NMR STUDIES FOR THE DETERMINATION OF THE STRUCTURE OF ALKOXIDES AND DOUBLE ISOPROPOXIDES FOR SOME TRIVALENT METALS

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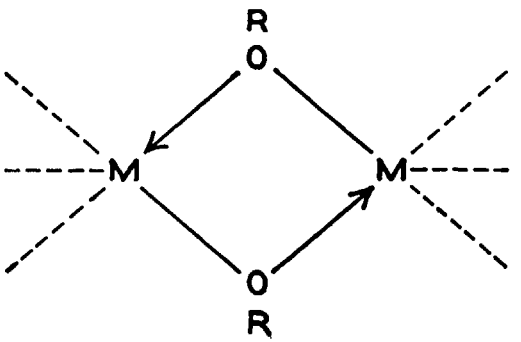
A brief review of the NMR studies of alkoxides of Vth, IVth and IIIrd group elements is presented. Fresh light has been thrown on the nature of splitting of the methyl protons of the bridged isopropoxy groups in tetrameric aluminium isopropoxide by a study of the methane proton of the spectrum.

NMR spectra of double isopropoxides of a few lanthanons with aluminium [$\{LnAl(OPr^i)_4\}_3$] have been discussed. In view of larger covalent radii of La (1.69 L°), Pr (1.65 A°) and Y(1.62 A°) the bridging and the terminal isopropoxy groups appear to undergo rapid exchange due to which only a single doublet is obtained in each case; this doublet is shifted upfield in the case of praseodymium due to its paramagnetic nature. In the case of Yb(1.56 °A) the broad peak due to methyl protons appears to resolve into two peaks of almost equal area at —35°C. In the case of Lu(1.56A°) the presence of two types of isopropoxy groups (bridged and terminal) is observed even at the room temperature. The spectrum of Sc(1.44A°) double alkoxide is identical with that of tetrameric aluminium isopropoxide, with the only difference that the doublet due to terminal methyl protons is also resolved into two doublets of almost equal area. This interesting splitting has been explained on the basis of magnetic non-equivalence of the methyl protons present in the non-bridging isopropoxy groups also.

The NMR spectra of [$In\{M(OPr^i)_4\}_3$] (with M=Al or Ga) have been shown to be similar to that of [$Al\{Al(OPr^i)_4\}_3$], with the difference that a splitting of the methyl protons of the terminal isopropoxy groups, as observed in case of Sc, is also observed in the *HA*-100 spectrum of [$In\{Al(OPr^i)_4\}_3$]. The NMR spectra of [$Ga\{Al(OPr^i)_4\}_3$] and [$Al\{Ga(OPr^i)_4\}_3$] have been discussed in the light of the possible interchange between terminal and central metal atoms.

INTRODUCTION

Although extensive studie. on the synthesis and chemical as well as physical properties of the alkoxides of various elements have been carried out, little information is available on the structure of these compounds. Most of the structures are generally based on their measured degree of association and only a few of these have been elucidated with the help of direct experimental evidence. Bradley *et al.* (1952 *a*, *b* and *c*) in a series of papers in early fifties showed that the degree of molecular association of alkoxides of group IVA elements could be explained on the basis of the formation of the alkoxy bridges of the type

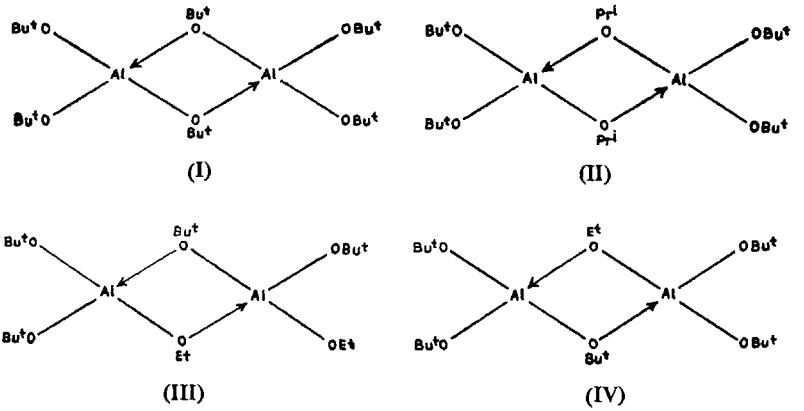


The nuclear magnetic resonance spectral studies of some metal alkoxides of group IVA and VA have only recently been made by Bradley and Holloway (1965). These studies, however, could not throw much light on the structure of the alkoxides. It was observed that at room temperature titanium ethoxide, normal propoxide and butoxide gave a single doublet only, suggesting the occurrence of a rapid exchange between the terminal and the bridged isopropoxy groups. In the cases of normal propoxide and normal butoxide more intense peaks are obtained on lowering the temperature indicating that a slowing down of the terminal-bridging exchange process occurs. However, in case of titanium ethoxide a more resolved spectrum is obtained at low temperature exhibiting the presence of new structures, most probably a tetramer, which are unstable in solution at room temperature. The isopropoxides of titanium, niobium and tantalum have been shown to exist as polymers in solution, the degree of polymerisation being concentration and temperature dependent. The relative abundance of the monomer and dimer species could also be roughly estimated.

Experimental and Discussions

Considerable light has, however, been thrown on the structures of aluminium alkoxides more recently by extensive studies of Shiner *et. al.* (1963) as well as of Oliver and Worrall (1970 *a*). Before presenting these interesting investigations, it would be worthwhile to summarise briefly the views about the structures of aluminium alkoxides arrived at from their other properties.

Considerable confusion prevailed in the literature on the molecular complexities of aluminium alkoxides (Ulrich & Nespital 1933; Wardlaw 1955; McElvain & Davies 1951; Mehrotra 1953; and Rudakoff 1960). It was observed by Mehrotra (1953) that aluminium isopropoxide showed an increase in the degree of association on being allowed to age. Based on the dimetric nature of aluminium tertiary butoxide and the steric factors involved in the alcoholysis of aluminium isopropoxide and ethoxide with tertiary alcohols, the following structures were suggested by Mehrotra (1953) for $Al_2(OBu^t)_6$, $Al_2(OPr^i)_2$ $(OBu^t)_4$, $Al_2(OEt)_2$ $(OBx^t)_4$, Al_2 (OEt) $(OBu^t)_5$ respectively.



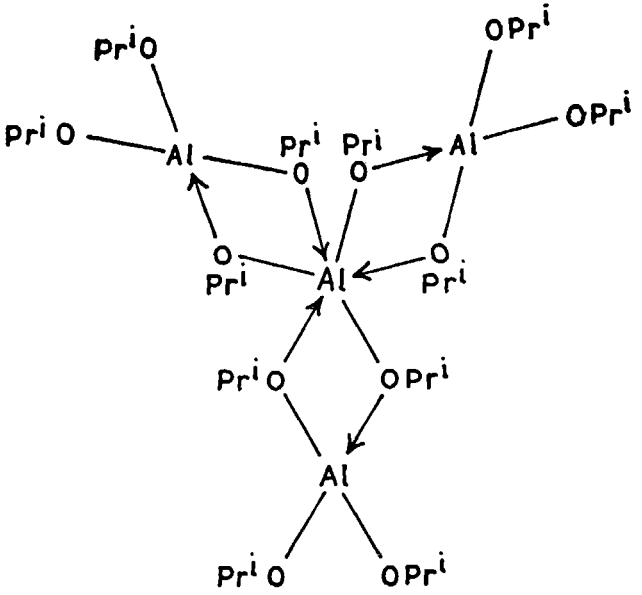
Evidence (N.M.R.) for structure (I) was provided by Shiner *et. al.* (1963). The spectrum shows the presence of only two singlets in the ratio of 1:2 as would be expected from structure (I). The spectrum further confirms the report of Bains (1962) that two distinguishable tertiary butyl groups exist in aluminium tertiary butoxide. It was presumed that the bridging tertiary butoxy groups give signals at 91 and 90 in benzene and carbon tetrachloride solution respectively and the non-bridging at 84 and 74H_z. No evidence for the dissociation of dimer at higher temperatures or by such basic solvents as dioxane or tertiary butyl alcohol has been obtained.

The NMR spectrum of $Al(OBu^t)_4$ $(OP^i)_2$ studied by Oliver and Worral (1970*b*) was found to be complex; it however, supported the unsymmetrical type of structure III. This structure contains three different tertiary butoxy groups and two isopropoxy groups. For such a structure it could be expected that the methyl part of the spectrum would consist of three due to tertiary butoxy groups and four doublets due to isopropoxy groups ; eleven peaks would therefore, be expected. The observed spectrum was found to be poorly resolved. Only seven at positions 66, 72, 76, 78, 84, 90 and 92 H_z could be obtained (measured from tetramethylsilane) and it was likely that the others were hidden beneath the broader peaks. The spectrum was a good evidence for the presence of unsymmetry in the molecule.

During ageing freshly distilled aluminium isopropoxide was found to change predominantly from trimeric to tetrameric units. Based on his theory that the metal alkoxides show minimum degree of polymerisation consistent with the attainment of higher covalency of metals, Bradley (1960) proposed the following structure for tetrameric aluminium isopropoxide :

The change in degree of association was ascribed by him to be due to the change of the tetra-coordinate aluminium atoms to hexa-coordinate.

In a recent publication, it has been shown by Fieggen *et al.* (1968) that physical properties like dipole moment and viscosity of liquid aluminium isopropoxide also change slowly on storage. This indicates the occurrence of some sort of molecular re-arrangement, the activation energy of which has been estimated to be about 12 kcal./mole although the end product of the rearrangement has not been identified.



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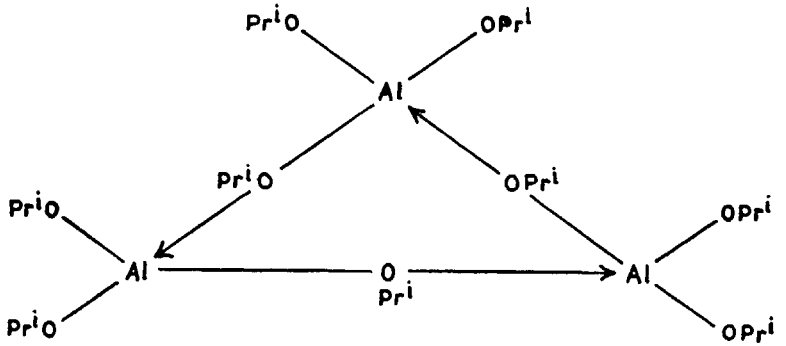
Shiner *et al.* (1963) observed that solid aluminium isopropoxide when dissolved in organic solvents gave spectra which gave evidence in favour of the tetrameric structure of the aluminium isopropoxide as proposed by Bradley (1960). Three sets of doublets of the methyl proton peaks were observed. The area of the upfield doublet was equal to the area of the two low field doublets which were found to be equal in themselves. The upfield doublet was explained to be due to the protons of the six-terminal groups and the low field doublet was explained to be due to the methyl protons of the six bridged isopropoxy groups. The explanation given by Shiner *et al.* (1963) for the presence of two low field doublets was the non-interchangeability of the isopropoxy groups attached to the central aluminium atom. Consequently, the methyl groups appear to have a fixed orientation which may be approximately equatorial or oxial tc the plane of aluminium atoms.

The tetrameric aluminium isopropoxide on being heated to 200°C, followed by a rapid cooling of the melt is converted into trimeric isopropoxide the structure of which appears to correspond to the cyclic form (as suggested by Robinson and Peak (1935) for tetrameric aluminium isopropoxide) as, only a single doublet of the methyl proton peaks is observed in the spectrum. The structure can be depicted as follows :

Shiner *et al.* (1963) explained this to be due to the ready interchangeability of the bridging and the terminal isopropoxy groups in a structure of the above type. On cooling, some splitting of the peaks was observed and rough estimate of the heights of the peak finally obtained was in the ratio of 1:1:2:2.

The spectrum obtained by Oliver *et al.* (1969) was almost identical to the NMR spectrum of Shiner *et al.* (1963) consisting of three sets of doublets thus further confirming the proposed structure for tetrameric aluminium isopropoxide.



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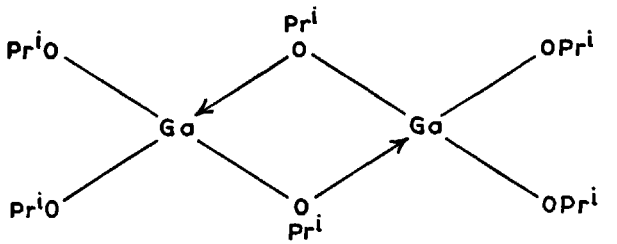
Huckerby *et al.* (1968), however, tried to explain the existence of two low field doublets in the bridged isopropoxy groups in the NMR spectrum of the tetrameric aluminium isopropoxide due to the assymetry of the bridging central aluminium atom. Oliver *et al.* (1969) observed that when freshly distilled aluminium isopropoxide was crystallised at 20°C, the crystillisation was complete after 48 hours. The NMR spectrum of the benzene solution of this solid consisted of three doublets showing the presence of tetrameric aluminium isopropoxide. However, when the solution of the solid was made in pyridine, partial dissolution occurred. The insoluble portion was filtered off and was then dissolved in benzene. The NMR spectrum of both the pyridine and the benzene solutions was taken. The benzene solution gave a spectrum identical to the one initially obtained whereas the NMR spectrum of the pyridine solution showed the presence of principally two peaks and a broad shoulder. The two very small low peaks were probably due to the presence of small amounts of the dissolved tetramer in the soluble pyridine solution. In order to identify the major components in the pyridine solution pure trimer was made by heating the isopropoxide to 200°C and then cooling rapidly. Separate solutions were made in pyridine and benzene and in both the cases a single doublet is obtained showing the presence of trimer only. Thus the original solid consisted of a mixture of trimer and tetramer. Some evidence for the existence of dimeric aluminium isopropoxide molecules observed by Mehrotra (1953) in vapour phase has also been obtained by Oliver *et al.* (1969) on changing the concentration of pyridine solution.

The NMR spectra taken in our laboratories (Mehrotra 1972) have also been found to consist of three sets of doublets in the ratio of 1:1:1:1:2:2 further confirming the tetrameric structure proposed for aluminium isopropoxide. The positions of the methyl proton peaks in the NMR spectra at room temperature in cycles per second can be given as below :

Solvent	A	B	C	D	E	F	Machine
CCl_4	91	85	80	74	69	63	A60
$CDCl_3$	93	87	82	76	71	65	A60
CCl_4	152	145	133	128	127	121	HA100

The HA-100 spectrum of the aluminium isopropoxide molecule was found to be very well resolved. In all the above cases discussions of only the methyl proton peaks have been done as the methine proton peaks have been found to be too weak and sometimes rather complex. However, in the case of the HA-100 spectrum of aluminium isopropoxide presence of two distinct sets of peaks with equal area have been observed. These peaks could be assigned to the methine proton of the terminal and bridging isopropoxy group. Following Huckerby *et al.* (1968), if the explanation of the splitting of the methyl protons in the spectra of some of the isopropoxides be sought in terms of magnetic non-equivalence of the two methyls on the same isopropoxy groups, then the corresponding methine protons on all the isopropoxy groups in similar environments could be expected to be identical. This general conclusion appears to be confirmed by the presence of only two sets of peaks of equal areas. According to Shiner *et al.* (1963) the spectrum ought to show the presence of three sets of peaks for the methine protons.

Attempts to elucidate the structure of analogous gallium isopropoxide have also been made by Worrall and Oliver (1969). The NMR spectrum of gallium isopropoxide was found to be identical to that of tetrametric aluminium analogue. However, on standing one of the doublets increased in intensity while the other two gradually became insignificant. This was explained by Worrall and Oliver (1969) to be due to the dissociation of the tetrameric molecule to dimeric forms. The structure proposed was similar to that proposed for dimeric aluminium isopropoxide.



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Similar results have been obtained in our laboratories (Mehrotra 1972). The spectrum has been studied at room temperature on a 60MH$_z$ machine in $CDCl_3$. The peaks were obtained at positions 91, 85, 79, 73, 73, 67. The peaks at positions 79 and 73 appeared to grow on allowing the solution to stand, at the expense of other peaks.

Related to the structure of aluminium isopropoxide, structures for a number of double isopropoxides of some other trivalent metal atoms have also been proposed. Mehrotra and Agarwal (1968) suggested the following structure for lanthanum aluminium isopropoxide,

The NMR spectra of the rare-earth double isopropoxides was studied for the first time by Oliver and Worrall (1970). They studied the spectrum of $[La\{Al(OPr^i)_4\}_3]$ and observed that only one doublet, centered at 1.48 ppm downfield from tetramethyl silane is obtained. They tried to explain the occurrence of a single doublet in the NMR spectrum of $[La\{Al(OPr^i)_4\}_3]$ to be due to the rapid exchange of the terminal and the bridging isopropoxy groups. In fact, they could

not resolve the peak even by cooling the solution to—60C°. However, they were able to confirm the proposed structure for $[La\{Al(OPr^i)_4\}_3]$ with the help of mass-spectroscopy.

The NMR spectra of $[Y\{Al(OPr^i)_4\}_3]$ and $[Pr\{Al(OPr^i)_4\}_3]$ studied in our laboratories (Mehrotra 1972) also showed the presence of a single doublet. The peak in $[Y\{Al(OPr^i)_4\}_4]$ was found to be at 1.25 ppm downfield from tetramethylsilane and in $[Pr\{Al(OPr^i)_4\}_3]$ at 3.22 ppm. upfield from tetramethylsilane. The shift of the position of the peak in the case of praseodymium can be explained to be due to the paramagnetic effect of the central praseodymium metal.

In view of the lanthanide contraction the atomic and ionic radii of lanthanons go on decreasing with the atomic number. It was conjuctured that the rate of exchange between the terminal and the bridging isopropoxy groups should be considerably reduced with the last members of the lanthanon series and that they should give more resolved spectra throwing some light on the structures of the compound. Ytterbium and lutecium were, therefore, chosen for the purpose. The covalent raaii of Y, La, Yb and Lu have been found to be 1.62, 1.69, 1.56 and 1.56 Å respectively. The NMR spectrum of ytterbium aluminium isopropoxide taken on a HA-100 machine showed the presence of a very weak peak at 1.19 ppm. downfield from tetramethylsilane. This is generally the usual position at which peaks due to methyl protons of isopropanol in diamagnetic metal isopropoxide occurs. However, upfield from tetramethylsilane two broad peaks centered at about 5.56 and 7.10 ppm. were also obtained. Integration showed them to have an area ratio of 6:1 indicating that these could be assigned to methyl and methine protons, contact shifted considerably, due to paramagnetic nature of ytterbium.

On cooling the solution to about —35°, further contact shift occurs. The peak at 7.1 ppm. due to methine proton appears to be shifted to 8.8 ppm. However, the peak at 5.56 ppm due to methyl protons is not only shifted at this lower temperature but appears to be resolved into two peaks of almost equal area centered at 5.6 and 7.1 p pm. The total area of these two peaks is again approximately six times the area of the peak at 8.8 ppm.

The reproducibility of the spectrum was confirmed by heating the solution again to about 40° (room temperature) when the spectrum originally obtained at room temperature was reproduced.

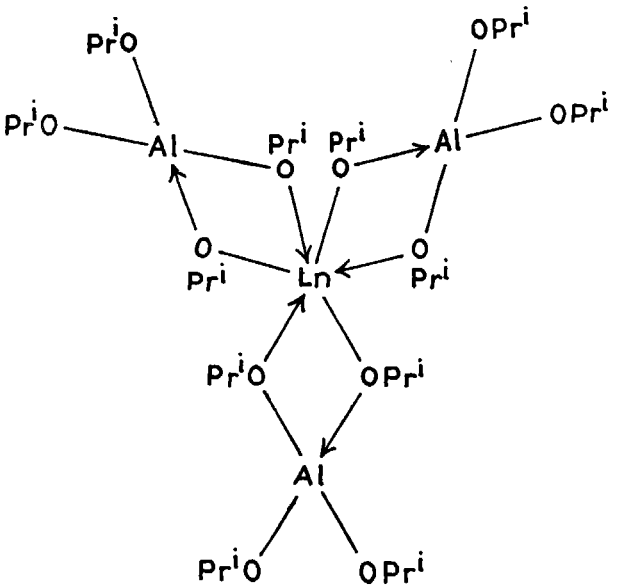
The spectrum of $[Yb\{Al(OPr^i)_4\}_3]$ at —35° appears to lend support to the presence of two type of isopropoxy groups in the molecule in almost equal numbers; this would correspond broadly to six terminal and six bridging isopropoxy groups as proposed in the structure for $[Ln\{Al(OPr^i)_4\}_3]$.

However, in case of $[Lu\{rA(OPr^i)_4\}_3]$ the presence of two types of isopropoxy groups bridged and terminal is observable even at room temperature. The peaks observed are found at 2.76, 2.56, 2.20, 2.03 ppm downfield from tetramethylsilane. The peaks due to methine protons were observed at 8.45 and 8.33 ppm. The area ratio of the methyl and the methine proton was found to be 6:1.

An interesting structural evidence has been obtained in our laboratories (Mehrotra and Mehrotra 1972) whilst studying the NMR spectrum of $[Sc\{Al(OPr^i)_4\}_3]$. Scandium having the same chemical properties as the rare-earths, was expected to form double isopropoxide similar to lanthanon double isopro-

poxides. However, it can be assumed that the intramolecular exchange of the bridging and the terminal isopropoxy groups in $[Sc\{Al(GPr^i)_4\}_3]$, would be comparatively much hindered due to the appreciably smaller radius of the scandium atom and hence a NMR spectrum, with better resolved peaks, could be expected. Diamagnetic nature was another advantage of using this metal for NMR studies.

The NMR spectrum of $[Sc\{Al(^iOPr)_4\}_3]$ was found to be almost identical to the spectrum of tetrameric aluminium isopropoxide suggesting a similar structure for $[Sc(Al(OPr^i)_4\}_3]$ also. The structure can be represented as follows :



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The positions of methyl proton peaks obtained in the NMR spectrum of $Sc\{Al(OPr^i)_4\}_3]$ in cycles per second from tetramethylsilane are given below :

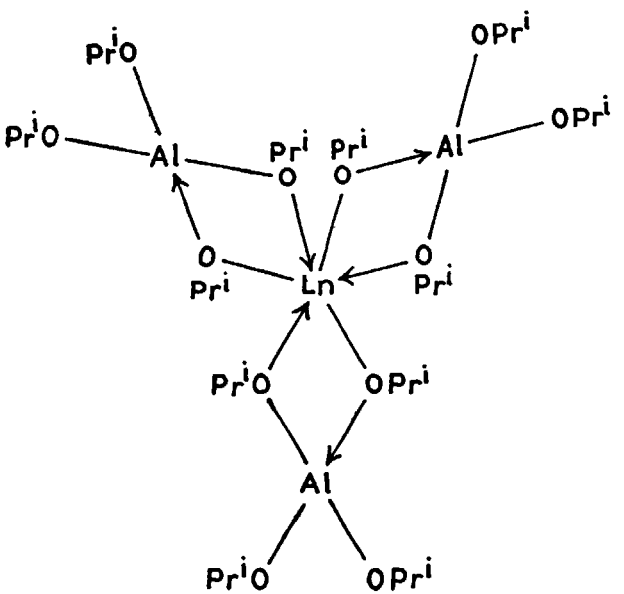
Solvent	A	B	C	D	E	F	G	H	Machine
CCl_4	151	145	135	129	115	109	112	106	HA100
CCl_4	90	84	81	75	68	62	67	61	A60
$CDCl_3$	95	89	85	79,	73	67	72	66	A60

However, in the case of $[Sc\{Al(OPr^i)_4\}_3]$ it has been observed that the peaks due to the methyl protons of the terminal isopropoxy groups also show splitting. In all the above spectra, however, the areas of doublet (A+B)+(C+D) (peaks due to methyl protons of the bridging isopropoxy groups) to that of (E+F) + (G+H) (peaks due to methyl protons of the terminal isopropoxy groups) are roughly in the ratio of 1:1:2 with the heights of the peaks E, F, G and H being almost equal. The splitting of the peaks of the terminal isopropoxy groups can be explained due to

magnetic non-equivalence of the methyl protons even in the non-bridging isopropoxy as observed in the case of bridging isopropoxy groups.

The existence of magnetic non-equivalence in methylene as well as methyl proton in a variety of compounds has been observed by a number of scientists (Waugh & Cottob 1961; Kaplan & Roberts 1961; Finegold 1960; Shafer *et al.* 1961; Pritchard & Lanterbur 1961; Bowman *et al.* 1965; Van Gorkam & Hall 1968; and Oliver & Worrall 1970). Oliver and Worrall in 1970 recorded $60MH_3$ spectra of tribenzyloxy aluminium and $220MH_3$ spectra of tri-benzyloxy aluminium and tri-(4-chloro benzyloxy) aluminium and found that methylene protons of both the terminal as well as the bridging alkoxy groups in the $220MH_z$ spectrum exhibit magnetic non-equivalence. Similarly the non-equivalence of methyl protons in some isopropyl esters has been exhibited by Bowman *et al.* (1965). The data obtained above support the presence of magnetic non-equivalence in the methyl protons of the non-bridging isopropoxy groups and thus throwing some light on the nature of the spectrum.

NMR spectra of $[In\{Al(OPr^i)_4\}_3]$ and $[(InGa(GPr_4)\}_3]$ have also been taken in our laboratories (Mehrotra and Mehrotra 1972). These also seem to be having a structure similar to tetrameric aluminium isopropoxide. The structure can be given as follows :



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The spectrum of $[In\{Al(OPr^i)_4\}_3]$ when run on a HA 100 machine was found to be similar to that of $[Sc\{Al(OPr^i)_4\}_3]$. The peaks due to the terminal isopropoxy groups also showing splitting.

In view of the identical covalent radii (1.44 Å) for both scandium and indium,

Methyl proton peaks of the isopropoxides in cycles per second at 60 MH_z from tetramethylsilane at room temperature

Compound	Solvent	A	B	C	D	E	F
$[In\{Al(OPr^i)_4\}_3]$	CCl_4	91	85	81	75	69	63
,,	$CDCl_3$	91	85	81	75	69	63
$[In(Ga(OPr^i)_4\}_3]$	$CDCl_3$	91	85	83	77	73	67

the identity of the spectra of $[Sc\{Al(OPr^i)_4\}_3]$ and $[In(Al(OPr^i)_4\}_3]$ can be easily understood.

Methyl proton peaks in the NMR spectra of $[In\{Al(OPr^i)_4\}_3]$ in cycles per second from tetramethylsilane at room temperature

Solvent	A	B	C	D	E	F	G	H
CCl_4	151	145	135	129	116	110	114	108
$CDCl_3$	151	145	135	129	116	110	114	108

The NMR spectra of $[Ga\{Al(OPr^i)_4\}_3]$ and $[Al\{Ga(OPr^i)_4\}_3]$ were also taken but they were found to be slightly complicated ; the nature of the spectra could, however, be easily understood if some interchange was assumed to be occurring between central and terminal metal atoms. Thus the spectrum of the double isopropoxide corresponding to the over-all compositoin $[Ga(Al(OPr^i)_4\}_3]$ can be explained, if it were actually a mixture of $[Ga\{Al(OPr^i)_4\}_3]$ and $[Al(Ga\{OPr^i)_4\}$ $\{Al(OPr^i)_4\}_2]$ in the molar ratio 1:2. Similarly, the spectrum of $[Al(Ga(^iOPr)_4\}_3]$ appeared to show the presence of $[Al\{Ga(OPr^i)_4\}_3]$ and $[Ga\{Al(OPr^i)_4\}$ $\{Ga(OPr^i)_4\}_2]$ in $\sim$ 1:2 molar ratio. These interchanges appear to be feasible as the covalent radii of Al and Ga (i.e., 1.18 and 1.26 Å) are close together. In view of the comparatively much larger covalent radius (1.44 Å) of indium. this type of interchange for double indium aluminium isopropoxides does not appear to take place and hence, the spectrum of this derivative corresponds to the structure $[In\{Al(OPr^i)_4\}_3]$ only.

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