Coordination Chemistry Reviews, 75 (1986) 1—99
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

Chapter 1

ELEMENTS OF GROUP 1

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0010-8545/86/$34.65

1.1 INTRODUCTION

The format of the first two Chapters of this review is similar to that adopted previously.[1] The chemistry of both the Group 1 and Group 2 elements is considered in sections which reflect subjects of topical interest and significance; certain aspects of their chemistry, particularly the formation of crown and related complexes, are so similar that they are reported once only, in the relevant section of the present Chapter.

The material chosen for inclusion in the review is selective, only those papers in which some unique aspect of the inorganic chemistry of these two groups of metals is described being abstracted; those papers in which their organometallic chemistry is discussed are omitted since they are reviewed in detail elsewhere. The remarkable upsurge in interest in the coordination chemistry of lithium, first noted in the 1983 review[2] has been maintained throughout 1984. To permit appropriate coverage of this exciting, rapidly expanding field, other topics including molten salts have, regretfully, had to be omitted from the present review.

Preliminary communications reporting that activated carbon supported alkali metals catalyse both the methanation of CO by H_2 ($T>750K$)[3] and the reduction of NO_x ($x = 1,2$) by C or CO ($T>500K$)[4] have been published. The activity of the catalysts, prepared by pore volume impregnation of an activated carbon with an aqueous solution of an alkali metal carbonate followed by slow evaporation of the water at 323K and drying at 400K, increases with increasing atomic number:

$$Na < K < Rb < Cs$$

Attempts to poison the catalysts by addition of H_2S (for the methanation process)[3] or Et_4Pb (for the NO_x reduction process)[4] were unsuccessful.

1.2 THE ELEMENTS

The application of the lighter alkali metals, particularly lithium and sodium, in nuclear energy and high energy battery technologies continues to stimulate interest in the chemistry of these metals. Mindful of their industrial significance, Addison[5] has written a book reviewing the chemistry of the liquid alkali metals; chapters covering aspects of the manipulation, purification and analysis of the liquids, the solubility, solvation and reactivity of solutes dissolved therein, the reactions of the liquids with non-metals, water, hydrocarbons and halogen-containing compounds, and the corrosion of transition metals including stainless steel containment materials, by the liquid metals, are included.[5] The proceedings of two conferences devoted, in part, to the specific roles of liquid alkali metals in nuclear reactor technology[6,7] and of one conference devoted exclusively to current applications of lithium in science, medicine and technology[8] have been published during 1984. Since the majority of the papers published in these proceedings are technologically oriented, they are of only peripheral interest to the average inorganic chemist and will not be considered in detail; the specialist reader is referred to the appropriate proceedings.[6-8] There are however a number of papers of more general interest; these have been abstracted and are reviewed, as appropriate, in the following sub-sections.

The development of battery systems using alkali metal, particularly lithium, electrodes has resulted in a large number of papers in the Journal of the Electrochemical Society. Again, owing to the mainly technological nature of these papers they are not reviewed here, the specialist reader being referred to the appropriate volume of the Journal.[9]

1.2.1 General Properties

An XPS study of lithium surfaces exposed to low levels of gaseous reactants has been undertaken.[10] Molecular oxygen and carbon monoxide yield Li_2O and Li_2O plus a material tentatively identified as Li_2C_2, respectively, under all exposure conditions. Water vapour always gives Li_2O and a species tentatively identified as LiOH; the ratio of the products varies with coverage, however, Li_2O being favoured at submonolayer levels and LiOH at higher exposures. Carbon dioxide and sulphur dioxide produce different products depending on coverage; whereas for submonolayer coverages Li_2O plus Li_2C_2 and Li_2O plus Li_2S are formed, for greater exposures, Li_2CO_3 plus a $Li_2O.CO_2$ adduct and Li_2SO_3, respectively, are formed.[10]

The kinetics of the reaction of molecular hydrogen or nitrogen with liquid lithium[11] may be explained by chemisorption of reactant followed by either conversion of reactant to product and solubilisation of product or solubilisation of reactant followed by conversion to product in the bulk liquid. The reactions proceed at a constant rate with apparent activation energies of 69.9 kJ.mol$(H_2)^{-1}$ and 45.2 kJ.mol$(N_2)^{-1}$ until the bulk liquid is saturated. Subsequently, the reaction rate is controlled by mass transport through the surface product layer.[11]

Novel high speed photographic methods have been used to study the reaction resulting on injection of a thread of liquid sodium or NaK alloy into liquid water ($293 < T/K < 333$).[12] The metal reacts rapidly ($K \sim 10^{-3}$ moles $s^{-1} mm^{-2}$) but incompletely (~15%) at the nozzle; the thread then breaks into globules which are carried away in a semi-protective bubble of hydrogen subsequent reaction being much slower ($K \sim 10^{-5}$ mole $s^{-1} mm^{-2}$). The reaction produces hydrogen both directly and via MH as an intermediate:

$$2M + 2H_2O \rightarrow 2MOH + H_2 \qquad \ldots(1)$$

$$2M + H_2O \rightarrow MOH + MH \qquad \ldots(2)$$

$$MH + H_2O \rightarrow MOH + H_2 \qquad \ldots(3)$$

1.2.2 The Alkali Metals as Solvent Media

The solution chemistry of both metals and non-metals has been extensively studied during the past year. For lithium as solvent non-metallic solutes predominate, whereas for sodium, both types of solute appear. For potassium, rubidium and caesium a limited number of papers have been published on the chemistry of dissolved oxygen.

The solubility of Ni in liquid lithium ($503<T/K<873$) has been determined[13] by chemical analysis (atomic absorption spectroscopy) of samples filtered from equilibrated specimens held in nickel crucibles. The data, which are described by the relationship:

$$\log_{10}(C_{Li}^{Ni}/\text{wppm}) = 6.5392 - 2845/T \qquad \ldots(4)$$

complement earlier data.

The results of several attempts to determine the solubilities of the transition metals, V,[14] Cr,[15] Fe,[13] Co,[15] Ni[13,15] and Mo[14] in liquid sodium have been published. With the exception of Co and Mo the results were scattered and temperature relationships could not be established. The solubility ranges observed for all solutes are summarised in Table 1 together with the quoted $\log_{10}(C^{M}_{Na}/\text{wppm})$ vs $(T/K)^{-1}$ relationships. The Co solubility was determined[14] by radiochemical analysis of samples obtained by equilibration in sealed nickel crucibles internally plated with cobalt. Analysis of the sodium for impurities showed it to contain 10-20 wppm oxygen. The Mo solubility was determined[13] by classical chemical analysis of samples obtained by equilibration in tantalum crucibles containing molybdenum foil and magnesium powder. The magnesium was added to ensure oxygen-free sodium.

Table 1. Solubility ranges for V, Cr, Fe and Ni in liquid sodium

Solute (M)	Solubility C^{M}_{Na}/wppm		Temperature Range/K	A*	B*	Ref
	Range	Average				
Vanadium	0.01 - 0.15	0.05	557 - 751	-	-	14
Chromium	0.89 -18.8	4.04	673 - 923	-	-	15
Iron	0.18 - 3.03	1.26	773 - 963	-	-	13
Cobalt	0.002- 0.123	0.034	673 - 973	0.101	1493	15
Nickel	0.16 -18.7	4.28	673 - 948	-	-	15
Nickel	0.09 - 0.30	0.16	773 - 963	-	-	13
Molybdenum	0.04 - 0.48	0.23	628 - 978	2.738	2200	14

* These constants refer to the solubility expression

$$\log_{10}(C^{M}_{Na}/\text{wppm}) = A - B(T/K)^{-1}$$

† wppm is equivalent to μgM/gNa.

As for several previous determinations of transition metal solubilities in liquid sodium the Cr[14] and Fe[15] solubility data appeared to be influenced by non-metallic contaminants, especially oxygen. In independent studies, two groups of authors have attempted to elucidate the role of oxygen in this context; they both consider the formation of ternary oxides to be of paramount importance. From a comparison of experimental and theoretically derived Fe solubility data Awasthi and Sundaresan,[16] have shown that, at high oxygen activities, the predominant species is Na_4FeO_3 and that the enhanced solubility of iron can be explained by the initial formation of FeO followed by its conversion to Na_4FeO_3. By deriving a thermochemical expression for the solubility of ternary oxides in sodium, Grundy[17] has calculated data for NaOH, Na_2CO_3, Na_2FeO_2, Na_4FeO_3, $NaCrO_2$, $Na_2Si_2O_5$, Na_2SiO_3 and Na_3PO_4 as a function of both temperature and third component activities.

The chemical status of Sr and Ba in reactor sodium has been assessed both theoretically and practically.[18] Thermodynamically based calculations indicate that MO formation is favoured over MH_2, MBr or MI formation. A fifth potential product, M_2N, cannot be included in this analysis owing to a dearth of appropriate thermochemical data. Its formation has been noted, however, in experimental studies of the reaction of both Na-Sr and Na-Ba solutions with nitrogen. The process occurs via a consecutive solution-precipitation mechanism, the extent of the solution process being dependent on the alkaline earth metal content of the solution. At saturation, N:Sr and N:Ba ratios of ~0.05:1 and ~0.25:1, respectively, are consistently obtained. The difference is attributed to the greater effect Ba has on reducing nitrogen activities in liquid sodium.[18]

As the technological potential of liquid lithium is being realised analytical methods for assessment of non-metallic impurity inventories are being perfected. Two papers[19,20] outlining chemical methods for the determination of carbon, nitrogen and oxygen, and in one case,[20] hydrogen and silicon, have been presented. The application of the foil equilibration technique to the estimation of carbon and nitrogen has also been established.[21] Activity-concentration relationships were derived from literature thermodynamic data for both non-metals in the foil material (304 SS) and in liquid lithium. Using these relationships, chemical analysis of foils after immersion in liquid lithium gave carbon and nitrogen concentrations in the liquid metal which showed significant correlation with values obtained by direct chemical analysis.[21]

Neither chemical nor foil equilibration methods are continuous. Experience in liquid sodium has shown that diffusion and/or electrochemical sensors can be used to monitor hydrogen, carbon and oxygen activities (see later). DeKeyser et al[22] have started a programme to consider the application of these sensors to liquid lithium systems. The hydrogen diffusion sensor was found to operate successfully except at very low hydrogen activities and low temperatures ($T < 673K$); preliminary experiments with the oxygen electrochemical sensor were encouraging, the electrolyte material (ThO_2-7.5wt% Y_2O_3) being found to be compatible with a liquid lithium environment.[22]

A large number of papers reporting the considerable effort applied during recent years to the development and testing of these sensors for use in liquid sodium systems were presented at the third international conference on "Liquid Metal Engineering and Technology".[7] Only one sensor, the electrochemical type, is available for oxygen.[23-29] It is very well established, being based on the cell:

$$M,M_xO_y \mid ThO_2 - 7.5wt\%\ Y_2O_3 \mid Na(O)$$

A variety of metal-metal oxide couples have been proposed, the most popular being In-In_2O_3. Recent developments to this sensor have been of detail rather than of principle. When treated carefully, it is a very effective sensor. When subjected to thermal shock, however, its operating lifetime is reduced considerably.[23] Both electrochemical[24,30] and diffusion[23,24,30,31] hydrogen sensors have been designed. The former is based on the cell:

$$Li\text{-}LiH \mid Fe \mid CaH_2\text{-}CaCl_2 \mid Fe \mid Na(H)$$

and the latter on the diffusion of hydrogen through a nickel[23,24,30,31] or iron[24] membrane. A flow of argon sweeps the inner surface of the membrane, the hydrogen partial pressure in the sweep gas being determined by a variety of methods including thermal conductivity,[24,30,31] and mass spectrometric analysis.[23] Comparative experiments have shown that the diffusion sensor, particularly that with a nickel membrane, is more reliable than the electrochemical sensor, the reproducibility of the calibration curves being much better. Carbon sensors also fall into the two categories of electrochemical type[23-25,32] and diffusion[24,28,32,33] type. The former is based on emf changes associated with carbon activity changes manifest in the cell:

Ref. electrode ¦ Li_2CO_3-Na_2CO_3 ¦ Fe | Na(C)

the reference electrode varying from CO/CO_2 gas mixtures,[23,25] through pure graphite[32] to Fe_3C.[24] The latter[24,28,32,33] depends on the diffusion of carbon through a pure iron membrane with a previously oxidised inner surface. After oxidation at this FeO surface layer the CO/CO_2 so formed is swept to a flame ionisation detector by a continuous flow of argon. The diffusion sensor is generally considered to be much more robust than the electrochemical sensor and to have a much longer working life.

After careful calibration of an electrochemical oxygen sensor, by both metered gas addition and cold trap equilibration ($433 < T/K < 773$) Smith and Simm[34] have estimated an expression for oxygen solubilities in liquid sodium:

$$\log_{10}(C_{Na}^{O}/\text{wppm}) = 5.52 - 1900(T/K)^{-1} \qquad \ldots(5)$$

Their data[34] and those of Nafe[26] for the concentration dependence of oxygen activity in liquid sodium both suggest that negative deviations from Henry's Law occur in these solutions particularly at concentrations close to saturation. Ivanovskii et al[35] have noted similar behaviour for potassium-oxygen (from electrochemical oxygen sensor measurements) and caesium-oxygen solutions (from vapour pressure measurements). It is suggested[35] that the observed deviations can be rationalised in terms of a heterophase oxygen state model composed of oxygen containing molecular-type particles and crystal like inclusions. For the metallic solvent, this disperse system is apparently single phased.

Hubberstey et al[36,37] have reported the results of detailed X-ray diffraction and electrical resistivity studies of aspects of the behaviour of dilute solutions of silicon,[36] nitrogen[37] and hydrogen[37] in liquid lithium ($x_{Li}>0.96$; $T = 675,750K$). Silicon is reported to be chemically reactive towards particulate nickel (but not iron or chromium) and towards dissolved nitrogen (but not hydrogen or oxygen). Whereas the reaction with particulate nickel follows a heterogeneous mechanism in which insoluble Ni_2Si is formed at the nickel-solution interface following attack by dissolved silicon, that with dissolved nitrogen is a simple homogeneous solution reaction resulting in formation of insoluble Li_5SiN_3. Neither nitrogen nor hydrogen was found to react with either lead or tin.[37] The presence of lead in lithium (x_{Li} = 0.99; $675 \leq T/K \leq 735$) was, however, observed to increase the solubility of hydrogen relative to that in the pure alkali metal. The enhanced solubilities are attributed to a decreased hydrogen activity in the ternary solutions relative to the binary solutions. Hubberstey[38] has also reviewed the chemistry of dissolved nitrogen in liquid lithium, noting that it adopts the corrosive role filled by oxygen in liquid sodium systems.

The extraction of hydrogen from impure lithium by yttrium has been analysed thermochemically by consideration of the Li-Y-O-H, Li-Y-N-H and Li-Y-O-N systems.[39] It is concluded that the ternary oxide $LiYO_2$ will be formed on the surface of yttrium in impure lithium thus influencing the ability of the yttrium to extract hydrogen. It is suggested that ternary oxide formation may be reduced at high hydrogen and/or low oxygen levels.[39]

Two independent studies of the reaction of hydrogen with carbon in the presence of alkali metals have been undertaken; whereas Barker et al[40] have shown, using mass spectroscopic methods (T = 823K) that the product in liquid lithium is C_2H_4, Borgstedt and Pillai,[41] using gas chromatographic methods ($723 < T/K < 823$) claim that in liquid sodium the reaction product is CH_4.

X-ray powder diffraction analysis of the products (isolated by filtration) of the reaction (T = 673K) between liquid sodium and a pump lubricating oil has shown the presence of NaH, Na_2S and residual sodium.[42] These materials form the minority of the product, the majority being a black, amorphous, material with a C:H molar ratio of 5:2. Comparison of d.s.c. and i.r. data for this material with those for the thermal decomposition product (T = 608K) of $NaHC_2$ showed many similarities. Despite considerable effort, the chemical identity of this product is still uncertain although it is thought to contain (-C≡C-) fragments bonded to alkyl groups.[42]

Solutions of non-metals in liquid alkali metals are known to corrode containment materials. The most deleterious impurities are nitrogen in lithium and oxygen in sodium; carbon transfer is also a problem in both lithium and sodium systems. A perspective of the corrosive behaviour of lithium and sodium has been written.[43] It is noted that although corrosion in sodium has been extensively studied, corrosion data for lithium are fragmentary and hence our understanding of corrosion processes in lithium lags far behind that for sodium. Striking similarities in the overall mass transfer processes for the two solvents in austenitic stainless steels is observed; preferential depletion of nickel and chromium leads to the development of a ferritic surface layer and a constant corrosion rate (with time). The corrosion processes do show, however, basic differences in their chemistry, the principal products being nitrogen containing species in lithium and oxygen containing species in sodium.[43] The corrosive behaviour of lithium has also been compared to that of liquid $Li_{17}Pb_{83}$, an alternative coolant/tritium breeder for the fusion reactor.[44] The mechanisms and kinetics of corrosion processes in the two liquids are examined and their influence on the degradation of structural material is discussed.

Well subscribed sessions devoted to the subject of corrosion in liquid metal systems were organised at both the "Fusion Reactor Materials"[6] and "Liquid Metal Engineering and Technology"[7] conferences. Sodium,[45-56] lithium[57-63] and $Li_{17}Pb_{83}$[64-66] were considered as solvents; surface depletion phenomena, ferrite layer production, grain boundary penetration and carburization/decarburization processes were studied for austenitic, ferritic and speciality stainless steels. The data reported for sodium[45-56] simply corroborate and extend previously reported information. Those presented for lithium[57-63] confirm the point, made earlier in the review of corrosion phenomena in lithium and sodium solutions,[43] that corrosion of austenitic steels in flowing lithium mirrors that in flowing sodium. Thus a surface loss of nickel and chromium results in a ferromagnetic corrosion layer of distorted bcc structure. The underlying austenitic matrix is depleted in carbon and nitrogen and lithium penetrates into the grain boundaries probably forming Li_9CrN_5. Evidence for lithium penetration has been obtained using secondary imaging mass spectrometry (SIMS) and metallographic techniques.[40] The potential of Auger electron spectroscopy (AES) as a technique for analysis and detection of lithium compounds on surfaces has been pointed out.[67] Interpretation of the spectra is at an embryonic stage but it does appear that they can be used to derive important bonding information.

Results presented for liquid $Li_{17}Pb_{83}$[64-66] indicate that corrosion rates for both austenitic and ferritic steels are 10x greater than in pure lithium. The influence of time, temperature and steel composition on corrosion behaviour is the same in $Li_{17}Pb_{83}$ as in lithium. Surface analysis (EDAX, XRD) of austenitic steels after exposure to $Li_{17}Pb_{83}$ indicated nickel depletion and formation of a ferritic layer which easily spalls from the specimen surface.

The chemical reactivity of $Li_{17}Pb_{83}$ towards hydrogen isotopes,[68-70] nitrogen[66,71] and oxygen[66] has been ascertained, often as part of a study of the entire Li-Pb system.[68-71] Independent studies of the equilibrium pressure of hydrogen,[68] deuterium[69] and tritium,[69] p_{X_2}, as a function of hydrogen isotope concentration, x_X, have shown that Sieverts relationship:

$$p_{X_2}^{\frac{1}{2}} = K_s . x_X \qquad \ldots(6)$$

where K_s is the Sieverts constant, is valid throughout the entire Li-Pb system at low concentrations of all three hydrogen isotopes; it becomes invalid, however, as the hydrogen isotope concentration approaches saturation. The variation of K_s with increasing lead content in the $Li-Pb-H_2$ system[68] exhibited three features of interest: (i) a 10^5-fold increase; (ii) an inflexion point at $x_{Pb} \sim 0.3$, presumably caused by the formation of partially ionic bonds; and (iii) a steady decrease in temperature coefficient resulting in a reversal at $x_{Pb} \sim 0.6$. The solubilities of hydrogen, deuterium and tritium have been derived as a function of composition and temperature using thermodynamic data for the binary systems.[70] The calculated values are considerably lower than those determined experimentally; a ternary Li-Pb-H interaction term is postulated to achieve agreement between experimental and calculated results.

Lithium-rich Li-Pb alloys react with nitrogen or Li_3N ($900<T/K<950$) until the lithium activity in the alloy equals that in equilibrium with Li_3N (i.e. at a composition close to $x_{Li} = 0.215$).[71] Thus alloys richer in lithium than $Li_{21.5}Pb_{78.5}$ are converted to this composition by reaction with nitrogen or Li_3N whereas alloys richer in lead are inert. These alloys, although inert to austenitic steels in the absence of nitrogen, will in its presence corrode the steel to give Li_9CrN_5 and the alloy $Li_{62}Pb_{38}$ ($T = 879K$). This limit defines the thermodynamic stability of Li_9CrN_5 for which a value of $\Delta G_f^\circ(Li_9CrN_5,c,879K) = -328kJ.mol^{-1}$ is calculated.[71]

Unlike nitrogen which is inert to $Li_{17}Pb_{83}$,[66,71] oxygen reacts with it to form Li_2O ($T > 673K$) which in the presence of air is hydrolysed to LiOH and ultimately $LiOH.H_2O$; complete reaction of the lithium content of the alloy is observed.[66]

The large deviations from ideality observed in Li-Pb solution thermodynamics have been explained by postulating the existence of LiPb molecules in solution and strong surface tension effects around dissolved impurity species.[72] The equilibrium constant for LiPb formation obeys the equation:

$$\ln K_{eq} = -1.44 + 7000(T/K)^{-1} \qquad \ldots(7)$$

Formulations which derive from these assumptions are used to calculate solubility data for hydrogen, nitrogen and oxygen in liquid $Li_{17}Pb_{83}$:

$$\ln(x_H/\text{mol.fr}) = 6.53 - 8370(T/K)^{-1} \qquad \ldots(8)$$

$$\ln(x_N/\text{mol.fr}) = 3.05 - 5770(T/K)^{-1} \qquad \ldots(9)$$

$$\ln(x_O/\text{mol.fr}) = -1.39 - 5480(T/K)^{-1} \qquad \ldots(10)$$

The values obtained for cold trap solubilities ($T = 508K$), $x_H = 4.8 \times 10^{-5}$, $x_N = 2.5 \times 10^{-4}$ and $x_O = 5.1 \times 10^{-6}$ are much lower than those observed in pure lithium. Sieverts constants for hydrogen and nitrogen in lead-rich Li-Pb solutions, calculated using the formulations, agree with experimentally derived constants.[72]

The reactions of metal oxides with liquid lithium have been reviewed by Barker.[73] Of the alkali metals, lithium is the most powerful reducing agent owing to the very high free energy of formation of Li_2O ($\Delta G_f^\circ(Li_2O,c,1000K) = -442$ kJ.mol^{-1}; cf. $\Delta G_f^\circ(Na_2O,c,1000K) = -277$ kJ.mol^{-1}, $\Delta G_f^\circ(K_2O,c,1000K) = -211$ kJ.mol^{-1}, $\Delta G_f^\circ(Rb_2O,c,1000K) = -186$ kJ.mol^{-1}, $\Delta G_f^\circ(Cs_2O,c,1000K) = -155$ kJ.mol^{-1}). Consequently, the majority of metal oxides are reduced by liquid lithium forming Li_2O and metal. In the presence of impurity nitrogen or carbon, some transition metals react further to form binary or ternary nitrides, binary carbides and even carbonitrides. Only ThO_2 has been found to be stable in liquid lithium. In the presence of impurity nitrogen, however, even ThO_2 reacts to form either ThN or Li_2ThN_2. Intermediate behaviour is exhibited by CeO_2 which undergoes partial reduction in liquid lithium forming the ternary product $LiCeO_2$. Again in the presence of nitrogen, binary or ternary nitride formation (CeN or Li_2CeN_2) occurs.[73]

Compatibility studies[74] of sintered specimens of AlN containing metal oxide (1% as a sintering aid) with liquid lithium containing nitrogen (~850 wppm N) at 873K indicate that the AlN ceramic is basically unreactive. Specimens containing CaO or Cr_2O_3 deteriorated slightly, however, owing to loss of calcium and chromium.[74]

Chemical interactions between liquid sodium and sintered specimens of UO_2, UO_2-PuO_2 and UO_2-PuO_2 doped with various cations to simulate the presence of fission products have been studied under both low $(773 < T/K < 1073)$[75] and high $(1323 < T/K < 1873)$[76] temperature regimes. Similar behaviour was observed at all temperatures; pure sodium and stoichiometric UO_2 are compatible whereas sodium reacts with UO_2-PuO_2 to form a reduced oxide phase and $Na_3U_{1-x}Pu_xO_4$. At low temperatures,[75] the threshold plutonium valency for reaction to occur decreased with increase in temperature; at 973 and 1073K it was 3.46(3) and 3.41(2), respectively. The addition of fission product cations to UO_2-PuO_2 resulted in increased changes in volume and increased reaction rates. Some of the specimens containing these cations were found to break up on reaction with sodium. At high temperatures,[76] for which kinetic data were not obtained, pronounced grain growth was observed during reaction of all the oxides with liquid sodium at 1873K.

Compatibility studies[77] of commercially available ceramics based on basalt and MgO with liquid sodium $(673 < T/K < 1173)$ have shown that whereas MgO is inert the basalt based ceramics exhibit complete loss of integrity, presumably owing to ternary oxide formation.[77]

Two reports describing the solution chemistry of liquid rubidium have been abstracted.[78,79] Confirmation that the rubidium-oxygen phase diagram $(0.00 < x_O < 0.25)$ is similar to that of the caesium-oxygen system has been achieved from the results of a preliminary thermal analysis study.[78] Evidence for the existence of Rb_7O and Rb_4O, which are thought to decompose in peritectic reactions at 262 and 293K respectively, is presented. Addition of oxygen to rubidium results in a depression of the freezing point (312K) to 259K at the eutectic composition (x_O = 0.095).[78]

Reaction of liquid rubidium with chromium oxides (T = 773K) leads, depending on the oxygen inventory in the liquid metal to Rb_4CrO_4 and Rb_3CrO_4;[79] the products were identified by chemical analysis and by analogy of their XRD patterns with those of Cs_4CrO_4 and Cs_3CrO_4. Similarly, reaction with iron oxides (T = 773K) leads to two products. Although that found at lower oxygen activities was identified by single crystal XRD studies as $Rb_6Fe_2O_6$ that found at higher oxygen activities was not identified; analytical data suggested a Rb:Fe stoichiometry similar to that in $Rb_2Fe_2O_6$.[79]

1.2.3 Metallic Solutions

Chemical short range order in liquid phase binary metallic solutions continues to arouse the interest of both experimentalists and theoreticians. Neutron diffraction studies have been completed for Li-Sn,[80] Li-Pb[81] and Li-Ag[81,82] solutions. Whereas van der Lugt et al[80] have studied Li-Sn solutions as a function of composition, Ruppersberg et al[81,82] have investigated lithium, $Li_{80}Pb_{20}$, $Li_{90}Ag_{10}$ and $Li_{70}Ag_{30}$ as a function of temperature. The results provide evidence for appreciable ordering in the liquid probably accompanied by charge transfer from lithium to tin, lead or silver. The concentration dependence data[80] indicate that chemical short range order is maximised at $Li_{80}Sn_{20}$. The temperature dependence data[81,82] suggest that the effect is pronounced at distances <400pm; at larger distances the atoms are distributed randomly and the global structure of the solutions is similar to that of pure lithium. Ruppersberg et al[81] also conclude that although the amount of charge transfer in the Li-Pb and Li-Ag systems is similar, the electronic screening in $Li_{90}Ag_{10}$ and $Li_{70}Ag_{30}$ is significantly stronger than that in $Li_{80}Pb_{20}$.

Electrical resistivity data for dilute solutions of group IV elements (Si, Ge, Sn and Pb) in liquid lithium[83] have been interpreted within the context of chemical short range order, the relationship between the existence of ordering in liquid phase binary metallic solutions and the formation of a Zintl phase which approximates to a normal valency compound in the solid state, being stressed.[83]

Evidence for chemical short range order in dilute solutions of lithium in mercury has been derived from the presence of a minimum (at $x_{Li} \sim 0.05$) in the thermoelectric power isotherms. The minimum is attributed to higher order atom-atom correlation effects which are caused by charge transfer from lithium to mercury.

Three models for the interpretation of thermodynamic data for solutions which exhibit chemical short range order have been presented.[85-88] Hafner et al[85,86] have developed a simple model which has been applied successfully to liquid Li-Mg, Li-Pb and Li-Ag solutions,[85] good agreement being obtained for enthalpy and entropy of formation data as well as for structural data. The model has also been applied to the more complex Na-Sn and Na-Pb systems which exhibit two anomalies in the thermodynamic excess functions (at $\sim Na_{50}M_{50}$, $Na_{80}M_{20}$; M = Sn, Pb) usually associated with the formation of two different compounds. The model shows that the anomaly at $Na_{80}M_{20}$ arises from a preferred A-B interaction (of electronic origin) and that at $Na_{50}M_{50}$ from packing effects. The structural implications inherent in this interpretation have been corroborated by recent neutron diffraction studies,[89] reported in the 1983 review.[90]

Enthalpy of mixing data for Na-Hg solutions have been successfully calculated by Khanna[87] using a semi-empirical model based on the simple hard-sphere theory.

Using equations derived by Kirkwood and Buff,[91] Saboungi and Corbin[88] have shown that the sign and magnitude of the limiting slope of the activity coefficient, ε, for the less electropositive component of binary metallic mixtures containing $x_M < 0.12$ (M = Li, Na) yield information on the attractions and repulsions between like and unlike atoms. A positive value for ε indicates repulsions between alkali metal atoms and attractions between solute and solvent. The magnitude of ε is indicative of the degree of ordering. The model has been applied to a number of Li-M (M = Ga, In, Pb, Te) and Na-M (M = In, Sn, Pb, Bi, Te, Au, Cd) systems (Table 2). With the exception of the Na-Au system, positive values of ε are obtained; the negative value of ε obtained for the Na-Au system requires confirmation. The zero values of ε for the tellurium systems, combined with very large

Table 2 Limiting slopes of the activity coefficients of the less electropositive member of dilute binary metallic mixtures ($x_M < 0.12$; M = Li, Na).[88]

System	ε	T/K	System	ε	T/K
Li-Ga	1.4	800	Na-In	3.9	717
Li-In	0.4	800	Na-Sn	0.8	673
Li-Pb	1.7	932	Na-Pb	2.3	723
Li-Te	0.0	823	Na-Bi	2.2	673
			Na-Te	0.0	800
			Na-Cd	6.1	673
			Na-Au	-1.1	1500

negative values of limiting excess chemical potential may indicate the existence of covalent bonding in these systems.

1.2.4 Intermetallic Compounds

High pressure (4 GPa), high temperature ($873 < T/K < 973$) modifications of MSi and MGe (M = K, Rb, Cs) have been synthesised from the elements under argon.[92] They adopt the tetragonal NaPb-type structure; pertinent crystallographic data are collected in Table 3. The crystal structure of $CsIn_3$ has been determined;[93] it is of the $RbGa_3$-type, tetragonal, space group $I\bar{4}m2$ with unit cell parameters, a = 704.7, c = 1680.3pm.

Table 3 Crystallographic parameters of the high pressure (4 GPa), high temperature ($873 < T/K < 973$) modifications of MSi and MGe (M = K, Rb, Cs).[92]

Compound	a/pm	c/pm	Compound	a/pm	c/pm	Compound	a/pm	c/pm
KSi	1057	1710	RbSi	1083	1758	CsSi	1123	1834
KGe	1069	1737	RbGe	1104	1787	CsGe	1138	1850

A theory to describe chemical bonding in intermetallic compounds has been developed.[94] The model, which involves the modified Bethe lattice, offers a general framework for discussing stability, clustering tendency and valency in charge-transfer compounds. Its viability was demonstrated by application to the transition from simple ionic octet compounds to clustered configurations as observed in alkali metal-group IV metal systems.[94]

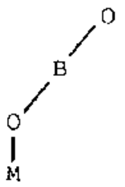
1.3 SIMPLE COMPOUNDS OF THE ALKALI METALS

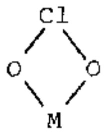
Following the precedent set in the 1982 and 1983 reviews, subsections devoted to the chemistry of ion pairs containing alkali metal cations and to the theoretical treatment of small molecules, particularly those containing lithium, have been incorporated in this section to cater for the continuing interest in these fields; subsections devoted to the chemistry of binary and ternary derivatives of the alkali metals have also been retained. To avoid unnecessary duplication with other chapters of this review, the ternary compounds considered are restricted to those containing both an alkali metal and a transition metal.

1.3.1 Ion pairs

The ion pairs $M[BO_2]$, (M = Li-Cs),[95] $M[AsO_3]$ (M = K-Cs),[96] $M[ClO_2]$ (M = Li-Cs),[95] $M[ClO_3]$ (M = Li, Na, Rb),[96] $M[ClO_4]$ (M = Na-Cs),[97] $M[ReO_4]$ (M = Li-Rb)[98] and $M[UF_6]$ (M = Na-Cs)[99] have been isolated in low temperature (nitrogen and/or argon) matrices by condensation from the vapour phase above the corresponding salts. Infra-red spectroscopic data, including those from $^{18}O/^{16}O$ isotopic substitution experiments reveal interesting structural information. Whereas $M[BO_2]$ ion pairs (1) have C_s symmetry with linear $[BO_2]^-$ groups and MOB bond angles between 100° ($Li[BO_2]$) and 127° ($Cs[BO_2]$), $M[ClO_2]$ ion pairs (2) have C_{2v} symmetry.[95] Differences also occur in the geometries of the $M[AsO_3]$ (3) and $M[ClO_3]$ (4) ion pairs. Whereas $[AsO_3]^-$ coordinates the metal in a bidentate fashion with C_{2v} symmetry, $[ClO_3]^-$ acts as a tridentate ligand forming a complex with C_{3v} symmetry.[96] The coordination geometry of the $M[ClO_3]$ ion pair also contrasts with that of the $M[ClO_4]$ ion pair (5) which adopts a C_{2v} bidentate interaction[97] similar to that of the $M[ReO_4]$ species.[98] The dimerisation of $M[ReO_4]$ ion pairs has also been studied spectroscopically in these matrices, a bridged structure of D_{2h} symmetry being suggested for the dimers, $\{M[ReO_4]\}_2$.[98]

Infra-red data for MUF_6 (M = K-Cs) suggest a C_{3v} symmetry - a


(1)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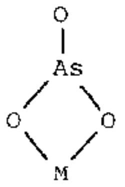
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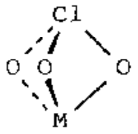
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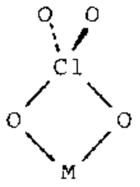
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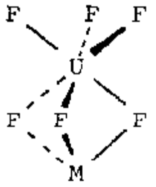
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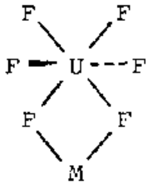
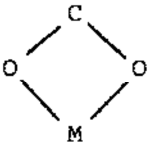

(7)

facial interaction (6) - for the species isolated in argon and a C_{2v} symmetry - an edge interaction (7) - for that trapped in nitrogen.[99] For $NaUF_6$, the spectra are complicated by decomposition reactions leading to UF_5 as one of the products; it is probable, however, that the isolated $NaUF_6$ species has a C_{2v} or lower symmetry in both matrices.[99]

Ion pair formation by reaction of alkali metals with carbon dioxide has been studied spectroscopically by two groups. Teghil et al[95] have investigated the $Li-CO_2$ reaction in argon matrices, while Margrave et al[100] have characterised the products of the $M-CO_2$ (M = Na, K, Cs) reaction in argon, nitrogen and neat matrices. Reaction of Li with CO_2 leads to both C_{2v} (8) and C_s (9) isomers of $Li[CO_2]$;[95] the C_s isomer photolytically rearranges to the C_{2v} structure after prolonged exposure to the i.r. source. The C_{2v} isomer of $Li[CO_2]$ has also been isolated in argon matrices by condensation from the vapour above lithium carbonate.[95] Very small amounts of $Na[CO_2]$ were produced when sodium was allowed to react with CO_2 in inert gas matrices; the product was found to have C_{2v} symmetry (8).[100] Similar $M[CO_2]$ ion pairs (8) were obtained when potassium or caesium were used as activating metals.[100] They were not the sole product, however, $M_2[CO_2]$ ion pairs of both C_{2v} (10) and C_s (11) symmetry also being formed, probably as a result of the reaction of the alkali metal dimer M_2 and CO_2. Photolysis of the C_{2v} isomers of $M_2[CO_2]$ with the i.r. source caused their rearrangement to the C_s form.[100]



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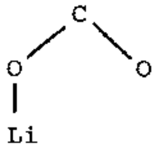

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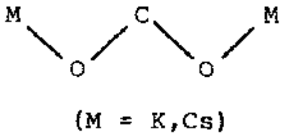

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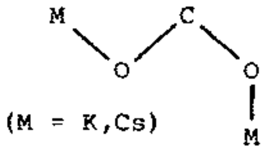


(11)

Reaction of HCHO with alkali metal halide salt molecules in argon matrices,[101] instead of yielding the anticipated halide transfer product, the $M[CH_2XO]$ ion pair, generally gave an unusual complex involving an ion-dipole interaction between the halide ion and the carbon centre of HCHO. For CsF, however, slight indication of a covalent interaction was noted.[101]

1.3.2 Theoretical Treatment of Small Moieties

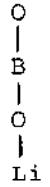
In a departure from previous practise, this subsection is divided into two parts. Firstly, theoretical studies of low molecular weight inorganic species containing lithium or sodium are considered; secondly, the theoretical and structural chemistry of selected organolithium compounds are discussed.

Ab initio SCF MO calculations of the electronic and geometrical structures and properties of lithium and sodium oxides and hydroxides,[102] of lithium borate[103] and of lithium and sodium complexes of aziridine and ethylene oxide rings[104] have been undertaken. Calculated data for MO and MOH (M = Li, Na) molecules are collected in Table 4 where they are compared with analogous data for corresponding beryllium and magnesium derivatives.[102] Calculations using various basis sets have shown that the $C_{\infty v}$ structure of $LiBO_2$ (12) is the equilibrium structure and that the alternative C_{2v} structure (13) is a saddle point on the potential energy surface of the molecule.[103] This conclusion contrasts slightly with the assertion, based on i.r. evidence, that the $M[BO_2]$ (M = Li-Cs) ion pair when isolated in cryogenic matrices adopts a C_s structure (1).[96] The calculated geometries of the alkali metal complexes of aziridine (14) and ethylene oxide (15) rings are as expected, the only difference being that whereas the Li^+ cation is positioned in the plane of the ethylene oxide ring (180°) the Na^+ cation is located marginally above it (169.3°).[104] Both aziridine and ethylene oxide exhibit a substantial Li^+ and Na^+ activity. Hence use of

Table 4 Electronic and geometrical structures and properties of MO, MOH and $(MOH)^+$ (M = Li,Na,Be,Mg) species.[102]

Species	State	$R_e(MO)$ pm	μ D	Species	State	$R_e(MO)$ pm	$R_e(OH)$ pm	μ D
LiO	$^2\Pi$	168.4	-7.02	LiOH	$^1\Sigma^+$	157.1	94.3	-4.51
NaO	$^2\Pi$	206.2	-8.52	NaOH	$^1\Sigma^+$	192.6	94.7	-6.71
BeO	$^1\Sigma^+$	132.1	-7.43	BeOH	$^2\Sigma^+$	139.9	93.4	0.85
MgO	$^1\Sigma^+$	179.5	-8.44	MgOH	$^2\Sigma^+$	177.4	94.1	-1.27
				$(BeOH)^+$	$^1\Sigma^+$	134.0	94.4	-5.41
				$(MgOH)^+$	$^1\Sigma^+$	170.9	94.5	-7.77

mitomycin (an aziridine-containing drug with anti-tumour activity) in conjunction with alkali metal salts may facilitate ring opening at neutral pH leading to enhanced drug activity.[104]



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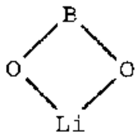

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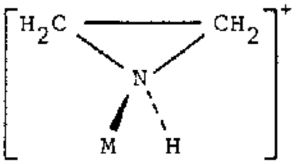

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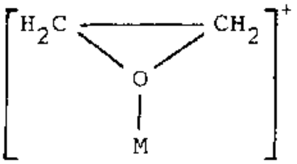
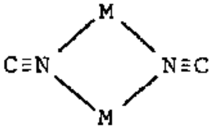
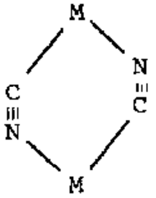
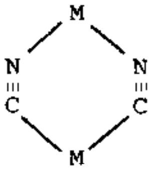


(15)

A considerable number of lithium containing dimers[105-108] and in one instance trimers,[106] have been treated theoretically using ab initio and/or semiempirical MO methods. Interest in these species arises from the marked tendency of lithium compounds to oligomerise. The formation of aggregates in solution has long been recognised; an increasing awareness of their presence in the solid state has resulted from recent X-ray crystallographic studies (section 1.4.9). The shapes and energetics of many different isomers of $(LiCN)_2$ and $(NaCN)_2$ have been determined.[105] For both dimers, there are three different isomers of very similar stability. The energy difference between the lowest-energy structure, a four membered planar ring of alternating M (M = Li,Na) and N atoms of D_{2h} symmetry (16) and two different six-membered planar rings of C_{2h} (17) and C_{2v} (18) symmetries is ~20 $kJ.mol^{-1}$ for $(LiCN)_2$ but only ~5 $kJ.mol^{-1}$ for $(NaCN)_2$. Linear structures are substantially less stable.[105]







	Li	Na
r(C...N)	117.5	117.3
r(M...N)	193.0	223.4
$N\hat{M}N$	103.1	98.3

(16)

	Li	Na
r(C...N)	116.1	116.2
r(M...N)	193.1	223.2
r(M...C)	209.0	235.4
$C\hat{M}N$	108.2	101.9
$M\hat{N}C$	118.2	121.3

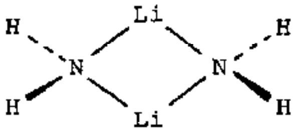
(17)

	Li	Na
r(C...N)	116.1	116.2
r(M...N)	194.9	223.7
r(M...C)	207.2	234.8
$N\hat{M}N$	117.5	108.5
$M\hat{N}C$	116.9	121.8
$N\hat{C}M$	134.7	136.0
$C\hat{M}C$	99.2	95.8

(18)

distances/pm angles/°

The calculated structures and energies of $LiNH_2$ dimers and trimers are in agreement with XRD data;[106] thus $(LiNH_2)_2$ and $(LiNH_2)_3$ prefer symmetrical D_{2h} (19) and D_{3h} (20) geometries with hydrogen atoms perpendicular to the $(LiN)_n$ rings. The



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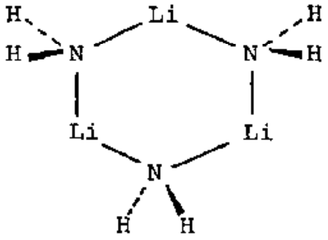


(20)

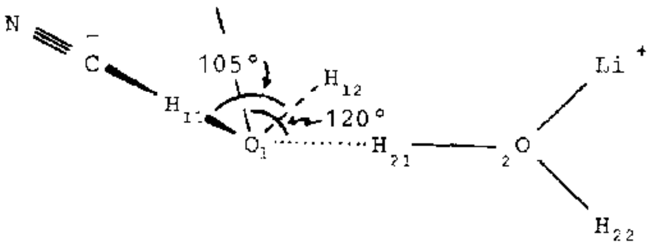
	r(N...H)	r(N...Li)	$H\hat{N}H$	$H\hat{N}Li$	$N\hat{Li}N$	$Li\hat{N}Li$
(19)	101.6	190.8	105.9	119.2	108.3	71.7
(20)	101.7	190.6	105.9	114.4	93.7	146.3

distances/pm angles/°

dimerisation energies of $LiNH_2$ have been compared with those of the other first row hydrides (LiBeH, $LiBH_2$, $LiCH_3$, LiOH) and lithium fluoride (LiF) by two independent groups;[107,108] the two sets of data are very similar. The dimerisation energy of $LiNH_2$

is comparable with those of LiOH and LiF, almost double those of $LiBH_2$ and $LiCH_3$ and approximately four times greater than that of LiBeH. A significant conclusion reached by both groups is that the dimerisation energies are dominated by electrostatic interactions.[107,108]

Theoretical analysis of the interaction of excited lithium atoms with molecular hydrogen,[109] of the hydrolysis of lithium cyanide[110] and of the reaction of lithium alkoxyamides with organolithium compounds[111] have been undertaken. A mechanism has been proposed for the hydrolysis[110] which involves (i) the approach of the hydrated ions Li^+ and CN^-, (ii) the formation of a hydrogen bonded intermediate (<u>21</u>), (iii) the coordinated proton transfer along the hydrogen bonds of the intermediate, and (iv) the dispersion of LiOH away from the hydrated neutral molecule, $NCH.H_2O$.

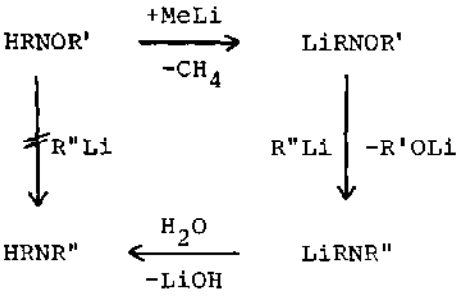


Distances/pm	$(C...N)$	$(C...H_{11})$	$(H_{11}...O_1)$	$(O_1...H_{12})$
Initial geometry	116	176	96	96
Final geometry	116	107	∞	96

Distances/pm	$(O_1...H_{21})$	$(H_{21}...O_2)$	$(O_2...H_{22})$	$(O_2...Li)$
Initial geometry	∞	96	96	184.2
Final geometry	96	∞	95.2	158.8

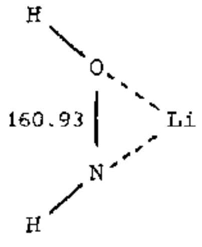
distances/pm angles/° (<u>21</u>)

Semi-empirical (MNDO) MO investigations[111] of the reactions in Scheme 1 have shown that the lithium alkoxyamides LiRNOR' (<u>22</u>) react (in contrast to the alkoxyamines HRNOR' (<u>23</u>)) with organolithium compounds R"Li owing to (i) formation of an intermediate dimer (<u>24</u>), (ii) a long N-O bond in (<u>22</u>), and (iii) the high stability of $LiNH^+$:



R = H,alkyl

Scheme 1



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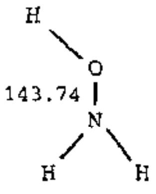
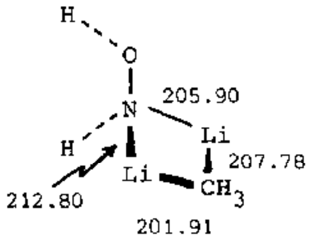


(23)

distances/pm

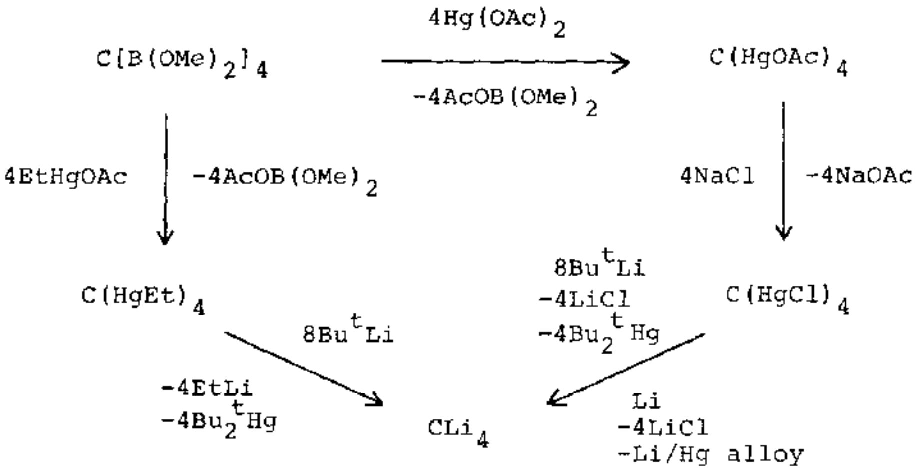


(24)

Continuing their studies of hypervalent molecules, Schleyer and Pople,[112] using ab initio SCF MO theory, have shown that ONa_3 (D_3h) and ONa_4 (T_d) are highly stable as isolated molecules towards all possible dissociation reactions (eg. loss of Na or Na_2). Further examples of hypermetalation are provided by $HONa_2$ (C_{2v}) and $HONa_3$ (C_{3v}). The ninth and tenth valence electrons in these hypervalent molecules are involved in metal-metal rather than in oxygen-metal bonding; the central oxygen atoms are content with the usual complement of eight electrons and do not have an expanded valence shell. Hypermetalation is predicted to be a general phenomenon involving all alkali metals in combination with many, if not most, of the other elements in the Periodic Table.[112]

New developments in the chemistry of polylithium compounds have been reviewed by Lagow et al.[113] Two novel synthetic routes to CLi_4 (Scheme 2) have been reported by Maercker and Theis.[114] Reaction of $C(HgEt)_4$ or $C(HgCl)_4$ with Bu^tLi in cyclopentane yields almost exclusively CLi_4; lithium dust in ether on reaction with $C(HgCl)_4$ leads to not only CLi_4 but also $Li_2C{=}CLi_2$ and Li_3CCLi_3 presumably owing to the radical reaction mechanism.[114]

Lagow et al have reported the synthesis of various isotopic forms of dilithiomethane ($(CH_2{}^6Li_2)_n$ and $(CD_2Li_2)_n$)[115] and of mono- and bis(trimethylsilyl)dilithiomethane[116] by reaction of lithium



Scheme 2

vapour with the corresponding dichloroderivatives. Preliminary XRD and solid phase ^{13}C-nmr studies of the isotopically substituted dilithiomethanes indicate a triclinic structure with a single highly symmetrical carbon environment.[115] The trimethylsilyl derivatives of dilithiomethane were characterised simply by hydrolysis using D_2O in a vacuum line.[116] The bonding in dilithiomethane has been elucidated by Streitwieser et al[117] from an ab initio SCF MO study at the 6-31** level. Singlet CH_2Li_2 structures are basically C^-Li^+ in character with a small amount of three-centre bonding. Three-centre bonding is less important for triplet CH_2Li_2 structures which have significant Li-Li bonding instead.[117]

Schleyer et al[118] have predicted the structures and stabilities of the organolithium and organosodium compounds MCH_2X (M = Li,Na; X = CH_3,NH_2,OH,F,SiH_3,PH_2,SH,Cl) by ab initio calculations. Comparisons are made with the corresponding free anions. The energetic results are summarised pictorially in Figure 1. The first row $LiCH_2X$ (X = NH_2,OH,F) species are more stable than the corresponding anions due to lithium bridging. Sodium displays a diminished tendency to bridge resulting in an absence of such extra stabilisation for the corresponding sodium compounds. The second-row systems behave differently. The MCH_2Cl species are stabilised to the same extent as the free anions. However the presence of the metals in MCH_2X (X = SH,SiH_3 and especially PH_2) cancels much of the α-substituent stabilising effects in the corresponding anions resulting in much less stable species.

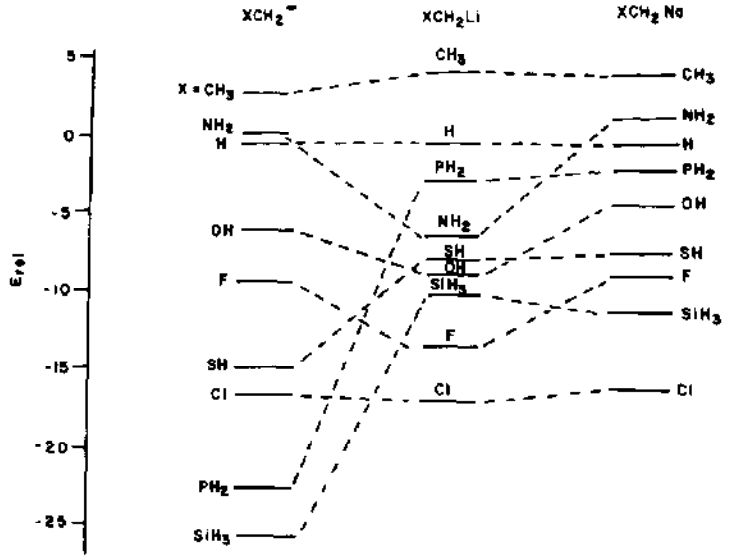
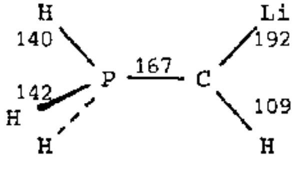


Figure 1. Comparison of stabilisation energies of substituted methyl anions and their corresponding organosodium and organolithium compounds (reproduced by permission from J. Am. Chem. Soc., 106(1984)6467).

Ab initio SCF MO studies of (α-lithiomethylene)phosphorane and the corresponding anion have also been completed. Geometries, optimised at the 3-21G+(*) level, exhibit but marginal differences.[119] It is concluded that the lithium derivative (25) is best described as an ion pair, the chemistry of which is largely that of the corresponding anion.[119]



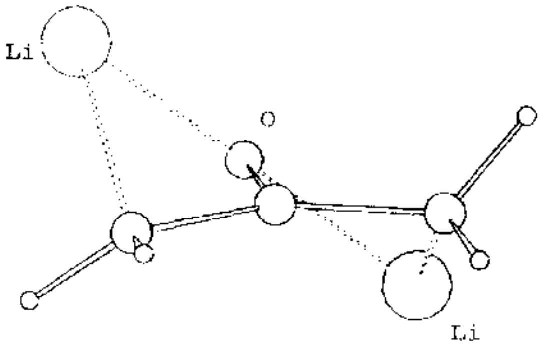
$\widehat{\mathrm{HPH}}$ = 95.4°
HPC = 112.9°
PCLi = 131.2°
PCH = 114°

(25) distances/pm

The production of the lithiated pentacoordinate carbocations $[CH_nLi_{5-n}]^+$ $(0 \le n \le 3)$ by flash vapourization and electron impact of polylithium organic molecules has been reported by Lagow et al.[120]

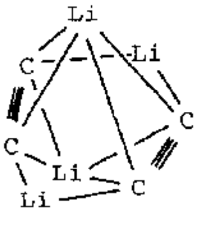
The 3-21G optimised structure of 1,3-dilithioacetone (26) has

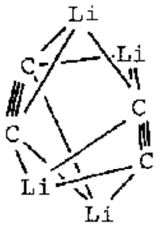
C_2 symmetry.[121] The two lithium cations bridge the oxygen and α-carbon atoms above and below the molecular plane of the dianion; some twisting of the CH_2 groups occurs as a result. This conformation is more favourable electrostatically than the alternative with both lithium atoms on the same side of the dianion moiety.[121]



(<u>26</u>)

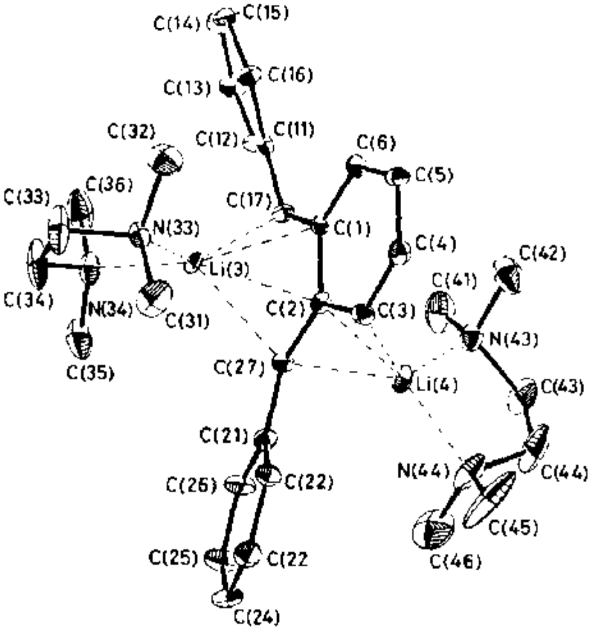
The C_4Li_4 potential surface has been examined theoretically using ab initio SCF MO methods.[122] Of the twelve structures considered, the most stable is a novel D_{2h} tetralithiodiacetylene (<u>27</u>) which lies 309.2 kJ.mol^{-1} below two molecules of dilithioacetylene and ~21 kJ.mol^{-1} above the corresponding D_{2d} tetralithiodiacetylene structure (<u>28</u>).[122]

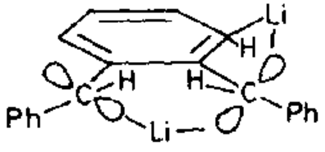




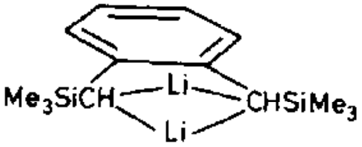
(<u>27</u>) D_{2h} (<u>28</u>) D_{2d}

Schleyer et al[123] have determined the crystal and molecular structure of $[\{o\text{-}C_6H_4(CHPh)_2\}\{Li(tmeda)\}_2]$ (<u>29</u>) by single crystal X-ray diffraction methods. The two lithium atoms (Figure 2) prefer quite different locations in contrast to the symmetrical C_{2v} double bridging exhibited by other 1,4-dilithium compounds such as $[\{o\text{-}C_6H_4(CHSiMe_3)_2\}\{Li(tmeda)\}_2]$ (<u>30</u>) and $[\{C_{12}H_8\}\{Li(tmeda)\}_2]$ (<u>31</u>). Model MNDO calculations[124] have shown, however, that symmetrical C_{2v} double bridging is not favoured in (29) since charge delocalisation in the dianion, hybridisation, and orbital orientation effects are more important than quadrupole-like electrostatic interactions. Thus, unlike $SiMe_3$ substituents, which stabilise carbanions very effectively and redistribute the electrons in part by polarisation,





(29)



(30)

(31)

Figure 2. Molecular structure of $[\{o\text{-}C_6H_4(CHPh)_2\}\{Li(tmeda)\}_2]$ and simplified structural formulae for $[\{o\text{-}C_6H_4(CHPh)_2\}\{Li(tmeda)\}_2]$ (29), $[\{o\text{-}C_6H_4(CHSiMe_3)_2\}\{Li(tmeda)\}_2]$ (30) and $[\{C_{12}H_8\}\{Li(tmeda)\}_2]$ (31) (reproduced by permission from J. Chem. Soc., Chem. Commun., (1984) 1493, 1495).

Ph substituents delocalise the charge into the aromatic ring preventing stabilisation of the two Li^+ ions by electrostatic interaction with the two $\alpha\text{-}CH_2$ groups in either C_{2v} or C_2 geometries. Thus only one Li^+ remains in a central position; the other prefers a benzyl-lithium-like location, the Huckel π-charges on the ring being greatest at the C(3) and C(6) positions.[124]

1.3.3 Binary Compounds

Once again there is a dearth of abstracted papers for this section; hence the data are considered en bloc rather than in separate subsections. As predicted in the 1982 review,[125] however, there has been a limited increase in interest in the chemistry of lithium containing ceramics owing to their potential application as tritium breeding materials in fusion reactors. Recent advances in this field were considered at, and published in the proceedings of, the third topical meeting on "Fusion Reactor Materials."[6] In a 'state-of-the-art' review, Johnson and Hollenberg[126] concluded that Li_2O is the prime ceramic candidate for tritium breeder owing to its high breeding potential and good thermal characteristics. Its chemical properties are also attractive to the fusion reactor technologist except in the presence of water when the highly deleterious LiOH is produced.

Several groups[127-129] have addressed the question of the chemistry of the Li_2O-LiOH-H_2O system. The adsorption of H_2O vapour from a helium gas stream onto solid Li_2O according to the equilibria:

$$Li_2O(s) \quad + \quad H_2O(g) \rightleftharpoons 2LiOH(s) \qquad \ldots(11)$$

$$Li_2O(s) \quad + \quad H_2O(g) \rightleftharpoons 2LiOH(\ell) \qquad \ldots(12)$$

has been studied using isothermal dynamic adsorption methods.[127] The temperature dependence ($573 < T/K < 890$) of the partial pressure of H_2O vapour above the $Li_2O(s)$-$LiOH(s,\ell)$ system has been measured in a sealed system;[128] the derived second law enthalpy and entropy data for equilibrium (11) are $\Delta H° = -128.5(2.5)$ kJ.mol^{-1} and $\Delta S° = -123.4(4.2)$ JK^{-1}mol^{-1}, while those for equilibrium (12) are $\Delta H° = -83.3(2.5)$ kJ.mol^{-1} and $\Delta S° = -61.9(3.3)$ JK^{-1}mol^{-1}. The melting point of LiOH was confirmed as 744K and its enthalpy of fusion as 22.6(1.7) kJ.mol^{-1}.[128] The activity coefficient of LiOH dissolved in solid Li_2O has also been determined for very dilute solutions using a thermobalance technique.[129]

The solubility of deuterium in solid Li_2O has been determined[130] by measuring the adsorption of deuterium gas by single crystals of

Li_2O located in a fused silica tube; the results ($10 < p_{D_2}/Pa < 130$) suggest that $x_D \propto p_{D_2}$ indicating that D_2 molecules are the dissolved species.

Chemical compatibility studies between solid Li_2O ($873 < T/K < 1273$)[131] or molten LiOH ($744 < T/K < 933$)[132] and transition metals (Ti, V, Cr, Mn, Fe, Ni and various stainless steels) have been undertaken by Pulham et al. Pure Li_2O is inherently stable towards transition metals except when equilibria such as:

$$4Li_2O + Fe \rightleftharpoons Li_5FeO_4 + 3Li \qquad \ldots(13)$$

$$2Li_2O + Cr \rightleftharpoons LiCrO_2 + 3Li \qquad \ldots(14)$$

are disturbed by removal of lithium by vacuum or chemical means.[131] Molten LiOH, however, corrodes transition metals according to the equations:

$$6LiOH + 2Fe \rightarrow LiFeO_2 + Li_5FeO_4 + 3H_2 \qquad \ldots(15)$$

$$6LiOH + 2Cr \rightarrow 2LiCrO_2 + 2Li_2O + 3H_2 \qquad \ldots(16)$$

The corrosion rates, determined from the rate of evolution of hydrogen gas, indicate that Cr reacts most rapidly, and that the corrosion of steels increases with increasing Cr and decreasing Ni content, 316 stainless steel being the most reactive steel studied.[132]

Other than those reporting on the chemistry of Li_2O and LiOH, the papers abstracted for this section do not portray a recurrent theme; they describe the results of diverse studies on varied compounds.

Evidence that alkali metal halide salts are not fully dissociated in aqueous solution has been obtained from fluoride ion selective electrode potentiometry studies of aqueous solutions of MF (M = Li-Cs) at T = 298K and I = 1.0M;[133] extremely weak monofluoride (MF) complexes are formed, their stability constants decreasing in the order:

$$Li^+ > Na^+ > K^+ > Rb^+ \sim Cs^+$$

The ions, K^+, K_2I^+, $K_3I_2^+$, I^-, KI_2^- and $K_2I_3^-$ have been recorded in the saturated vapour over KI; in the presence of KOH, however, the ions observed were K^+, K_2I^+, $K_2(OH)^+$, I^-, KI_2^-, $(OH)^-$, $K(OH)_2^-$, K^- and K_2I^-.[134] The enthalpies of formation (kJ.mol^{-1}) of the ions K_2I^+[233(8)], $K_3I_2^+$[-35(15)], KI_2^-[-483(8)], $K_2I_3^-$ [-760(15)] and K_2I^-[-244(11)], the electron affinities (kJ.mol^{-1}) of KI_2[386(20)] and K_2I[135(20)] and the ionisation enthalpy (kJ.mol^{-1}) of K_2I[347(20)] have been estimated.[134]

The LiF-LiOH and LiF-LiH phase diagrams have been constructed from the results of dta, XRD and ac-impedance studies.[135] Whereas the former system is a simple eutectic one with eutectic parameters, $T = 705K$, $x_{LiOH} = 0.85$, the latter system exhibits, at sufficiently high temperatures ($T>823K$), a continuous series of solid solutions throughout the composition range. At lower temperatures ($T < 823K$) a miscibility gap, which extends over the composition range $0.60 < x_{LiH} < 0.90$ at $T = 298K$, is observed.[135]

Structural studies have been completed on a small number of novel interalkali metal compounds; pertinent crystallographic parameters for KLiS,[136] $RbLiBr_2$,[137] $CsLiBr_2$,[137] $Cs_2Na_2Cl_3.H_2O$[138] and $Cs_{0.57}(Na,H_2O)_{0.43}Cl$[138] are collected in Table 5. The sulphide[136] and bromides[137] were prepared by thermal treatment of equimolar mixtures of the appropriate binary compounds; the chlorides[138] were crystallised from the CsCl-NaCl-H_2O system. The structure of $CsNa_2Cl_3.2H_2O$ consists of a slightly distorted cubic CsCl framework in which 2/3 of the Cs atoms are replaced by H_2O molecules and Na atoms are inserted into the Cl_4 face centres between pairs of H_2O molecules to form coiled $(Na.H_2O)_n$ chains. This structural principle also accounts for the unusual solid solution series $Cs_{1-x}(Na.H_2O)_xCl$ ($0 < x < 0.43$) in which H_2O molecules replace Cs atoms and $(Na.H_2O)_n$ chains are looped or coiled at random in the cubic structure.[138]

A variety of techniques have been used for structural elucidation of Li_3N,[139] NaN_3,[140] $[Li(tmeda)]_3P_7$,[141] $Na_2S,5H_2O$[142] and MOH,H_2O (M = K,Rb).[143] The electron density distribution in Li_3N has been investigated using Compton scattering techniques;[139] the results are interpreted within an ionic model. A temperature dependent ($12 < T/K < 293$) diffraction study of NaN_3 has shown[140] that the low temperature (monoclinic, C2/m) phase results from a discontinuous shear in the (010) plane of the high temperature (rhombohedral, $R\bar{3}m$) structure. The magnitude of the shear increases from 0.5° at the transition temperature of 292.2K to a value of 5.3° at 12K.[140]

Table 5. Crystallographic parameters for a number of interalkali metal compounds.

	symmetry	space group	a/pm	b/pm	c/pm	β/°	ref.
KLiS	tetragonal	P4/nmm*	431.8	-	696.2	-	136
$RbLiBr_2$	orthorhombic	Ccmm	1512.0	436.4	765.4	-	137
$CsLiBr_2$	tetragonal	-	518.7	-	992.4		137
$CsNa_2Cl_3.2H_2O$	monoclinic	I2/c	1362.4	583.2	1070.5	91.26	138
$Cs_{0.57}(Na,H_2O)_{0.43}Cl$	cubic	-	412.3				138

* alternative P$\bar{4}$m2.

Crystalline $[Li(tmeda)]_3P_7$, formed by reaction of white phosphorus with $LiCH_2PPh_2$(tmeda), has been studied by XRD analysis.[141] It comprises an isolated, ionic complex with approximately 3m (C_{3v}) symmetry. The Li atoms are each coordinated in a distorted tetrahedron to the two nitrogen atoms of one tmeda molecule, $r(Li...N)_{av}$ = 207.1pm, and to two twofold bonded phosphorus atoms of the heptaphosphane (3) moiety, $r(Li...P)_{av}$ = 255.5pm; the threefold bonded phosphorus atoms of the latter unit do not participate in the coordination of the Li atoms, which is typical of solvent-free polyphosphides.[141] This paper is only one of many, submitted primarily by Baudler or von Schnering, on the chemistry of alkali metal polyphosphides; the others, however, concentrate on the polyphosphide unit and hence are considered in detail in Chapter 5 of this review.

The crystal and molecular structures of $Na_2S,5H_2O$ have been redetermined with greater precision to define the hydrogen bonding.[142] It contains two crystallographically distinct Na atoms located in NaO_6 distorted octahedral (D_{4h}), r(Na(1)...O(1)) = 246.3pm, r(Na(1)...O(2)) = 236.1pm and NaO_4S square based pyramidal (C_{4v}) coordination spheres, r(Na(2)...O(2)) = 239.7pm, r(Na(2)...S) = 288.7pm. A vibrational (i.r. and Raman) study has also been undertaken.[142]

Recrystallisation of MOH,H_2O (M = K,Rb) from supercritical ammonia afforded crystals suitable for structure determination.[143] Their closely related structures, ($RbOH,H_2O$ has more symmetry) contain metal cations in distorted octahedral coordination spheres generated by four H_2O molecules r((K...O) = 278.8-293.9, r(Rb...O) = 292.8, 304.0pm, and two OH^- anions, r(K...O) = 283.9, 284.7, r(Rb...O) = 299.6pm; they are compared with the structures of PbFCl and γ-AlO(OH).[143]

1.3.4 Ternary Pnictides

Schuster et al[144,145] have provided the only papers abstracted for this subsection. They have synthesised and structurally characterised a large number of phosphides, arsenides, stibnides and bismuthides; the compounds synthesised are listed in Table 6 together with representative crystallographic data.

1.3.5 Ternary Oxides and Chalcogenides

The apparant loss of interest in the chemistry of ternary oxides

Table 6. Ternary pnictides synthesised by Schuster et al.[144,145]

$CaAl_2Si_2$ - structure type tetragonal $P\bar{3}m1$ a = 425.1, c = 690.6pm*			
Li_3LaP_2	Li_3NdAs_2	Li_3LaSb_2	Li_3LaBi_2
		Li_3YSb_2	Li_3YBi_2
$ThCr_2Si_2$ - structure type tetragonal I4/mmm a = 380.8, c = 1297.2pm*			
KFe_2P_2	KCo_2P_2	$RbFe_2As_2$	$RbCo_2As_2$
KRu_2P_2	$RbCo_2P_2$	KRu_2As_2	$RbRh_2As_2$
$RbRu_2P_2$	$RbRh_2P_2$	$RbRu_2As_2$	KIr_2As_2
	KIr_2P_2		$RbIr_2As_2$
	$RbIr_2P_2$		
K_2PdP_2 - structure type orthorhombic Cmcm a = 645.4, b = 1371.6, c = 560.2pm*			
K_2NiP_2	Rb_2PdP_2	K_2NiAs_2	Rb_2PdAs_2
Rb_2NiP_2	Rb_2PtP_2	Rb_2NiAs_2	Rb_2PtAs_2

* The crystallographic parameters refer to Li_3LaP_2, KFe_2P_2 and K_2NiP_2.

and chalcogenides continues; as for the 1983 review[146] the number of papers abstracted for this subsection is again exceeded by the number devoted to ternary halides. A significant development, however, is the publication, by Hoppe et al, of crystallographic data (Table 7) for several oxides containing two alkali metals, viz KLi_3TiO_4,[147] K_2NaFeO_3,[148] KNa_2CuO_2,[149] $KNaZnO_2$[150] and $K_3NaTh_2O_6$.[151] These materials were synthesised by high temperature reaction of either three binary oxides or two ternary oxides. For example, mixtures of $KO_{0.48}$, $NaO_{0.5}$ and Cu_2O, sealed at 913K for 30 days, afford KNa_2CuO_2 while mixtures of K_2ZnO_2 and Na_2ZnO_2 at 873K for 14 days yield $KNaZnO_2$. Unit cell parameters for these materials are listed in Table 7 together with corresponding data for those regular ternary oxides which have been synthesised and structurally characterised.[152-161] Preparation of the ternary oxides was generally achieved in high temperature reactions involving either combination of binary oxides:

$$4NaO_{0.5} + 5TiO_2 \rightarrow Na_4Ti_5O_{12} \text{ ; 1273K ; 6 days} \quad ...(17)$$

or exchange between binary and ternary oxides:

$$5Li_2O + 2NaFeO_2 \rightarrow 2Li_5FeO_4 + 2NaO_{0.5} \text{ ; 973K ; 16 days} \quad ...(18)$$

β-$NaVO_3$, however, was prepared by topotactic dehydration of synthetic $NaVO_3,2H_2O$.[153] With the exception of $NaNb_7O_{18}$[154] and $LiCoO_2$,[158] structural analysis of the ternary oxides was achieved using single crystal XRD data. For $NaNb_7O_{18}$,[154] a combination of high resolution electron microscopy and powder XRD methods, and for $LiCoO_2$[158] powder neutron diffraction techniques were used. The results of the latter study confirm the earlier XRD structure, showing it to be a completely ordered rock salt arrangement with alternating planes of Li and Co atoms.[158]

A novel potassium trivanadate, $K_{1+x}V_3O_8$ has been produced[162] by rapid quenching of high temperature melts (T = 1023K) containing K_2CO_3 and V_2O_5 in the approximate molar ratio 1:3. It is metastable and isomorphous with lithium and sodium trivanadates (γ-phase). No further details are quoted.[162]

The vibrational spectra ($33<\bar{\nu}/cm^{-1}<4000$) of isotopically substituted $Li_2Ti_3O_7$ have been measured;[163] the observed wavenumber shifts confirm that the structure contains both tetrahedrally and octahedrally coordinated Li atoms.

The only report of a novel ternary sulphide to be abstracted for this review is that of $Na_2Co_2S_5$ which was prepared by reaction of Co powder and Na_2CO_3 with dry H_2S at 1000K;[164] the crystallographic parameters of this material, which is sensitive to both air and moisture, are included in Table 7.

1.3.6 Ternary Halides

Discussion in this section is restricted to the chemistry of anhydrous ternary halides; solvated species are not considered.

Phase relationships in the KCl-$NiCl_2$,[165] MCl-$PdCl_2$ (M = Rb,

Table 7. Crystallographic parameters for diverse ternary oxides and sulphides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	β/°	Ref.
KLi_3TiO_4	triclinic	$P\bar{1}$	1040.0	757.0	592.5	–	147
			(100.4°)	(110.1°)	(90.6°)		
K_2NaFeO_3	orthorhombic	Cmma	1101.2	619.7	670.6	–	148
KNa_2CuO_2	tetragonal	I4mm	432.7	–	1089.1	–	149
$KNaZnO_2$	monoclinic	$P2_1/c$	582.4	970.0	551.3	103.7	150
$K_3NaTh_2O_6$	monoclinic	C2/c	629.6	1089.9	1259.8	99.7	151
$Na_4Ti_5O_{12}$	monoclinic	C2/m	2654.4	295.2	632.2	95.8	152
β-$NaVO_3$	orthorhombic	Pnma	1414.7	365.0	536.4	–	153
$NaNb_7O_{18}$	orthorhombic	Immm	1428.4	2622.4	384.1	–	154
Na_5MnO_4	orthorhombic	$P2_1mn$	582.2	776.9	600.5	–	155
Li_5ReO_6	monoclinic	C2/m	506.8	873.2	502.9	110.2	156
Na_5ReO_6	monoclinic	C2/m	568.8	973.1	560.7	111.0	156
Li_5FeO_4	orthorhombic	Pbca	921.8	921.3	915.9	–	157
$LiCoO_2$	rhombohedral	$R\bar{3}m$	281.5	–	1405	–	158
Li_2IrO_3	orthorhombic	–	513.0	886	971	–	159
Li_8IrO_6	hexagonal	–	541	–	1494	–	159
Li_2CuO_2	orthorhombic	Immm	365.4	285.9	937.4	–	160
$LiCeO_2$	monoclinic	$P12_1/c1$	582.4	616.6	579.3	102.5°	161
$Na_5Co_2S_5$	tetragonal	I4mm	915.0	–	622.2	–	164

Cs),[166] MBr-$TaBr_5$ (M = Na-Cs),[167] CsBr-$DyBr_3$,[168] MBr-$HoBr_3$,[169] and CsBr-$HoBr_3$[168,169] systems have been investigated using dta, tga, and/or XRD methods. The compounds formed in these systems are listed in Table 8 together with their thermal properties. Two significant features arise from these studies. Firstly, the results for the KCl-$NiCl_2$ system[165] contrast with those of an earlier study[170] which indicated the formation of K_2NiCl_4 as well as $KNiCl_3$. Secondly, the two sets of results for the CsBr-$HoBr_3$ system differ. Whereas Podorozhnyi and Safonov[168] claim the formation of Cs_3HoBr_6 and $Cs_3Ho_2Br_9$, Dudareva et al[169] conclude that Cs_3HoBr_6 and $CsHo_2Br_7$ are produced. Furthermore, they disagree in the detail of the thermal properties of Cs_3HoBr_6.

A significant proportion of commitment in this field lies in the

Table 8. Thermal properties of the ternary halides formed in the $KCl-NiCl_2$, $MCl-PdCl_2$, $MBr-TaBr_5$, $CsBr-DyBr_3$, $MBr-HoBr_3$ and $CsBr-HoBr_3$ systems.

$KCl-NiCl_2$[165]		
	$KNiCl_3$	d. peritectic 948K
$RbCl-PdCl_2$[166]		
	Rb_2PdCl_4	m.p. 799K
	$RbPd_3Cl_7$	d. peritectic 613K
$CsCl-PdCl_2$[166]		
	Cs_2PdCl_4	m.p. 759K
	$CsPd_3Cl_7$	d. peritectic 634K
$NaBr - TaBr_5$[167]		
	$NaTaBr_6$	β→α trans. 573K d. peritectic 679K
$KBr-TaBr_5$[167]		
	$KTaBr_6$	β→α trans. 443K d. peritectic 723K
	$K_2Ta_3Br_{17}$	d. peritectic 543K
$RbBr-TaBr_5$[167]		
	$RbTaBr_6$	β→α trans. 603K m.p. 677K
$CsBr-TaBr_6$[167]		
	$CsTaBr_6$	β→α trans. 675K m.p. 798K
$CsBr-DyBr_3$[168]		
	Cs_3DyBr_6	β→α trans. 710K m.p. 1063K
	$Cs_3Dy_2Br_9$	d. peritectic 908K
$LiBr-HoBr_3$[169]		
	$LiHo_9Br_{28}$	ε→δ trans. 473K δ→γ trans. 469K γ→β trans. 648K d.peritectic 781K
$NaBr-HoBr_3$[169]		
	Na_3HoBr_6	d. peritectic 753K
	Na_2HoBr_5	β→α trans. 499K d. peritectic 651K
$CsBr-HoBr_3$[169]		
	Cs_3HoBr_6	β→α trans. 749K m.p. 1045K
	$CsHo_2Br_7$	d. peritectic 537K
$CsBr-HoBr_3$[168]		
	Cs_3HoBr_6	β→α trans. 736K m.p. 1101K
	$Cs_3Ho_2Br_9$	d. peritectic 918K

Abbreviations:

m.p. - melts congruently

d. peritectic - decomposes in a peritectic reaction

β→α trans. - polymorphic transformation

synthesis, preferably as single crystals, of ternary halides for structural elucidation. Those compounds which have been characterised at ambient temperature[166,171-179] are listed in Table 9 together with salient crystallographic parameters; those compounds which exhibit polymorphism and have been studied as a function of temperature[180,181] are listed in Table 10 together with pertinent thermal and crystallographic parameters. Polymorphism has also been studied in Li_2UBr_6, for which structural data are absent; techniques used include electrical conductivity, differential thermal and differential enthalpic analyses.[182] Two thermal effects (ΔH_{trans} = 1.70(40) and 0.35(15) $kJ.mol^{-1}$ at 505(2) and 740(2)K, respectively) were observed before melting (ΔH_m = 48(2) $kJ.mol^{-1}$ at 781(2)K). The data are discussed by comparison with those of Na_2UBr_6 for which more reliable structural data are available.

A variety of synthetic routes have been employed for the preparation of these ternary halides. The majority are variants of classical solid state methods. Meyer,[176] for example, has obtained $LiGdCl_4$ by reaction of $GdCl_3$ with liquid lithium, by synproportionation of $GdCl_3$ and LiCl and by thermal decomposition of $(NH_4)_2LiGdCl_6$. Hoppe et al[183] have also reported an alternative preparation of $MLnF_3$ (M = K-Cs; Ln = Eu, Yb) which involves reduction of $MLnF_4$ by liquid alkali metal, it being more effective than the normal method which involves LnF_3 as substrate.

X-ray diffraction studies have been completed on the interstitial compounds Rb_xCrF_3 (x = 0.18, 0.20, 0.225, 0.25, 0.275, 0.30),[184] Li_xYCl (x = 0.2),[185] Li_xGdCl (x = 0.5)[185] and $K_xZr_6I_{14}$ (x = 0.46, 1.0). For Rb_xCrF_3,[184] a hexagonal bronze like system spans the range $0.18 \leq x \leq 0.29$. An orthorhombic sublattice (a ~ 1270, b ~ 740, c ~ 740pm) was identified in every sample. Modulated structures, designated $\alpha(x)$, resulting from 1/2, 2/3 and 3/4-filled Rb^+ sites occur for x = 0.167, 0.222 and 0.250. The $\alpha(0.167)$ unit cell has the same dimensions as the orthorhombic sublattice, but unlike the sublattice, which is primitive, the superstructure is body centered. The $\alpha(0.222)$ unit cell has the same a and b dimensions as the sublattice but it is base centered with c(super) = (3/2)c(sub). The $\alpha(0.250)$ phase has a primitive unit cell with dimensions a(super) = 2a(sub), b(super) = 3b(sub) and c(super) = 2c(sub). An undistorted

Table 9. Crystallographic parameters for a number of ternary halides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	β/°	Ref
Na_3GdCl_6	rhombohedral	$R\bar{3}$	700.7	-	1879.1	-	171
Rb_2PdCl_4	tetragonal	P4/mmm	727	-	478	-	166
Cs_2PdCl_4	tetragonal	P4/mmm	753	-	465	-	166
Cs_2YbCl_4	tetragonal	I4/mmm	541.8	-	1727.6	-	172
K_2PtCl_6	cubic	Fm3m	974.3	-	-	-	173
$Cs_6Ni_5F_{16}$	orthorhombic	Cmca	618.4	1455.5	2145.1	-	174
$KCdCl_3$	orthorhombic	Pnma	879.2	400.9	1459.7	-	175
$LiGdCl_4$	tetragonal	$I4_1/a$	645.8	-	1316.0	-	176
$CsReF_6$	rhombohedral	$R\bar{3}$	785.3	-	814.0	-	177
$CsCu_2Cl_2$	orthorhombic	Cmcm	950.8	1189.8	559.9	-	178
$CsCu_2Br_2$	orthorhombic	Cmcm	987.3	1235.5	581.8	-	178
KLn_2Cl_7*	monoclinic	$P2_1/a$	1283.1	694.7	1277.4	89.90	179
$RbLn_2Cl_7$*	orthorhombic	Pnma	1293.2	702.4	1278.7	-	179
$CsLn_2Cl_7$*	orthorhombic	Pnma	1320.5	709.9	1295.2	-	179

* Ln = Sm-Yb, Y; the data quoted refer to the samarium compound.

hexagonal bronze phase was also observed in samples where x = 0.20, 0.225, 0.25 and 0.275.[184] Both $Li_{0.2}YCl$ (a = 375.13, c = 2780.3pm)[185] and $Li_{0.5}GdCl$ (a = 381.5, c = 2783.2pm)[185] occur in the ZrBr-type structure (rhombohedral, $R\bar{3}m$) with lithium evidently randomly distributed in trigonal antiprismatic interstices.

The phase KZr_6I_{14}[186] is the first example of an unprecedented structural configuration (Figure 3) in which a potassium atom is located in the centre of an octahedral zirconium cluster, r(K...Zr) = 239.3, 246.0pm; iodine atoms bridge both the edges of the cluster $r(Zr...I)_{av}$ = 289.8pm and between clusters $r(Zr...I)_{av}$ = 312.4, 340.8pm. The cluster (Figure 3) has C_{2h} symmetry resulting from a 2-fold axis, which passes through K and I(5), together with a mirror plane that contains K, I(4) and Zr(2).[186]

The electron density distribution in K_2PtCl_6 has been determined from a detailed single crystal XRD study (Final R value = 0.009).[173] X-X synthesis shows a peak of 0.5(2) x 10^{-6}e pm^{-3} in

Table 10. Polymorphism of K_3VF_6,[180] Cs_2CdBr_4[181] and Cs_2HgBr_4.[181]

Compound	Transition Temperature K*	Symmetry	Space Group	a/pm	b/pm	c/pm	β/°
K_3VF_6	-	monoclinic		1210.2	1745.6	1200.7	92.6
	453	monoclinic		1714	1237	547.9	91.5
	483	tetragonal†		1370.8	-	875.2	-
Cs_2CdBr_4	-	triclinic	$P\bar{1}$	1020.0	778.8	1389.8	-
				(90.0)	(90.0)	(90.0)	
	158	monoclinic	$P2_1/n$	1020.1	785.6	1394.9	90.0
	237		incommensurate phase				
	252	orthorhombic	Pnma	1022.8	793.1	1396.6	-
Cs_2HgBr_4	-	triclinic	$P\bar{1}$	1010	1540	1380	-
				(90.0)	(90.0)	(90.0)	
	85	triclinic	$P\bar{1}$	1014.8	775.4	1383.7	-
				(90.0)	(90.0)	(90.0)	
	167	monoclinic	$P2_1/n$	1016.2	781.3	1379.6	90.0
	232		incommensurate phase				
	245	orthorhombic	Pnma	1024.8	792.7	1390.1	-

* This temperature is the lower limit of existence of the associated phase.

† This phase can be stabilised at room temperature by incorporation of trace quantities of Na^+.

the (111) direction at 50pm from the Pt nucleus which is tentatively attributed to the non-bonding 5d electrons in t_{2g} orbitals.[173]

Transfer of electronic excitation energy has been studied[187] in crystals of the antiferromagnetic compounds $RbMnCl_3$, $CsMnCl_3$, $CsMnBr_3$ and Rb_2MnCl_4.

Finally, the standard enthalpies of formation (ΔH_f°(298K,c,x)) of K_2NiF_6 (-1963 kJ.mol^{-1}), K_2PdF_6 (-2040 kJ.mol^{-1}) and K_2PtF_6 (-2055 kJ.mol^{-1}) have been determined by solution calorimetry.[188]

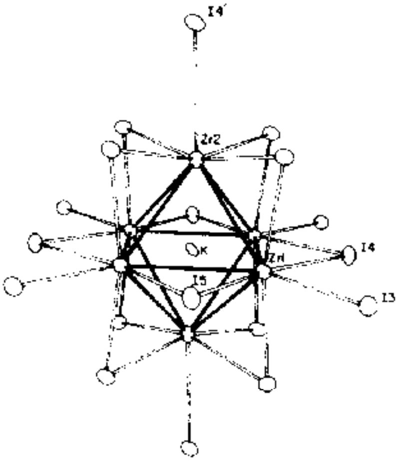


Figure 3. The molecular structure of the KZr_6I_{14} cluster with all exo iodines (reproduced by permission from J. Am. Chem. Soc., 106(1984)4618).

1.4 COMPOUNDS OF THE ALKALI METALS CONTAINING ORGANIC MOLECULES OR COMPLEX IONS

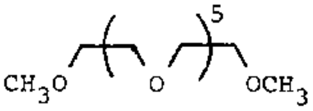
The format adopted for this section is similar to that used for the 1983 Review.[189] Thus the text is simplified by incorporation of subdivisions for specialised topics of current interest and significance; these include complexes of acyclic and macrocyclic lipophilic ionophores, salts of carboxylic and thiocarboxylic acids, and heterobimetallic complexes. The subdivision previously included for derivatives of nucleotides and related species has been omitted owing to a marked reduction in pertinent data. Those which have been abstracted are considered in the subdivisions for the individual alkali metals. Of these, that for lithium is very extensive, reflecting recent developments in the chemistry of lithium-containing oligomers.

1.4.1 Complexes of Acyclic Lipophilic Ionophores

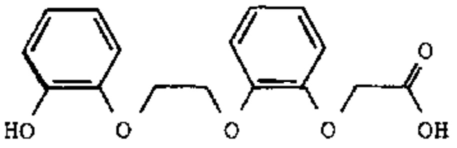
Complex formation between lithium and lipophilic ionophores, including acyclic oligoethers, crowns and cryptands has been reviewed by Pacey.[190] Emphasis is put on the production of chromogenic derivatives which act as colorimetric reagents for alkali metals; their formation involves the addition of a chromophore to a monoanion or azo-type linkage on the ionophore.[190]

Competition reactions between linear oligoethers or crowns anchored to solvent swollen microporous polystyrene resins and soluble ligands for lithium or sodium picrate in toluene at 298K have been studied;[191] the results are used to generate a scale of relative ligand affinities for linear oligoethers and oligoamines, crowns, cryptates and other cation binding ligands. The linear oligoethers have much lower cation affinities than the corresponding macrocyclic polyethers; for example, glyme 7 has an affinity for sodium picrate lower than that of B18C6 by a factor of 265.[191]

Single crystal XRD studies have been completed on three complexes containing acyclic oligoethers; viz the barium thiocyanate complex of (29),[192] the sodium salt of (30)[193] and the potassium acid salt of (30).[194] The structure of the former is the first of a complex between an unsubstituted oligoglyme and an alkaline earth metal cation to be determined.[192]



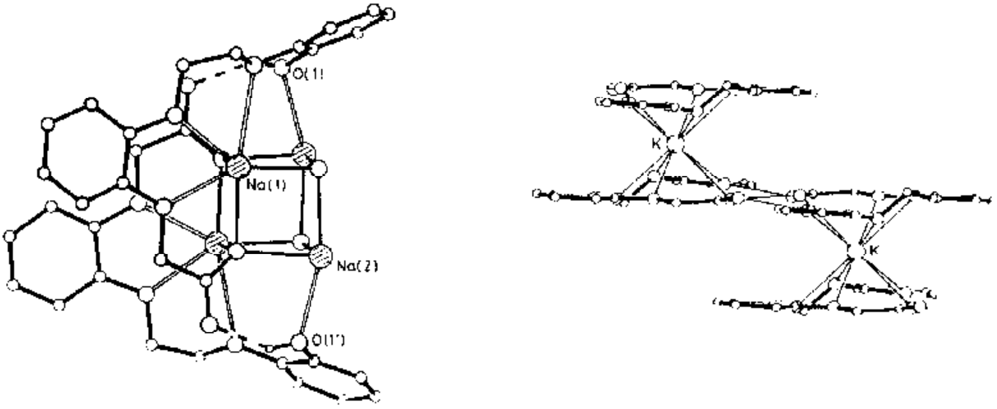
(29)



(30)

The open chain oligoether approximates to one turn of a helix, thus facilitating coordination of the cation to all seven ether oxygen atoms (287.9-294.1pm) and to the nitrogen atoms of the two anions located on the same side of the helix (282.5, 284.2pm).

Despite the apparent similarity of the latter two salts, they exhibit markedly different structural chemistry; whereas the sodium salt shows a tetrameric association,[193] the potassium acid salt contains monomeric units joined by hydrogen bonding in a step-polymer formation.[194] The molecular structure of the sodium salt (Figure 4a)[193] shows alternating oxygen and sodium atoms at the corners of a fairly regular cube which is at the centre of an Na_4L_4 tetramer. The symmetry of the cube is such that there are two crystallographically distinct Na atoms which have similar pentagonal bipyramidal coordination spheres (Figure 4a). Each Na atom is coordinated by the carboxylate oxygen atoms of three ligands (located at the corners of the cube) and also by three ether oxygen atoms from one of these ligands. The seventh coordination position is filled by the



(a) (b)

Figure 4. Aspects of the molecular structure of (a) the sodium salt of (30) showing the sodium-oxygen cube and two ligands, related by two-fold symmetry, and the saddle-shape of the hydrogen bonded dimer unit, and (b) the potassium acid salt of (30) showing the linking of hydrogen bonded anions through coordinated potassium cations (reproduced by permission from (a) J. Chem. Soc., Chem. Commun., (1984)408 and (b) J. Chem. Soc., Dalton Trans., (1984)1187).

phenolic oxygen atom of the fourth ligand. For each Na atom, one equatorial Na-O bond is significantly longer, $r(Na(1)...O) = 285$, $r(Na(2)...O) = 270pm$, than the others, $r(Na...O) = 232-251pm$. The molecular structure of the potassium acid salt (Figure 4b) shows it to be composed of K atoms sandwiched between planar hydrogen bonded acid salt anions. Thus each K atom is irregularly coordinated by eight oxygen atoms, four (three ether and one phenolic) from each of two ligands, (271-287pm) with two somewhat more remote carboxylate oxygen atoms (319pm) completing the 10-fold coordination sphere.

Cox et al[195,196] have reported stability constant data for complexes of the anionic ionophores monensin and lasalocid with M^+ (M = Li-Cs) and M^{2+} (M = Mg-Ba) ions, measured in both protic and polar aprotic solvents. The monensin complexes are very stable.[195,196] They exhibit the same stability sequences:

$$Li^+ < Na^+ > K^+ > Rb^+ > Cs^+ \ ; \quad Mg^{2+} > Ca^{2+} < Sr^{2+} < Ba^{2+}$$

in all solvents except dmso for which Ca^{2+} appears at a maximum. The lasalocid complexes are less stable.[195] They exhibit the same stability sequence as the monensin complexes for M^{2+} ions in all solvents (dmso was not studied) but no consistent trends were discernable for M^+ ions. Cox et al[196] have also reported kinetic data for the formation and dissociation of the monensin complexes of M^+ ions in ethanol. Whereas the dissociation rate constants are sensitive to cation size, their variation:

$Li^+ > Na^+ < K^+ < Rb^+ < Cs^+$

reflecting the stability sequence noted above, the formation rate constants increase monotonically with increasing cation size.

Fuhrhop and Liman[197] have synthesised the monopyromellitic ester of monensin. Unlike monensin, which prefers a cyclic conformation, the ester adopts a stretched conformation owing to the presence of the negative charges at both ends of the molecule. Incorporation of the ester into monolayer membranes during sonication resulted in the formation of channels (Figure 5a) through which alkali metal ions could proceed. Incorporation into bilayer membranes, however, did not result in channel formation, the ester being too short to cross the bilayer lipid membrane (Figure 5b).[197]

1.4.2 Crown complexes

In view of the continuing significance of alkali and alkaline earth metal complexes of crown and related macrocyclic ligands, this topic has again been divided into three subsections in which complexes formed by (i) 'classical' crown compounds and their substituted derivatives, (ii) lariat ethers, and (iii) novel macrocyclic ligands of unusual design are considered.

Holton et al[198] have measured the nmr spectra of the alkalide anions, Na^- and Rb^-, present in solutions of sodium and rubidium in 12C4. Cation resonances were not detected, presumably due to broadening of the absorption. These M-12C4 (M = Na,Rb) solutions are shown to represent a convenient stable source of high concentrations of alkalide anions. It is proposed that, in view of recent evidence for alkalide anions, the reducing power of metal-amine and metal-hexamethylphosphoramide solutions may be attributable to these anions rather than to the solvated

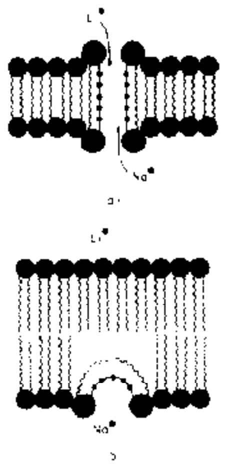


Figure 5. Models of (a) an ~2000pm monolayer membrane prepared by sonication of a symmetric α,ω-bifunctional amphiphile (●~~~●) in the presence of the monopyromellitic ester of monensin (●~~~~●), and (b) an ~4000pm bilayer membrane similarly prepared by sonication of a monofunctional amphiphile (●~~~) in the presence of the monensin derivative (reproduced by permission from J. Am. Chem. Soc., 106(1984)4643).

electron.[198]

Solvent extraction of alkali metal salts (picrates,[199-202] phenolates,[201] and o-nitrophenolates[201]) by 15C5,[199,200] 18C6,[199,201] DB18C6[201,202] and DCH18C6[201] has been studied in H_2O-$CHCl_3$,[199] H_2O-CH_2Cl_2,[201] H_2O-C_6H_6[200] and H_2O-$C_6H_5NO_2$[202] solvent systems. The results for the H_2O-$C_6H_5NO_2$ system[202] were used to calculate stability constant data for 1:1 complexes of M^+ (M = Li-Cs) with DB18C6 in $C_6H_5NO_2$ saturated with water. The stability of the complexes increases in the sequence:

$Li < Cs < Rb < K < Na$

Stability constants have also been determined conductometrically for 1:1 complexes of M^+ (M = Na-Cs) with B18C6 in a variety of solvents (CH_3OH, CH_3CN, dmf and dmso)[203] and of M^+ (M = Na,K) with DB18C6 or DCH18C6 in aqueous isopropyl alcohol.[204] In general, the selectivity of B18C6 for the alkali metals is governed primarily by the size-fit concept. It varies in the sequence:

Na < K > Rb > Cs

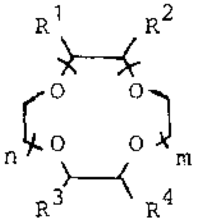
and is independent of solvent.[203] A clearly defined K^+/Cs^+ selectivity is also observed for DB18C6 in aqueous isopropyl alcohol. The selectivity is dependent, however, on the dielectric constant of the solutions, decreasing with increasing alcohol content.[204]

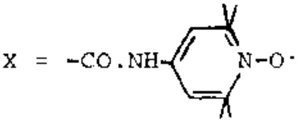
A number of novel alkyl- and aryl-substituted crown ether derivatives have been synthesised and their complexing ability towards alkali and/or alkaline earth metal cations assessed;[205-210] they are listed in Table 11. The complexing abilities of alkyl and aryl substituted 12C4, 15C5 and 18C6 (31) have been assessed by consideration of the transport of alkali metal picrates (M = Li,Na,K) across a bulk $CHCl_3$ membrane.[205] As the substituents render the crown ethers more lipophilic the complexes become more soluble in $CHCl_3$. For Na^+ and K^+ this leads to a reduction in transport; for Li^+, however, transport is improved although the overall rate is much leass than that for Na^+ or K^+.[205] The analogous dodecyl substituted 18C6 (32) has been coated onto insoluble supports through hydrophobic interactions.[206] The resultant material provides a relatively cheap stationary phase for efficient chromatographic separation of alkali metal cations. Comparative studies have been undertaken with decyl substituted C221.[206]

The use of epr methods to study the effect of K^+ ion binding on the geometrical properties of syn- and antichiral dinitroxide substituted 18C6 (33,34) and of tetranitroxide susbstituted 18C6 (35) has been described.[207]

The complexation of M^+ (M = Li–Cs) and M^{2+} (M = Mg–Ba) ions by crown ether carboxylic acids (36-39) in aqueous methanol solution has been studied both spectroscopically (i.r. and nmr) and potentiometrically.[208] Complexation is governed by electrostatic interactions between the cation and carboxylate residues; hence discrimination among cations on the basis of ionic radius is poor. The syn- and antichiral isomers (38,39) exhibit differing complexation behaviour, the antichiral isomer giving the stronger complexes.[208] The extraction and transport of M^{2+} (M = Mg–Ba) from a basic to an acidic solution across an artificial membrane by crown ether carboxylic acids (38-44) has also been investigated.[209] Monocarboxylate 15C5 and 18C6 carriers (40,41) achieve transport via 2:1 complexes, whereas

Table 11. Novel alkyl- and aryl-substituted crown ethers which have been assessed as complexing agents for alkali and/or alkaline earth metal cations.





Y = $-CO.NH.C_8H_{17}$

Z = $-CO.N(C_8H_{17})_2$

Identifier	Description	Ref
(31)	$R^1 = -CH_3, -C_2H_5, -C_8H_{17}, -C_{10}H_{21}, -C_{14}H_{29}$ or $-C_6H_5$; $R^2 = R^3 = R^4 = -H$; $n+m = 2, 3$ or 4	205
(32)	$R^1 = -C_{12}H_{25}$; $R^2 = R^3 = R^4 = -H$; $n+m = 4$	206
(33)	$R^1 = R^4 = -COOH$; $R^2 = R^3 = X$; $m = n = 2$	207
(34)	$R^1 = R^3 = -COOH$; $R^2 = R^4 = X$; $m = n = 2$	207
(35)	$R^1 = R^2 = R^3 = R^4 = X$; $m = n = 2$	207
(36)	$R^1 = R^2 = -COOH$; $R^3 = R^4 = -H$ or $C_{10}H_{21}$; $m+n = 4$	208
(37)	$R^1 = -COOH$; $R^2 = Y$; $R^3 = R^4 = -H$; $m+n = 3$ or 4	208
(38)	$R^1 = R^4 = -COOH$; $R^2 = R^3 = Y$; $m = n = 2$	208,209
(39)	$R^1 = R^3 = -COOH$; $R^2 = R^4 = Y$; $m = n = 2$	208,209
(40)	$R^1 = -COOH$; $R^2 = -CONHC_{18}H_{37}$; $R^3 = R^4 = -H$; $n+m = 3$	209
(41)	$R^1 = -COOH$; $R^2 = -CONHC_{14}H_{29}$ or Z; $R^3 = R^4 = -H$; $n+m = 4$	209
(42)	$R^1 = -COOH$; $R^2 = -CONHC_{14}H_{29}$ or Z; $R^3 = R^4 = -H$; $n+m = 4$	209
(43)	$R^1 = R^4 = -COOH$; $R^2 = R^3 = Z$; $n = m = 2$	209
(44)	$R^1 = R^3 = -COOH$; $R^2 = R^4 = Z$; $n = m = 2$	209
(45)	$R^1 = R^2 = R^3 = R^4 = -C_6H_5$; $n = m = 2$ or 3	210
(46)	$R^1 = R^4 = -(CH_2)_4C_6H_5$; $R^2 = R^3 = -H$; $n = m = 2$	210

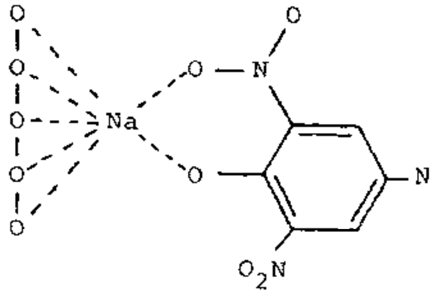
dicarboxylate 18C6 carriers (38,39,42-44) transport ions as 1:1 complexes.[209]

The ability of phenyl and 4-phenylbutyl substituted 18C6 and 24C8 (45,46) to complex M^+ (M = Li-Ba) and M^{2+} (M = Sr,Ba) ions has been assessed.[210] The 18C6 derivatives form the most stable complexes with K^+, Sr^{2+} and Ba^{2+}; the 24C8 derivatives prefer K^+, Rb^+ and Ba^{2+}.[210]

Single crystal XRD studies have been completed for $[(12C4)_2Li]^+PPh_2^-$,[211] $[(12C4)_2Li]^+AsPh_2^-$, thf,[211] $[(12C4)Li]^+N(SiMe_3)_2^-$,[212] $[(B15C5)Na]^+[OC_6H_2(NO_2)_3]^-$,[213] $[(B15C5)Ba]^{2+}[O_2CC_6H_3(NO_2)_2]_2^-$,[214] $[(18C6)Cs_2]^{2+}[Al_3Me_9SO_4]^{2-}$,[215] $[(DB30C10)K]^+SCN^-$,[216] $[(DB30C10)K]^+SCN^-.H_2O$,[216] and $[(DB36C12)Na_2]^{2+}(PF_6^-)_2$.[217] Contrasting Li atom coordination geometries are observed in the structures of the 12C4 complexes. That in the diorganophosphides and arsenides[211] is novel; it consists of a LiO_8 unit with approximate D_{4d} symmetry generated by two 12C4 polyether rings. The coordination number of 8, previously unknown for lithium, results in unusually long Li-O distances, (average r(Li...O) = 235pm). That in the bis(trimethylsilyl)amide[212] is more conventional; it consists of a square pyramidal LiO_4N unit generated by the 12C4 polyether ring (basal positions) and the amide nitrogen atom (apical position). Disparate Li-O distances are observed; two are typical for this bond (209.4, 210.8pm) and two are abnormally long (233.2, 239.3pm). The Li-N bond distance (196.5pm) is similar to those reported for comparable compounds.

Considerably different cation geometries (47,48) are found for the two B15C5 complexes. The Na atom in the picrate (47)[213] is seven-coordinate; the NaO_7 unit is composed of all five heteroatoms of the B15C5 ring (240.0-250.1pm), as well as two oxygen atoms, the phenolate (235.0pm) and one from an ortho nitro moiety (251.0pm), of the anion. It is displaced by 90pm from the crown ether cavity in the direction of the picrate.[213] The Ba atom in the 3,5-dinitrobenzoate (48)[214] is nine-coordinate. Two symmetry related Ba atoms are linked by four anions through their carboxylate groups (263.9-269.4pm). The BaO_9 unit is completed by the five heteroatoms of the B15C5 ring (288.8-309.2pm), the Ba atom lying 187.7pm out of the crown ether cavity in the direction of the bridging anions.[214]

A novel coordination geometry has been observed for the cation



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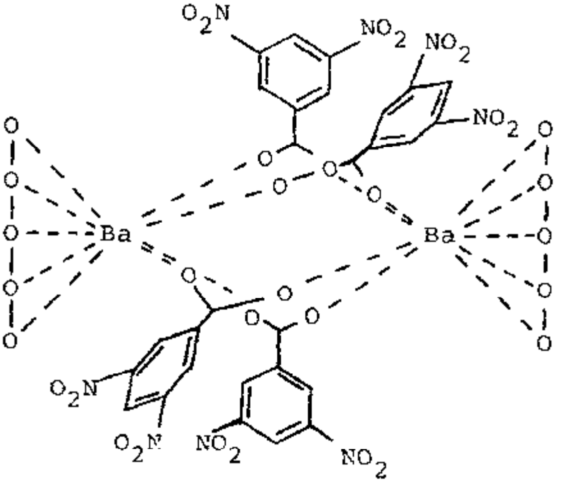

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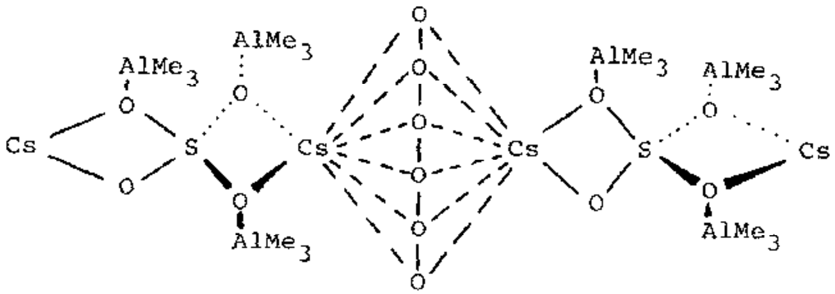
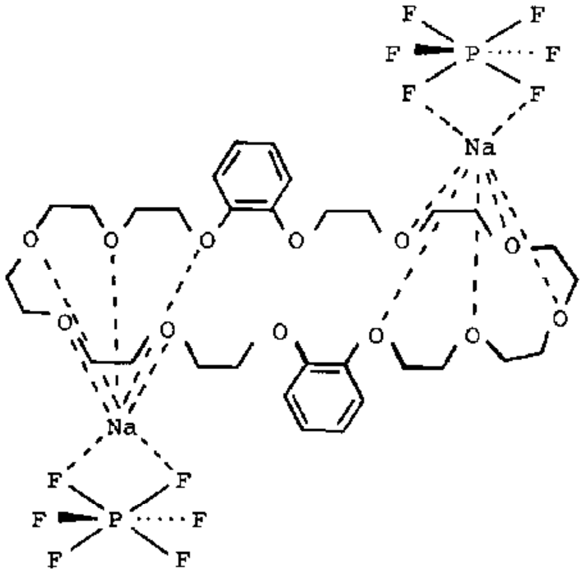


(49)

in the structure of $[(18C6)Cs_2]^{2+}[Al_3Me_9SO_4]^{2-}$ (49);[215] it contains a Cs...Cs contact (392pm) only slightly longer than the sum of the ionic radii (356pm). The two Cs atoms, which are crystallographically distinct, are located on either side of the 18C6 ring (r(Cs(1)...O) = 333-359, r(Cs(2)...O) = 313-348pm) and are bridged by the anion (r(Cs(1)...O) = 308,324, r(Cs(2)...O) = 316,320pm). Considerable asymmetry is observed in the disposition of the two Cs atoms relative to the crown ether cavity, Cs(1) being much closer to the plane of oxygen atoms (179pm) than Cs(2) (237pm) (49).[215]

Only marginal differences occur in the structures of the $[(DB30C10)K]^+$ cations in the anhydrous and monohydrated thiocyanate salts.[216] Whereas that in the anhydrous material is located on a two-fold axis, that in the monohydrate exhibits no symmetry. The K atom is coordinated by all ten heteroatoms of the DB30C10 molecule in both complexes; the water molecule does not enter the coordination sphere. The two structures show a different pattern of K-O distances. In the anhydrous salt they vary from 285.7 to 293.5pm with the mean distance to aromatic oxygen atoms being greater than that to aliphatic oxygen atoms, while in the monohydrate the range is 286.1-310.6pm with the mean distance to aromatic oxygen atoms being less than that to aliphatic oxygen atoms.[216]



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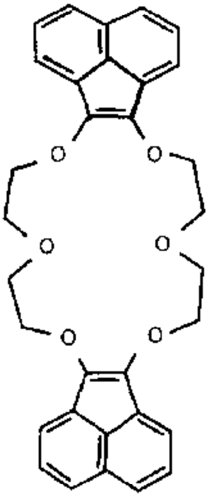


(51)

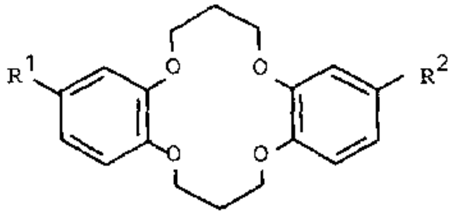
The DB36C12 macrocycle in the hexafluorophosphate salt (50)[217] contains a centre of symmetry and is twisted such that it possesses two complexing faces at opposite ends of the molecule each of which accommodates a Na atom bound to a PF_6^- anion. The Na atom is seven coordinate with bonding to five oxygen atoms of the DB36C12 molecule (241.9-254.4pm) and two fluorine atoms of the anion (242.4, 252.8pm). It is displaced 45pm from the mean plane of the five heteroatoms towards the phosphorus atom.[217]

The crystal and molecular structures of two more complex crown ether derivatives have also been reported.[218,219] The coordination geometry of the Na atom in (dibenzo-18-crown-6)bis-(tetrahydrofuran)sodium(meso-tetraphenylporphinato)ferrate, $[(DB18C6).Na(thf)_2]^+[FeTPP]^-$,[218] consists of a NaO_8 hexagonal bipyramidal unit; the six oxygen atoms of the DB18C6 molecule provide the equatorial plane (257.3-274.5pm) and the thf oxygen atoms occupy the apical positions (227.9, 229.9pm). The coordination geometry of the K atom in 2,3,11,12-(bis-1,2-acenaphtho)-18-crown-6 potassium thiocyanate, $[(51)K]^+NCS^-$,[219] consists of a KO_6N hexagonal pyramidal unit. The K atom is located in the centre of and bonded to the six heteroatoms of the macrocycle (270.6-299.4pm) with a N-bonded thiocyanate anion on one side only (272.7pm).[219]

Several papers have been published in which the complexation of alkali metal cations by ring contracted[220] and ring expanded[221-224] crown ethers is discussed. Ring contracted 14C5, 17C6 and their sila-analogues showed a drastic decrease in cation binding ability when compared with the corresponding crown ethers;[220] this decrease is attributed not to the diminished cavity size but to the disordered conformation induced by ring contraction.

In an attempt to obtain highly selective ionophores for Li^+ ions, ring expanded 13C4, 14C4, 15C4 and 16C4 derivatives bearing a long aliphatic chain have been synthesised.[221] The Li^+ selectivities of these materials were in accord with the size-fit concept, the 14C4 and 15C4 derivatives being the most effective. Incorporation of a methyl group geminal to the aliphatic chain prevents formation of sandwich-type 2:1 complexes with alkali metals other than lithium and hence improves Li^+ selectivity.[221]

N.m.r. (^7Li) spectroscopic studies[222] of the complexation of Li^+ by ring expanded DB14C4 and its alkyl substituted derivatives (52)



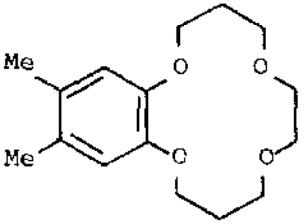
$R^1=R_2=$ -H

$R^1=$ -H; $R^2=$ -Me

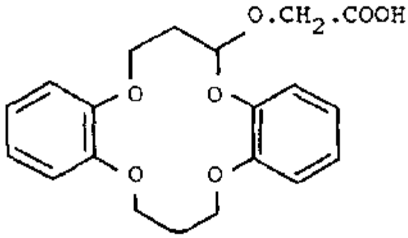
R^1 = -H; $R^2=$ -Bu^t

$R^1=R^2=$ -Bu^t

(<u>52</u>)



(<u>53</u>)



(<u>54</u>)

provide evidence for the formation of 1:1 complexes; no clear cut evidence for the existence of 2:1 complexes was obtained. Complex formation was found to be solvent dependent, the stability of the complexes varying with the coordinating power of the solvent. The presence of substituent groups on the benzene rings of the crown ethers also influences the stability of the complexes which decreases in the sequence:

MeDB14C4 > Bu^tDB14C4 > Bu^t_2DB14C4 > DB14C4

Structural analysis of the $LiNO_3$ complexes of ring expanded B14C4[223] and its chiral dimethyl derivative (<u>53</u>)[224] has been effected using the results of single crystal XRD studies. The coordination geometry of the Li atom is very similar in the two complexes; although based on a LiO_6 unit it is best perceived as square pyramidal with a bidentate nitrate group occupying the apical position and the four heteroatoms of the crown ether located in the basal plane. Pertinent molecular dimensions for the two complexes are summarised in Table 12.

The crystal and molecular structures of the hydrated lithium salt of the oxyacetic acid derivative of DB14C4 (<u>54</u>) have also been elucidated.[225] The Li atom is coordinated by the four

Table 12. Pertinent molecular dimensions in $[B14C4Li]^+NO_3^-$ [223] and in $[Me_2B14C4Li]^+NO_3^-$.[224]

Complex	Average r(Li...O)/pm Crown ether	r(Li...O)/pm Nitrate	$\hat{ONO}$/°	Displacement of Li^+ from plane of heteroatoms/pm
$[B14C4Li]^+NO_3^-$	205.0	207.2, 230.0	57.6	24
$[Me_2B14C4Li]^+NO_3^-$	206.6	207.4, 228.6	51.7	6

heteroatoms of the coronand proper (203.8-207.7pm) and an axial water molecule (191pm) in a near square pyramidal geometry. The water molecule forms a link between the Li atom and the carboxylate moiety which does not directly coordinate the cation.[225]

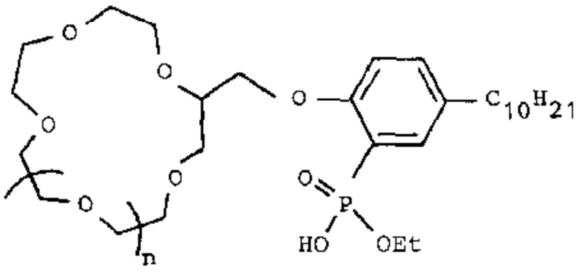
1.4.3 Complexes of Lariat Ethers

Novel lariat ethers based on crown compounds and their monoaza- and diaza- derivatives have been synthesised and the specificity of their complexing ability for alkali and/or alkaline earth metal cations assessed. The dynamics of the complexation of M^+ (M = Na,K,Ca) by various lariat ethers (2-substituted 15C5, N-substituted monoaza 15C5 and N-substituted monoaza 18C6) have been elucidated by ^{13}C nmr spectroscopic techniques.[226]

Comparison of the complexing abilities of lariat ethers bearing alkyl and polyether side chains (2-substituted-12C4, -15C5, -18C6, N-substituted monoaza-12C4, -15C5 and -18C6) for M^+ (M = Li-Cs) has been effected;[227] the incorporation of oxygen atoms in the side chains did not significantly improve the complexing abilities of the lariat ethers towards Na^+ and K^+.

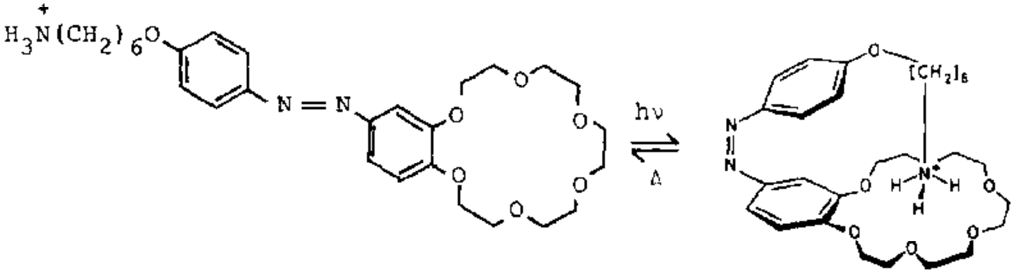
The series of 2-substituted crown ethers (55) have been prepared.[228] They have been tested in competitive alkali metal solvent extraction experiments (M = Li-Cs) and have been shown to be capable of anion independent metal ion transport from acidic and neutral aqueous solutions into organic media. Whereas the 15C5 and 18C6 derivatives were fairly selective for Na^+ and K^+, respectively, the 21C7 and 24C8 derivatives were less discriminating, the extracts containing at least 10% of each alkali metal.[228]

A novel photoresponsive crown ether with an ammonium group tail (56) has been synthesised.[229] Its photoresponsive ionophoric properties have been evaluated through solvent extraction of alkali metal toluene-p-sulphonates (M = K–Cs). Trans (56) clearly exhibits a higher affinity for K^+ than for Rb^+ or Cs^+.



n = 1, 2, 3, 4.

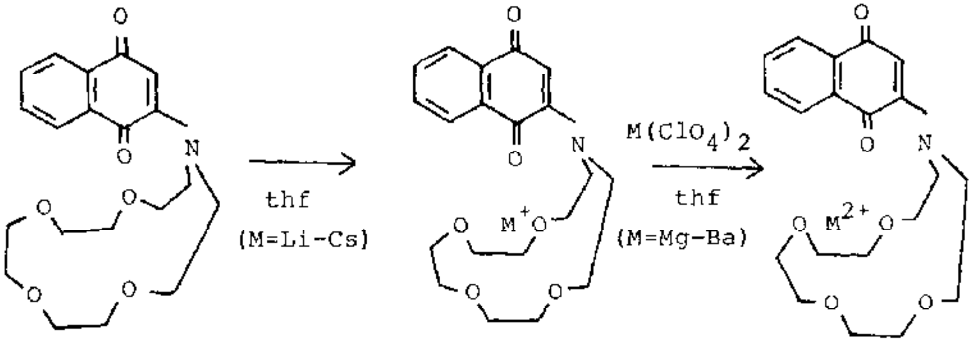
(55)



trans (56) cis (56)

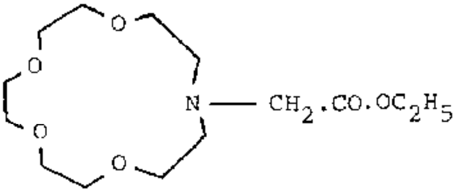
Cis (56), however, is capable of ejecting K^+, but not Rb^+ or Cs^+ from the crown ether ring. Presumably, the K^+ ion nests in the B18C6 cavity while the larger Rb^+ and Cs^+ ions perch on its edge. Thus interaction with Rb^+ and Cs^+ would be less affected by an ammonium group bound (probably) to the opposite side of the crown ether ring.[229]

Reduction of 1,4-naphthoquinone N-substituted monoaza 15C5 (57) by an alkali metal in thf at 298K generates the azacoronand-naphthoquinone radical anion which forms a cage into which the cation can be inserted (58).[230] Reaction of this product with alkaline earth metal perchlorates yields the corresponding alkaline earth metal complex (59). Characterisation of all products was achieved using esr/endor spectroscopy.[230]



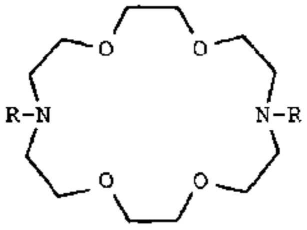
(57) (58) (59)

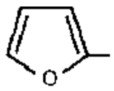
The molecular structure of the complex formed between NaBr and the N-substituted monoaza-15C5 (60) has been determined.[231] It is the first structurally characterised example of a lariat ether in which an ester carbonyl group interacts directly with a ring bound cation. Thus, the Na atom is coordinated by the five heteroatoms of the monoaza 15C5 coronand (r(Na...O) = 248.3-251.5 pm; r(Na...N) = 257.8pm), the carbonyl oxygen atom of the lariat side chain (245.1pm) and the bromide anion (311.6pm) in a pentagonal bipyramidal geometry.[231]

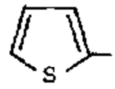


(60)

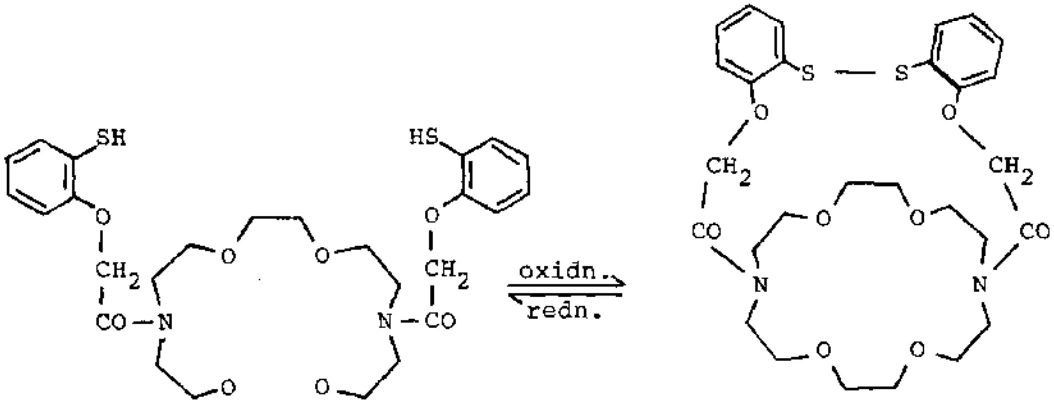
N,N'-disubstituted diaza 18C6 coronands, having two functionalised side chains for cation binding, provide new and characteristic transport selectivities. Tsukube[232] has shown that the furan derivative (61) exhibited clearly enhanced complexing and transporting abilities for the K^+ ion when compared with those of simple diazacrown ethers. Replacement of furan with thiophene, however, resulted in a carrier (62) which exhibited decreased transport efficiencies for K^+ and Ba^{2+} ions.[232] Gokel et al,[233] in a separate study, have shown that utilisation of polar yet uncharged donor groups such as carbethoxymethyl gives a "bibracchial" lariat ether (63) capable of selectivity of Ca^{2+} over Na^+ or K^+.



(61) R = 

(62) R = 

(63) R = $EtOCOCH_2$-



(64)

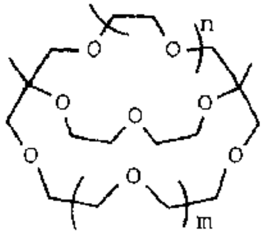
(65)

Synthesis of a disubstituted N,N'-diaza 18C6 bearing redox functional thiol groups has been achieved;[234] redox-responsive interconversion between the "bibracchial" lariat ether (64) and the cryptand (65) readily occurs. For Na^+ ions, (64) and (65) showed a similar affinity. For M^+ (M = K-Cs), however, (65) was a more effective complexing agent presumably because of coordination of the complexed metal ions by the bridging oxygen atoms.[234]

1.4.4 Complexes of Macrocyclic Polyethers of Novel Design

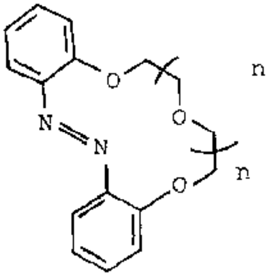
Japanese chemists are interested in the design, synthesis and coordination properties of novel macrocyclic polyethers to such an extent that papers submitted by six independent groups[235-240] have been abstracted for this subsection. The macrocyclic polyether

(66) with novel ring structures complex with Na^+ and K^+ in accordance with the size-fit concept.[235] Crown ethers containing an azo-linkage (67) are somewhat ineffective as ligands for M^+ (M = Li-Cs) and M^{2+} (M = Mg-Ba) ions;[236] it is concluded that incorporation of the azo moiety into the macrocycle does not lead to stabilisation of complexes. Acyclic polyethers containing two cinnamoyl moieties (68) and their cyclised derivatives (69) exhibit but little difference in their selectivity and complexing ability for M^+ (M = Na,K);[237] it is suggested that the cyclobutane structure distorts the macrocyclic polyether to such an extent that its presence negates the anticipated increase in complexing ability on cyclisation. The bis(polyetheramide) derivative (70) is more selective than the corresponding monocyclic analogue (71) for the Ca^{2+} ion.[238] Furthermore, the potentiometric selectivity for Ca^{2+} relative to



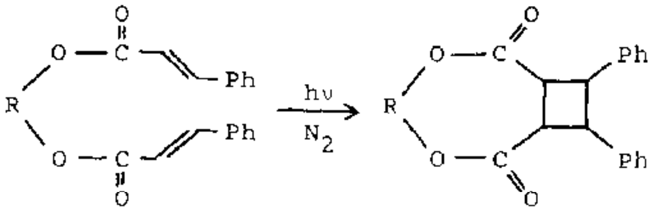
n=2, m=1
n=1, m=1
n=1, m=0

(66)



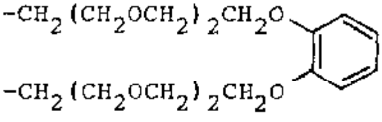
n=1,2,3 or 4

(67)

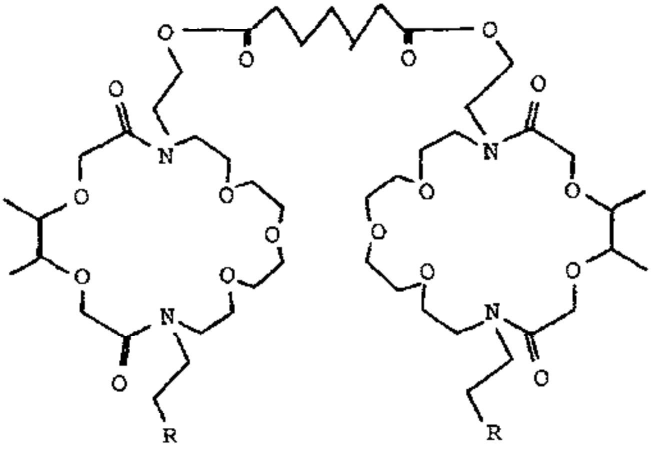


(68) (69)

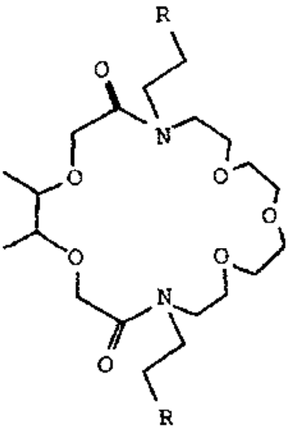
R = $-CH_2(CH_2OCH_2)_3CH_2-$



R = $\begin{matrix}-CH_2(CH_2OCH_2)_2CH_2O \\ -CH_2(CH_2OCH_2)_2CH_2O\end{matrix}$

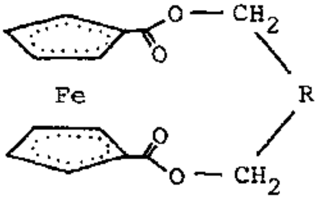


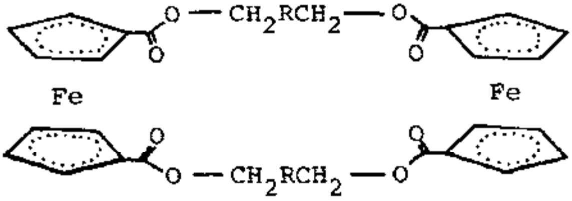
(<u>70</u>)



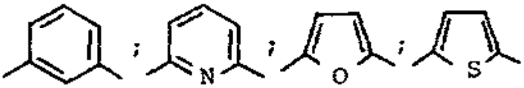
(<u>71</u>)

R = $-CO.O(CH_2)_6CH_3$

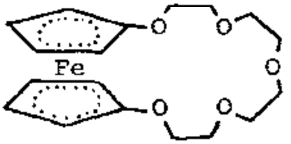




R = $-(CH_2OCH_2)_n-$; $-(CH_2SCH_2)_n-$;



(<u>72</u>) (<u>73</u>)



(<u>74</u>)

Mg^{2+} is improved by more than an order of magnitude.

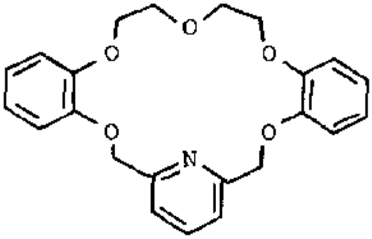
A number of novel crown ethers containing a ferrocene unit as an integral part of the ring have also been reported.[239,240] The complexing ability of some of these ferrocenophanes (72,73) towards, inter alia, M^+ (M = Li-Cs) and M^{2+} (M = Mg-Ba) has been examined;[239] in general they exhibit low complexing power and little selectivity for these ions. Alkali metal thiocyanate complexes with polyoxa[n]-ferrocenophanes (e.g. 74) have been studied[240] using multinuclear (^1H and ^{13}C) nmr spectroscopic methods; chemical shift data are rationalised in terms of an electronic field effect and a conformational change on metal complexation. The crystal and molecular structures of $[(74)Na]^+NCS^-$ have also been determined in a complementary single crystal XRD study.[240] The Na atom is coordinated by the five heteroatoms of the cyclic moiety (239.6-263.1pm) and the nitrogen atom of an anion (254.1pm) in a pentagonal pyramidal geometry. The Fe-Na distance (412.9pm) is too long relative to the sum of the van der Waals radii for the iron atom to take part in complex formation although the possibility of a very weak Fe...Na interaction cannot be excluded.[240]

Four other papers, all of which describe the results of structural studies,[241-244] have been abstracted for this section; as for the 1983 review the majority are submitted by either Weber[241] or Owen.[242,243] Weber has determined the crystal structure of $[(75)Na]^+NCS^-$,[241] Owen those of $[(76)Na_2]^{2+}(SCN)_2^-,2H_2O$[242] and $[(77)K_2]^{2+}(OC_6H_2(NO_2)_3)_2^-$[243] and Casini et al that of $[(78)K]^+SCN^-$.[244]

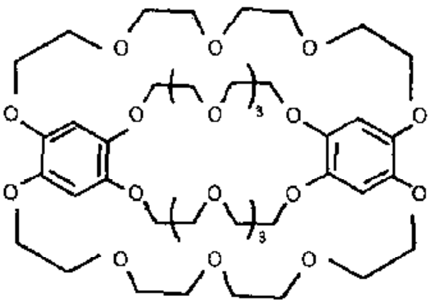
The crystal structure of $[(75)Na]^+NCS^-$[241] contains two crystallographically distinct complexes. The Na atom is located close to the centre of the macrocycle in both complexes; it is coordinated by all six heteroatoms of the ring (r(Na(1)...O) = 263.1-277.2; r(Na(1)...N) = 260.1; r(Na(2)...O) = 259.6-269.6; r(Na(2)...N) = 250.1pm) and the nitrogen atom of the NCS anion (r(Na(1)...N) = 233.5; r(Na(2)...N) = 238.2pm), the NaO_5N_2 coordination geometries being essentially hexagonal pyramidal.[241]

In $[(76)Na_2]^{2+}(SCN)_2^-,2H_2O$,[242] two Na atoms, separated by 816.9 pm are coordinated by each ligand molecule. Na(1) is surrounded by the five heteroatoms of one polyether chain (there are four normal Na-O distances (241.5-250.4pm) and one longer interaction

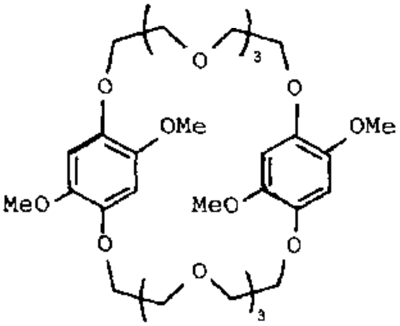
(298.8pm)), an adjacent methoxy oxygen atom (249.5pm) and the nitrogen atom of an NCS anion; the NaO_6N coordination geometry is approximately pentagonal bipyramidal. Na(2) forms part of an eight coordinate NaO_8 unit, of no particular geometry, generated by the five heteroatoms of the other polyether chain (245.0-266.1 pm), two methoxy oxygen atoms (248.4,259.2) and a water molecule (237.6pm). Neither the second anion nor the second water molecule is coordinated to a Na atom.[242] Two metal atoms are also coordinated by a single ligand molecule in the structure of $[(\underline{77})K_2]^{2+}(OC_6H_2(NO_2)_3)_2^{-}$;[243] two K atoms, related by a crystallographic centre of symmetry are each encapsulated by ten oxygen atoms of the ligand (282.2-319.5pm) to the exclusion of the picrate anions.[243]



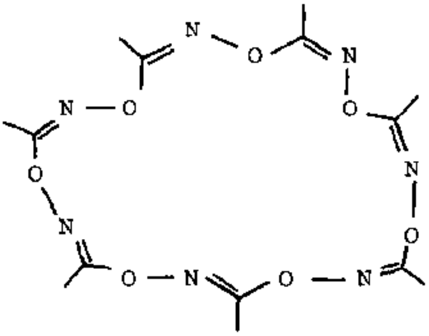
(<u>75</u>)



(<u>77</u>)



(<u>76</u>)



(<u>78</u>)

The K atom in the KNCS complex of acetonitrile oxide cyclic heptamer (78)[244] is located in a heptagonal bipyramidal KO_7NS unit generated by the seven oxygen atoms of the macrocycle (average r(K...O) = 282pm), the nitrogen atom of the anion (287pm) and, to a weaker extent, the sulphur atom of a symmetry related anion (323pm); it is displaced by 10pm from the plane of the seven oxygen atoms in the direction of the N-bonded NCS anion.[244]

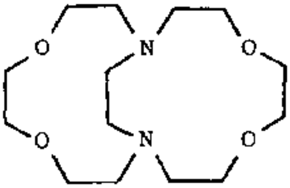
1.4.5 Cryptates and Related Complexes

Thermodynamic[245,246] and kinetic[246,247] data for the complexation of alkali and/or alkaline earth metal cations by diverse cryptates have been reported. Enthalpies of complexation for M^+ (M = Na-Cs) with C222 in dmf and dmso and for Li^+ with C222 in methanol have been determined[245] using a calorimetric technique; corresponding entropy data were derived from known free energy data.[245] The stability constants of complexes of M^{2+} (M = Ca-Ba) with C211, C221, C222, $C2_B22$ and $C2_B2_B2$ have also been measured[246] in dmf, dmso, methanol and water. The formation and dissociation rate constants of M^{2+} (M = Ca-Ba) complexes of C222, $C2_B22$ and $C2_B2_B2$ have been determined independently by two groups of authors;[246,247] in one study[246] the results are compared with analogous data for complexes containing C211 and C221. The introduction of the benzene rings in the sequence C222 - $C2_B22$ - $C2_B2_B2$ causes (i) a progressive decrease in the formation rate constants for all three cations, (ii) no change in the dissociation rate constants for Ca^{2+}, and (iii) a marked increase in the dissociation rate constants for Sr^{2+} and Ba^{2+}.[247]

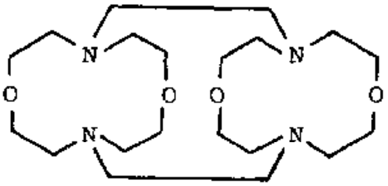
Reaction of KGeSb with C222 in ethylenediamine(en) produces a dark red solution from which crystals of both $[C222K]_2^+Sb_4^{2-}$ and $[C222K]_3^+Sb_7^{3-}$,2en have been isolated.[248] Whereas the structure of the former complex is centrosymmetric, that of the latter complex contains three crystallographically independent $[C222K]^+$ cations. All of the cations have normal configurations with the K atom centrally located along the N...N axis. Details of the K atom coordination spheres are only available as supplementary material.[248]

Coloured 1:1 complexes of diaza-18C6 with potassium 4-nitrophenolate and with potassium 2,4-dinitrophenolate and of diaza-15C5 with sodium and potassium 4-nitrophenolate have been isolated and characterised using chemical analytical and spectroscopic (i.r.; u.v.-visible; n.m.r.) techniques;[249] no complexes of diaza-18C6 with sodium salts could be isolated.

Groth et al have isolated and structurally characterised alkali metal thiocyanate complexes of (79) (M = Li,Na,K)[250] and of (80) (M = K);[251] with the exception of the lithium complex which is a hemihydrate, the complexes are anhydrous. Significant features of the structures of the MNCS (M = Li-K) complexes of (79)[250] are shown in Figure 6; details are only available as supplementary material. The structures are similar. As the size of the alkali metal atom increases it moves from a location within the trigonal bipyramidal N_2O_4 cage of the ligand (for Li^+), through a point close to the centre of the O_4 square plane (for Na^+) to a position above the O_4 square plane (for K^+). The gap in the coordination spheres of Na^+ and K^+ is filled by the nitrogen atom of the NCS^- anion. Only the Na atom (CN = 7) attains its optimum coordination number, the K atom (CN = 7) being coordinatively unsaturated and the Li atom (CN = 6) having too many neighbours. As a result the ligand clearly has the least conformational strain in the sodium complex.[250] The structure of the KNCS complex of (80)[251] is such that the K atom is located inside a cavity generated by all eight heteroatoms (r(K...O) = 258-284; r(K...N) = 274-281pm) in a pseudo cubic arrangement.



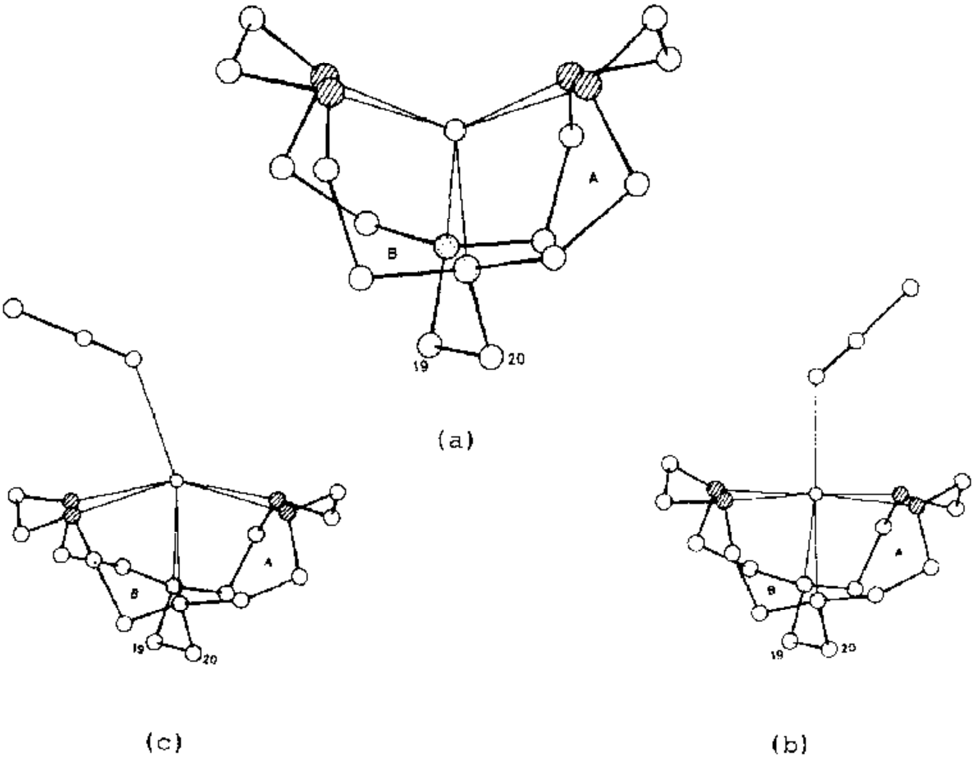
(79)



(80)

1.4.6 Complexes of Macrocyclic Polyimine and Related Ligands

Russian authors have considered the complexation of alkali metal 2,4-dinitrophenolates (M = Li-K,Cs)[252] and of alkaline earth metal iodides (M = Mg,Ca)[253] by the tripodand triaza-[9]-annulene (81). Solution (thf-$CHCl_3$;4/1) studies[252] of the alkali metal complexes using conductometric methods indicate that their stabilities decrease with increasing cation size. Formation constant studies[253] of the alkaline earth metal complexes in organic



(a)

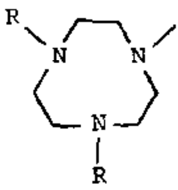
(c)

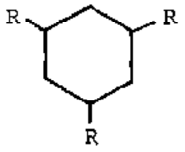
(b)

Figure 6. The molecular geometries around the alkali metal atom in (a) $[(\underline{79})Li]^{+}SCN^{-},\frac{1}{2}H_2O$, (b) $[(\underline{79})Na]^{+}SCN^{-}$, and (c) $[(\underline{79})K]^{+}SCN^{-}$ (reproduced by permission from J. Chem. Soc., Chem. Commun., (1984)1502).

solvents suggest that complex formation involves interaction with not only the phosphoryl groups but also the nitrogen atoms of the macrocycle. Two complexes, $[(\underline{81})_2Mg_3]^{6+}6I^{-},3H_2O$ and $[(\underline{81})Ca]^{2+}2I^{-},3H_2O$ have been isolated from these solutions.[253] In both investigations, the results were compared with analogous data for the ligands, $Ph_2P(O)CH_2P(O)Ph_2$, $Ph_2P(O)CH_2NH(CH_2)_2.NH.$-$CH_2P(O)Ph_2$ and ($\underline{82}$).[252,253]

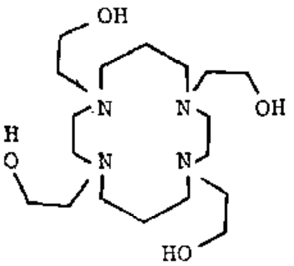
Complex formation between Na^{+} and the tetrapodand tetraaza-[14]-annulene ($\underline{83}$) has been monitored in aqueous solution by ^{23}Na nmr using Dy^{3+} as a shift reagent.[254] The spectra are consistent with the formation of a complex in which three of the arms of the ligand coordinate a Na atom located in the macrocyclic cavity and the fourth arm interacts with Dy^{3+}.[254] An analogous Na atom coordination geometry has been observed previously in the solid phase.[255]





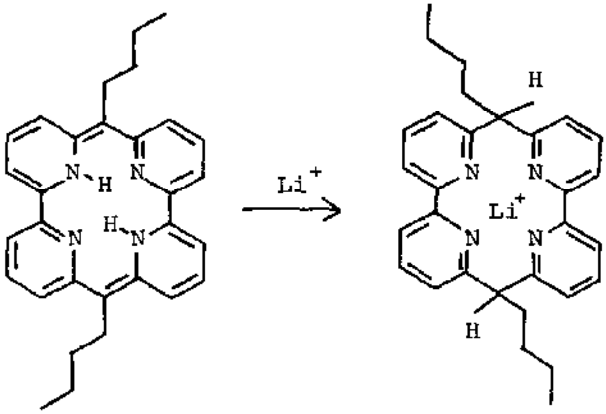
R = $-CH_2P(O)Ph_2$

(81) (82)



(83)

A tetraaza-[1,4]-annulene (84) that selectively binds Li^+ with a concomitant colour change has been synthesised.[256] Addition of solid LiCl to the red solution of (84) in CH_2Cl_2 results in its decolourisation. Incorporation of Li^+ into the cavity of the macrocycle, induces proton transfer from nitrogen to bridging carbon and hence reduction of the ligand's conjugated π-system (85). Neither sodium, potassium nor alkaline earth metal salts are capable of effecting this spectral change.[256]

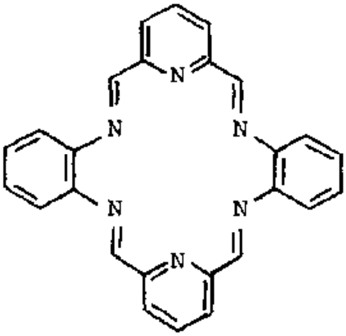


(84) (85)

^1H-nmr studies of the $KClO_4$ complex of the hexaaza-[18]-annulene (86) indicate that the stability of $[(86)K]^+ClO_4^-$ is an order of magnitude greater than that of the corresponding 18C6 complex in the same solvent (dmso).[257]

Novel complexes, $[(87)Mg]^{2+}(ClO_4)_2^-,2H_2O$ and $[(88)Mg]^{2+}(ClO_4)_2^-,H_2O$ have been isolated and identified by field desorption mass spectroscopic methods.[258] It is inferred that the Mg atom is located in cavities formed by just four of the nitrogen atoms of the pentaaza-[17]- and hexaaza-[14]-annulenes; incorporation of the water molecules into the Mg coordination sphere is also thought to be possible.

The crystal and molecular structures of the magnesium tetraphenylporphyrin complexes, MgTPP(1-methylimidazole)$_2$, MgTPP(4-picoline)$_2$ and MgTPP(piperidine)$_2$ have been reported.[259] All three complexes exhibit distorted octahedral Mg coordination spheres with the four nitrogen atoms of the tetraaza-[16]-annulene in the equatorial positions and the nitrogeneous bases in



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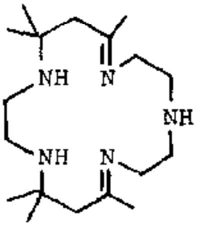

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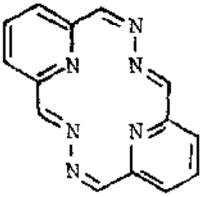


(88)

the axial positions. Compared with the Mg-N equatorial bond distances, which fall in a very limited range (206.9-208.2pm), the Mg-N axial bond distances are long, varying from 229.7pm (for 1-methylimidazole) through 238.6pm (for 4-picoline) to 241.9pm (for piperidine).[257]

1.4.7 Salts of Carboxylic and Thiocarboxylic Acids.

A significant number of papers, have been abstracted, mainly from Acta Crystallographica, for this subsection. They are concerned exclusively with structural chemistry, four lithium,[260-263] seven sodium,[264-269] four potassium[266,270-272] and a single caesium salt[273] being considered. The salts studied are listed in Table 13 which also incorporates pertinent features of the cations' coordination spheres. Whereas the coordination number of Li$^+$ is exclusively 4, for Na$^+$ it is either 5 or 6, for K$^+$ it ranges from 6 to 8 and for the single Cs$^+$ example it is 8. Although in anhydrous salts the cations are normally coordinated by either the carboxylate oxygen atoms or the thiocarboxylate sulphur atoms, as appropriate, a preference for coordination by water molecules is shown in the hydrated

Table 13. Pertinent features of the cation coordination spheres in a number of salts of carboxylic and thiocarboxylic acids.

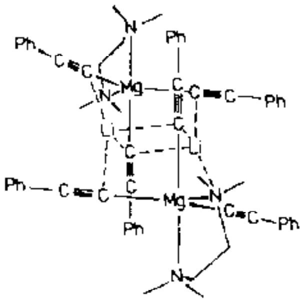
Structural Formula	Cation Unit	Coordination Geometry	Interatomic Distances/pm			Ref.
			Anion		Water	
			M...O	M...X	M...O	
$[HO_2C(CH_2)_4CO_2]Li$	LiO_4	dist. T_d	189.6-197.7	-	-	260
$[(CH_3)_2NCS_2]Li,4H_2O$	LiO_4	dist. T_d	-	-	190.7-195.4	261
$[(C_2H_5)_2NCS_2]Li,3H_2O$	LiO_4	dist. T_d	-	-	189.5-204.9	262
$[(C_3H_7)_2NCS_2]Li,3H_2O$	LiO_4	dist. T_d	-	-	187.0-203.1	263
$[HO_2C.CO_2]Na,H_2O$	NaO_6	irregular	235.2-244.3	-	230.7,238.3	264
$[HO_2C.CH{=}CH.CO_2]Na,3H_2O$	NaO_6	dist. O_h	237.4-244.6	-	237.6	265
$[HO_2C(CH_2)_2.CO.CO_2]Na$	NaO_6	dist. O_h	235.5-260.5	-	-	266
$[HOCH_2(CHOH)_4CO_2]Na$	NaO_6	dist. O_h	234.0-254.0	-	-	267
$[HN(CH_2CO_2)_3]Na_2$	NaO_6	O_h	230.4-243.2	-	-	268
	NaO_6	O_h	241.6-251.2	-	-	
$[N(CH_2CO_2)_3]NaZn,H_2O$	NaO_5	irregular	224.2-241.0	-	231.0	268
$[S_2C.N\bigcirc N.CS_2]Na_2,6H_2O$	NaO_4S	dist. O_h	-	299.0(X=S)	231.6-245.0	269
$[PhSCH_2CO_2]K,PhSCH_2CO_2H$	KO_7	irregular	272.9-303.4	-	-	270
$[HO_2C(CH_2)_2.CO.CO_2]K$	KO_8	irregular	274.7-301.3	-	-	266
$[SC(CH_3)_2CH(NH_2)CO_2]K_2,3H_2O$	KO_5N	dist. O_h	268.4-293.3	296.5(X=N)	268.3,282.7	271
	KO_6	dist. D_{3h}	274.6-288.7	-	287.6,291.7	
$[S_2C.NH.NH.CS_2]K_2,4CH_3OH$	KO_4S_4	D_{4d}	-	341.2,342.6(X=S)	276.6,292.0 (methanol)	272
$[\overline{CH(CO_2)\{CH(CO_2H)\}_3O}]Cs$	CsO_8	irregular	300.9-334.2	-	-	273

materials.

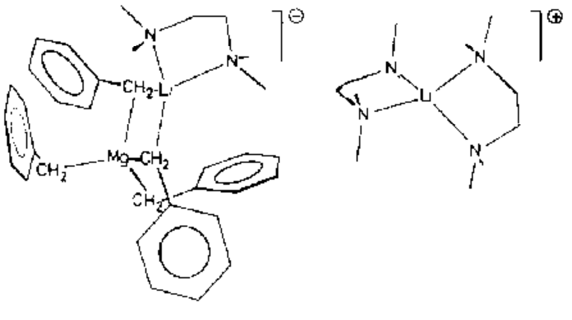
1.4.8 Heterobimetallic Complexes containing Alkali Metals

A significant number of heterobimetallic complexes containing lithium[274-278] and sodium[279,280] have been isolated. In every instance they have been structurally characterised using single crystal XRD methods.

The Li-Mg complexes, $[Li_2Mg_2(tmeda)_2(PhC{\equiv}C)_6]$ (89) and $[Li(tmeda)_2]^+[LiMg(tmeda)(C_6H_5CH_2)_4]^-$ (90) have been synthesised[274] by reaction of PhC≡CLi with $(PhC{\equiv}C)_2Mg$ in the presence of tmeda and by reaction (273K) of EtLi with Et_2Mg and toluene in hexane solution containing tmeda. The asymmetric unit of (89) is centrosymmetric.[274] The Li atom is surrounded by four carbon atoms of separate acetylide molecules; two bridge to Li (r(Li...C) = 230.1,231.5pm) and two bridge to Mg (r(Li...C) = 225.7,234.2pm) in a distorted tetrahedral arrangement. The Mg atom is coordinated by three carbon atoms of separate acetylide molecules, (r(Mg...C) = 218.3,218.8,230.7pm) all of which bridge to Li, and the two nitrogen atoms of a tmeda molecule (220.2, 235.0pm) in a distorted trigonal pyramidal geometry. The structure of (90) contains clearly separated $[Li(tmeda)_2]^+$ cations and $[LiMg(tmeda)(C_6H_5CH_2)_4]^-$ anions.[274] The Li atom in the cation is surrounded by the four nitrogen atoms of two tmeda molecules (207.6-221.3pm) in a distorted tetrahedral configuration. The anion is based on a LiCMgC ring containing bridging benzyl molecules (r(Li...C) = 222.9,227.2; r(Mg...C) = 231.3,232.2pm) with the approximately tetrahedral coordination geometries of the metal atoms being completed by (for Li) the two



(89)



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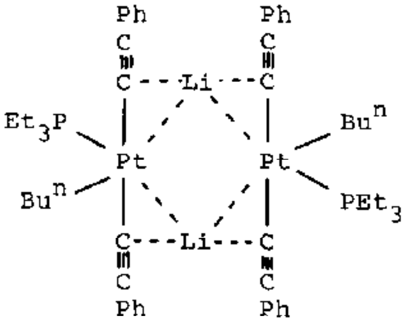

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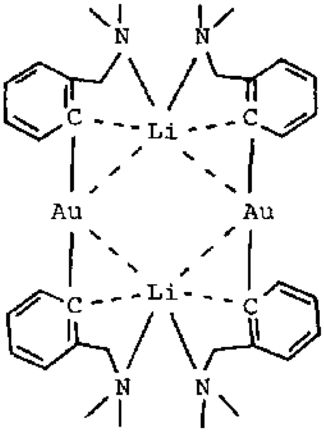

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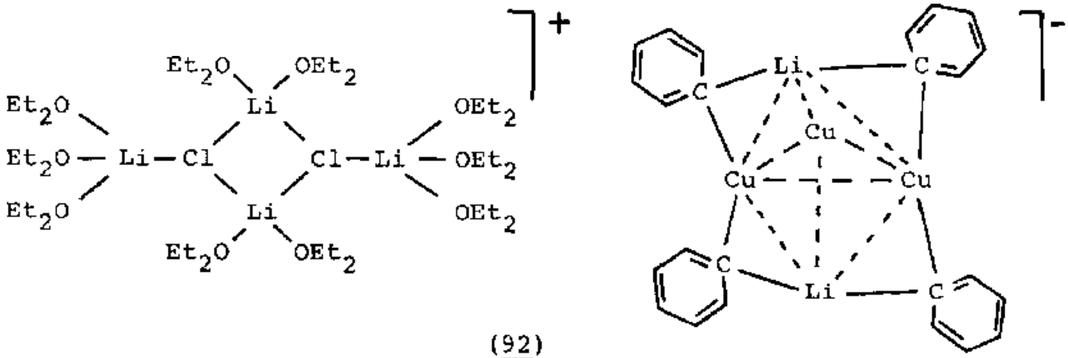
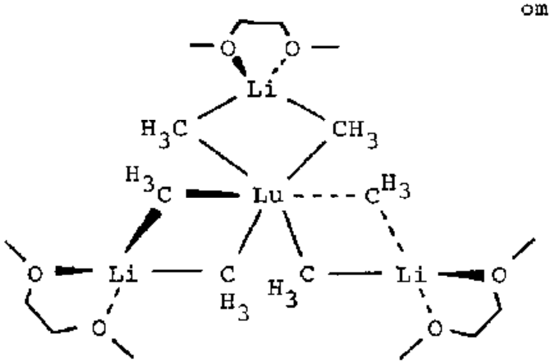


(92)

Two phenyl groups have been omitted for clarity



(94)

nitrogen atoms of a tmeda molecule (210.9,216.7pm) and (for Mg) the carbon atoms of two terminal benzyl molecules (222.5,226.3 pm).[274]

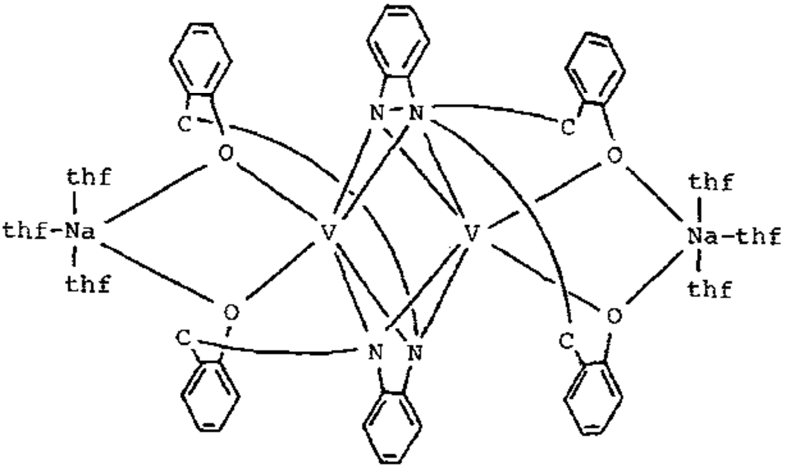
Treatment of $[(PhC{\equiv}C)_2Pt(PEt_3)_2]$ with Bu^nLi results in loss of one equivalent of PEt_3 and formation of the Li-Pt complex $[Li_2Pt_2(PEt_3)_2(PhC{\equiv}C)_4Bu^n{}_2]$ (91).[275] The bonding in this material, which does not exhibit a centre of symmetry, is complex. Close contacts occur between the Li atoms and both the Pt atoms (average r(Li...Pt) = 280.7pm) and the acetylenic carbon atoms (average r(Li...C) = 215.5pm). The relative significance of the Li-Pt and Li-C interactions is as yet unresolved, despite a detailed multinuclear nmr (^{1}H, ^{7}Li, ^{13}C, ^{31}P, ^{195}Pt) study of this, and several related, complexes.[275]

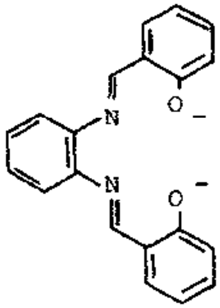
Addition of PhLi to CuCN in ether at 253K yields yellow crystals of the Li-Cu complex, $[Li_4Cl_2(Et_2O)_{10}]^{4+}[Li_2Cu_3Ph_6]_2^{2-}$ (<u>92</u>).[276] The cation consists of a planar Li_2Cl_2 core (250.5,253.7pm) each Cl atom also being coordinated by a terminal Li atom (269.7pm). All the Li atoms are four coordinate due to the presence of either two or three ether molecules (average r(Li...O) = 196pm). The anion is based on a trigonal bipyramid containing two Li (axial) and three Cu(equatorial) atoms, each Li-Cu vector being bridged by a phenyl group (typical r(Li...C) = 224.0; typical r(Cu...C) = 192.9pm). The Li atoms are essentially three coordinate, the sites along the 3-fold axes of the Li_2Cu_3 cluster being blocked by protons of the phenyl group.[276]

The structure of the Li-Au complex, $[Li_2Au_2(Me_2NC_6H_4CH_2)_4]$ (<u>93</u>),[277] for which no preparative details are given, is comparable to that of the Li-Pt complex (<u>91</u>). Close contacts occur between the Li atoms and both the Au atoms (typical r(Li...Au) = 286, 290 pm) and the ipso carbon atoms of the aryl anion (typical r(Li...C) = 245,258pm). Although the relative significance of these two interactions is still uncertain, multinuclear nmr (^{1}H, ^{13}C, ^{6}Li, ^{7}Li) studies of $[Li_2M_2(Me_2NC_6H_4CH_2)_4]$ (M = Cu,Ag,Au) in solution indicate that the carbon sp^2 lone pair of the aryl anion interacts with both Li and M atoms.[277] The Li coordination sphere is completed by nitrogen atoms (average r(Li...N) = 224pm) of two pendant amine groups.

Reaction of MeLi with $LuCl_3$ in ether containing 1,2-dme gives $[Li_3Lu(dme)_3(CH_3)_6]$ (<u>94</u>).[278] Structural analysis shows it to contain an octahedral $Lu(CH_3)_6$ arrangement bridged to each of the three Li atoms via two methyl groups (202-219pm), the distorted tetrahedral geometry of each Li atom being completed by a bidentate chelating 1,2-dme molecule (194-214pm).[278]

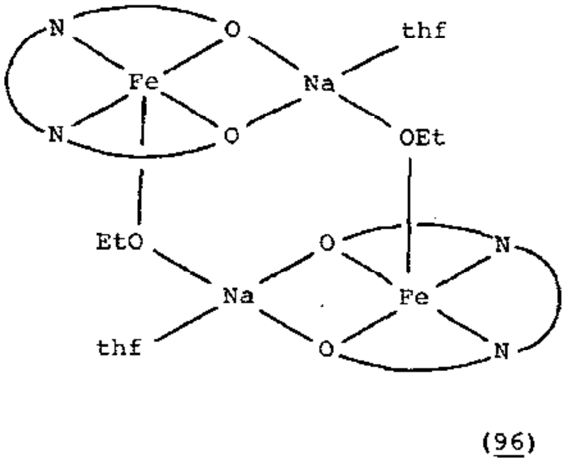
Na-V and Na-Fe heterobimetallic complexes have been synthesised and characterised by Floriani et al[279,280] using tetradentate Schiff bases (salophen or acacen) to stabilise the metal cluster. The Na-V complex $[Na_2V_2(salophen)_2(thf)_6]$ (<u>95</u>)[279] was prepared by reduction of [V(salophen)(thf)Cl] with sodium metal. The approximately trigonal bipyramidal Na coordination sphere is composed of the two oxygen atoms of a salophen molecule (equatorial; 228.0,233.4pm) which bridge to a vanadium atom (199.4,200.3pm) and three thf oxygen atoms (one equatorial, two axial; bond distances not quoted). The two vanadium atoms are bridged by the four nitrogen atoms of the two salophen molecules (205.0-208.7pm) and are joined by a V(III)-V(III) double bond (240.6pm).[279] Reaction of $FeCl_2$ with acacen in the presence of MeONa affords $[Fe(acacen)_2]$ which reacts with EtONa to form the

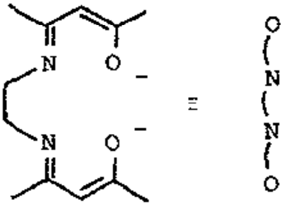




salophen

(95)





acacen

(96)

Na-Fe complex, $[Na_2Fe_2(acacen)_2(thf)_2(EtO)_2]$ (96).[280] It contains two centrosymmetrically related, five coordinate Fe^{II} atoms doubly bridged by EtONa ion pairs. The distorted tetrahedral Na coordination sphere consists of four oxygen atoms provided by the acacen molecule (234.7,235.5pm) the ethoxy anion (224.1pm) and the thf molecule (236.9pm). The approximately square pyramidal Fe coordination geometry is composed of the heteroatoms of the Schiff base (equatorial; r(Fe...O) = 206.2, 207.1; r(Fe...N) = 206.5,209.9pm) and the oxygen atom of the ethoxy anion (axial; 193.1pm).[280]

1.4.9 Lithium Derivatives

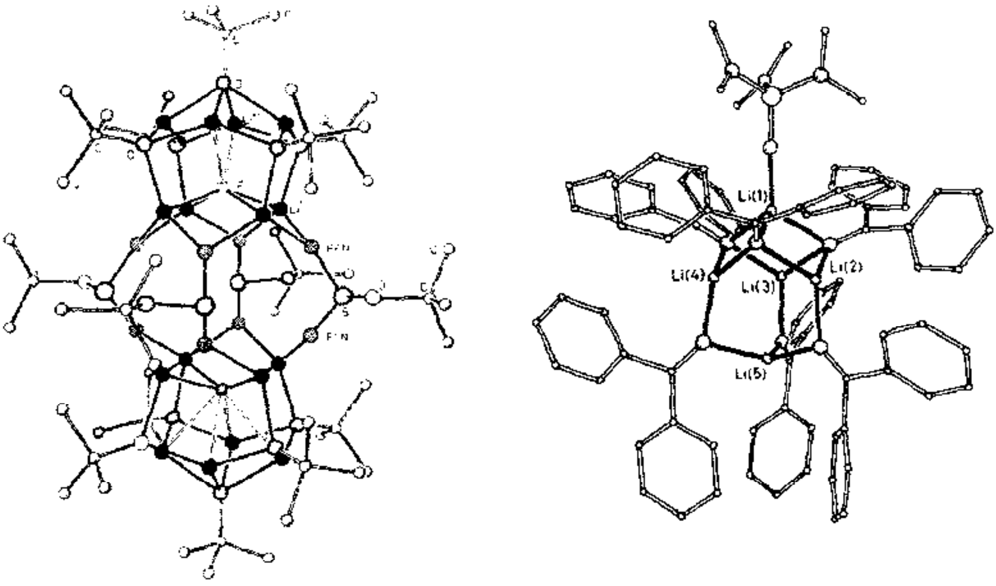
Following the precedent set for the 1983 review,[281] many papers have been abstracted in which the inorganic chemistry of lithium is discussed. Four principle of areas interest can be perceived: (i) theoretical analysis of small molecules containing lithium, including low molecular weight organolithiums, (ii) synthesis of novel heterobimetallic complexes of lithium, (iii) characterisation of lithium containing oligomers, and (iv) structural analysis of diverse monomeric lithium derivatives. The former two topics are considered in subsections 1.3.2 and 1.4.8, respectively, the latter two in the present subsection.

It is important to remind the reader that, with the sole exception of novel structural data, the organometallic chemistry of lithium is not covered here since it is the subject of a separate annual review.

Oligomerisation is currently of great interest to lithium chemists. Reports describing the synthesis and characterisation, principally by single crystal XRD structural methods, of octameric,[282] pentameric,[283] tetrameric,[284-287] trimeric[288] and dimeric[288-302] lithium derivatives have been published. The complex $[Li_8(Me_3COS(N)F)_4F_2][Li_4(OCMe_3)_5]_2,4C_5H_{12}$,[282] which was isolated from a reaction mixture of $N\equiv SF$ and Me_3COLi in n-pentane, contains an unprecedented octanuclear Li_8 cluster. Its structure (Figure 7a) arises from the linkage of two $Li_8(OCMe_3)_5F$ clusters by four $Me_3COS(N)F^-$ anions, which act as bridges. The eight Li atoms form a tetragonal antiprism, bond distances between the inner Li' atoms (Figure 7a), which are bridged by fluorine or nitrogen are 264-270pm, those between the outer Li" atoms (Figure 7a), which are oxygen bridged are 233-243pm, and the Li'-Li" distances lie between 275 and 280pm. The triangular faces of the antiprism are bridged by four Me_3CO groups (r(Li'...O) = 190.1; r(Li"...O) = 188.3pm) and the outer quadrangular face is capped by an additional Me_3CO moiety (r(Li"...O) = 199.1pm). The fluorine atom which bridges the inner quadrangular face lies within the antiprism (Figure 7a) and hence interacts with all the Li atoms (r(Li'...F) = 198.5, r(Li"...F) = 246.4pm).[282]

A novel pentanuclear Li_5 cluster is present in the anion of the complex $[Li(hmpa)_4]^+[Li_5(hmpa)\{N{=}CPh_2\}_6]$[283] which has been crystallised from an ether/toluene solvent mixture containing $[LiN{=}CPh_2]$ and hexamethylphosphoramide (hmpa). The five Li atoms in the anion (Figure 7b) are arranged in a distorted trigonal bipyramidal arrangement such that four Li atoms (Li(2)-Li(5)) form a tetrahedron (average r(Li...Li) = 302pm) while the fifth Li atom (Li(1)), which is bonded to the single hmpa molecule (r(Li...O) = 183pm), caps the face at the base of the tetrahedron but with significantly shorter contacts (average r(Li...Li) = 260pm). Three imido nitrogen atoms bridge the Li_3 faces involving this unique Li atom (average r(Li...N) = 205pm) while the remaining three bridge the Li_2 edges involving Li(5) (average r(Li...N) = 202pm). The structure of the cation is conventional with the Li atom tetrahedrally coordinated by four oxygen atoms (average r(Li...O) = 184pm) of the hmpa molecules.[283]

Tetrahedral Li_4 clusters have been observed in the structures of $[CH_3OCH_2CH_2(CH_3)CHLi]_4$ (<u>97</u>),[284] $[(Ph_2C{=}N)Li.C_5H_5N]_4$ (<u>98</u>),[285] $[LiCl.hmpa]_4$ (<u>99</u>),[285] and $[Bu^t{}_2Si(NH_2)OLi]_4$ (<u>100</u>).[286] In (<u>97</u>),[284] each face of the Li_4 tetrahedron (average r(Li...Li) = 249.0pm) is capped by a μ_3-bridging anion attached at the chiral C(2) atom, to form a pseudo-cubane Li_4C_4 configuration (average r(Li...C) = 231.4pm). In addition each Li atom is coordinated intramolecularly by the pendant oxygen atom of an ether side chain (192.3pm).[284] Similar structures are adopted by (<u>98</u>), obtained by reaction of $[LiN{=}CPh_2]$ with pyridine in hot toluene,[285] and by (<u>99</u>), isolated from the reaction of a 1:1 mixture of $[LiN{=}CBu^t{}_2]$ and hmpa in hexane with 1/3 molar equivalent of $AlCl_3$ in ether.[285] The faces of the tetrahedral Li_4 cluster in the former complex (r(Li...Li) = 257.1-274.6pm) are capped by μ_3-bridging $Ph_2C{=}N$ anions attached at the nitrogen atom (r(Li...N) = 201.9-217.1pm) whereas those in the latter complex (r(Li...Li) = 306.4-312.1pm) are capped by μ_3-bridging Cl atoms (r(Li...Cl) = 235.7-244.1pm) to form pseudocubane Li_4N_4 and Li_4Cl_4 frameworks. In the former complex the coordination sites along the 3-fold axes of the Li_4 tetrahedron are occupied by the nitrogen atom of a donor pyridine



(a) (b)

Figure 7. Molecular structures of (a) the two Li_8 clusters in $[Li_8(Me_3COS(N)F)_4F_2][Li_4(OCMe_3)_5]_2, 4C_5H_{12}$ and of (b) the Li_5 cluster in $[Li_5(hmpa)\{N{=}CPh_2\}_6]^-$ (reproduced by permission from (a) Angew. Chem., Int. Ed. Engl., 23(1984)795, and (b) J. Chem. Soc., Chem. Commun., (1984)220).

molecule (207.5-211.4pm); those in the latter complex are filled by the oxygen atom of a donor hmpa molecule.[285] In (100),[286] prepared by reaction of $Bu^t{}_2Si(Cl)OH$ with NH_3 followed by Bu^nLi, the pseudocubane Li_4O_4 configuration is generated by attachment of μ_3-bridging anions via the oxygen atom (r(Li...O) = 191-211pm) to each face of the Li_4 tetrahedron (r(Li...Li) = 255-262pm). The Li coordination sphere is completed by the amine nitrogen atom of the anion (r(Li...N) = 220-230pm).[286]

The room temperature solution structures of phenyllithium have been established by nmr techniques.[287] In ether-rich, cyclohexane-ether mixtures, it is tetrameric with essentially the same geometry as in the solid state. In cyclohexane-rich solutions, however, tetramers and dimers exist in equilibrium. In thf solutions, it is invariably dimeric.[287]

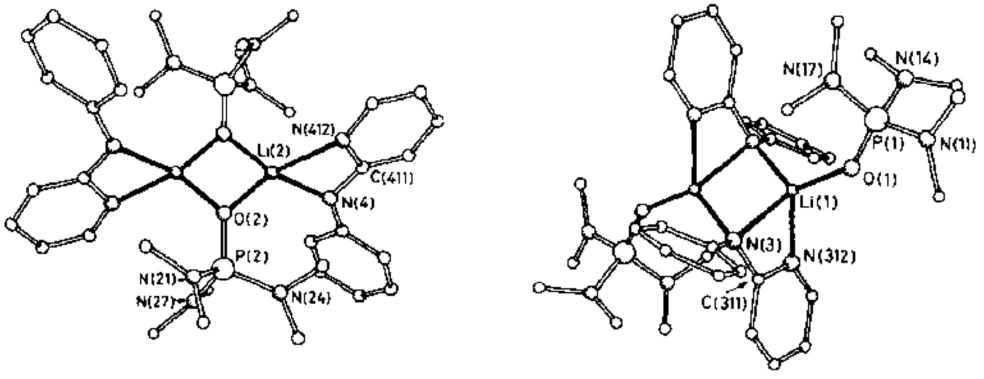
Addition of Bu^nLi in hexane to chilled solutions of $(PhCH_2)_2NH$ in hexane, diethylether-hexane or hmpa-hexane yields trimeric

$[(PhCH_2)_2NLi]_3$ (101), dimeric $[(PhCH_2)_2NLi.OEt_2]_2$ (102) and dimeric $[(PhCH_2)_2NLi.(hmpa)]_2$ (103), respectively.[288] The molecules contain planar Li_3N_3 ((101) — 190.7-203.8pm) or Li_2N_2 ((102) — 198.2-199.1; (103) — 200.1-201.3pm) rings with formal Li coordination numbers of 2 or 3, the third coordination site in the dimers being occupied by either ether ((102) — 200.9pm) or hmpa ((103) — 185.0pm) molecules.[288] In the trimer, however, all the benzyl units bend towards neighbouring Li atoms of the Li_3N_3 ring to give each Li atom contacts to four CH_2 units (average r(Li...C) = 281, average r(Li...H) = 280, to two α-C ring carbon atoms (average r(Li...C) = 280pm) and to two ortho-CH units (average r(Li...C) = 280; average r(Li...H) = 266pm).[288,289] It is suggested[289] that these Li-benzyl interactions are responsible for the changed state of association in the absence of coordinating ligands, in that the decrease in formal Li coordination number from 3 (in 102, 103) to 2 (in 101) may cause the much closer approach of the benzyl units to the Li atoms (in 101) which in turn necessitates expansion to a larger ring system. Spectroscopic studies[289] of the coloured solutions from which these complexes crystallise, are thought to provide evidence for a low association (monomeric) $(PhCH_2)_2NLi$ species which absorbs in the visible region of the spectrum owing to a benzyl → Li charge transfer excitation.

Although no other trimeric lithium derivatives have been studied in 1984, many novel dimers have been prepared and structurally characterised. Of these, one contains a planar Li_2X_2 framework with 3-coordinate Li atoms similar to those in (102, 103). Treatment of 2,4,6-tri-t-butylaniline (NH_2Ar) with Bu^{n}Li in ether yields $[ArNHLi.Et_2O]_2$ (104) in which the Li_2N_2 framework (204.1pm) has ether substituents to complete the Li coordination sphere (190.6pm).[290]

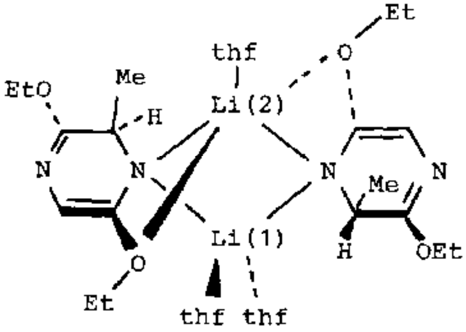
More conventional 4-coordinate Li atoms are found in the Li_2O_2 frameworks of $[Ph_2(O)P\text{-}P\text{-}P(O)Ph_2Li,MeCN]_2$ (105),[291] obtained by degradation of P_4 by $LiOPPh_2$, $[LiCl,dmf,\tfrac{1}{2}H_2O]_2$ (106),[292] prepared by interaction of solid LiCl with neat dmf, $[Li(H_2O)_2,(hmpa)]_2{}^{2+}2Cl^-$ (107),[293] isolated from the reaction of hydrated LiCl and hmpa in toluene, and [Ph(2-pyridyl)NLi,(hmpa)]$_2$ (108),[294] synthesised in the 1:1:1 reaction of 2-anilinopyridine with Bu^{n}Li and hmpa. Whereas the former complex contains a conventional oxygen bridging anion, the latter three complexes exhibit formally neutral oxygen bridging molecules, a previously unknown phenomenon. The centrosymmetric Li_2O_2 ring in (105)[291] is bridged by one of the two oxygen atoms of the $(Ph_2(O)P{-}P{-}P(O)Ph_2)^-$ anion (198.9pm); the other oxygen atom completes the distorted tetrahedral Li coordination sphere (185.0pm) together with the nitrogen atom of an acetonitrile molecule. The two Li atoms of the Li_2O_2 ring of (106),[292] which contains bridging dmf molecules, are crystallographically distinct; whereas Li(1) is surrounded by the bridging oxygen atoms (195.2, 198.4pm), a chlorine atom (236.1pm) and a water molecule (190.4 pm), Li(2) is associated with the bridging oxygen atoms (194.9, 197.5pm) and two chlorine atoms (234.1,234.7pm). The Li_2O_2 frameworks of (107)[293] and (108)[294] are centrosymmetric with bridging hmpa molecules. The Li atom in (107) is coordinated by two bridging oxygen atoms (198.4,201.3pm) and two water molecules (193.6,194.0pm).[293] That in (108) is surrounded by the two bridging oxygen atoms (average r(Li...O) = 192.4pm) and the two nitrogen atoms of a bidentate anion (198.3,217.2pm),[294] The structure of the latter complex (Figure 8a) is of particular interest because it is one of two entirely different structural isomers. The structure of the alternative isomer (Figure 8b) is based on a centrosymmetric Li_2N_2 framework, the amido nitrogen atoms of the anions providing the bridging atoms (average r(Li...N) = 214.2pm). The terminal positions of the distorted tetrahedral coordination geometry of the Li atom are occupied by a pyridyl nitrogen atom of the anion (205.5pm) and an oxygen atom of the hmpa molecule (187.0pm).[294] In the presence of excess 2-anilinopyridine, neither of the dimeric isomers is found. The product, [Ph(2-Pyr)NLi,Ph(2-pyr)NH,hmpa],[304] is a monomeric species in which the 4-coordinate Li atom is surrounded by the two nitrogen atoms of the anion (209.1,211.1pm), the pyridyl nitrogen atom of a neutral 2-anilinopyridine molecule (207.8pm) and the oxygen atom of a hmpa molecule (181.5pm). The protonated ligand forms a hydrogen bond to the amido nitrogen atom of the anion resulting in a short Li-H contact (251.6pm).[304]

Another two dimers based on Li_2N_2 frameworks for which structural data are now available are the lithiated bis-lactim ether of the diketopiperazine from alanine (109),[295] and the lithium complex derived by metallation of $2\text{-}(Me_3Si)CH_2C_5H_4N$ (110).[296] The Li atoms in (109), although lying on an



(a) (b)

Figure 8. Molecular structures of (a) the μ_2-O-isomer and (b) the μ_2-N-isomer of $[Ph(2\text{-}pyr)NLi,hmpa]_2$ (reproduced by permission from J. Chem. Soc., Chem. Commun., (1984) 700).



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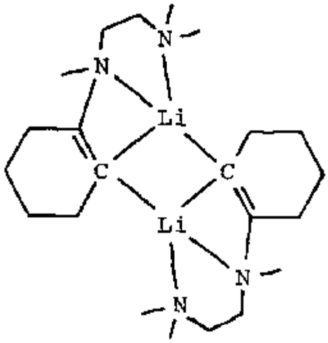

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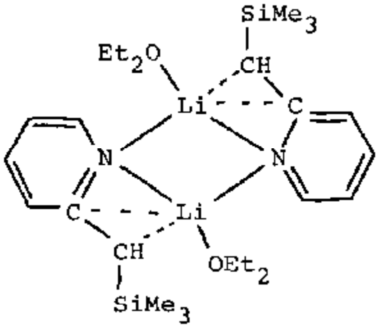


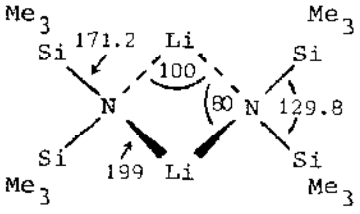
(110)

approximate 2-fold axis are crystallographically distinct. Whereas Li(1) is coordinated by the two bridging nitrogen atoms of the anions (205,206pm) and two thf oxygen atoms (198,198pm) in an approximately tetrahedral geometry, Li(2) is surrounded by the two bridging nitrogen atoms (204,206pm), a single thf oxygen atom (192pm), and the two oxygen atoms of the ethoxy moieties attached to the heterocycles in the 2-position (224,225pm) to form a distorted square pyramidal geometry.[295]

In the centrosymmetric structure of (110),[296] the anion adopts a novel η^3-azaallyl ligand geometry (r(Li...N) = 219, r(Li...C) = 234,236pm), the nitrogen atom bridging to the related Li atom (204pm). The coordination geometry of the Li atom is completed by an ether oxygen atom (191pm).[296]

The only Li_2C_2 4-membered ring structurally characterised this year is that which forms the basis of the dimeric vinyllithium derivative N-(2-lithiocyclohexenyl)-N,N',N'-trimethyl-1,3-propane diamine (111).[297] The bridging carbon atoms are provided by the cyclohexenyl ring (216,220pm) and the four-coordinate geometry of the Li atom is completed by the two nitrogen atoms of the pendant diamine side chain (205,210pm).[297]

Lappert et al[298-300] have synthesised the two lithiated trimethylsilyl derivatives $[(Me_3Si)_2NLi]_2$ (112) and $[\{(Me_3Si)_2CH\}_2PLi]_2$ (113). Whereas the former (112) has been structurally characterised in the gas phase using electron diffraction methods,[298,299] the latter (113) has been studied in the solid phase using conventional XRD techniques.[300] Structurally similar, they are dimeric with Li_2X_2 frameworks, none of the Li atoms bearing any other substituents. Although the Li_2N_2 ring exhibits D_2 symmetry,[298,299] the Li_2P_2 ring has no



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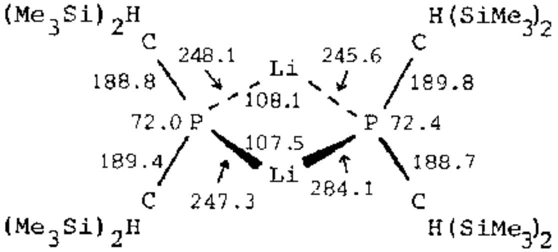
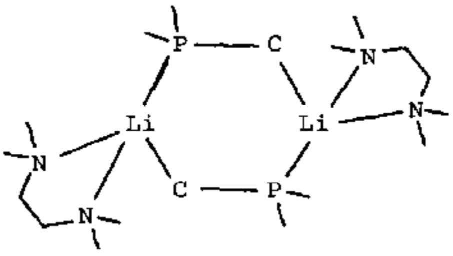


(113)

distances/pm; angles/°

apparent symmetry.[300]

The crystal and molecular structures of the related lithiated phosphine complexes $[\mathrm{Me_2PCH_2Li,tmeda}]_2$ (114)[301] and $[(\mathrm{Me_2P})_3\mathrm{CLi,thf}]_2$ (115)[302,303] have been reported by two independent groups. White et al[301] have shown that (114) is a dimer with a simple $\overline{\mathrm{LiCPLiCP}}$ ring structure. Thus the Li atoms are coordinated by a carbon atom (r(Li(1)...C) = 214.1, r(Li(2)...C) = 215.0pm) and a phosphorus atom (r(Li(1)...P) = 261.5, r(Li(2)...P) = 259.3pm) from separate bridging anions and by the two nitrogen atoms of a bidentate tmeda molecule (r(Li(1)...N) = 216.9,221.6, r(Li(2)...N) = 217.7,221.8pm) in a distorted tetrahedral geometry.[301] Karsh, Muller et al[302,303] have ascertained that $[(\mathrm{Me_2P})_3\mathrm{CLi,thf}]_2$ is also a dimer, but in this case, despite the centrosymmetric structure, the bridging



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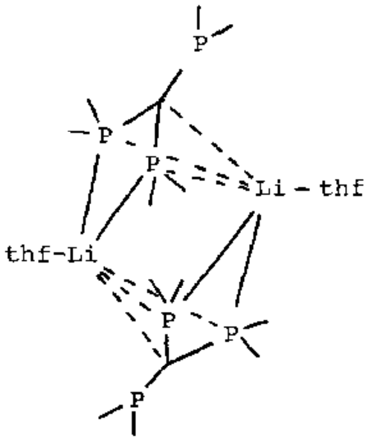


(115)

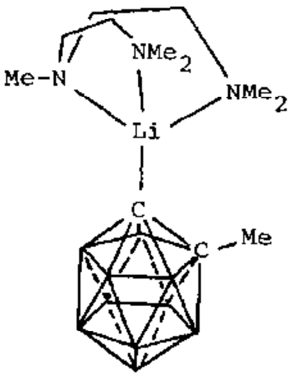
conformation is much more complex (115). Each Li atom is bonded to the oxygen atom of a thf molecule (192.3pm) and to the phosphorus atoms of two phosphino groups of one $[(\mathrm{Me_2P})_3\mathrm{C}]^-$ anion (258.8,268.4pm). The pseudo-tetrahedral Li coordination sphere is completed by an η^3-contact ion pair interaction with the carbanionoid centre of the second anion.[302,303]

Several monomeric lithium complexes have been structurally characterised. They fall into two categories: those with conventional σ-bonded ligands only and those also containing η^n-bonded ligands. With two exceptions, namely the 3- and 6-coordinate Li atoms in $[2,4,6\text{-}\mathrm{Bu^t{}_3C_6H_2NHLi,tmeda}]$ (116)[298] and

$[(PhMe_2Si)_3CBH_3Li,(thf)_3]$ (117),[305] respectively, 4-coordinate Li atoms are found in the former compounds;[304,306-309] in the latter complexes, however, higher coordination numbers are generally favoured.[296,310-315] The Li atom in (116) is simply attached to the anilino nitrogen atom of the anion (189.5pm) and the two nitrogen atoms of a bidentate tmeda ligand (213.7,216.5pm).[298] That in (117) is located on the three-fold axis of symmetry, $(Me_3Si)_3C$-B-Li$(thf)_3$, implying tridentate coordination of the Li atom by the hydrogen atoms of the alkyltrihydroborate moiety; in conjunction with the three oxygen atoms of the thf solvate molecules (average r(Li...O) = 200pm) this gives a distorted octahedral coordination sphere. If the hydrogen atoms are ignored (they were not located owing to the relatively poor quality of the diffraction data) the Li atom is situated in a pseudo-tetrahedral coordination geometry comprising the thf oxygen atoms and the boron atom of the anion (219pm).[305]

Four-coordinate Li atoms have been observed in the cations of $[Li(thf)_4]^+[\{(Me_3Si)_3C\}_2Ag]^-$[306] and $[Li(tmeda)_2]^+[(C_5H_5)Lu(CH_3)_3]^-$[307] and in the molecular species, $[C_2B_{10}H_{10}MeLi,pmdeta]$ (118),[308] [Ph(2-pyr)NLi,Ph(2-pyr)NH,hmpa] (119),[304] and $[Me_2Al(CH_2PMe_2)_2Li,tmeda]$ (120).[309] The structures of the cations are conventional and need not be discussed further.[306,307] Those of the molecular species, however, are novel. Both the dicarbadodecaborane[308] and phosphinomethyl substituted aluminate[309] derivatives exhibit mirror symmetry. In the former complex (118),[308] the Li atom is bonded to a six coordinate carbon atom (217.6pm) of the carborane unit and to the three nitrogen atoms of a tridentate pmdeta molecule (213.4,216.9 pm). In the latter complex (119),[309] the Li atom has a distorted tetrahedral coordination geometry provided by the two phosphorus atoms of the chelating anion (260.5pm) and the two nitrogen atoms of the bidentate tmeda molecule. The structure of the monomeric 2-anilinopyridine derivative [Ph(2-pyr)NLi,Ph(2-pyr)NH,hmpa][304] is compared to that of the corresponding dimeric complex $[Ph(2$-$pyr)NLi,hmpa]_2$[294] earlier in this section.

The classical example of a lithiated compound containing a η^n-bonded ligand is cyclopentadienyllithium. Ab initio SCF MO calculations[310] have shown that the hydrogen atoms on this molecule are bent away from the lithium atom to a significant degree (1.9° using the 4-31G** basis set level) thereby increasing



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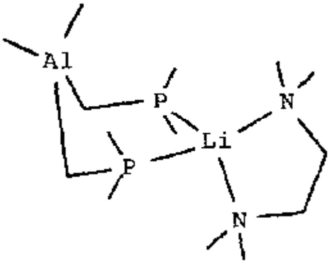
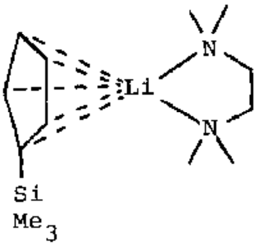


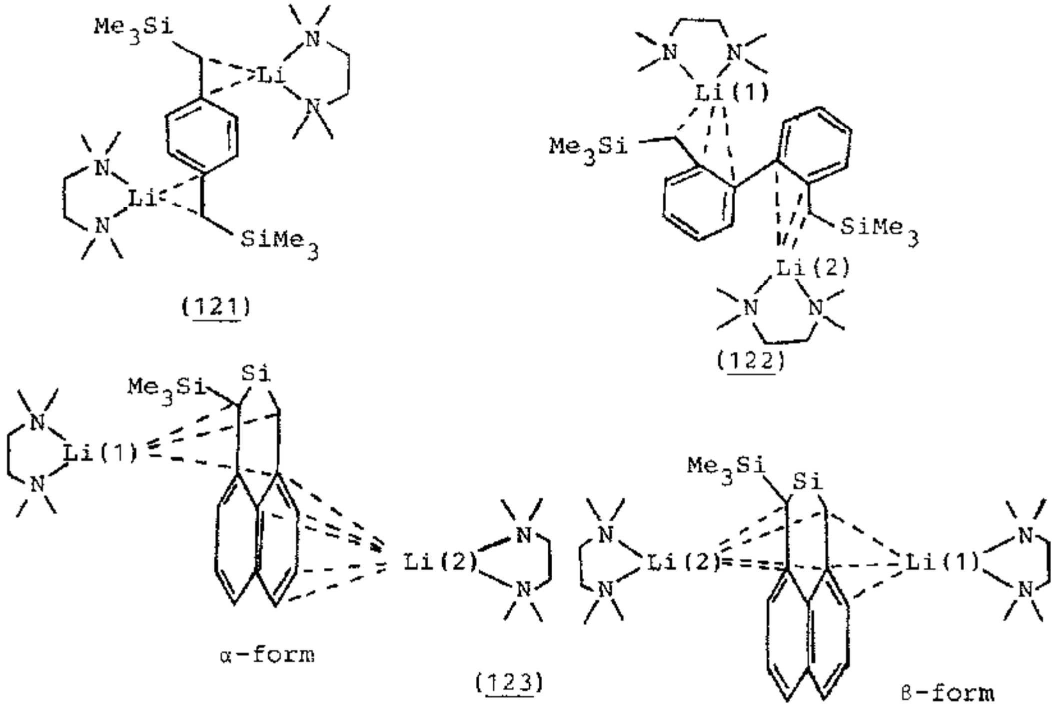
(119)

the negative charge on the side of the ring adjacent the Li atom. These results imply that (η^5-C_5H_5)Li is an ion pair and that the binding therein is essentially a Coulombic effect of the Li^+ cation.[310] Structural analysis of the cyclopentadienyllithium derivative, [η^5-$C_5H_4SiMe_3Li$,tmeda] (120),[311] synthesised by addition of an equimolar mixture of Bu^nLi and tmeda in n-hexane to trimethylsilylcyclopentadiene and recrystallised from n-pentane, has shown that the Li atom has a pseudo-trigonal planar coordination sphere with bonds to the centroid of the planar η^5-$C_5H_4SiMe_3$ ring (r(Li...C) = 225.7-228.6pm) and to the two nitrogen atoms of the bidentate tmeda molecule (211.9,214.2 pm).



(120)

Figure 9. Schematic representation of the structures of the lithiated trimethylsilyl derivatives of 1,4-xylene (121),[312] 2,2'-dimethylbiphenyl (122)[313] and 1,8-dimethylnaphthalene (123).[314]



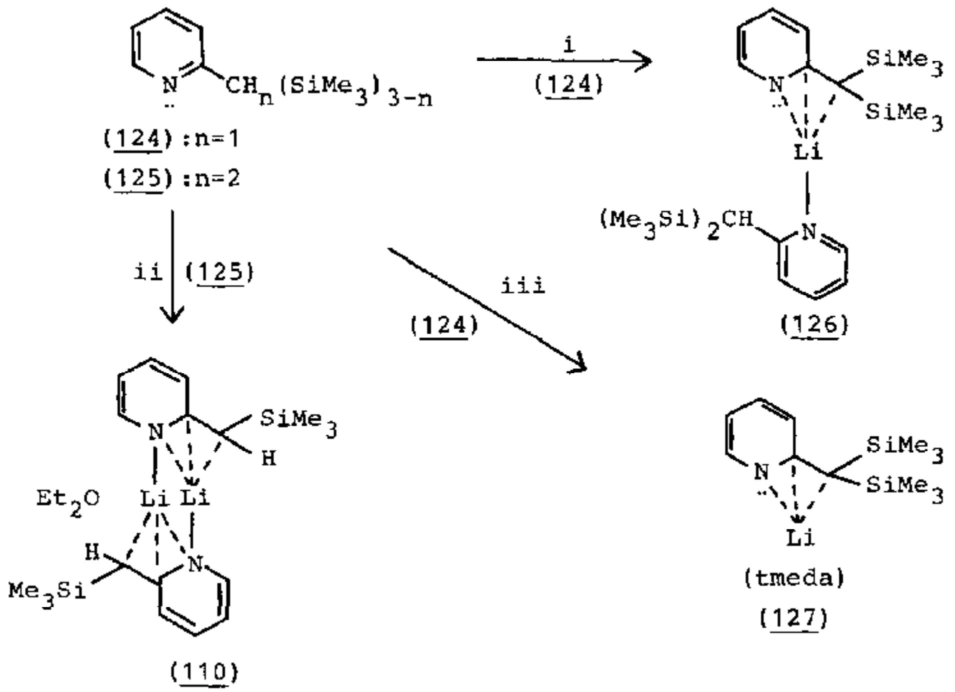
Pertinent interatomic distances/pm in (121)-(123):

	(121)†	(122) Li(1)	(122) Li(2)	α-(123) Li(1)	α-(123) Li(2)	β-(123) Li(1)	β-(123) Li(2)
r(Li...tmeda)	204	204	204	213	208	*	*
	206	210	210	218	212	*	*
r(Li...η^nC_n)	210	219	222	235	234	212	224
	238	233	242	246	240	217	239
		248	263	251	243	219	249
					243		264
					249		
					249		

†centrosymmetric

*Not quoted

Figure 10. Schematic representations of, and synthetic routes to, lithium η^3-azaallyl derivatives (110, 126, 127).[296]



Reagents and conditions: (i) Bu^nLi (ca. 1.6M in hexane); (ii) as for (i) + OEt_2; (iii) as for (i) + tmeda.

Pertinent interatomic distances/pm in (110), (126) and (127).

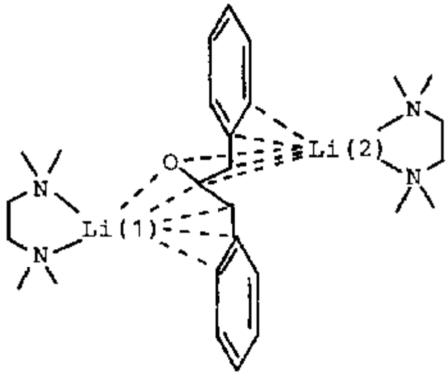
	r(Li...N)	r(Li...η^3C_2N)			r(Li...tmeda)	r(Li...OEt_2)
		N	C	C		
(110)	204	219,	234,	236	-	191
(126)	201	200,	222,	232	-	-
(127)	-	196,	243,	246	206, 207	-

Raston, White et al[312-314] have made a substantial contribution to the study of the chemistry of lithiated complexes of trimethylsilyl derivatives of aromatic materials. As part of their investigation they have determined the crystal and molecular structures of the 1,4-xylene, 2,2'-dimethylbiphenyl and

1,8-dimethylnaphthalene derivatives, $[1,4\text{-}(Me_3SiCH)_2C_6H_4Li_2,(tmeda)_2]$ (121),[312] $[2,2'\text{-}(Me_3SiCH)_2C_{12}H_8Li_2,(tmeda)_2]$ (122)[313] and $[C(SiMe_3)SiMe_2CHC_{10}H_6Li_2,(tmeda)_2]$ (123),[314] respectively. Their structures are shown schematically in Figure 9; the 1,8-dimethylnaphthalene derivative exists in two polymorphic modifications.[314] The asymmetric units of all four structures contain two $[Li(tmeda)]^+$ cations and a single dicarbanion; they differ in the configuration of the contact ion pair interaction. Whereas the two cations in (121)[312] bond to the π-system of the anion by an η^2-interaction, those in (122)[313] interact through an η^3-configuration. The α-polymorph of (123) exhibits η^3- and η^6-configurations; the β-polymorph contains η^3- and η^4-arrangements.[314] Pertinent interatomic distances are summarised in Figure 9.

Raston, White et al[296] have also effected a detailed study of lithium η^3-azaallyl-type complexes derived from the metallation of $2\text{-}(Me_3Si)_{3-n}CH_nC_5H_4N$. Details of the synthetic routes and products are summarised in Figure 10. Metallation of (124) with Bu^nLi in hexane yields the monomeric pyridine adduct (126); in the presence of tmeda, however, the chelating agent replaces the pyridine molecule to form the monomeric tmeda adduct (127). Metallation of (125) with Bu^nLi in hexane-ether mixtures affords the dimeric solvated product (110). [This product has been discussed previously in the section covering dimeric complexes with Li_2N_2 frameworks]. Single crystal XRD structural analysis of the three products has shown them all to contain novel η^3-aza-allyl ligand geometries.[296] Pertinent details are incorporated in Figure 10.

A similar contact-ion pair interaction occurs in lithiated dibenzylketone, $[(C_6H_5CH)_2COLi_2,(tmeda)_2]$ (128).[315] Each of the two crystallographically distinct Li atoms is involved in an η^5-C_4O interaction with the dicarbanion. The pseudo trigonal coordination of the Li atoms is completed by the nitrogen atoms of a bidentate tmeda molecule. Experimental structural data for the contact ion pair interaction were compared with those calculated in a MNDO theoretical study. Although they agreed in principle, they differed in detail; calculated Li-C contacts were too short and the calculated Li-O contact too long.

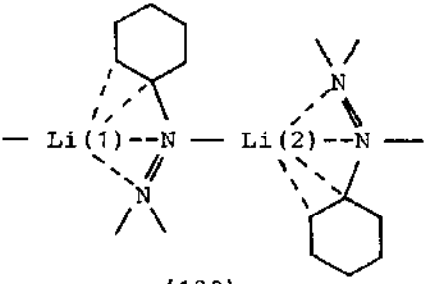


	Li(1)	Li(2)	MNDO
r(Li...C)	215.0	241.5	216.7
	246.9	242.5	225.5
	265.3	250.5	232.6
	273.1	255.0	244.1
r(Li...O)	184.9	187.0	201.3

distances/pm

(128)

Single crystal XRD studies have shown that the three lithiated species, $[C_6H_{10}N{=}NMe_2Li]_n$ (129),[316] $[(2\text{-}CH_2C_6H_4)_2Li_2(\text{tmeda})_2]_n$ (130),[313] and $[(SiMe_3)_2CHLi]_n$ (131),[317] adopt polymeric extended arrays in the solid state. The two crystallographically distinct Li atoms in (129)[316] are coordinated to one anion in an η^4-C_2N_2 configuration (r(Li(1)...C) = 219.6,229.8; r(Li(1)...N) = 206.2,215.6, r(Li(2)...C) = 225.5,229.8, r(Li(2)...N) = 199.5, 217.6pm and to a second anion by a simple Li-N contact (r(Li(1)...N) = 193.4, r(Li(2)...N) = 193.4pm). In the other two compounds (130,131), the Li atom coordination sphere does not involve any η^n-type (n>1) interactions. One of the Li atoms in (130)[313] bridges the two methylene groups of a biphenyl dianion



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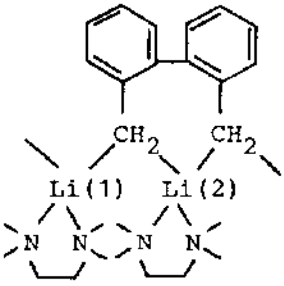

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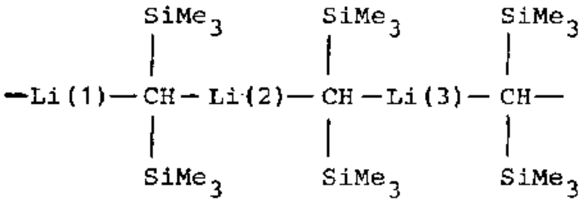

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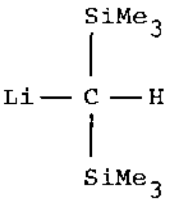


$Li{-}C(SiMe_3)_2{-}H$

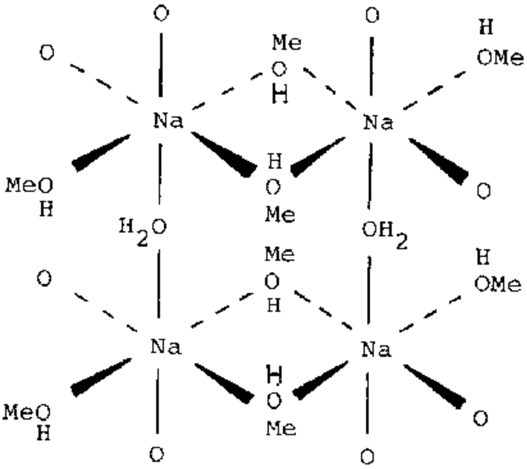
(132)

(r(Li(1)...C) = 216,228pm); the other bridges two methylene groups of adjacent biphenyl dianions (r(Li(2)...C) = 228,246pm). The four-fold, approximately tetrahedral, coordination geometries of the two Li atoms are completed by nitrogen atoms of bidentate tmeda molecules (r(Li(1)...N) = 210,221, r(Li(2)...N) = 214,218 pm). The three Li atoms in the asymmetric unit of (131)[317] simply bridge alkyl groups (r(Li(1)...C) = 214,221, r(Li(2)...C) = 218,222, r(Li(3)...C) = 213,227pm) forming nearly linear 2-fold coordination geometries (C-Li(1)-C = 152°, C-Li(2)-C = 147°, C-Li(3)-C = 151°). This latter compound has also been the subject of a gas-phase electron diffraction study at 413K;[317] it adopts a monomeric configuration (132) with r(Li...C) = 203pm.

1.4.10 Sodium Derivatives

As for previous reviews, the majority of the papers abstracted for this subsection contain novel structural data for diverse sodium salts. The compounds studied fall into two broad classifications; those containing inorganic anions[318-320] and those containing organic anions.[321-325]

Novel tetrameric cations, $[(\mu\text{-}CH_3OH)_4(CH_3OH)_4(\mu\text{-}H_2O)_2Na_4]^{4+}$ (133)[318] have been found in the structure of $[(CH_3OH)_8(H_2O)_2Na_4]^{4+}Mo_8O_{26}{}^{4-}$. They consist of four planar Na atoms, two bridging water molecules (240.8pm), four symmetrically bridged methanol molecules (238.0,238.8pm) and four terminal methanol molecules (233.3pm); the octahedral coordination of the cation is completed by eight oxygen atoms from $Mo_8O_{26}{}^{4-}$ anions (240.3,242.1 pm).

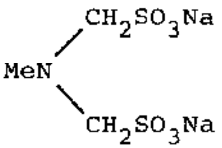


(133)

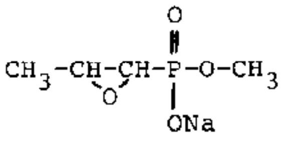
Extended array structures are formed by $[(C_4H_8O_2)Na]^+AsPh_2^-$ (134)[319] and $[(Me_2NCOCMe_2CONMe_2)_2Na]^+ClO_4^-$ (135).[320] The diphenylarsenide salt (134) consists of an alternating sequence of bis(dioxane) coordinated Na atoms (230.7,232.0pm) and Ph_2As anions which gives rise to infinite Na-As-Na-As chains (293.7,296.2pm) parallel to (100). Although nearly linear at arsenic (NaAsNa = 173.6°), the chains are bent at sodium (AsNaAs = 121.5°) resulting in a distorted tetrahedral Na coordination sphere.[319] In the perchlorate salt (135), each bidentate $Me_2NCOCMe_2CONMe_2$ molecule bridges two Na atoms by coordination through oxygen (229.7-232.5pm). The five-fold coordination of the Na atom, which is intermediate between trigonal bipyramidal and square pyramidal, is completed by an oxygen atom of a ClO_4^- anion (237.8pm).[320]

Structural elucidation using single crystal XRD methods have been successfully completed for sodium salts of N-methyliminobis-(methanesulphonic acid) (136),[321] the monomethyl ester of fosfomycin (137),[322] 1-(phospho)glucose (138)[323] and 1-(uridinediphospho)glucose (139).[324] Although six-coordinate Na atoms predominate, five-coordinate Na atoms are found in the fosfomycin and 1-(phospho)glucose salts; coordination geometries are invariably irregular.

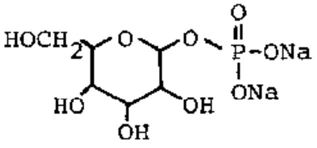
The two symmetry related Na atoms in the sulphonate dihydrate, (136),$2H_2O$[321] are coordinated by four anion oxygen atoms (242.6-252.3pm) and two water molecules (236.1,239.7pm). The structure



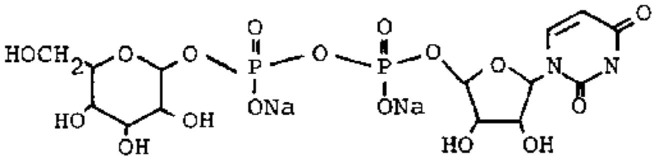
(136)



(137)



(138)

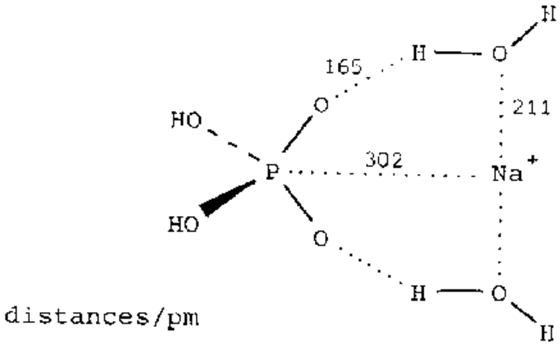


(139)

of the fosfomycin salt, (137),[322] contains two crystallographically independent molecules. In both cases, four short Na-O bonds are formed with oxygen atoms of phosphite groups (r(Na(1)...O) = 227.5-240.3, r(Na(2)...O) = 230.1-236.2pm) and a longer Na-O bond involves the epoxy oxygen atom of a fosfomycin molecule (r(Na(1)...O) = 266.6, r(Na(2)...O) = 261.2pm).

Interactions between phosphate anions and Na^+ ions have been studied both experimentally[323,324] and theoretically.[326] The structures of two 1-(phospho)glucose derivatives have been determined. Very few details of the cation coordination geometries are given in the paper reporting the structure of the disodium salt of 1-(phospho)glucose hydrate, (138),$3.5H_2O$.[323] It contains three crystallographically distinct Na atoms; two are located on 2-fold axes, the other has no apparent symmetry. Two of the Na atoms are six-coordinate, the other is five-coordinate; their coordination spheres comprise both unidentate phosphate anions and water molecules. The structure of the related disodium salt of 1-(uridinediphospho)glucose dihydrate, (139),$2H_2O$,[324] contains two six-coordinate crystallographically distinct Na atoms. Na(1) is surrounded by three oxygen atoms from different anions (229.9-235.6pm), two water molecules (237.0, 263.1pm) and a remote oxygen atom of a fourth anion (299.3pm). Na(2) is coordinated by four oxygen atoms from different anions (230.8-245.6pm), one water molecule (237.9pm) and a remote oxygen atom from one of the four original anions (280.0pm).

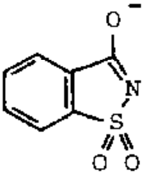
Interactions of the phosphate anion with Na^+ ion in the presence of water have also been studied by ab initio MO theory.[326] The results predict that the most stable structures for $H_2PO_4^-.Na^+.2H_2O$ complexes have the water molecules located partially between the anion and cation (140); these bridging water



(140)

molecules increase the separation between the ions to optimise the water-ion interactions.

The last of the novel structures to be abstracted for this subsection is that of sodium dipotassium trisaccharinate monohydrate.[325] The coordination polyhedra around the three alkali metal atoms (the two K atoms are crystallographically independent) are highly irregular. The Na atom has a six-fold coordination geometry generated by two water molecules (241.2, 284.1pm) and by three oxygen (229.0-235.3) and one nitrogen (253.8) atom of separate anions (141). The two K atoms adopt eight- and six-fold coordination geometries; K(1) is surrounded by one water molecule (292.8pm), five oxygen (274.9-311.3pm) and two nitrogen (288.9,323.6pm) atoms from different anions, while K(2) interacts with five oxygen (259.9-280.2pm) and one nitrogen (287.8pm) atom provided solely by anions.[325]

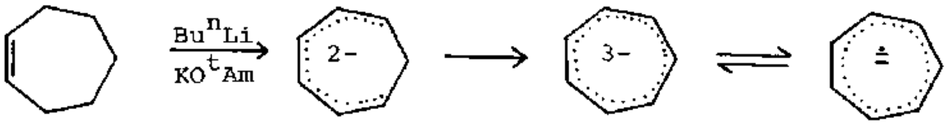


(141)

1.4.11 Potassium, Rubidium and Caesium Derivatives

A limited number of papers pertinent to this subsection were found during the literature search; a total of seven were abstracted for potassium,[327-333] one for rubidium[334] and none for caesium.

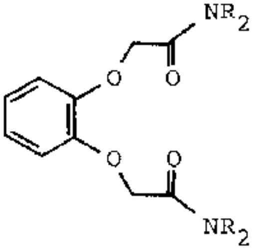
The esr spectrum[327] of the cycloheptatrienyl radical dianion (145) which is in equilibrium with the corresponding trianion (144), generated together with the cycloheptadienyl dianion (143), by the reaction of cycloheptane (142) with a 1:1 n-butyllithium - potassium t-amyloxide mixture is characteristic of the potassium



(142) (143) (144) (145)

rather than the lithium salt. Although this suggests that potassium salts of hydrocarbon anions are favoured, it may be due to preference of lithium for oxygen containing anions.[327]

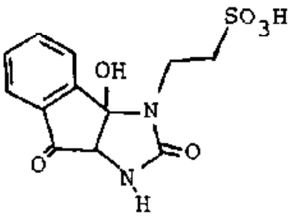
The chelation ability and coordination modes of a number of 1,2- and 1,3-phenylenedioxydiacetamides for K^+ ion have been systematically studied[328] using i.r. and nmr (^1H and ^{13}C) spectroscopy. Only the 1,2-diphenylenedioxydiacetamides (146) function as ligands; they act as tetradentate chelating ligands using all four oxygen atoms to bind the cation.



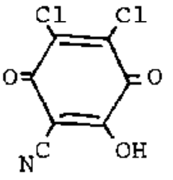
(146)

The structures of five potassium derivatives, pertinent to this subsection, have been determined. They fall into two broad classifications; those in which the K atom is surrounded by chelating ligands[329] and those in which the K atom interacts with organic anions and/or solvent (water) molecules.[330-333] The dimeric cationic moiety in the crystal structure of $[K(phen)_3]_2^{2+}, 2[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ [329] is located on an inversion centre and hence contains cubic K atom coordination spheres. All six o-phenanthroline (phen) molecules act as bidentate chelating ligands; two bridge the K atoms (290.7-334.2pm) and four simply chelate them (283.5-311.7pm).[329]

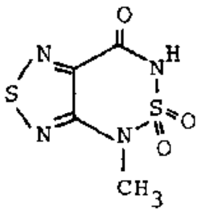
The structures of the monopotassium salts of (147),[330] (148)[331] and (149)[332] and of dipotassium 1,3-dithiosquarate dihydrate (T = 140K)[333] contain KO_6, KO_5N, KO_7 and KO_5S_2 coordination units, respectively. The K-O contacts in the six-coordinate species, r(K...O) = 265.1-287.8pm (KO_6) and 279.8-288.9pm (KO_5N) are considerably shorter than those in the KO_7 unit, average r(K...O) = 291pm, but similar to those in the KO_5S_2 unit, average r(K...O) = 279.5pm. The K-N (282.6pm) and K-S (344.5,346.9pm) contacts in the KO_5N and KO_5S_2 units are typical of these coordination geometries.



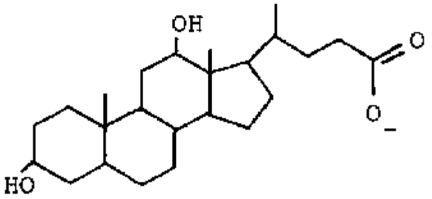
(147)



(148)



(149)



(150)

In the structure of rubidium deoxycholate-water (3/10),[334] the three crystallographically different Rb atoms are surrounded by water molecules and located within the interior of 2_1 helices formed by the anions (150). Rb(1) is linked to six water molecules (294-332pm), the two oxygen atoms of a bidentate carboxylate group (310,337pm) and the oxygen atom of a monodentate carboxylate group (291pm), Rb(2) interacts solely with eight water molecules (291-332pm) and Rb(3) is coordinated by five water molecules (283-333pm), the oxygen atoms of two monodentate carboxylate groups (303,305pm) and the oxygen atom of the hydroxyl group (294pm) of a chelating anion. None of the Rb coordination units have a regular geometry.[334]

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