (1979) L33.
173 M. Ciampolini and N. Nardi, Inorg. Chim. Acta, 32 (1979) L9.
174 R.C. Mehrotra and M.M. Agarwal, J. Chem. Soc. Chem. Commun., (1968) 469.
175 A. Mehrotra and R.C. Mehrotra, Inorg. Chim. Acta Rev., 5 (1971) 127.
176 A. Mehrotra and R.C. Mehrotra, Indian J. Chem., 10 (1972) 532.
177 R.C. Mehrotra, M.M. Agarwal and A. Mehrotra, Synth. Inorg. Met.-Org. Chem., 3 (1973) 181.
178 R.C. Mehrotra, M.M. Agarwal and A. Mehrotra, Synth. Inorg. Met.-Org. Chem., 3 (1973) 407.
179 R.C. Mehrotra and A. Mehrotra, Inorg. Chem., 11 (1972) 2170.
180 D.C. Bradley, Progr. Inorg. Chem., 2 (1960) 303.
181 V.J. Shiner, D. Whittaker and V.P. Fernades, J. Am. Chem. Soc., 85 (1963) 2318.
182 J.G. Oliver, P.K. Philips and I.J. Worrall, J. Inorg. Nucl. Chem., 31 (1969) 1609.
183 R.C. Mehrotra and A. Mehrotra, J. Chem. Soc. Chem. Commun., (1972) 189.
184 J.G. Oliver and G.J. Worrall, J. Chem. Soc. Dalton Trans., (1970) 845.
185 R.C. Mehrotra and A. Mehrotra, Proc. Indian Acad. Sci., Sect. A, 40 (1974) 215.
186 J.G. Oliver and G.J. Worrall, J. Chem. Soc. A, (1970) 1389.
187 W. Fieggen, H. Gerding and N.M.M. Nibbering, Rec. Trav. Chim. Pays-Bas, 87 (1968) 377.
188 N.K. Dutt, K. Nag and T. Sheshadhari, J. Inorg. Nucl. Chem., 31 (1969) 1435.
189 D. Brown, D.G. Holah and C.E.F. Rickard, J. Chem. Soc. A, (1970) 786 and references cited therein.
190 A.A. Pinkerton, Inorg. Nucl. Chem. Lett., 10 (1974) 495.
191 A.A. Pinkerton and D. Schwarzenbach, J. Chem. Soc. Dalton Trans., (1976) 2464.
192 Y. Meseri, A.A. Pinkerton and G. Chapins, J. Chem. Soc. Dalton Trans., (1977) 725.
193 A.A. Pinkerton, Y. Meseri and C. Rieder, J. Chem. Soc. Dalton Trans., (1978) 85.
194 A.A. Pinkerton and W.L. Earl, J. Chem. Soc. Dalton Trans., (1978) 267.
195 A.A. Pinkerton and D. Schwarzenbach, J. Chem. Soc. Dalton Trans., (1976) 2466.
196 K. Nag and M. Chaudhury, J. Inorg. Nucl. Chem., 38 (1976) 309. Inorg. Nucl. Chem. Lett., 12 (1976) 307.
197 D.C. Bradley, J.S. Ghotra, F.A. Hart, M.B. Hursthouse and P.R. Raithby, J. Chem. Soc. Dalton Trans., (1977) 1166; D.G. Bradley, J.S. Ghotra, F.A. Hart, M.B. Hursthouse and P.R. Raithby, J. Chem. Soc. Chem. Commun., (1974) 40.
198 T.S. Srivastava, R. Hershberg and T. Yonetani, Biophys. J., 15 (1975) 1469.
199 W.D. Horrocks, Jr., R.F. Venteicher, C.A. Spilburg and B.L. Valk, Biochem. Biophys. Res. Commun., 64 (1975) 317.
200 M. Gouterman, C.D. Schumaker, T.S. Srivastava and T. Yonetani, Chem. Phys. Lett., 40 (1976) 456.
201 L.A. Martarano, C.P. Wong, W.D. Horrocks and A.M.P. Gonclaves, J. Phys. Chem., 80 (1976) 2389.
202 F.A. Cotton and G. Wilkinson, Advances in Inorganic Chemistry, Wiley-Interscience, New York, 1976.
203 T.S. Srivastava, Bio-inorg. Chem., 8 (1978) 61.