

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/232028074>

# Coordination compounds of alkali and alkaline earth metals with covalent characteristics

ARTICLE *in* COORDINATION CHEMISTRY REVIEWS · OCTOBER 1974

Impact Factor: 12.24 · DOI: 10.1016/S0010-8545(00)82031-7

---

CITATIONS

7

---

READS

664

2 AUTHORS, INCLUDING:



[Pramesh N Kapoor](#)

University of Delhi

121 PUBLICATIONS 1,652 CITATIONS

SEE PROFILE

## COORDINATION COMPOUNDS OF ALKALI AND ALKALINE EARTH METALS WITH COVALENT CHARACTERISTICS

P.N. KAPOOR and R.C. MEHROTRA

*Chemistry Department, Rajasthan University, Jaipur 302004 (India)*

(Received March 19th, 1973; revised September 17th, 1973)

### CONTENTS

A. Introduction . . . . .	1
B. Addition Compounds . . . . .	2
C. Compounds containing metal–carbon bonds . . . . .	5
D. Compounds containing metal–oxygen–carbon bonds . . . . .	8
E. Macrocyclic polyether complexes . . . . .	9
F. Macrocyclic rings containing nitrogen and sulphur . . . . .	12
G. Cryptates . . . . .	13
H. Bimetallic compounds containing metal–carbon bonds . . . . .	14
I. Bimetallic compounds containing metal–oxygen–carbon bonds . . . . .	15
References . . . . .	24

### A. INTRODUCTION

Synthesis of apparently covalent volatile double alkoxy derivatives of a few electropositive metals<sup>1</sup> promoted a study of the literature regarding coordination compounds of strongly electropositive elements with significant covalent metal–ligand bonding. Although only a few coordination complexes of alkali and alkali earth metals have been reported, interest in this field has grown recently because of their importance in the metabolism of plants, e.g. a number of macrocyclic neutral compounds of alkali metals have been found to enhance respiration of fungal metabolics. The importance of sodium, potassium, magnesium and calcium ions in bio-chemical processes has been recently reviewed by Williams<sup>2</sup>.

On the Pauling scale, the electronegativity values of all alkali and alkali earth metals vary from 0.7–1.2. Taking the electronegativity of oxygen as 3.5, the bonds between these metals and oxygen should be about 85–70% electrovalent in character. Further, in view of the low ionisation potential of such metals and their hard acidic character, the concept of any covalent compounds between these and hard bases like oxygen and nitrogen is rather difficult to understand. Nyholm and coworkers<sup>3</sup> appear to be confronted with similar difficulties when, in the first of a recent series of papers on alkali metal complexes, they tried to define such complexes; “Rightly or wrongly, we shall use the word complex here to imply the existence of a discrete unit of the type  $ML_n^{q\pm}$ , where  $n$  is number of donor

groups and  $a$  is the number of the charges; if  $a$  is zero we have a 'neutral complex'. We imply nothing concerning the nature of the electron distribution between the metal and the donor atom when we use the word complex".

Truter<sup>4</sup> in a recent review on the "Crystal Chemistry of  $d^0$  Cations" has attempted to suggest the criteria for defining a complex of an alkali metal. The first plausible criterion could be the capacity to volatilise as a distinct species, e.g.  $\text{Cs}[\text{Y}(\text{CF}_3\text{COCHCOCF}_3)_4]$  (ref. 5), and  $\text{M}[\text{Sc}(\text{C}_2\text{F}_3\text{COCHCOCF}_3)_4]$  (ref. 6) (where  $\text{M} = \text{K}, \text{Rb}$  or  $\text{Cs}$ ). Another criterion for defining an alkali metal complex is the formation of a neutral extractable molecule, e.g.  $\text{NaCl}$  ( $p, p'$ -methylene dianiline)<sub>3</sub> adduct which is soluble in chloroform<sup>7</sup>. A third criterion may be the extent of sequestration e.g. that of the alkali earth ions by complexones like EDTA or highly polymeric metaphosphate salts like Calgon. To this list have been added the tricyclic (so called Football) ligands like  $\text{N}(\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2)_3\text{N}$ , synthesised by Lehn et al.<sup>8</sup> which have the capacity to enclose alkali and alkaline earth atoms so completely that even  $\text{BaSO}_4$  can be rendered soluble. Derived from the Greek word "Kruptos" meaning "hidden", such ligands have been appropriately named as "Cryptate". A review on cryptates has recently been published<sup>9</sup>.

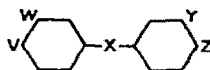
In this article, some of the recent work on coordination compounds of alkali and alkaline earth metals is summarised. A review dealing mainly with structural aspects of adducts, crown compounds and cryptates of alkali ions as well as some molecules of biological interest is in print<sup>10</sup> and therefore, the present review is being limited to non-structural aspects only as far as the above class of compounds is concerned. In addition, this article will include derivatives with metal-carbon and metal-oxygen-carbon bonds including double alkoxy derivatives. Some related reviews<sup>10a</sup> have recently appeared.

## B. ADDITION COMPOUNDS

The first reported coordination compounds of alkali metals were synthesised by Sidgwick and Brewer<sup>11</sup>; these were salicylaldehyde and  $\beta$ -diketonate derivatives consisting of a salt  $\text{M}^+\text{L}^-$ . These workers showed that electrovalent (insoluble in an organic solvent) sodium benzoylacetate, when recrystallised from 96% ethanol takes up two molecules of water; this new derivative is soluble in organic solvents such as benzene and chloroform. Sodium benzoylacetate also becomes soluble in non-aqueous solvents by the addition of ethylene glycol, giving non-conducting solutions. The crystal structure of this addition compound ( $\text{Na}(\text{PhCOCHCOCH}_3) \cdot (\text{HOCH}_2\text{CH}_2\text{OH})$ ) has been determined<sup>12</sup>.

Alkali metal halides form solid addition compounds with nitrogen donor ligands, e.g.  $\text{MX} \cdot (\text{amine})_3$  (amine = racemic  $p, p'$ -diamino-2-3-diphenylbutane<sup>13</sup> or  $p, p'$ -methylene dianiline<sup>7</sup>). Some of these, for example ( $\text{NaCl}$  ( $p, p'$ -methylene dianiline)<sub>3</sub>), precipitate out from aqueous solution, but are soluble in chloroform; the analogous bromide complex although isomorphous is insoluble in chloroform. NMR Studies have shown that only half the hydrogen atoms of the ligand,  $p, p'$ -methylene dianiline, are involved in hydrogen bonding<sup>14</sup>. Further, the lowering ( $53 \text{ cm}^{-1}$ ) of the N-H vibration in the derivative, ( $\text{NaCl}$ -( $p, p'$ -diamino-2, 3-diphenylbutane)<sub>3</sub>), is strong evidence for sodium to nitrogen bonding<sup>13</sup>.

TABLE 1



Ligand	V	W	X	Y	Z	Compound isolated
I	MeCO <sub>2</sub>	H	CH <sub>2</sub>	H	MeCO <sub>2</sub>	NaX(IV) <sub>3</sub>
II	MeCO <sub>2</sub>	Me	CH <sub>2</sub>	Me	MeCO <sub>2</sub>	
III	MeCONH	H	CH <sub>2</sub>	H	MeCONH	
IV	NH <sub>2</sub>	H	CH <sub>2</sub>	H	NH <sub>2</sub>	
V	NH <sub>2</sub>	H	SO <sub>2</sub>	H	NH <sub>2</sub>	
VI	MeCO <sub>2</sub>	H	SO <sub>2</sub>	H	MeCO <sub>2</sub>	NaX(XV) <sub>3</sub>
VII	H	MeCONH	SO <sub>2</sub>	MeCONH	H	
VIII	NH <sub>2</sub>	H	SO <sub>2</sub>	H	CO <sub>2</sub> H	
IX	HO(CH <sub>2</sub> ) <sub>2</sub> O	H	CMe <sub>2</sub>	H	HO(CH <sub>2</sub> ) <sub>2</sub> O	
X	MeCHOHCH <sub>2</sub> O	H	CMe <sub>2</sub>	H	MeCHOHCH <sub>2</sub> O	
XI	MeCO <sub>2</sub>	H	CMe <sub>2</sub>	H	MeCO <sub>2</sub>	
XII	MeCO <sub>2</sub>	Me	CMe <sub>2</sub>	Me	MeCO <sub>2</sub>	
XIII	NH <sub>2</sub>	H	(CH <sub>2</sub> ) <sub>2</sub>	H	NH <sub>2</sub>	
XIV	NH <sub>2</sub>	H	(CH <sub>2</sub> ) <sub>3</sub>	H	NH <sub>2</sub>	
XV	NH <sub>2</sub>	H	CH <sub>3</sub> CH-   CH <sub>3</sub> CH-	H	NH <sub>2</sub>	

Steric factors play an important role in the formation of these adducts, since a number of other compounds of varied functionalities, although structurally similar to these ligands (Table 1) do not form any crystalline complexes with sodium chloride, potassium chloride or calcium chloride<sup>7, 14</sup>. This indicates that the above interactions are highly selective and the mechanisms involved may well be similar to those responsible for the behaviour of membranes which are selectively permeable to inorganic ions<sup>14</sup>. The crystal structure of [NaCl(*p, p'*-methylene dianiline)<sub>3</sub>] has been determined<sup>15</sup>.

A number of crystalline, water soluble adducts of the alkali metal salts are known; X-ray structures of some of these [LiCl·dioxane] (ref. 16), [NaBr·2MeCONH<sub>2</sub>] (ref. 17), [LiCl·2C<sub>6</sub>H<sub>5</sub>N·H<sub>2</sub>O] (ref. 18) and [LiCl·2en] (ref. 19), have also been determined. Addition compounds with triphenylphosphine oxide, [MX·5Ph<sub>3</sub>PO] (M = Li<sup>+</sup> or Na<sup>+</sup> and X = univalent anion varying in size from Br<sup>-</sup> to BPh<sub>4</sub><sup>-</sup>), are stable in water<sup>20</sup>. The ease of the formation of these adducts can be represented by: Li > Na > K and I > Br > Cl. There appears to be a fairly good parallelism between the salts which form hydrates and those which form adducts with triphenylphosphine oxide. The crystal structure<sup>21</sup> of [LiI·5Ph<sub>3</sub>PO] indicates that four triphenylphosphine oxide molecules are tetrahedrally

coordinated to the lithium ions through oxygen, and the iodide ions occupy isolated positions distant from lithium. The fifth triphenylphosphine oxide molecule is enclosed by the rest of the structure. The adduct,  $[\text{LiI} \cdot 4\text{Ph}_3\text{PO}]$ , is also known<sup>22</sup> and this presumably contains a tetrahedrally coordinated lithium cation without the loose fifth triphenylphosphine oxide molecule. Calcium and magnesium perchlorates<sup>23</sup> and tetrafluoroborates<sup>24</sup> form addition compounds with triphenylphosphine oxide of the type,  $[\text{Mg}(\text{TPO})_4] [\text{BF}_4]_2$ ;  $[\text{Mg}(\text{TPO})_4] [\text{ClO}_4]_2$ ;  $[\text{Ca}(\text{TPO})_4(\text{OClO}_2)] [\text{ClO}_4]$  and  $[\text{Ca}(\text{TPO})_4] [\text{BF}_4]_2$ . Phenacyldiphenylphosphine oxide,  $(\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{C}(\text{O})\text{Ph})$  forms 1:1 complexes with lithium bromide and lithium iodide, and a 3:1 complex with magnesium perchlorate. The IR spectra of these compounds through the shifting of  $\text{C}=\text{O}$  ( $45\text{ cm}^{-1}$ ) and  $\text{P}=\text{O}$  ( $25\text{ cm}^{-1}$ ) frequencies, indicate chelation by neutral ligands<sup>25</sup>. Surprisingly, larger alkali cations such as rubidium and caesium do not form any complexes<sup>25</sup> of this type. The adducts of the alkali halides  $\text{MX}$  (where  $\text{M} = \text{Li}^+, \text{Na}^+, \text{K}^+, \text{Cs}^+$  and  $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$ ) with chelating ditertiaryphosphine oxide,  $(\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{Ph}_2)$  and of sodium iodide with  $\text{R}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})\text{R}_2$  (where  $\text{R} = \text{Bu}, \text{BuO}, p\text{-MeOC}_6\text{H}_4$ ) and  $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{P}(\text{O})(\text{OEt})\text{CH}_2\text{P}(\text{O})\text{Ph}_2$  have been studied conductometrically in acetonitrile<sup>26</sup>. It was found that during the introduction of the ligand in a few cases, the electrical conductance of the solutions decreased due to the formation of an undissociated complex  $[\text{MXL}]$ ; in other cases the electrical conductance increased due to the formation of a dissociating complex  $[\text{ML}]^+\text{X}^-$ . The nature of the complex formed appears to be determined by the following three factors: (i) the sizes of  $\text{M}^+$  and  $\text{X}^-$ , (ii) the polarizability of  $\text{X}^-$  which appears to play an important role in the formation of the undissociated complex  $[\text{MXL}]$  whereas the formation of the dissociated complex  $[\text{ML}]^+\text{X}^-$  seems to depend on the ionisation potential of the cation, and (iii) the nature of the substituent on the phosphorus atoms<sup>26</sup>.

Alkali metal salts also form adducts with thiourea<sup>27</sup> and sulphur dioxide<sup>28</sup>. Lithium iodide gives unstable adducts with ammonia<sup>29</sup> and alcohols<sup>30</sup>. More recently, some alkali metal xanthates<sup>31</sup>, malonates<sup>32</sup> and glycines<sup>33</sup> have been reported. Complexes of alkali and alkali earth metals with carbohydrates have also been reviewed<sup>34</sup>.

Nyholm and coworkers<sup>3</sup> have described the formation of adducts of the type  $\text{ML} \cdot n\text{HL}$ , by mixing the metal hydroxide or ethoxide with the ligand in a medium of low dielectric constant (usually absolute ethanol), (where  $\text{M} = \text{alkali metal}$  and  $\text{HL} = 8\text{-hydroxy quinoline (I), isonitroso-acetophenone (II), 1-nitroso-2-naphthol (III), } o\text{-nitrophenol (IV), anthranilic acid (V), 2,4-dinitrophenol (VI), } o\text{-nitro benzoic acid (VII), 1,10-phenanthroline (VIII) or 2,9-dimethyl-1,10-phenanthroline (IX)} (fig. 1).$

In some of the above systems, only one product is isolated irrespective of the proportion of the reactants; in others, it has been possible to obtain  $\text{ML}$  (i.e.,  $n = 0$ ) or  $\text{ML} \cdot n\text{HL}$  ( $n = 1$  or  $2$ ) by increasing the proportion of  $\text{HL}$  in the system. These adducts have been characterised as true compounds using the following criteria: (a) these have higher melting points than the approximate mixtures, (b) distinct infrared spectra and (c) capacity to form single crystals for which X-ray data were obtained. It has been shown by measuring the molar conductance in *N*-methyl pyrrolidone for a series of compounds that

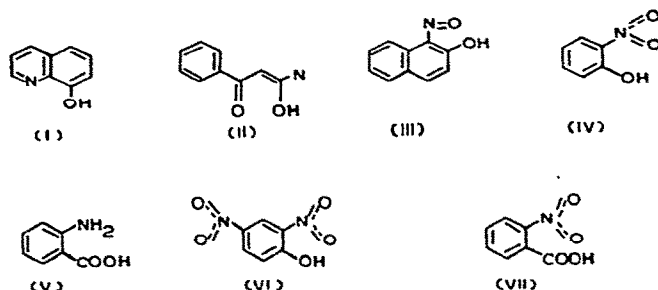


Fig. 1. The structure of ligands which form adducts of the type  $ML_nHL$ .

potassium, rubidium caesium derivatives behave similarly while there are considerable differences amongst potassium, sodium and lithium compounds. All the ligands were found to chelate the metal, forming five membered rings for (I), six membered rings for (II), (III), (IV), (V) and (VI) and a seven membered ring for (VII), which actually forms an acid salt. Increase in radius (or decrease in ionisation potential) of the metal appears to facilitate the isolation of adducts in the solid state whereas ion pairing in solution is naturally stronger for smaller cations. It was also found that hydrogen bonding is not essential for the formation of adducts between the chelating ligand and the alkali metal salt of the chelate anion. Crystal structures of  $K^+[PhC(O)CH=NO]^-HON-CHC(O)Ph$  (ref. 35),  $K^+[ONCHC(O)Ph]^- \cdot C_6H_4(NO_2)OH$  (ref. 36) and the sodium perchlorate adduct of bis- $[N,N'$ -ethylenebis (salicylidene iminato) copper (II)] ref. 37) have been determined.

### C. COMPOUNDS CONTAINING METAL-CARBON BONDS

Organic derivatives of alkali metals are highly reactive and are useful chemical reagents. Most of these depict the expected ionic character<sup>38</sup>, but a few depict apparently covalent behaviour also. Organolithium compounds e.g. ethyl lithium, *n*-propyl lithium, *n*-butyl lithium, tertiary butyl lithium and  $Me_3SiCH_2Li$ , are in general readily soluble in hydrocarbon solvents and can be purified by distillation or sublimation under reduced pressure whereas corresponding sodium, potassium, rubidium and caesium compounds are non volatile and insoluble in benzene; the latter are, therefore, commonly regarded as salts  $M^+R^-$  ( $M = Na, K, Rb, Cs$ ;  $R = \text{alkyl or aryl}$ ). The above difference appears to arise from the small size and higher polarising power of the lithium ion making the lithium-carbon bond more covalent in nature. Most of the organolithium compounds, however, involve lithium being associated in different coordination states (Table 2).

The existence of the addition compound,  $(EtLi) \cdot (EtOLi)_2$ , was shown by molecular weight determination in cyclohexane solution indicating that the initial coordination of two lithium ethoxide molecules takes place at two coordination sites of the hexamer<sup>45</sup>. Ethyl and tertiary butyl lithium form volatile pentane soluble complexes when they are

TABLE 2

Properties of some lithium alkyls

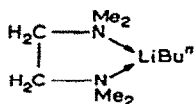
Compound	B.p. (°C/mm)	Degree of association	Solvent
CH <sub>3</sub> Li		4	Ether or THF (ref. 39)
C <sub>2</sub> H <sub>5</sub> Li	90/*	6 <sup>a,b</sup>	Benzene <sup>40,38</sup>
C <sub>4</sub> H <sub>9</sub> <sup>n</sup> Li	80–90/*	6	Benzene or cyclohexane <sup>41,38</sup>
C <sub>4</sub> H <sub>9</sub> <sup>n</sup> Li		4	Ether or THF (ref. 39)
C <sub>4</sub> H <sub>9</sub> <sup>t</sup> Li	70/0.1	4	Benzene or hexane <sup>42</sup>
CH <sub>2</sub> :CHLi		3	THF (ref. 43)
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Li		1	Ether or THF (ref. 39)
(CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> Li	100/0.0001	4	Benzene or hexane <sup>44</sup>

\* Under highly reduced pressure (not clearly specified).

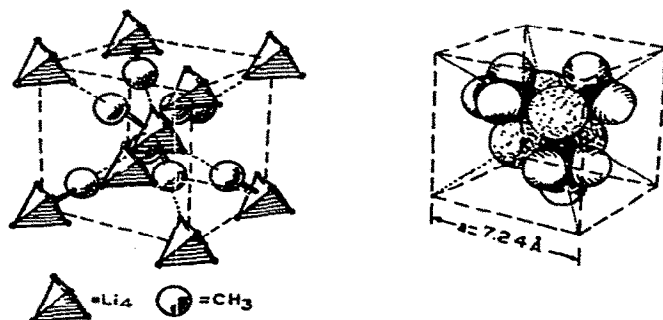
<sup>a</sup> = Tetrameric in crystal.<sup>b</sup> = Hexameric in vapour.

THF = Tetrahydrofuran.

mixed together<sup>46</sup>. *n*-Butyl lithium forms with tetramethyl ethylenediamine a chelate complex which is monomeric, soluble in paraffins and acts as a catalyst for the polymerisation of ethylene<sup>47</sup>.



The crystal structure<sup>48</sup> of methyl lithium reveals tetrameric units of (CH<sub>3</sub>Li)<sub>4</sub> (Figure 2). In this structure, the carbon atoms are apparently six coordinate (almost octahedral), and each can be regarded as being bound to three hydrogen atoms in a normal

Fig. 2. The structure of a methyl lithium tetramer<sup>48</sup>.

way and to three lithium atoms by two-electron four-center bonds. The methyl groups of each tetramer unit appear to be quite close to the lithium atoms of an adjacent tetramer. This results in strong three dimensional association which is responsible for the low volatility and the stability of methyl lithium. The structure of ethyl lithium<sup>49</sup> on the other hand may be regarded as a polymer derived from weakly associated tetramers, each of which consists of two strongly associated dimers. The mass spectrum of vaporised ethyl lithium indicates that the hexamer and tetramer units are the predominant species<sup>50</sup>. Recently, evidence for some covalent bonding in benzyl lithium<sup>51</sup> and 1 and 2-naphthyl methyl derivatives of lithium, sodium and potassium<sup>52</sup> has been provided by  $^7\text{Li}$  and  $^{13}\text{C}$  NMR spectroscopy.

Organic derivatives of bivalent electropositive elements calcium, strontium and barium have been comparatively much less studied due to loss in stability in the metal-carbon bond in passing from beryllium and magnesium to calcium, strontium and barium; these have been reviewed elsewhere<sup>53</sup>. Magnesium forms highly reactive organic derivatives which are essentially covalent in structure. Dimethyl magnesium is a white solid and can be sublimed in poor yield<sup>54</sup> whereas the dimethyl derivatives of calcium, strontium and barium are insoluble in common organic solvents and are non-volatile<sup>55</sup>. The polymeric structure involving metal-metal interactions of dimethyl magnesium has been confirmed by X-ray diffraction<sup>56</sup>. Diethyl, dipropyl and dibutyl magnesium can be volatilised under reduced pressure; these are insoluble in benzene and are likely to be electron-deficient polymers. By contrast, di-*n*-amylmagnesium has been reported to dissolve as a dimer in benzene<sup>57</sup>. That this difference may be due to steric factors appears to be confirmed by the recent synthesis<sup>57A</sup> of hydrocarbon soluble dineopentylallyl magnesium, the NMR spectrum of which indicates a dynamic allyl system with almost equal *cis* and *trans* forms.

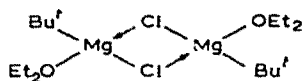
Ionic formulations closely related to ferrocene have been suggested for the bis-cyclopentadienyl derivatives of magnesium, calcium, strontium and barium which are soluble in organic solvents and can be purified by vacuum sublimation<sup>58</sup>.

A number of organo-calcium halides have been prepared by the reaction between calcium and organic halides in ethereal solvents, the reactivity of which appears to follow the order  $\text{RI} > \text{RBr} > \text{RCl}$  (ref. 59). The red complex  $[\text{Ph}_3\text{CCaCl} \cdot 2\text{THF}]$  formed from calcium amalgam and triphenylchloromethane in tetrahydrofuran is monomeric in benzene but probably contains triphenyl-methyl anions and could be in the form of ion pairs<sup>60</sup>. Bis(triphenylmethyl) calcium forms an adduct with tetrahydrofuran,  $[\text{Ca}(\text{CPh}_3)_2 \cdot 7\text{THF}]$  (ref. 61). Bis-(2-phenylethynyl)calcium, strontium and barium have been prepared recently and are soluble in tetrahydrofuran<sup>61</sup>. A benzene soluble complex of strontium,  $[\text{Et}_2\text{Sr} \cdot \text{Et}_2\text{Zn}]$ , has been reported<sup>62</sup>. The tetrahydrofuran complex  $[\text{Bu}_2\text{Mg} \cdot 2\text{THF}]$ , is soluble in benzene but cryoscopic molecular weight measurements show that it is partly dissociated<sup>63</sup>.

Most of the Grignard reagents are soluble in ether, tetrahydrofuran, 1,2-dimethoxyethane and diglyme forming solvated species<sup>64</sup>. A number of soluble organomagnesium halides may also be prepared in hydrocarbons<sup>65</sup> indicating a certain amount of covalent character, e.g., ethylmagnesiumiodide is soluble in boiling benzene, The mono-etherate of tertiary butyl



magnesium chloride is dimeric in benzene and this has been assigned the following bridged structure<sup>63</sup>.



A number of Grignard reagents are formed in good yields in benzene solution when one mole of triethylamine is present for every gram atom of magnesium. The monoamine complex of ethyl magnesium bromide is dimeric in benzene<sup>66</sup>. Benzene soluble thiomagnesium alkyls are also known<sup>67</sup>. Several alkyl magnesium alkoxides have been prepared by alcoholysis of the dialkyls in ether and can be obtained free from ether. Derivatives like ethyl magnesium isopropoxide, ethyl magnesium tertiary butoxide and isopropyl magnesium isopropoxide are tetrameric in benzene, whereas ethyl magnesium *n*-propoxide, isopropyl magnesium methoxide and isopropyl magnesium ethoxide yield higher oligomers, but in poor yields some of these can be purified by sublimation<sup>68</sup>.

On the basis of NMR and molecular weight data, evidence has been recently presented<sup>68A</sup> regarding the existence, in solution, of a stable alkoxy-alkyl mixed bridged organo-magnesium compound, which appears to be essentially dimeric in concentrated solutions with the following forms in dynamic equilibrium.



#### D. COMPOUNDS CONTAINING METAL-OXYGEN-CARBON BONDS

A number of alkali metal alkoxides, e.g. lithium ethoxide, lithium isopropoxide, lithium tertiary butoxide, sodium isopropoxide and potassium tertiary butoxide are soluble in benzene and cyclohexane and can be volatilised<sup>69</sup> under reduced pressure (Table 3).

It is interesting to note that the molecular weight of lithium tertiary butoxide is lower in benzene than cyclohexane indicating that the solvent also plays a role in the dissociation of such compounds. From NMR data<sup>69</sup>, it was suggested that the M-O bond in these alkali metal alkoxides exhibits a degree of covalency, which depends on the inductive effect of the alkyl group.

Lithium methoxide has a two-dimensional layer structure analogous to that of the hydroxide. Each oxygen is bonded to four lithiums and a methyl group in the form of square pyramid with oxygen at the center and methyl at the apex. Each lithium is surrounded by four oxygens in the form of a squashed tetrahedron. In view of the environment of the oxygens, the simplest view would be to consider it to be ionic

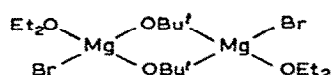
TABLE 3

Properties of some alkali metal alkoxides<sup>69</sup>

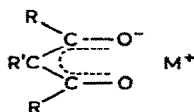
Compounds	B.p. (°C/mm)	Degree of association	Solvent
LiOEt	155/0.001		
LiOPr <sup>i</sup>	170/0.1	11	Cyclohexane
LiOBu <sup>t</sup>	110/0.1	4	Benzene
LiOBu <sup>f</sup>	110/0.1	6	Cyclohexane
KOBu <sup>f</sup>	145/0.001		

although a giant covalent polymeric form can not be entirely ruled out<sup>70</sup>.

The alkoxides of magnesium, calcium, strontium and barium are insoluble in common organic solvents due to their polymeric nature and have not been studied in detail. The products formed<sup>70A</sup> in the reactions of magnesium alkoxides with magnesium halides have been characterised by X-ray and IR techniques to be  $3\text{Mg}(\text{OR})_2 \cdot \text{MgHal}_2 \cdot n\text{ROH}$  and not the normally expected entities,  $(\text{HalMgOR})$ . Acetone reacts with methyl magnesium bromide to yield tertiary butoxide magnesium bromide which is dimeric in benzene and ether. It forms an adduct with ether, tertiary butoxide magnesium bromide diethyl ether, which has the following structure<sup>68</sup>.



The metal chelates containing the anions of  $\beta$ -diketones as ligands were reported<sup>71</sup> and a few of these can be volatilised under reduced pressure. The dipivaloylmethane derivatives were found to be exceptional in that sublimates of lithium, sodium and potassium were obtained<sup>72</sup>; magnesium acetylacetonates can also be sublimed in poor yields<sup>54</sup>. The acidic hydrogen atoms of the enol tautomer of the ligand is replaced by an alkali metal to give a compound of the type



where M is an alkali metal. The lowest sublimation temperatures in the series were exhibited by fluorine-containing  $\beta$ -diketonate complexes (Table 4).

#### E. MACROCYCLIC POLYETHER COMPLEXES

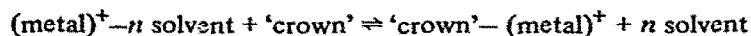
Pedersen<sup>73</sup>, described a large number of macrocyclic polyether "crown" compounds with Li, Na, K, Rb, Cs,  $\text{NH}_4$ , Ca, Sr, Ba, Ag,  $\text{Au}^{\text{I}}$ , Cd and  $\text{Ce}^{\text{III}}$  ions.

TABLE 4

Properties of some alkali metal  $\beta$ -diketonates<sup>72</sup>

Compound	M.p. (°C)	Sublimation temperature (°C/0.01 mm)
Li[(CH <sub>3</sub> ) <sub>3</sub> CCOCHCOC(CH <sub>3</sub> ) <sub>3</sub> ]	256 d	200
[Na[(CH <sub>3</sub> ) <sub>3</sub> CCOCHCOC(CH <sub>3</sub> ) <sub>3</sub> ]	180 d	200
K[(CH <sub>3</sub> ) <sub>3</sub> CCOCHCOC(CH <sub>3</sub> ) <sub>3</sub> ]	180	170 d
Na[CF <sub>3</sub> COCHCOCH <sub>3</sub> ]	246 d	190
Na[CF <sub>3</sub> COCHCOOC <sub>2</sub> H <sub>5</sub> ]	46(176–177)	150
Na[CF <sub>3</sub> COCHCOOCH <sub>3</sub> ]	125(164–167)	160
Na[CF <sub>3</sub> COC(CH <sub>3</sub> )COOC <sub>2</sub> H <sub>5</sub> ]	110(188–190)	180
Li[CF <sub>3</sub> COCHCOC(CH <sub>3</sub> ) <sub>3</sub> ]	250 d	190
Na[CF <sub>3</sub> COCHCOC(CH <sub>3</sub> ) <sub>3</sub> ]	230–232	185
K[CF <sub>3</sub> COCHCOC(CH <sub>3</sub> ) <sub>3</sub> ]	204–205	195
Rb[CF <sub>3</sub> COCHCOC(CH <sub>3</sub> ) <sub>3</sub> ]	159–162	180
Cs[CF <sub>3</sub> COCHCOC(CH <sub>3</sub> ) <sub>3</sub> ]	186–187	190
Li[CF <sub>3</sub> COCHCOCF <sub>3</sub> ]	300 d	200
Na[CF <sub>3</sub> COCHCOCF <sub>3</sub> ]	250 d	185
K[CF <sub>3</sub> COCHCOCF <sub>3</sub> ]	230 d	200
Rb[CF <sub>3</sub> COCHCOCF <sub>3</sub> ]	200 d	195 d
Cs[CF <sub>3</sub> COCHCOCF <sub>3</sub> ]	215–217	195
Na[CF <sub>3</sub> COCHCOC <sub>7</sub> H <sub>11</sub> ]	300 d	200

The complexing power of crowns for alkali metal ions is so strong as to leach sodium ions from the walls of an ordinary glass container<sup>74</sup>. Dicyclohexyl-15-crown-5 so far appears to be the best complexing agent for sodium ions. Most of the alkali and alkaline earth metal salts give a complex with 1 metal : 1 crown, which are formed by the ion-dipole interaction between the cations (held in the center of ring) and the negatively charged coplanar four, five or six oxygen atoms



Amongst the factors which appear to determine the stability<sup>73</sup> of metal–crown complexes, the following may be mentioned: (i) the number of coplanarity of oxygen atoms in the polyether ring and their symmetry, (ii) the basicity of the oxygen atoms and the electrical charge on the ions (iii) the solvation tendency of the cations and (iv) the steric hindrance in the polyether ring, i.e., the relative sizes of the cations and the hole in the ring. (Table 5). Rings containing four coplanar ligand atoms are quite common, for example in porphyrins. However, six oxygen atoms provide octahedral coordination for

TABLE 5

Ionic diameters and hole sizes (Å) (refs. 73, 77)

Cation	Ionic diameter	Polyether ring	Hole size
Li <sup>+</sup>	1.36	14-crown-4	1.2–1.5
Na <sup>+</sup>	1.94	15-crown-5	1.7–2.2
K <sup>+</sup>	2.66	18-crown-6	2.6–3.2
Rb <sup>+</sup>	2.94	21-crown-7	3.4–4.3
Cs <sup>+</sup>	3.34		

transition metals<sup>75</sup>. In some cases, where the cation appears to be too large to fit in the hole, the complex probably has a sandwich structure, since 2:1 and even 3:2, crown:cation ratios were obtained. Selectivity towards different cations varies with polyether ring size, the optimum ring size being such that the cation can just fit into the hole, i.e., 15–18 for Na<sup>+</sup>, 18 for K<sup>+</sup> and 18–21 for Cs<sup>+</sup> (Table 5)..

It is reported that the small lithium ion is not efficiently complexed by most of the common crown ligands. On the other hand, bis-tertiary butyl cyclohexyl-14-crown-4 with a small 1.2–1.5 Å cavity shows a preference for lithium over other alkali ions. Slightly larger tertiary butyl cyclohexyl-15-crown-5 complexes sodium the best of the alkali metal ions, and dicyclohexyl-18-crown-6 is best with potassium ion. The importance of these crown complexes has been shown<sup>74</sup> in their possible use as polymerisation catalysts, in cation separation and in preparing ion sensitive electrodes. Recently, the potassium permanganate complex of dicyclohexyl-18-crown-6 has been used as efficient oxidising agent; e.g. olefins are cleaved, alkyl benzenes are oxidised to aromatic acids, and alcohols and aldehydes give the corresponding acids<sup>76</sup>.

Employing the ultraviolet absorption maximum<sup>74</sup> of the picrate anion at 357 mμ followed by detailed potentiometric studies<sup>77</sup> using cation selective electrodes, Frensdorff has determined the stability constants for the 1:1 complexes of a number of cyclic polyethers (12 to 60 membered rings of C–C–O units) with several alkali cations (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup>) in water and methanol (Table 6). A comparison of the stability constants (log *K*) of the three cations (Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup>) with dicyclohexyl-18-crown-6 reveals that the constant for potassium ion is the highest by more than one order of magnitude<sup>77</sup>. The data for stability constants of derivatives formed by two biological species nonactin and monactin with lithium, sodium and potassium ions also show selectivity towards potassium ions<sup>78</sup> (Table 6). This can be understood on the basis of a competition between complex atom and solvation tendencies. Thus, the largest cations have the lowest stability constants due to their weaker attraction for ligand molecules. Conversely, the smallest cations exhibit the greatest attraction for ligand as well as solvent molecules, but the latter factor sometimes makes them too strongly solvated for the polyether to compete successfully for them. In such cases, obviously the medium sized ions like potassium show the highest

TABLE 6

Stability constants ( $\log K$ ) for the reaction  $[M^{n+}] (\text{solvated})_x + L = [ML^{n+}] (\text{solvated})_y + (x - y) \text{ solvent}$ 

Ligand	Refer- ence	Solvent	Li <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Rb <sup>+</sup>	Cs <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Sr <sup>2+</sup>	Ba <sup>2+</sup>
EDTA	79	H <sub>2</sub> O	2.8	1.7				3.6	10.6	8.6	7.8
Nonactin	78	CH <sub>3</sub> OH		2.1	3.7						
Monactin	78	CH <sub>3</sub> OH		3.0	5.4						
Dicyclohexyl- 14-crown-4	77	CH <sub>3</sub> OH		2.18	1.30						
Dicyclohexyl- 15-crown-5	77	CH <sub>3</sub> OH		3.71	3.58		2.78				
		H <sub>2</sub> O	<1.0	<0.3	0.6						
18-crown-6	77	CH <sub>3</sub> OH		4.32	6.10		4.62				
		H <sub>2</sub> O		0.3	2.06		0.8				
Cyclohexyl- 18-crown-6	77	CH <sub>3</sub> OH		4.09	5.89		4.30				
		H <sub>2</sub> O	<0.7	0.8	1.90		0.8				
Dicyclohexyl- 18-crown-6 isomer A	77	CH <sub>3</sub> OH		4.08	6.01		4.61				
		H <sub>2</sub> O	0.6	1.6	2.2		1.2				
Dicyclohexyl- 18-crown-6 isomer B	77	CH <sub>3</sub> OH		3.68	5.38		3.49				
Dibenzo-21- crown-7	77	CH <sub>3</sub> OH		2.40	4.30		4.20				
Cryptate	8	H <sub>2</sub> O		3.6	5.1	3.7			4.1	13.0	15.0

stability constants. The effect of solvent on these stability constants can be seen in Table 6, wherein the constants in aqueous solutions are three to four decades lower compared to those in methanol. This suggests a much stronger solvation of the cations by water, compared to that by methanol, with which the polyether has to compete<sup>77</sup>.

An account of the properties including crystal structures<sup>80-82</sup> of crown complexes of alkali metals appears in a recent review<sup>10</sup>. In addition, light has been thrown on the crystal structures of somewhat similar biological systems, e.g., silver salt of Nigercin or Polyetherin A (refs. 83, 84), potassium salt of nonactin<sup>85, 86</sup>, potassium salt of valinomycin<sup>87</sup> and ferroverdin<sup>88</sup>.

#### F. MACROCYCLIC RINGS CONTAINING NITROGEN AND OXYGEN OR SULPHUR

Replacement of two or four oxygen atoms by sulphur in the crown-5 or crown-6 compounds drastically reduces their complexing power for alkali and alkali earth metals while

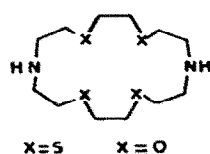


Fig. 3. The structure of macrocyclic rings containing nitrogen and oxygen or sulphur.

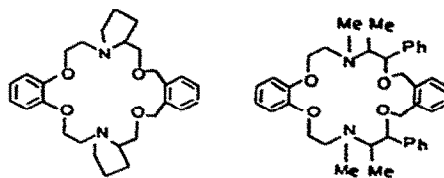


Fig. 4. Structures of chiral macrocyclic ethers.

maintaining it for silver<sup>73</sup>. The ligand (Fig. 3) containing four oxygen and two nitrogen atoms is able to form chloroform soluble complexes with alkali metal thiocyanates, which are unstable in water<sup>8</sup>. When oxygen atoms are replaced by sulphur in this ligand, it loses its complexation tendency with alkali metals<sup>89</sup>.

Recently, chiral macrocyclic amino ethers have been isolated (Fig. 4) which form complexes with alkali and alkali earth cations in neutral media<sup>90</sup>.

#### G. CRYPTATES

Cryptates are formed by the incorporation of ether linkages in place of some of the methylene groups in macrobicyclic diamines<sup>8</sup>. A few of these are shown in Fig. 5; they are also called "Football ligands". These cryptates are powerful complexing agents: even barium sulphate can be dissolved in their aqueous solutions and potassium permanganate is taken up by benzene solutions. The rate of uptake appears to be related to the nature of the anion, the presence of traces of water and temperature<sup>8</sup>. The stability constants of the complexes (Fig. 5(a)) between alkali and alkali earth chlorides are shown in Table 6. Potassium has a greater stability constant than sodium or rubidium while lithium and caesium have values too small to measure, indicating that the ligand is highly selective on the basis of the radius of the metal. Shifts in the NMR spectra of the proton of the methylene groups takes place as the metal salt is added to a chloroform solution of ligand,

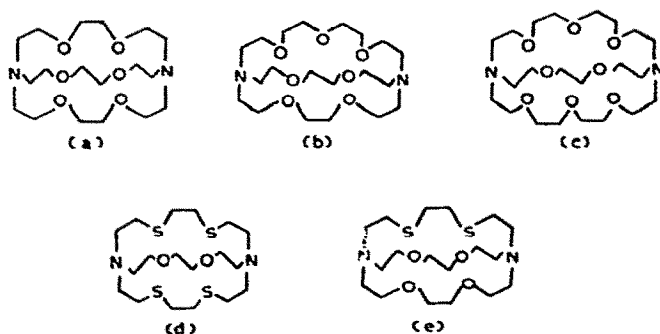
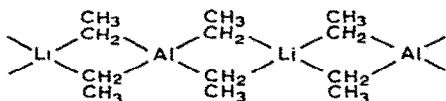


Fig. 5. Structures of some cryptates (Football ligands).

(Fig. 5(a)) indicating that the complex formation is complete when the ratio of metal: ligand is 1:1. More detailed studies were made<sup>91</sup> of sodium, potassium, rubidium, caesium, calcium, strontium and barium halide complexes in both deuterium oxide and deuteriochloromethane ( $\text{CDCl}_3$ ). When ligands (Fig. 5(d) and 5(e)) were used<sup>91</sup> cryptate compounds having 1:1 composition were obtained with alkali metals, but NMR spectra showed that the only hydrogens affected are on the methylene groups attached to the nitrogen. The crystal structure of the rubidium thiocyanate complex,  $\text{Rb}(\text{C}_{18}\text{H}_{36}\text{N}_2\text{O}_6) \text{SCN} \cdot \text{H}_2\text{O}$ , has been determined<sup>92</sup>.

#### H. BIMETALLIC COMPOUNDS CONTAINING METAL-CARBON BOND

In hydrocarbon solvents, finely divided alkali metals react with trimethylaluminium at room temperature to yield compounds of type  $\text{M}[\text{AlMe}_4]$  ( $\text{M} = \text{Li}, \text{Na}$  and  $\text{K}$ ). The order of reactivity has been found<sup>93</sup> to be  $\text{Li} < \text{Na} < \text{K}$ . Similarly, ethyl complexes have also been prepared which have lower melting points than the corresponding methyl complexes. The potassium compounds are almost insoluble in saturated hydrocarbons, and can be regarded as salts:  $\text{K}^+[\text{AlR}_4]^-$ , but the sodium and more particularly the lithium compounds are soluble in hydrocarbons, e.g.,  $\text{Li}[\text{AlEt}_4]$ . These may be recrystallised from a benzene-hexane mixture and can be sublimed in vacuum.  $\text{Li}[\text{AlEt}_4]$  has a polymeric structure, in which both lithium and aluminium atoms are tetrahedrally surrounded by methylene groups<sup>94</sup>



$\text{Na}[\text{AlBu}_4]$  is freely soluble in hydrocarbon solvents including cyclohexane<sup>95</sup>. However, the ionic character<sup>96</sup> of  $\text{Na}[\text{AlR}_4]$  salts can be substantiated by their equivalent conductances being comparable to those of the tetraalkyl ammonium salts.

The preparation, IR spectra and crystal structures of alkali tetramethyl, as well as some tetraphenyl indates,  $\text{M}[\text{In}(\text{R})_4]$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$  and  $\text{R} = \text{Me}$  or  $\text{Ph}$ ) have been described by Hoffmann and Weiss<sup>96A</sup>. In all these, the  $[\text{InR}_4]^-$  anions are tetrahedral and are isolated from alkali cations. Differences in structure amongst similar derivatives from different alkali cations are explained by their ionic sizes.

Alkali metal hydrides react with aluminium alkyls, giving adducts of the type  $\text{Li}[\text{Al}_2\text{HEt}_6]$  and  $\text{Na}[\text{AlHMe}_3]$  (ref. 97, 98). These hydride complexes are commonly soluble in hydrocarbons; e.g.  $\text{Na}[\text{AlHEt}_3]$  and  $\text{K}[\text{AlHEt}_3]$  are soluble in benzene. The order of reactivity<sup>93</sup> of these derivatives increases from lithium to potassium through sodium. The difference is mainly due to the hydride of the smallest cation ( $\text{Li}^+$ ) having the highest lattice energy which has to be broken before the initiation of the reaction. Similar effects also occur in the reactions of alkali halides to aluminium alkyls<sup>98</sup>. The formation of complexes is favoured when the cation is large and the anion is small. The

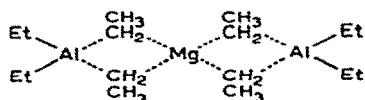
1:1 fluoride complexes, e.g.  $\text{Na}[\text{AlEt}_3\text{F}]$ ,  $\text{K}[\text{AlEt}_3\text{F}]$ , are more soluble in saturated hydrocarbons and have lower conductances in a fused state than the 1:2 complexes, e.g.  $\text{Na}[\text{Al}_2\text{Et}_6\text{F}]$ , and  $\text{K}[\text{Al}_2\text{Et}_6\text{F}]$  (ref. 99). Crystal structure of the 1:2 potassium fluoride complex has shown that the fluorine atom is symmetrically placed between the aluminium atoms<sup>100</sup>.

The lithium derivatives,  $\text{R}_2\text{AlOLi}$ , which are soluble in toluene, act as donors toward  $\text{R}'_3\text{Al}$



These are useful catalysts for the polymerisation of acetaldehyde<sup>101</sup>.

The coordination chemistry of organo aluminium compounds has been discussed critically in a recent review by Lehmkuhl<sup>102</sup>. Dimethyl and diethyl magnesium, which are polymeric insoluble substances, are slowly dissolved by trimethyl or triethyl aluminium forming viscous complexes of the form  $\text{Mg}[\text{Al}_2\text{R}_6]$ . These are soluble in aliphatic hydrocarbons and have an electron-deficient structure analogous to that of  $\text{Li}[\text{AlEt}_4]$



Attempted distillation of  $\text{Mg}[\text{Al}_2\text{Me}_6]$  results in the separation of trimethyl aluminium and the formation of crystalline  $\text{MeMg}[\text{AlMe}_4]$  which can be distilled<sup>103</sup> in a high vacuum at 70–75°C. Alkali earth complexes are formed<sup>104</sup> by reaction of the type



where  $\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$ .

#### I. BIMETALLIC COMPOUNDS CONTAINING METAL–OXYGEN–CARBON BONDS

An interesting example of an apparently covalent compound of this class reported recently appears to be the volatile bi-metallic derivative  $\text{Cs}[\text{Y}(\text{HFA})_4]$  (ref. 5), where

TABLE 7

Properties of some of alkali earth complexes of triethylaluminium<sup>104</sup>

Complex	M.p. (°C)	B.p. (°C/mm)
$\text{Ca}[\text{AlEt}_4]_2$	40	90–95/10 <sup>–3</sup>
$\text{Sr}[\text{AlEt}_4]_2$	109	122–123/10 <sup>–3</sup>
$\text{Ba}[\text{AlEt}_4]_2$	38	> 160/10 <sup>–3</sup>



HFA is hexafluoroacetylacetone. Apart from volatility, the feature of this derivative which attracted attention is that the caesium ion appears to be held so strongly to the complex anion that the loss of the ligand can occur, as depicted in the mass spectrum of the derivative, without prior loss of a caesium ion. This strength of the ion pair has been ascribed to the interaction between strongly electropositive caesium ion and the sheath of the electronegative fluorine atoms of the ligand. The work has been extended<sup>6</sup> to complexes of the type  $M[ScL_4]$ , where  $M = K, Rb$  or  $Cs$  and  $L =$  acetylacetone, trifluoroacetylacetone or hexafluoroacetylacetone. In this series also, the hexafluoroacetylacetone derivative depicts the highest thermal stability.

In the crystal<sup>5</sup> of  $Cs[Y(CF_3COCHCOCF_3)_4]$ , the yttrium atom is surrounded by eight oxygen atoms at the corners of a dodecahedron; this arrangement allows the electronegative atoms to be further apart than in the cubic form. The oxygen atoms are in contact with only one yttrium atom, so the whole anion is a complex (Fig. 6).

Another series of compounds of electropositive elements showing apparently covalent behaviour is that of double alkoxides. The formation of a large number of such derivatives was noticed about 50 years ago by Meerwin and Bersin<sup>105</sup> who carried out titrations of the alkoxides of a number of less basic metals such as  $Sb, Sn, Se^{IV}, Ti, Zr, B, Al, Zn, Be, Mg$  and  $Ca$  with alkoxides of strongly electropositive elements like,  $Li, Na$ , and  $K$ , using thymolphthalein as an indicator. Generally, the titrations were carried out in parent alcohols, but some of these could be accomplished even in inert solvents such as benzene. These alkoxo salts, e.g.  $K[Zn(OEt)_3], Na[Sb(OEt)_4], Na[Sb(OEt)_6], Na_2[Sn(OEt)_6], K[Al(OPr^i)_4], Ca[Al(OEt)_4]_2, Mg[Al(OPr^i)_4]_2, Mg[Al(OEt)_4]_2$  are quite stable, the last three could be volatilised under reduced pressure. Even  $K[Al(OPr^i)_4]$  and  $Cs[Al(OPr^i)_4]$  have recently been sublimed in poor yields<sup>106, 107</sup>. Compared to alkali aluminium isopropoxides, the corresponding boron derivatives  $M[B(OR)_4]$  (refs. 105, 108) appear to be less stable, disproportionating to give volatile alkyl borates.

Using the technique of Meerwein and Bersin<sup>105</sup>, Gilman and coworkers<sup>109</sup> synthesised a green crystalline compounds,  $Na[U(OEt)_6]$  in 1956 which could not be volatilised. How-

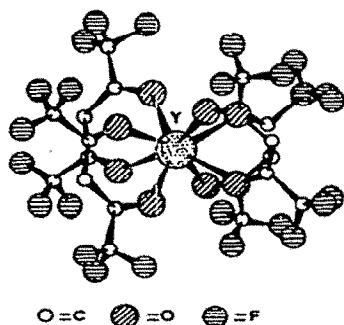


Fig. 6. Structure<sup>5</sup> of the anion in  $Cs^+[Y(CF_3COCHCOCF_3)_4]^-$ .

ever, the corresponding calcium derivative  $\text{Ca}[\text{U}(\text{OEt})_6]_2$  could be volatilised under reduced pressure. Similarly, Bartley and Wardlaw<sup>110</sup> were able to isolate a number of double alkali zirconium ennea-alkoxides of the type,  $\text{M}[\text{Zr}_2(\text{OR})_9]$ , (where  $\text{M} = \text{Li}, \text{Na}, \text{K}, \frac{1}{2} \text{Ca}, \text{Ti}$ , and  $\text{R} = \text{Et}, \text{Pr}^n, \text{Pr}^i, \text{Bu}^n$  or  $\text{Bu}^s$ ) by titrating alkali alkoxides with zirconium alkoxides in alcoholic media using thymolphthalin as the indicator. Compounds of the type  $\text{M}[\text{Ti}_2(\text{OR})_9]$  are also known<sup>111</sup>. A pH metric titration technique has been more recently used to show evidence for the existence of anionic species such as  $[\text{B}(\text{OMe})_4]^-$ ,  $[\text{Al}(\text{OMe})_4]^-$ ,  $[\text{Ti}_2(\text{OMe})_9]^-$ ,  $[\text{Nb}(\text{OMe})_6]^-$  and  $[\text{Ta}(\text{OMe})_6]^-$  in the titrations of corresponding metal chlorides with lithium methoxide in methanol<sup>112</sup>.

The sublimate obtained from the reactions of zirconium isopropoxide, isopropanolate and  $\text{MOPr}^i$  in isopropanol in 1:1 and 2:1 molar ratios corresponded<sup>106, 107</sup> to the formulae,  $\text{M}_2[\text{Zr}_3(\text{OPr}^i)_{14}]$  and  $\text{M}[\text{Zr}_2(\text{OPr}^i)_9]$  (where  $\text{M} = \text{Li}, \text{Na}, \text{K}$  and  $\text{Cs}$ ). For both of these double alkoxides, the measured molecular weights in boiling benzene correspond to their formula weights. All the isopropoxy groups in these derivatives are readily interchanged with ethanol and methanol. However, when exchange reactions were carried out with branched alcohols, replacement of the isopropoxy groups seemed to be hindered, e.g.  $\text{M}_2[\text{Zr}_3(\text{OBu}^s)_8(\text{OPr}^i)_6]$ , appears to be the final product in the alcoholysis reaction with secondary butanol. Similar steric effects were also observed with tertiary alcohols as indicated by the nature of the products, e.g.  $\text{Li}[\text{Zr}_2(\text{OPr}^i)_4(\text{OBu}^t)_5]$ ,  $\text{Li}[\text{Zr}_2(\text{OPr}^i)_4(\text{OAm}^t)_5]$ . In contrast to the isopropoxides, the reaction of zirconium tertiary butoxide with alkali tertiary butoxide, in all molar ratios, yielded the volatile products  $\text{M}[\text{Zr}(\text{OBu}^t)_5]$ , which were found to be dimeric in boiling benzene. The compounds  $\text{M}[\text{Th}_2(\text{OPr}^i)_9]$ ,  $\text{M}[\text{Ti}(\text{OPr}^i)_5\text{Pr}^i\text{OH}]$ ,  $\text{Li}[\text{Ti}_2(\text{OPr}^i)_9]$ ,  $\text{Li}[\text{Ti}_2(\text{OBu}^n)_9]$ ,  $\text{M}[\text{Sn}(\text{OPr}^i)_5]$  and  $\text{M}[\text{Sn}_2(\text{OPr}^i)_9]$  (where  $\text{M} = \text{Li}$  or  $\text{Na}$ ) have also been prepared<sup>113</sup> and are soluble in common organic solvents but disproportionate on heating to yield their respective alkoxides.

Double alkoxides of the type  $\text{M}[\text{M}'(\text{OR})_6]$ , ( $\text{M}' = \text{Nb}$  or  $\text{Ta}$ ;  $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Cs}, \frac{1}{2} \text{Ca}$  and  $\text{R} = \text{Me}, \text{Et}, \text{Pr}^i$  or  $\text{Bu}^t$ ) were prepared<sup>107, 114</sup> by reaction of the corresponding metal alkoxides with alkali alkoxides in the parent alcohols. Solubility of these derivatives appears to decrease from lithium to potassium. The tantalum derivatives are more stable than niobium derivatives which tend to disproportionate on heating. The derivatives,  $\text{M}[\text{Ta}(\text{OR})_6]$ , (where  $\text{M} = \text{Na}$  or  $\text{K}$ ;  $\text{R} = \text{Pr}^i$  or  $\text{Bu}^t$ ), sublime under reduced pressures with slight decomposition. Complexes of the type  $\text{M}[\text{M}'(\text{OR})_4]$ , (where  $\text{M}' = \text{Al}$  or  $\text{Ga}$ ,  $\text{M} = \text{Li}, \text{Na}$  and  $\text{R} = \text{Pr}^i, \text{Bu}^t$  and  $\text{Me}, \text{Et}$  for  $\text{Ga}$ ) and  $\text{M}[\text{Al}(\text{OMe})_4]$ , (where  $\text{M} = \text{Li}, \text{Na}, \text{K}, \frac{1}{2} \text{Ca}, \text{Sr}, \text{Ba}$ ) were prepared<sup>106, 115, 116</sup> by the reactions of  $\text{M}'(\text{OR})_3$  with  $\text{MOR}$  in a 1:1 molar ratio. These complexes are almost insoluble in their respective alcohols as well as in benzene.  $\text{M}[\text{M}'(\text{OPr}^i)_4]$ , ( $\text{M} = \text{K}$  or  $\text{Cs}$ ), is however, soluble in isopropanol and on heating it sublimes in a poor yield. If the component isopropoxides are taken in the ratio 3:2, the products correspond in analysis to  $\text{M}_3[\text{Al}_2(\text{OPr}^i)_9]$  (where  $\text{M} = \text{Li}, \text{Na}$  or  $\text{K}$ ). The potassium derivative is in this case also soluble in isopropanol. A number of double alkoxides of beryllium, e.g.  $\text{Li}_2[\text{Be}(\text{OMe})_4 \cdot 2\text{LiOMe}]$ ,  $\text{Li}_2[\text{Be}(\text{OEt})_4]$ ,  $\text{Li}[\text{Be}(\text{OPr}^i)_3]$  and  $\text{Na}[\text{Be}(\text{OPr}^i)_3]$  were also isolated<sup>117</sup> by the reactions of beryllium alkoxides with alkali

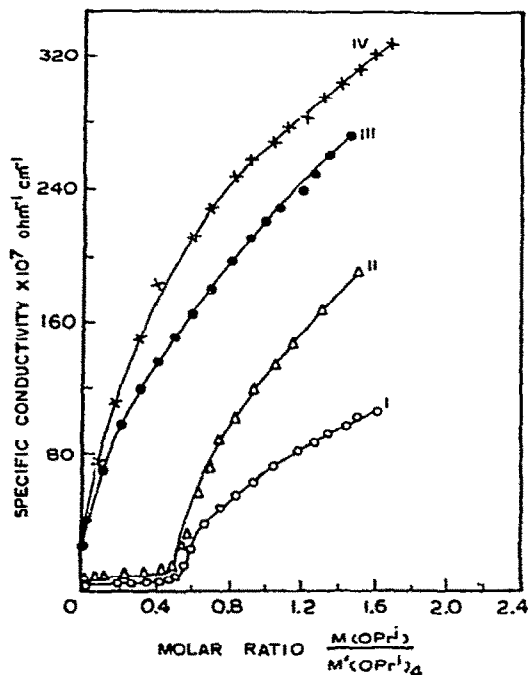


Fig. 7. Titration between  $M(OPr^i)_4$  and  $M(OPr^i)_3$ . I (o)  $NaOPr^i$  M/4.77 vs  $Zr(OPr^i)_4$   $Pr^iOH$  M/80.49. II ( $\Delta$ )  $KOPr^i$  M/9.97 vs  $Zr(OPr^i)_4$   $Pr^iOH$  M/43.01. III ( $\bullet$ )  $NaOPr^i$  M/9.20 vs  $Ti(OPr^i)_4$  M/37.7. IV (X)  $KOPr^i$  M/9.94 vs  $Ti(OPr^i)_4$  M/37.7. M = Na or K,  $M' = Ti$  or Zr.

alkoxides in parent alcohols. The complex  $Li[Be(OPr^i)_3]$  is dimeric in boiling isopropanol where other complexes, e.g.,  $Li_2[Be(OEt)_4]$  and  $Li_2[Be(OMe)_4 \cdot 2LiOMe]$ , once isolated from clear solution, could not be redissolved in the parent alcohols. Complexes of the type,  $Li_4[Zn(OMe)_6]$ ,  $Li_4[Zn(OEt)_6]$ ,  $Li_2[Zn(OEt)_4]$ ,  $Li[Zn(OEt)_3]$ ,  $Li[Zn_2(OEt)_5]$ ,  $Na[Zn_2(OEt)_5]$ ,  $Li[Zn(OPr^i)_3]$  have also been reported<sup>118</sup>. Only  $Li[Zn(OEt)_3]$  is monomeric in benzene whereas all other double alkoxides show dissociation in the parent alcohol.

The very low conductivity of  $Na[Zr_2(OPr^i)_9]$  measured in isopropanol indicates that it does not dissociate to give highly conducting sodium isopropoxide. The conductometric titrations of zirconium and hafnium isopropoxide in isopropanol with sodium and potassium isopropoxides in isopropanol show that on addition of alkali isopropoxide to  $M(OPr^i)_4 \cdot Pr^iOH$ , the conductivity was almost constant till the molar ratio of alkali isopropoxide to  $M(OPr^i)_4$  reaches 0.5 after which the conductivity curve (Fig. 7) shows a sharp rise, indicating that excess of alkali isopropoxide begins to contribute its conductivity to the solution<sup>113</sup>.

However, titrations of titanium isopropoxide with alkali isopropoxides showed a rise in conductivity from almost the beginning indicating that although  $Na[Ti_2(OPr^i)_9]$  can be

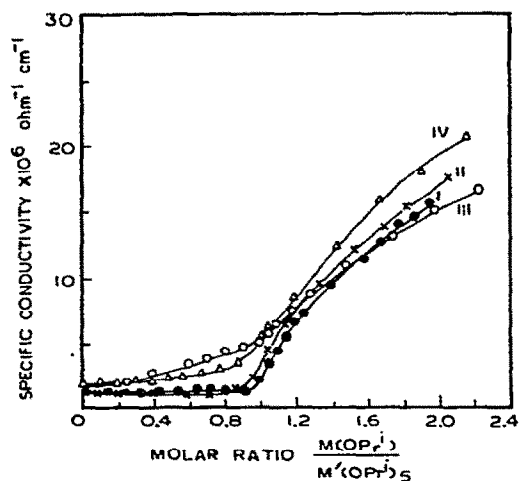


Fig. 8. Titration between  $M'(OPr^i)_5$  and  $M(OPr^i)$ . I (●)  $NaOPr^i$  M/4.77 vs  $Ta(OPr^i)_5$  M/93.74. II (x)  $KOPr^i$  M/4.96 vs  $Ta(OPr^i)_5$  M/93.74. III (O)  $NaOPr^i$  M/4.77 vs  $Nb(OPr^i)_5$  M/94.24. IV (Δ)  $KOPr^i$  M/4.98 vs  $Nb(OPr^i)_5$  M/94.91.  $M = Na$  or  $K$ ,  $M' = Nb$  or  $Ta$ .

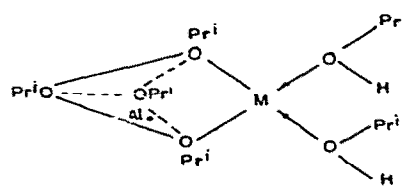


Fig. 9. The structure of double alkali aluminium isopropoxides.

isolated, it is appreciably dissociated in isopropanol solution<sup>113</sup>. Titration of niobium and tantalum isopropoxides with sodium and potassium isopropoxides in isopropanol gave sharp inflexions at 1:1 molar ratio<sup>114</sup> (Fig. 8).

The lower stability of mixed methoxides and ethoxides compared to the isopropoxides and the higher stability of tantalum compared to niobium analogues are reflected in the corresponding titration curves (Figs. 7 and 8).

The boiling points and molecular complexities of some double alkoxides are shown in Table 8.

The structure of double alkali aluminium isopropoxides,  $M[Al(OPr^i)_4]$  (where  $M$  is  $Li$ ,  $Na$  or  $K$ ) is suggested by Mehrotra and Mehrotra<sup>1, 119</sup> as shown in Fig. 9 indicating the solvation of two molecules of isopropanol. This tendency of solvation is facilitated by the increasing size of the alkali metals from lithium through sodium to potassium, increasing the solubility of these derivatives respectively. Similar observations were also noted<sup>12</sup> for  $Na^+[PhCOCHCOCH_3]^- [HOCH_2CH_2OH]$ . Remarkably, covalent and volatile derivatives  $M[M'_2(OPr^i)_9]$  (where  $M = Li, Na$  or  $K$ ,  $M' = Zr$  or  $Hf$ ) may have structures of the type in which nine isopropoxy groups are arranged around the two zirconium atoms by sharing the faces of two octahedra (Fig. 10). This structure assumes that the oxygen atoms of the alkali isopropoxide forms two donor linkages with each zirconium or hafnium atom. The alkali atom, in its turn, may be accepting donor linkages from two or three isopropoxy groups linked to the zirconium or hafnium atoms. This structure is supported by the alcoholysis studies of Bartley and Wardlaw<sup>110</sup> in which they found that treatment of

TABLE 8

Properties of some double alkoxides of electropositive elements

Compounds	Boiling points or sublimation temp. (°C/mm)	Molecular complexity	Solvent	Reference
K[Al(OPr <sup>i</sup> ) <sub>4</sub> ]	180–85/0.5			106
Cs[Al(OPr <sup>i</sup> ) <sub>4</sub> ]	300–310/0.25			107
Ca[Al(OMe) <sub>4</sub> ] <sub>2</sub>	220/4.0			105
Ca[Al(OPr <sup>i</sup> ) <sub>4</sub> ] <sub>2</sub>	230–40/3.0			105
Mg[Al(OPr <sup>i</sup> ) <sub>4</sub> ] <sub>2</sub>	130–42/2.0			105
K[Ga(OPr <sup>i</sup> ) <sub>4</sub> ]	260–70/0.4			106
Li[Zr(OBu <sup>t</sup> ) <sub>5</sub> ]	130–40/0.2	1.34	Benzene	113
Na[Zr(OBu <sup>t</sup> ) <sub>5</sub> ]	200–10/1.0			113
K[Zr(OBu <sup>t</sup> ) <sub>5</sub> ]	130–40/0.2	1.40	Benzene	113
Li[Zr <sub>2</sub> (OEt) <sub>9</sub> ]	260/0.2	2.10(1)*	Benzene	110
Li[Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> ]	226/0.3	1.7(1)*	Benzene	110
Li[Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> ]	207/3.0	1.00	Benzene	110
Li[Zr <sub>2</sub> (OBu <sup>n</sup> ) <sub>9</sub> ]	221–35/0.3	1.60	Benzene	110
Li[Zr <sub>2</sub> (OBu <sup>s</sup> ) <sub>9</sub> ]	200–10/0.2	1.00	Benzene	110
Li[Zr <sub>2</sub> (OEt) <sub>4</sub> (OBu <sup>t</sup> ) <sub>5</sub> ]	200/7.0	1.00	Benzene	110
Li[Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> .Pr <sup>i</sup> OH]	160/0.2	1.00(1)*	Benzene	110
Na[Zr <sub>2</sub> (OMe) <sub>9</sub> ]	360/0.005			110
Na[Zr <sub>2</sub> (OEt) <sub>9</sub> ]	230/0.1	1.2(1)*	Benzene	110
Na[Zr <sub>2</sub> (OPr <sup>n</sup> ) <sub>9</sub> ]		1.10	Benzene	110
Na[Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> ]	220/0.29	1.00	Benzene	110
Na[Zr <sub>2</sub> (OBu <sup>n</sup> ) <sub>9</sub> ]	218–25/0.37	1.00	Benzene	110
K[Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> ]	200/0.2	1.00	Benzene	110
Cs[Zr <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> ]	190–200/0.1			107
K[Zr <sub>2</sub> (OBu <sup>n</sup> ) <sub>9</sub> ]	238/0.38	1.00	Benzene	110
Ca[Zr <sub>4</sub> (OEt) <sub>18</sub> ]	280/vacuum			110
Li <sub>2</sub> [Zr <sub>3</sub> (OEt) <sub>14</sub> ]	200–10/0.5	1.10	Benzene	106
Li <sub>2</sub> [Zr <sub>3</sub> (OPr <sup>i</sup> ) <sub>14</sub> ]	200–10/0.5	0.97	Pr <sup>i</sup> OH	113
Na <sub>2</sub> [Zr <sub>3</sub> (OPr <sup>i</sup> ) <sub>14</sub> ]	185–95/2.0	1.00	Benzene	113
Cs <sub>2</sub> [Zr <sub>3</sub> (OPr <sup>i</sup> ) <sub>14</sub> ]	220–230/0.1			107
K <sub>2</sub> [Zr <sub>3</sub> (OPr <sup>i</sup> ) <sub>14</sub> ]	200–10/0.2			113
K[Hf(OBu <sup>t</sup> ) <sub>5</sub> ]	178/0.5	1.40	Benzene	120
Li[Hf <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> ]	200/0.7	1.00	Benzene	120
Na[Hf <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> ]	170–90/0.1	0.90	Benzene	120
K[Hf <sub>2</sub> (OEt) <sub>9</sub> ]	235/0.6	1.10	Benzene	120
K[Hf <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> ]	180–90/0.2	1.10	Benzene	120
Cs[Hf <sub>2</sub> (OPr <sup>i</sup> ) <sub>9</sub> ]	230–40/0.1			107
K[Hf <sub>2</sub> (OBu <sup>n</sup> ) <sub>9</sub> ]	220–40/0.3	1.00	Benzene	120
Li <sub>2</sub> [Hf <sub>3</sub> (OPr <sup>i</sup> ) <sub>14</sub> ]	200/0.5	1.00	Benzene	120
Na <sub>2</sub> [Hf <sub>3</sub> (OPr <sup>i</sup> ) <sub>14</sub> ]	170–80/0.3	0.70	Benzene	120
K <sub>2</sub> [Hf <sub>3</sub> (OPr <sup>i</sup> ) <sub>14</sub> ]	190/0.4	1.00	Benzene	120
K <sub>2</sub> [Hf <sub>3</sub> (OEt) <sub>14</sub> ]	180–90/0.1	1.00	Benzene	120
Cs <sub>2</sub> [Hf <sub>3</sub> (OPr <sup>i</sup> ) <sub>14</sub> ]	160–70/0.2			107
Li[Ta(OMe) <sub>6</sub> ]	260/0.1			114
Li[Ta(OEt) <sub>6</sub> ]	330/0.2	1.00	EtOH	114
Li[Ta(OPr <sup>i</sup> ) <sub>6</sub> ]	160–80/0.1	0.95	Pr <sup>i</sup> OH	114

TABLE 8 (continued)

Compounds	Boiling points or sublimation temp. (°C/mm)	Molecular complexity	Solvent	Reference
Na[Ta(OPr <sup>i</sup> ) <sub>6</sub> ]	200–10/0.2	0.92	Pr <sup>i</sup> OH	114
K[Ta(OPr <sup>i</sup> ) <sub>6</sub> ]	210–20/0.1			114
Cs[Ta(OPr <sup>i</sup> ) <sub>6</sub> ]	210–20/0.15			107
Li[Nb(OBu <sup>t</sup> ) <sub>6</sub> ]	110–20/0.1	0.80	Bu <sup>t</sup> OH	114
Na[Nb(OBu <sup>t</sup> ) <sub>6</sub> ]	110–20/0.1			114
K[Nb(OBu <sup>t</sup> ) <sub>6</sub> ]	110–20/0.1			114
Cs[Nb(OPr <sup>i</sup> ) <sub>6</sub> ]	180–90/0.15			107
Li[Ta(OBu <sup>t</sup> ) <sub>6</sub> ]	110–20/0.1	0.65	Bu <sup>t</sup> OH	114
Na[Ta(OBu <sup>t</sup> ) <sub>6</sub> ]	110–20/0.1			114
Ca[Nb(OEt) <sub>6</sub> ] <sub>2</sub>	165/0.2	0.97	Benzene	107
Ca[Nb(OPr <sup>i</sup> ) <sub>6</sub> ] <sub>2</sub>	185–95/0.3	1.2	Benzene	107
Ca[Ta(OEt) <sub>6</sub> ] <sub>2</sub>	153/0.2	0.91	Benzene	107
Ca[Ta(OPr <sup>i</sup> ) <sub>6</sub> ] <sub>2</sub>	195–215/0.2	0.8	Benzene	107
Ca[Ta(OEt) <sub>3</sub> (OBu <sup>t</sup> ) <sub>3</sub> ] <sub>2</sub>	190–200/0.2			107
Ca[U(OEt) <sub>6</sub> ] <sub>2</sub>	200/0.001			109

\* Molecular weight in parent alcohol.

M[Zr<sub>2</sub>(OPr<sup>i</sup>)<sub>9</sub>] with excess tertiary butanol yielded M[Zr<sub>2</sub>(OPr<sup>i</sup>)<sub>4</sub>(OBu<sup>t</sup>)<sub>5</sub>] (where M = Li, Na, K). The NMR spectra<sup>119</sup> of alkali hafnium double isopropoxides (Fig. 11) e.g. Li[Hf<sub>2</sub>(OPr<sup>i</sup>)<sub>9</sub>] and K[Hf<sub>2</sub>(OPr<sup>i</sup>)<sub>9</sub>], show two pairs of methyl protons, of which peak areas are approximately in the ratio of 1:1:2:2 which corresponds to six terminal and three bridging isopropoxy groups (as shown in the structure given in Fig. 10).

On similar lines, the following structures (Fig. 12) have been suggested<sup>1</sup> for derivatives like M<sub>2</sub>[M'<sub>3</sub>(OPr<sup>i</sup>)<sub>14</sub>] (where M = Li, Na, K, M' = Zr, or Hf). However, the NMR spectra of Li<sub>2</sub>[Hf<sub>3</sub>(OPr<sup>i</sup>)<sub>14</sub>] and K<sub>2</sub>[Hf<sub>3</sub>(OPr<sup>i</sup>)<sub>14</sub>] lend greater support structure (ii). This structure possesses four bridging isopropoxy groups and ten terminal isopropoxy groups attached to the three hafnium atoms. The NMR spectra (Fig. 13) of both compounds also shows the existence of two types of methyl proton peaks. Although the ratios of the areas of the observed peaks A, C and D could not be accurately measured, they are approximately represented as 1:3 : 5:2.5, which would indicate that the ratio of the area of the doublets

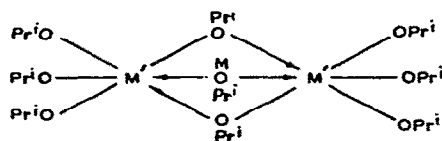


Fig. 10. The structure of M(M'<sub>2</sub>(OPr<sup>i</sup>)<sub>9</sub>) where M = Li, Na or K, M' = Zr or Hf.

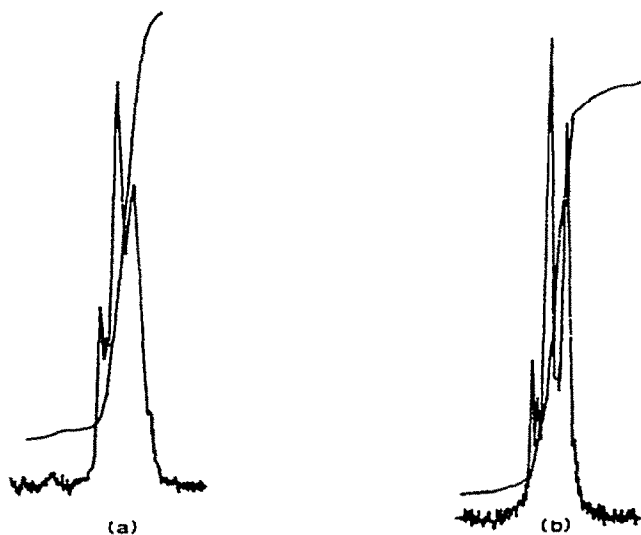


Fig. 11. (a) The NMR spectrum of the methyl group protons of  $K(Hf_2(OPri)_9)$  in  $CCl_4$  in cycles per second at 60 MHz. (b) The NMR spectrum of the methyl group protons of  $Li(Hf_2(OPri)_9)$  in  $CCl_4$  in cycles per second at 60 MHz.

$(A + B):(C + D)$  is about 1:2.5 (Fig. 13). The methyl proton peaks reported for the above compounds are given in Table 9.

The structures of  $M[Zr(Obu^t)_5]$  (dimer) (Fig. 14) and double alkali tantalum (niobium) alkoxides (Fig. 15) could then be represented by the following plausible structures<sup>1</sup>.

The difference in behaviour between the double alkali zirconium isopropoxides and tertiary butoxides may be due to steric factors hindering the sharing of  $Zr(OR)_6$  octahedra through a face as has been suggested for  $Na[Zr_2(OPri)_9]$  (Fig. 10).

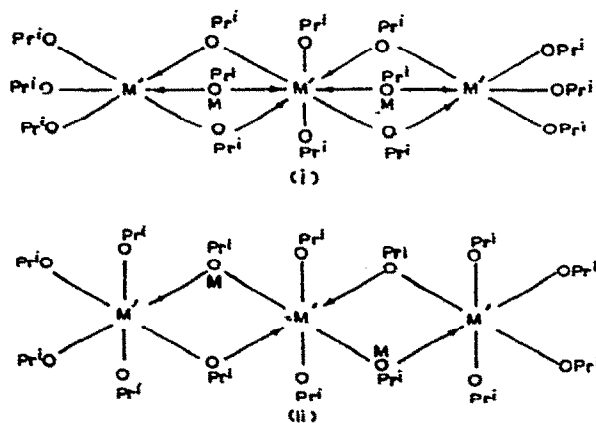


Fig. 12. Structures suggested for derivatives such as  $M_2[M'_3(OPri)_{14}]$ .  $M = Li, Na, K$ ;  $M' = Zr$  or  $Hf$ .

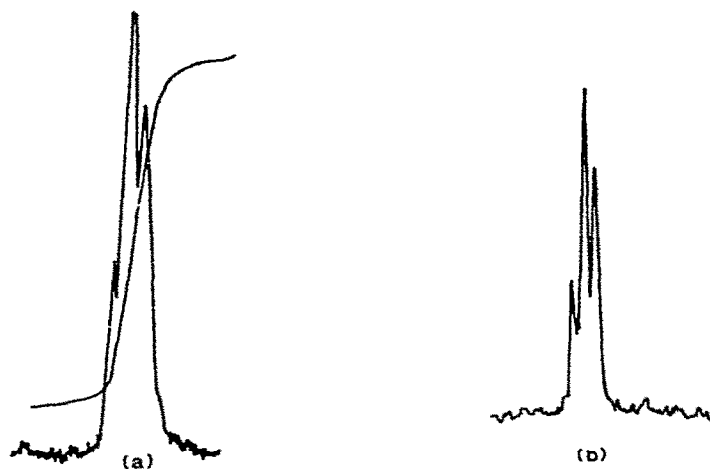


Fig. 13. (a) The NMR spectrum of the methyl group protons of  $K_2[Hf_3(OPr^i)_{14}]$  in  $CCl_4$  in cycles per second 60 MHz. (b) The NMR spectrum of the methyl group proton of  $Li_2[Hf_3(OPr^i)_{14}]$  in  $CCl_4$  in cycles per second.

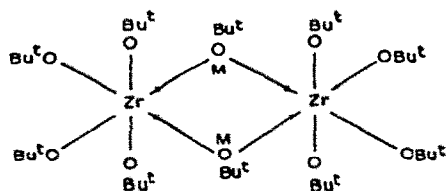


Fig. 14. The structure of  $M[Zr(OBu^t)_5]$  (dimer).

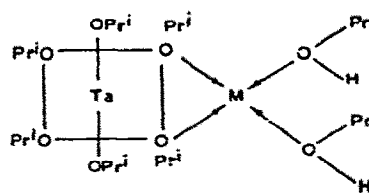


Fig. 15. The structure of double alkali tantalum (niobium) alkoxides.

TABLE 9

Methyl proton peaks of some double isopropoxides of hafnium in c.p.s. from tetramethylsilane<sup>119</sup>

Compound	Solvent	Peaks				Area ratio
		A	B <sup>a</sup>	C	D	
$Li[Hf_2(OPr^i)_9]$	$CCl_4$	81	(74.5)	74.5	68	1 : 1 : 2 : 2
$K[Hf_2(OPr^i)_9]$	$CCl_4$	79	(73)	73	67	1 : 1 : 2 : 2
$Li_2[Hf_3(OPr^i)_{14}]$	$CDCl_3$	81	(75)	75	69	1 : 1 : 2.5 : 2.5
$K_2[Hf_3(OPr^i)_{14}]$	$CCl_4$	81	(74.5)	74.5	68	1 : 1 : 2.5 : 2.5

<sup>a</sup> Values within parenthesis indicate overlapping peaks.



## ACKNOWLEDGEMENTS

One of authors, P.N. Kapoor is thankful to the Council of Scientific and Industrial Research and Indian National Science Academy, New Delhi for providing financial assistance.

## REFERENCES

- 1 R.C. Mehrotra and Miss. A. Mehrotra, *Inorg. Chim. Acta Rev.*, 5 (1971) 127.
- 2 R.J.P. Williams, *Quart. Rev.*, 24 (1970) 331; *Advan. Chem. Ser.*, 100 (1971) 155.
- 3 A.K. Banerjee, A.J. Layton, R.S. Nyholm and M.R. Truter, *Nature* 217 (1968) 1147; *J. Chem. Soc. A*, (1969) 2536; *J. Chem. Soc. A*, (1970) 292; A.J. Layton, R.S. Nyholm, A.K. Banerjee, D.E. Fenton, C.N. Lestas and M.R. Truter, *J. Chem. Soc. A*, (1970) 1894.
- 4 M.R. Truter, *Chem. Brit.*, 7 (1971) 203.
- 5 S.J. Lippard, *J. Amer. Chem. Soc.*, 88 (1966) 4300; M.J. Bennett, F.A. Cotton, P. Legzdins and S.J. Lippard, *Inorg. Chem.*, 7 (1968) 1770.
- 6 M.Z. Gurevich, B.D. Stepin, L.N. Komissarova, N.E. Lebedeva and T.M. Sas, *Zh. Neorg. Khim.*, 16 (1971) 93; *Chem. Abstr.*, 74 (1971) 71120.
- 7 T.C. Shields, *Chem. Comm.*, (1968) 832; F.C. McCoy, R.R. Reinhard and H.V. Hess, *Chem. Ind. (London)*, (1970) 531.
- 8 B. Dietrich, J.M. Lehn and J.P. Sauvage, *Tetrahedron Lett.*, (1969) 2885, 2889.
- 9 M.R. Truter and C.J. Pedersen, *Endeavour*, 30 (1971) 142.
- 10 M.R. Truter, *Struct. Bonding (Berlin)*, 16 (1973) 71.
- 10a J.M. Lehn, *Struct. Bonding (Berlin)*, 16 (1973) 1; W.E. Mort and P.Ch. Meier, *Struct. Bonding (Berlin)*, 16 (1973) 113; R.M. Izatt, D.J. Eatough and J.J. Christensen, *Struct. Bonding (Berlin)*, 16 (1973) 161.
- 11 N.V. Sidgwick and F.M. Brewer, *J. Chem. Soc., London*, (1925) 127, 2379; F.M. Brewer, *J. Chem. Soc., London*, (1931) 361.
- 12 D. Bright, A.J. Kolombos, G.H.W. Milburn, R.S. Nyholm and M.R. Truter, *Chem. Comm.*, (1970) 49; D. Bright, G.H.W. Milburn and M.R. Truter, *J. Chem. Soc. A*, (1971) 1582.
- 13 N.P. Marullo and R.A. Lloyd, *J. Amer. Chem. Soc.*, 88 (1966) 1076.
- 14 I. Goodman, S.J. Kettle and P.G. Owston, *Chem. Ind. (London)*, (1971) 1300.
- 15 J.A.J. Jarvis and P.G. Owston, *Chem. Comm.*, (1971) 1403.
- 16 F. Durant, Y. Gobillon, P. Piret and M. van Meerssche, *Bull. Soc. Chim. Belge.*, 75 (1966) 52.
- 17 P. Piret, L. Rodrique, Y. Gobillon and M. van Meerssche, *Acta Crystallogr.*, 20 (1966) 482.
- 18 F. Durant, P. Piret and M. van Meerssche, *Acta Crystallogr.*, 22 (1967) 52.
- 19 F. Durant, P. Piret and M. van Meerssche, *Acta Crystallogr.*, 23 (1967) 780.
- 20 A.R. Hands and A.J.H. Mercer, *J. Chem. Soc. A*, (1968) 449 and references cited therein.
- 21 Y.M.G. Yasin, O.J.R. Hodder and H.M. Powell, *Chem. Comm.*, (1966) 705.
- 22 K. Issleib and K. Krech, *Z. Anorg. Chem.*, 328 (1964) 69.
- 23 N.M. Karayannis, C.M. Mikulski, M.J. Strocko, L.L. Pytlewski and M.M. Labes, *J. Inorg. Nucl. Chem.*, 32 (1970) 2629.
- 24 M.W.G. DeBolster, I.E. Kortram and W.L. Groeneveld, *J. Inorg. Nucl. Chem.*, 34 (1972) 575.
- 25 C.N. Lestas and M.R. Truter, *J. Chem. Soc. A*, (1971) 738.
- 26 M.I. Kabachnik, K.B. Yatsimirskii, Z.A. Sheka, T.Ya. Medved, M.Ya. Polikarpov and E.V. Sinyavskaya, *Redk. Shchelochnye Elem., Sb. Dokl. Soveshch.*, (1969) 461; *Chem. Abstr.*, 74 (1971) 106651.
- 27 J.C.A. Foyens and F.H. Herbstein, *Inorg. Chem.*, 6 (1967) 1408.
- 28 G. Jander and W. Ruppolt, *Z. Phys. Chem. A*, 179 (1937) 43; G. Jander, *Naturwissenschaften*, 26 (1938) 793; E.R. Lippincott and F.E. Welsh, *Spectrochim. Acta*, 17 (1961) 123.
- 29 A.B. Hart and J.R. Partington, *J. Chem. Soc., London*, (1943) 104.
- 30 W.E.S. Turner and C.C. Bissett, *J. Chem. Soc., London*, (1914) 1777.

- 31 K. Baessler and G. Folz, *Ger. Offen.* 1, 934, 175; *Chem. Abstr.*, 74 (1971) 63932.  
32 J.B. Grenet, *Ger. Offen.* 2,038, 725; *Chem. Abstr.*, 75 (1971) 5290.  
33 M.A. Bernard and A. Busnot, *Bull. Soc. Chim. Fr.*, (1970) 4271.  
34 J.A. Rendleman, *Advan. Carbohydr. Chem.*, 21 (1966) 209.  
35 M.A. Bush, H. Luth and M.R. Truter, *J. Chem. Soc. A*, (1971) 740.  
36 M.A. Bush and M.R. Truter, *J. Chem. Soc. A*, (1971) 745.  
37 S.J. Gruber, C.M. Harris and E. Sinn, *Inorg. Chem.*, 7 (1968) 268.  
38 G.E. Coates, M.L.H. Green and K. Wade, *Organometallic Compounds of Main Group Elements*, Vol. 1, Methuen and Co. Ltd., London, (1967), pp. 1-176.  
39 P. West and R. Waack, *J. Amer. Chem. Soc.*, 89 (1967) 4395.  
40 T.L. Brown, R.L. Gerteis, D.A. Bafus and J.A. Ladd, *J. Amer. Chem. Soc.*, 86 (1964) 2135 and references cited therein.  
41 D. Margerison and P.J. Newport, *Trans. Faraday. Soc.*, 59 (1963) 2058.  
42 M. Weiner, G. Vogel and R. West, *Inorg. Chem.*, 1 (1962) 654.  
43 R. Waack and P. West, *J. Organometal. Chem.*, 5 (1966) 188.  
44 R.H. Baney and R.J. Krager, *Inorg. Chem.*, 3 (1964) 1657; J.W. Connolly and G. Urry, *Inorg. Chem.*, 2 (1963) 645.  
45 T.L. Brown, J.A. Ladd and G.N. Newman, *J. Organometal. Chem.*, 3 (1965) 1.  
46 M.A. Weiner and R. West, *J. Amer. Chem. Soc.*, 85 (1963) 485.  
47 A.W. Langer, *Trans. N.Y. Acad. Sci.*, (1965) 741.  
48 E. Weiss and E.A.C. Lucken, *J. Organometal. Chem.*, 2 (1964) 197.  
49 H. Dietrich, *Acta Crystallogr.*, 16 (1963) 681.  
50 J. Berkowitz, D.A. Bafus and T.L. Brown, *J. Phys. Chem.*, 65 (1961) 1380.  
51 R. Waack, L.D. McKeever and M.A. Doran, *Chem. Comm.*, (1969) 117.  
52 F.J. Kronzer and V.R. Sandel, *Chem. Ind. (London)*, (1972) 210.  
53 G.A. Baluveva and S.T. Ioffe, *Russ. Chem. Rev.*, 31 (1962) 439.  
54 H. Gilman and R.E. Brown, *J. Amer. Chem. Soc.*, 52 (1930) 4480 and references cited therein.  
55 D.A. Payne and R.T. Sanderson, *J. Amer. Chem. Soc.*, 80 (1958) 5324.  
56 E. Weiss, *J. Organometal. Chem.*, 2 (1964) 314.  
57 W.H. Glaze and C.M. Selman, *J. Organometal. Chem.*, 5 (1966) 477.  
57A W.H. Glaze and C.R. McDaniel, *J. Organometal. Chem.*, 51 (1973) 23.  
58 K. Ziegler, H. Froitzheim-Kuhlhorn and K. Hafner, *Chem. Ber.*, 89 (1956) 434; K. Ziegler, *Angew. Chem.*, 66 (1954) 239; E.O. Fischer and G. Stolzle, *Chem. Ber.*, 94 (1961) 2107.  
59 D. Bryce-Smith and A.C. Skinner, *J. Chem. Soc., London*, (1963) 577; N. Kawabata, A. Matsumura and S. Yamashita, *Tetrahedron*, 29 (1973) 1069.  
60 R. Masthoff and G. Krieg, *Z. Chem.*, 6 (1966) 433; R. Masthoff, H. Schuler and G. Krieg, *J. Organometal. Chem.*, 13 (1968) 37.  
61 M.A. Coles and F.A. Hart, *Chem. Ind. (London)*, (1968) 423; *J. Organometal. Chem.*, 32 (1971) 279.  
62 H. Gilman, R.N. Meals, G. O'Donnell and L. Woods, *J. Amer. Chem. Soc.*, 65 (1943) 268.  
63 G.E. Coates and J.A. Heslop, *J. Chem. Soc. A*, (1968) 514.  
64 B.J. Wakefield, *Chem. Ind. (London)*, (1972) 450 and references cited therein.  
65 D. Bryce-Smith and G.F. Cox, *J. Chem. Soc., London*, (1958) 1050; (1961) 1175.  
66 E.C. Ashby and R. Rees, *J. Org. Chem.*, 31 (1966) 971; E.C. Ashby, *J. Amer. Chem. Soc.*, 87 (1965) 2509.  
67 G.E. Coates and J.A. Heslop, *J. Chem. Soc. A*, (1968) 631.  
68 G.E. Coates and J.A. Heslop, *Chem. Comm.*, (1968) 514; G.E. Coates, J.A. Heslop, M.E. Redwood and D. Ridley, *J. Chem. Soc. A*, (1968) 1118.  
68A J.A. Nacckashi and E.C. Ashby, *J. Organometal. Chem.*, 35 (1972) C1.  
69 M.S. Bains, *Res. Bull. Punjab Univ.*, 15 (1964) 303; *Can. J. Chem.*, 42 (1964) 945.  
70 P.J. Wheatley, *Nature*, 185 (1960) 681.  
70A N.Ya. Turova and E.P. Turevskaya, *J. Organometal. Chem.*, 42 (1972) 9.  
71 G.S. Hammond, D.C. Nonhebel and C.S. Wu, *Inorg. Chem.*, 2 (1963) 73.

- 72 R. Belcher, A.W.I. Dudeney and W.I. Stephen, *J. Inorg. Nucl. Chem.*, 31 (1969) 625.  
73 C.J. Pedersen, *J. Amer. Chem. Soc.*, 89 (1967) 7016; 92 (1970) 386, 391; *Proc. Fed. Amer. Soc. Exp. Biol.*, 27 (1968) 1305; *J. Org. Chem.*, 36 (1971) 254.  
74 *Chem. and Eng. News*, 2nd March (1970), p. 27.  
75 P.A. Tasker and E.B. Fleischer, *J. Amer. Chem. Soc.*, 92 (1970) 7072.  
76 D.J. Sam and H.E. Simmons, *J. Amer. Chem. Soc.*, 94 (1972) 4024.  
77 H.K. Frensdorff, *J. Amer. Chem. Soc.*, 93 (1971) 600.  
78 L.A.R. Pioda, H.A. Wachter, R.E. Dohner and W. Simon, *Helv. Chim. Acta*, 50 (1967) 1373; M.K. Wipt, L.A.R. Pioda, Z. Stefance and W. Simon, *Helv. Chim. Acta*, 51 (1968) 371.  
79 *Stability Constants*, Chem. Soc., Special Publication No. 17 (1964).  
80 D. Bright and M.R. Truter, *J. Chem. Soc. B*, (1970) 1544.  
81 M.A. Bush and M.R. Truter, *Chem. Commun.*, (1970) 1439; *J. Chem. Soc. B*, (1971) 1440; *J. Chem. Soc. B*, (1972) 341, 345.  
82 D.E. Fenton, M. Mercer, N.S. Poonia and M.R. Truter, *J. Chem. Soc. Chem. Commun.*, (1972) 66; K. Dalley, D.E. Smith, R.M. Izatt and J.J. Christensen, *J. Chem. Soc. Chem. Commun.*, (1972) 90.  
83 L.K. Steinrauf, M. Pinkerton and J.W. Chamberlin, *Biochem. Biophys. Res. Commun.*, 33 (1968) 29.  
84 T. Kubota, S. Matsutani, M. Shiro and H. Koyama, *Chem. Commun.*, (1968) 1541; M. Shiro and H. Koyama, *J. Chem. Soc. B*, (1970) 243.  
85 M. Dobler, J.D. Dunitz and B.T. Kilbourn, *Helv. Chim. Acta*, 52 (1969) 2573.  
86 M. Dobler, J.D. Dunitz and J. Krajewski, *J. Mol. Biol.*, 42 (1969) 603.  
87 M. Pinkerton, L.K. Steinrauf and P. Dawkins, *Biochem. Biophys. Res. Commun.*, 35 (1969) 512.  
88 S. Candeloro, D. Grdenic, N. Taylor, B. Thompson, M. Viswamitra and D.C. Hodgkin, *Nature*, 224 (1969) 589.  
89 C.N. Lestas and M.R. Truter, Unpublished work (1969), quoted in reference (9).  
90 F. Wudi and F. Gaeta, *J. Chem. Soc., Chem. Commun.*, (1972) 107.  
91 J.M. Lehn, J.P. Sauvage and B. Dietrich, *J. Amer. Chem. Soc.*, 92 (1970) 2916; *Chem. Commun.*, (1970) 1055.  
92 R. Weiss, B. Metz and D. Moras, *Proc. XIII Int. Conf. Coord. Chem.*, Vol. II., 1970, p. 85; *Chem. Commun.*, (1970) 217.  
93 L.I. Zakharkin and V.V. Gavrilenko, *J. Gen. Chem. USSR.*, 32 (1962) 688.  
94 R.L. Gertcis, R.E. Dickerson and T.L. Brown, *Inorg. Chem.*, 3 (1964) 872.  
95 E. Schaschel and M.C. Day, *J. Amer. Chem. Soc.*, 90 (1968) 503.  
96 M.C. Day, H.M. Barnes and A.J. Cox, *J. Phys. Chem.*, 68 (1964) 2595.  
96A K. Hoffmann and E. Weiss, *J. Organometal. Chem.*, 37 (1972) 1; 50 (1973) 17, 25.  
97 K. Ziegler, H. Lehmkuhl and E. Lindner, *Chem. Ber.*, 92 (1959) 2320.  
98 K. Ziegler, R. Koster, H. Lehmkuhl and K. Reinert, *Ann.*, 629 (1960) 33.  
99 K. Ziegler, in H. Zeiss (Ed.), *Organometallic Chemistry*, Reinhold, New York, 1960, ch. 5.  
100 G. Allegra and G. Perego, *Acta Crystallogr.*, 16 (1963) 185.  
101 H. Tani, R. Araki, N. Oguni, T. Aoyagi and H. Yasuda, *Chem. and Eng. News*, 9th August 1965, p. 40.  
102 H. Lehmkuhl, *Angew. Chem. Int. Ed. Engl.*, 3 (1964) 107.  
103 K. Ziegler and E. Holzkamp, *Ann.*, 605 (1957) 93.  
104 H. Lehmkuhl and W. Eisenbach, *Ann.*, 705 (1967) 42.  
105 H. Meerwein and T. Bersin, *Ann.*, 476 (1929) 113; *Chem. Abstr.*, 24 (1930) 586.  
106 R.C. Mehrotra, M.M. Agarwal and P.N. Kapoor, *Proc. IX Int. Conf. Coord. Chem.*, St. Moritz Bad 1966, p. 253; M.M. Agarwal, Ph. D. Thesis, Rajasthan University, 1968.  
107 S. Govil, P.N. Kapoor and R.C. Mehrotra, Unpublished work, 1973.  
108 H. Steinberg, *Organoboron Chemistry*, Wiley, New York, 1963, p. 612.  
109 R.G. Jones, E. Bindshadler, D. Blume, G. Karmas, G.A. Martin, J.R. Thirtle and H. Gilman, *J. Amer. Chem. Soc.*, 78 (1956) 6027.

- 110 W.G. Bartley and W. Wardlaw, *J. Chem. Soc.*, (1958) 422.
- 111 D.G. Carter, Ph.D. Thesis, London University, 1959.
- 112 R. Gut, *Helv. Chim. Acta*, 47 (1964) 2262.
- 113 R.C. Mehrotra and M.M. Agarwal, *J. Chem. Soc. A*, (1967) 1026.
- 114 R.C. Mehrotra, M.M. Agarwal and P.N. Kapoor, *J. Chem. Soc. A*, (1968) 2673.
- 115 G. Rietz and H. Mothes, *Z. Chem.*, 11 (1971) 114; *Chem. Abstr.*, 75 (1971) 14481.
- 116 V.R. Scholder and H. Protzer, *Z. Anorg. Allg. Chem.*, 340 (1965) 23.
- 117 R.C. Mehrotra and M. Arora, *Indian J. Chem.*, 7 (1969) 399.
- 118 R.C. Mehrotra and M. Arora, *Z. Anorg. Allg. Chem.*, 370 (1969) 300.
- 119 R.C. Mehrotra and A. Mehrotra, *J. Chem. Soc. A*, (1972) 1203; Unpublished work.
- 120 A. Mehrotra, Ph.D. Thesis, Rajasthan University, Jaipur, 1972.