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Chapter 1

ELEMENTS OF GROUP 1

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1.1 INTRODUCTION

When abstracting data from the literature for an annual review of the chemistry of the alkali and alkaline earth metals it is essential to be selective. Papers considered to be appropriate for inclusion are those in which some unique aspect of the inorganic chemistry of these metals is described. Papers omitted fall into two broad categories - those containing reports of the chemistry of either organometallic derivatives or compounds containing the metals as simple counter cations. The former are not included since they are discussed in detail in separate annual reviews published in the Journal of Organometallic Chemistry, the latter, since the identity of the metal is of little chemical significance.

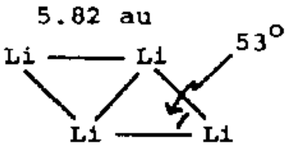
As for the 1982 review,[1] the format of Chapters 1 and 2 is such that the chemistry of both groups of elements is considered in sections which reflect subjects of topical interest and significance. For certain subjects, particularly crown complexes, and related derivatives, the chemistry of the two groups of metals is so closely interwoven that it is appropriate to consider it once only in the relevant section of this Chapter.

1.2 THE ELEMENTS

Interest in the chemistry of the alkali metals is fuelled both by academic curiosity and by technological necessity. Metallic solutions containing the alkali metals are of current interest in the academic world because of the contentious question of the existence of chemical short range order in these solutions. The majority of papers dealing with this subject are published in the Journal of Physics (Section F).[2] Lithium and sodium are also of interest because of their significance in energy production and storage. Whereas lithium is being considered for use as a coolant/tritium breeder in the thermonuclear fusion reactor, sodium is presently used as the heat transfer medium in prototype fast breeder fission reactors. Both metals also find application as electrode materials in battery systems. Papers of relevance to these topics are normally published in the Journal of Nuclear Materials[3] and the Journal of the Electrochemical Society.[4] Not all of the papers published in these three Journals on alkali metal chemistry have been abstracted and included in the following sections, however, since they are often biased towards theoretical physics or structural metallurgy and hence are considered not to be of sufficient interest to the average chemist to warrant inclusion. For a more extensive coverage, the specialist reader is referred to the appropriate Journal.[2-4]

1.2.1 Alkali Metal Cluster Molecules

Several authors[5-7] have reported properties of lithium cluster molecules. Thermodynamic properties of the diatomic lithium molecules, $^{6}Li_2$, $^{6}Li^{7}Li$ and $^{7}Li_2$ have been computed ($100 \leq T/K \leq 2000$) from the latest spectroscopic data.[5] The existence of the stable lithium cluster Li_4 has been proved experimentally by mass spectrometry[6]. From various gas phase equilibria data, the atomisation enthalpies ($D^{o}_{o}(Li_4) = 325.5 \pm 12.6$ kJ.mol^{-1}; $D^{o}_{o}(Li_4^{+}) = 393.3 \pm 20.9$ kJ.mol^{-1}), ionisation enthalpy ($IP(I_4) = 445 \pm 8$ kJ.mol^{-1}) and formation enthalpy ($\Delta H^{o}_{o}(Li_4) = 322.2 \pm 12.6$ kJ.mol^{-1}) have been derived.[6] Ab initio C.I. calculations[7] on Li_4 indicate that the cluster with minimum energy exists in a singlet state and has a planar rhombic geometry (1) reminiscent of the rhombus which is part of the f.c.c. lattice of solid lithium. Similar low energy singlet state configurations (2,3) based on the geometry of the f.c.c. lattice are computed for Li_6, although the most stable Li_6 arrangement (4) has C_{5v} symmetry and a singlet ground state.



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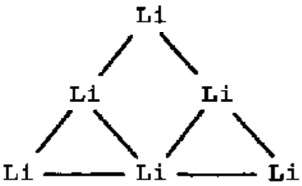

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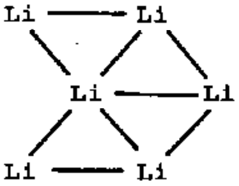

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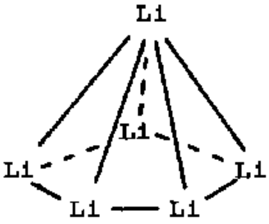


(4)

More compact structures such as tetrahedral Li_4 and octahedral Li_6 are less favoured energetically and have a triplet ground state.[7]

1.2.2 The Alkali Metals as Solvent Media

Three review articles in which different aspects of the solution chemistry of lithium and sodium are compared and contrasted have been published.[8-10] It is stressed in all three articles that it is the presence of dissolved non-metals (carbon, nitrogen, oxygen) which renders these metals corrosive towards stainless steel containment materials. Thus, Chopra[8] concludes that liquid alkali metal environments of controlled purity have little influence on the properties of structural materials, that long term exposure to sodium containing dissolved oxygen or lithium containing dissolved nitrogen results in a substantial degradation of mechanical properties and that carbon transfer (due to either thermal or carbon concentration gradients) gives rise to a loss of structural integrity.[8] Nateson[9] has used free energy of formation data for carbides, nitrides, oxides together with solubility data for the non-metals in the liquid alkali metals and in the structural metals to determine equilibrium distribution coefficients for these non-metallic elements. The types of interactions that occur in the alkali metal/structural metal systems are thus related to the magnitudes of these distribution coefficients.[9] Pulham and Hubberstey[10] report that the products of chemical reactions between transition metals (chromium, iron) and nitrogen dissolved in liquid lithium or oxygen dissolved in liquid sodium are the corresponding ternary nitrides (Li_3FeN_2; Li_9CrN_5) or oxides (Na_4FeO_3; $NaCrO_2$). They also note that these products have been found on stainless steel surfaces exposed to contaminated alkali metals and suggest that these reactions are responsible, in part, for the deterioration in the integrity of structural materials. The data for the lithium-chromium-nitrogen ternary system (750K) are published in much greater detail in a separate communication by Hubberstey et al.[11] The ternary nitride, Li_9CrN_5, was identified as the product of the reactions of particulate chromium and of austenitic stainless steel with nitrogen dissolved in liquid lithium using X-ray powder diffraction and electrical resistivity methods; the minimum nitride activity required for the formation of the product was shown to be less than 0.0025 at 750K.[11] The presence of a Li-Cr-N compound (assumed to be Li_9CrN_5)

has also been observed by Reudl and Sasaki[12] on the surface of a nitrogen alloyed Cr-Mn austenitic steel after immersion in pure lithium at 873K for 1000 hours. Surface analytical techniques, including electron microscopy, X-ray and Auger electron analyses, were used to investigate the effect of lithium grain boundary penetration on the steel in question. As well as the observation of the Li-Cr-N ternary compound, the analysis showed that the complex carbides, $M_{23}C_6$, formed in the grain boundaries rearrange and change their composition in the presence of lithium.[12]

In their review, Pulham and Hubberstey[10] also considered reactions between group 4 elements and nitrogen in both liquid lithium and liquid sodium. In the former solvent, carbon and silicon react with nitrogen to form Li_2NCN and Li_5SiN_3, respectively. In the latter solvent, the product of the reaction between carbon and nitrogen is NaCN; in the presence of barium, however, BaNCN is formed.[10]

Solubility data for chromium,manganese, iron and nickel in liquid sodium have been critically reviewed;[13] particular note was taken of the analytical method, of the effect of oxygen concentration (increasing oxygen content gives rise to increasing solubility values) and of the possibility of the formation of particulates. With the exception of chromium, for which a solubility curve cannot be deduced owing to the diversity of the published data, the recommended solubility equations are:

$$\text{Mn}: \quad \log c_{sat}^{Mn} = 2.325 - 2017/T \qquad \Delta H_{soln} = 38.6\ \text{kJ.mol}^{-1} \quad \ldots(1)$$

$$\text{Fe}: \quad \log c_{sat}^{Fe} = 4.720 - 4116/T \qquad \Delta H_{soln} = 78.7\ \text{kJ.mol}^{-1} \quad \ldots(2)$$

$$\text{Ni}: \quad \log c_{sat}^{Ni} = 2.07 - 1570/T \qquad \Delta H_{soln} = 30.0\ \text{kJ.mol}^{-1} \quad \ldots(3)$$

$$(c_{sat}^{M} - \text{wppm};\ T - \text{K})$$

A density functional approach to the electronic structure of dissolved impurities in liquid alkali metals has been developed.[14] Calculated values of the enthalpy of solution (at constant volume; ΔH_v) of oxygen, fluorine and chlorine in liquid sodium show satisfactory agreement with experimental data (at constant pressure; ΔH_p); the two sets of data are compared in Table 1.

Table 1. Enthalpy of solution data*/kJ.mol^{-1} for non-metallic solutes in liquid sodium.[14]

	O	F	Cl
ΔH_v (calc.)	-405	-558	-617
ΔH_p (exptl.)	-384	-405	-322

* $|\Delta H_p - \Delta H_v| < 20$ kJ.mol^{-1} - the accuracy of the experimental value

The performance of the yttria doped thoria ceramic electrochemical oxygen meter in liquid sodium has been assessed.[15] The emf data obtained in response to oxygen level changes are in good agreement with thermodynamic predictions. The lifetime of the ceramic varies up to 400 days, the major cause of failure being grain boundary attack by oxygen dissolved in the liquid sodium.[15]

A mechanistic study of the reactions between liquid sodium and UO_{2+x} $(0.0 < x < 0.1)$[16] or $U_{1-x}Ce_xO_{2-y}$ $(0.03 < x < 0.80;$ $0.00 < y < 0.03)$[17] has been completed. In the Na-U-O ternary system,[16] reaction at low temperatures results in the formation of Na_2O in the grain boundaries; at higher temperatures, however, the reaction product is Na_3UO_4. The appearance of Na_2O has a more damaging effect on the structural integrity of the ceramic than that of Na_3UO_4.[16] In the Na-Ce-U-O quaternary system,[17] the reaction product could not be identified as either Na_3UO_4 or $NaCeO_2$, the phases in equilibrium with the corresponding ternary systems. It is suggested that compounds of the type $Na_{2-z}(U_{1-x}Ce_x)O_3$, in which the value of z increases with increasing cerium content, are formed in equilibrium with liquid sodium and a reduced oxide solid solution. The value of the Ce/(U+Ce) ratio in both the product and the reduced oxide solid solution is thought to be the same as that in the original oxide solid solution.[17]

Activity data for liquid K-KF solutions $(0.2 < x_{KF} < 0.9;$ $1000 < T/K < 1065)$ have been obtained from novel vapour pressure data.[18] Both a_K and a_{KF} exhibit large positive deviations from ideality in accord with the extensive liquid phase immiscibility region at lower temperatures. Derived excess partial molar functions, $\Delta\bar{G}_i^E$ and $\Delta\bar{H}_i$, are compared with data calculated from a phase diagram analysis; there is surprisingly good agreement between the two sets of data.[18]

The solubility of deuterium in liquid Li-Pb solutions ($0.0 < x_{Pb} < 1.0$; $T < 1100K$) has been determined.[19] It decreases drastically with increasing lead content, Sieverts' Law constant increasing from ca. 10^0 for pure lithium to ca. 10^5 for pure lead. Although the solution process is exothermic for lithium-rich solutions, it is endothermic for lead-rich solutions; the transition occurs close to $x_{Pb} = 0.83$, the composition of the lead-rich eutectic mixture.[19]

1.2.3 Metallic Solutions

The existence of chemical short range order in metallic solutions has been studied both experimentally[20-23] and theoretically.[24-29] Experimental data have been accrued for Cs-Sb,[20] Na-Sn[21] and Na-Pb[22,23] solutions. Neutron diffraction measurements of Cs-Sb ($0.0 < x_{Sb} < 0.5$)[20] and of Na-Sn ($0.0 < x_{Sn} < 1.0$) provide evidence for the presence of both appreciable salt-like ordering and covalently bonded oligomers (of antimony or tin) in the two liquids. Analysis of the Cs-Sb data[20] indicates that the nearest neighbour atomic arrangement in liquid $Cs_{75}Sb_{25}$ is very similar to that in the intermetallic Cs_3Sb. The stability of the compound in the liquid state is such that at low antimony concentrations ($0.0 < x_{Sb} < 0.25$) a microsegregation tendency exists between compound forming regions and excess caesium. At higher antimony concentrations ($0.25 < x_{Sb} < 0.50$) a continuous change in structure occurs as covalently bonded negatively charged Sb_n chains, reminiscent of those in the corresponding CsSb intermetallic compound, are formed.[20] The interpretation of the Na-Sn data,[21] although the work of different authors, is comparable. At low tin concentrations ($0.0 < x_{Sn} < 0.2$) the liquid is similar to a simple ionic mixture with maximum separation between the negatively charged tin atoms. At higher tin concentrations ($0.2 < x_{Sn} < 1.0$), the formation of covalently bound negatively charged Sn_4 tetrahedra (or fragments thereof) similar to those in the intermetallic NaSn, is observed. There is no evidence, however, for a stable compound at $Na_{57}Sn_{43}$ as suggested by electronic behaviour and emf measurements.

Liquid Na-Pb solutions have been studied using both emf[22] and electrical resistivity[23] techniques. Temperature dependent

(575 < T/K < 825) emf data[22] obtained using a concentration cell with a β-alumina electrolyte have been used to derive various thermodynamic parameters. The concentration dependence of the concentration structure factor in the long wavelength limit, $S_{CC}(0)$, which is considered by many to be potentially one of the best quantities to indicate chemical short range order in liquid metal solutions, exhibits three kinds of atomic associations at the compositions of $Na_{80}Pb_{20}$, $Na_{50}Pb_{50}$ and $Na_{20}Pb_{80}$ (Figure 1(a)). The temperature dependent (600 < T/K < 823) electrical resistivity data, however, are consistent with the existence of chemical short range order at $Na_{80}Pb_{20}$, the composition of the intermetallic $Na_{15}Pb_4$. The concentration dependence of the resistivity and of its temperature dependence exhibit a maximum and a negative minimum, respectively, at this particular composition (Figure 1(b).

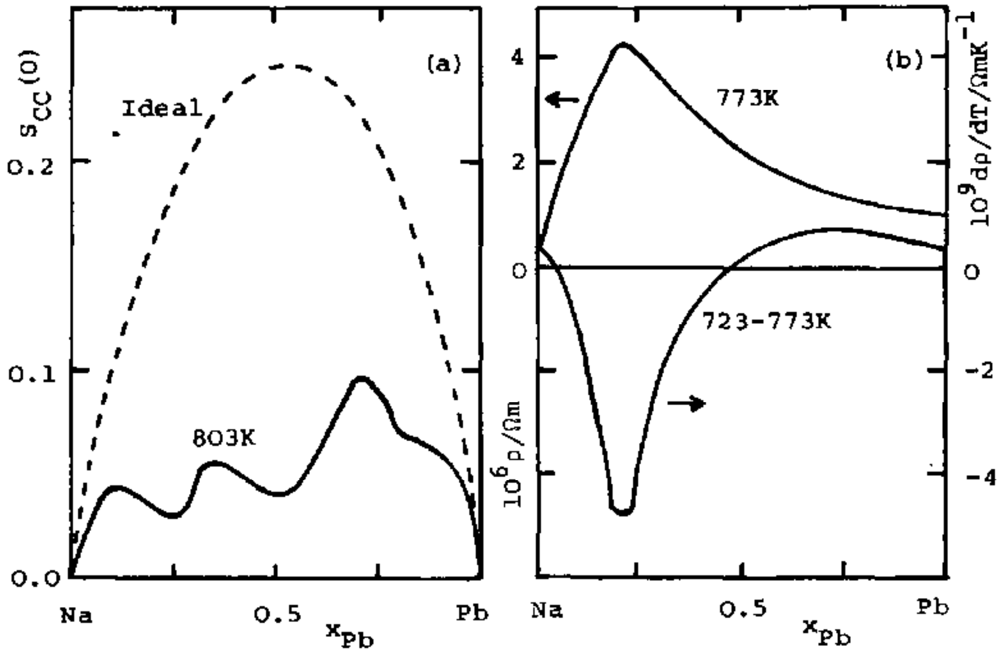


Figure 1. Experimental data indicating the existence of chemical short range order in Na-Pb metallic solutions. Concentration dependence of (a) the concentration structure factor in the long wavelength limit, $S_{CC}(0)$ and (b) the electrical resistivity, ρ, and its temperature dependence, dρ/dT.

Theoretical analyses of chemical short range order in metallic solutions have been published by Hoshino,[24,25] Evans, Ruppersberg et al[26] Ishiguro and Tamaki,[27] and Wang et al.[28,29] Hoshino[24,25] and Evans, Ruppersberg et al[26] have concentrated on interpreting behaviour in liquid Li-Pb solutions. Hoshino's theory[24] is based on a model in which the formation of a molecule with a finite lifetime is assumed, the solution being considered as a ternary mixture of lithium atoms, lead atoms and 'Li_4Pb' molecules. These species are further approximated by hard spheres with different diameters. Calculated values of the concentration structure factor, $S_{CC}(q)$, of liquid $Li_{80}Pb_{20}$ are in good agreement with the experimental results.[24] The marked temperature dependence of $S_{CC}(q)$ is rationalised within this model by taking into account the temperature dependence of the total packing fraction and the fraction of the molecules.[25] On the other hand, Evans, Ruppersberg et al[26] have proposed a theory based on a simple charged hard sphere model. Assuming effective changes of ~+0.5 and ~-2.0 on the lithium and lead atoms, this model accounts reasonably well for the observed values of $S_{CC}(q)$ for $Li_{80}Pb_{20}$. In order to explain the observed temperature dependence of $S_{CC}(q)$ using this theory it is necessary to assume that the extent of charge transfer between species decreases with increasing temperature.[26]

Ishiguro and Tamaki have developed a more general theoretical model for charge transfer in liquid metallic solutions.[27] Application to the Na-K and Na-Hg solutions has shown that whereas in the former system the electrons are transferred from potassium to sodium over the entire composition range, in the latter system electron transfer occurs from sodium to mercury at the dilute limits of each constituent ($0.0 < x_{Na} < 0.1$; $0.6 < x_{Na} < 1.0$) but from mercury to sodium at intermediate concentrations ($0.1 < x_{Na} < 0.6$).[27]

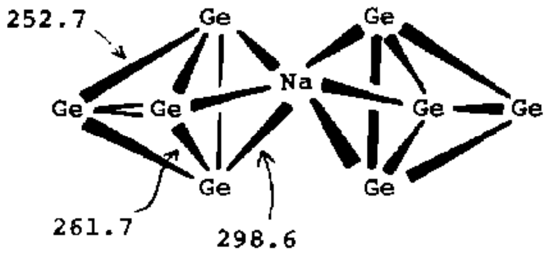
Theoretical models for the calculation of Knight shift[28] and magnetic susceptibility[29] data have been developed by Wang et al; the significance of the extent of charge transfer in these systems is stressed.

A preliminary Cs-Te phase diagram has been prepared;[30] it is based on limited thermal analysis data. The chalcogenide, Cs_2Te, was found to melt at 1083K. A tentative melting point of 708K is proposed for Cs_2Te_3 and evidence for other peritectically decomposing polytellurides at x_{Te} = 0.40, 0.50 is put forward.

Phase relationships in this system were shown to be sensitive to the presence of oxygen, the melting point of Cs_2Te being reduced by over 100K to at least 973K.[30]

1.2.4 Intermetallic Compounds

The intermetallics, M_7NaGe_8 (M = K,Rb) have been synthesised by melting mixtures of the constituent elements (Na:M:Ge = 2:3:3) at 1170K. After cooling over a period of 12 hours excess alkali metal was removed by distillation in vacuo (500K; 1 Pa; 6 hours). The two compounds are isomorphous (cubic, space group Pa3, a = 12.684 (M = K) a = 13.165 (M = Rb)). Their structures contain the novel $[Na(Ge_4)_2]^{7-}$ unit (5) in which two Ge_4 tetrahedra are linked by a sodium atom via six equivalent Na-Ge bonds; the two tetrahedra adopt a staggered conformation about the three fold axis of the $[Na(Ge_4)_2]^{7-}$ unit. The K^+ or Rb^+ ions are located in cavities in the structure.



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1.3 MOLTEN SALTS

As for the 1982 review,[32] the papers abstracted for this section deal exclusively with either structural or solution properties of molten salt systems; the section is subdivided accordingly. One particularly significant feature to emerge from an analysis of the data discussed herein and those considered in earlier reviews is the increasing diversity of the molten salts being considered as non aqueous solvent media.

1.3.1 Structural Properties

The structures of molten Cs_2SO_4,[33] K_2SO_4,[33] and KBr[34] have been elucidated by Ohno, Furukawa et al from X-ray diffraction data using the correlation method; the structural analysis for molten Cs_2SO_4 is novel, those for molten K_2SO_4 and molten KBr are redeterminations. The SO_4 tetrahedron of the solid state structure of Cs_2SO_4 is preserved in the liquid {r(S...O) = 145 pm; cf. r(S...O) = 147 pm of the solid state structure}. The short range structure of liquid Cs_2SO_4 is that in which ~7/8 of the Caesium atoms occupy the corner sharing sites {r(Cs...O) = 307 pm} the other 1/8 occupying the face sharing sites {r(Cs...O) = 348 pm}. The long range structure (>1000 pm) is best simulated by CaF_2-type packing, the SO_4 tetrahedra and Caesium atoms replacing the calcium and fluorine atoms, respectively. Refinement[33] by Ohno, Furukawa et al, of their earlier structure of K_2SO_4,[35] discussed in the 1979 review,[36] has shown that a similar situation pertains as for Cs_2SO_4. The main difference lies in the short range structure where only ~3/4 of the potassium atoms occupy the corner sharing sites {r(K...O) = 261 pm} the other 1/4 occupying the face sharing sites {r(K...O) = 333 pm}.

The mean interatomic distance and coordination number (318 pm and 3.5) derived by Ohno, Furukawa et al[34] for molten KBr differ somewhat from those (335 pm and 4.9) obtained by Antonov[37] in a similar but less extensive study. As an adjunct to their paper,[34] Ohno, Furukawa et al have collated all the experimental parameters for molten alkali metal halides obtained from X-ray or neutron diffraction data.

Raman and near-infrared absorption spectra of molten $K_2S_2O_7$-$KHSO_4$ mixtures (703K; $0.0 < x_{K_2S_2O_7} < 1.0$),[38] measured under the equilibrium vapour pressure of water, are consistent with the presence of the three species in the temperature sensitive equilibrium:

$$2HSO_4^- \rightleftharpoons H_2O + S_2O_7^{2-} \qquad ...(4)$$

The structure of $S_2O_7^{2-}$ in the melts was found to have C_{2v} symmetry and that of HSO_4^- C_s symmetry. Although no intermediate compound of the three species was detected, hydrogen bonding between the species seems to be characteristic of the melts.[38]

Thermodynamic parameters of the molten KCl-$MnCl_2$ system,[39] derived from mass spectrometric data determined by the ion-current ratio method ($900 \leq T/K \leq 1100$; $0.0 < x_{KCl} < 1.0$), exhibit large negative deviations from Raoult's Law suggesting a very strong interaction between KCl and $MnCl_2$. Indeed, the concentration dependence of the entropy of mixing has a minimum close to

x_{MnCl_2} = 0.33 consistent with the presence of the complex species $[MnCl_4]^{2-}$ in the melt.[39]

The solubility and diffusivity of chlorine in molten NaCl, CsCl and NaCl-CsCl (x_{NaCl} = 0.35)[40] and in molten $CsCl-AlCl_3$ ($0.425 < x_{AlCl_3} < 0.52$)[41] have been studied using manometric and chronopotentiometric techniques, respectively. For the alkali metal chlorides,[40] solubility increases from NaCl to CsCl, a positive enthalpy of dissolution being observed for all three solvents. For the chloroaluminate melts,[41] there is no drastic change in solubility as a function of melt composition (even at x_{AlCl_3} = 0.50); it does, however, exhibit a negative enthalpy of dissolution. The diffusivity of chlorine in the molten alkali metal chlorides[40] is insensitive to the identity of the cation; its relatively high magnitude is attributed to a chain conduction mechanism based on the equilibrium:

$$Cl_2 + Cl^- \rightleftharpoons Cl_3^- \qquad \ldots(5)$$

The diffusivity of chlorine in the chloroaluminate melts[41] does not differ markedly from acidic to basic melts.

1.3.2 Solution Properties

The solution chemistry of diverse solutes in molten halides, nitrates, carbonates and sulphates has been described during the period of this report.

An i.r. study of water molecules dissolved in molten MBr (M = Na-Cs) has been undertaken.[42] The spectra contain a single broad strong absorption band in the 3000 - 4000 cm^{-1} region. The frequency of the band maximum decreases from NaBr to CsBr and with decreasing temperature. These trends are similar to those observed for the analogous chloride systems and are rationalised by consideration of the existence of hydrogen bonding between the dissolved water molecules and the halide ions.[42]

The electrochemical oxidation of S^{2-} ions has been studied in both LiF-NaF[43] and LiCl-KCl[44,45] molten eutectics. In LiF-NaF melts, linear sweep voltammetry studies (1023K)[43] have shown that the oxidation is reversible and diffusion controlled. A detailed analysis of the experimental results suggests the following oxidation process:

$$2S^{2-} \rightleftharpoons S_2^{2-} + 2e \qquad \ldots(6)$$

In LiCl-KCl melts, cyclic voltammetry studies ($673 < T/K < 733$)[44] suggest three successive sulphide ion oxidation stages and a complex reduction electrochemistry. Although several different redox mechanisms can be postulated from a detailed analysis of the data, an overall definitive mechanism cannot be proposed on the basis of these data alone owing to the numerous ionic sulphur species which can exist in molten salts. In an attempt to resolve this problem, spectroscopic evidence has been put forward[45] for the formation of the polysulphide species, S_2^- and S_3^- in LiCl-KCl eutectic during both the controlled addition of oxygen to solutions of Li_2S or Li_2S-FeS mixtures and the electrolysis of Li_2S solutions. The solubility and diffusivity of Li_2S in molten LiCl-KCl has been investigated as a function of both composition ($0.54 < x_{LiCl} < 0.66$) and temperature ($633 < T/K < 727$);[44] whereas the solubility increases with both increasing temperature and increasing LiCl concentration, the diffusivity is relatively insensitive to both variables.[44]

Voltammetry studies[46] of the electrochemical reduction of $CaCrO_4$ in LiCl-KCl and $CaCl_2$-NaCl-KCl molten eutectics have shown that the overall reaction mechanism and ultimate reaction products are determined by the reaction of a chromium(V) intermediate with the available cations. Thus, in LiCl-KCl melts, $CaCrO_4$ is initially reduced to $Ca_5(CrO_4)_3Cl$ which is further reduced to $LiCrO_2$. In $CaCl_2$-NaCl-KCl melts, however, it is reduced to the stable intermediate $Ca_2(CrO_4)Cl$. Neither $Ca_5(CrO_4)_3Cl$ nor $Ca_2(CrO_4)Cl$ is further reduced in $CaCl_2$-NaCl-KCl melts, although both are reduced to $LiCrO_2$ in the presence of Li^+ ions.[46]

Raman and visible-u.v. spectroscopic studies[47] of LiCl-CsCl and LiI-KI molten eutectics equilibrated with either I_2 or I_2/ICl vapour gave evidence for the presence of the dissolved trihalide anions, I_3^-, I_2Cl^- and ICl_2^-. The Raman spectra of the LiI-KI melt equilibrated with I_2 vapour also contained features indicative of the presence of a polyiodide of higher molecular weight than the triiodide.[47]

Addition of $AlCl_3$ (as $KAlCl_4$) to the LiCl-KCl molten eutectic results in the solubilisation of several diverse metal oxides {MO (M = Mg,Co,Ni), M_2O_3 (M = Al,Cr,Y,La,Dy,Eu), MO_2 (M = Si, Ti,Mn,Zr,Th,U)}.[48] The dissolution process is attributed to the formation of the complex cation, AlO^+:

$$MO_n(s) + nAlCl_3(soln) \rightarrow MCl_{2n}(soln) + nAlOCl(soln) \qquad ...(7)$$

which is readily soluble in the molten salt medium.[48]

Several features of the chemistry of chloroaluminate[49,50] and chlorogallate[51] melts have been investigated. Raman studies[49] of tungsten(VI) chloride dissolved in NaCl-$AlCl_3$ melts have demonstrated that it exists predominantly as WCl_6 molecules and that its solubility increases with both increasing temperature and increasing $AlCl_3$ concentration.

Molten NaCl-$AlCl_3$ (1:2) mixtures act as solvents for the 'homogeneous Fischer-Tropsch catalysis' process.[50] Using $Ir_4(CO)_{12}$ precatalyst at 448K and 10^5 Pa of hydrogen and CO (3:1), CH_4, C_2H_6 and CH_3Cl were produced as the major carbon-containing species. In addition, a stoichiometric amount of CH_4 is formed when $Ir_4(CO)_{12}$ is introduced in the NaCl-$AlCl_3$ melt at the start of the catalysis. Detailed analysis of kinetic data suggests that the process involves the homogeneous reduction of CO to CH_3Cl, followed by homologation and/or hydrogenation reactions leading to the hydrocarbon products.[50]

Raman spectroscopic methods have been used to study the chemistry of sulphur in CsCl-$GaCl_3$ melts.[51] Under basic conditions (excess CsCl), polymeric chains $[Ga_nS_{n-1}Cl_{2n+2}]^{n-}$ are formed; the degree of polymerisation of these species is unknown and their chemistry is very complex. Under acidic conditions (excess $GaCl_3$) a precipitate is formed probably consisting of 'GaSCl' or $[Ga_nS_{n-1}Cl_{2n+2-m}]^{(n-m)-}$ salts with $n \geq m$.[51]

The vexed question of the identities of the species present in equimolar $NaNO_3$-KNO_3 melts has been investigated by chemical analytical methods ($773 < T/K < 873$).[52] In the absence of evidence for any anionic oxygen species such as O^{2-} O_2^{2-} or O_2^- it is concluded that the sole decomposition reaction of significance can be represented by the equilibrium:

$$NO_3^- \rightleftharpoons NO_2^- + \tfrac{1}{2}O_2 \qquad ...(8)$$

The standard free energy of this reaction ($\Delta G/kJ.mol^{-1} = 96.230 + 86.2\ T/K$) has been derived from equilibrium data for equation (8). The activation energy for the oxidation of nitrite (110.5 kJ. mol^{-1}) has also been calculated from a study of the kinetics of the reaction ($673 < T/K < 773$) which is first order with respect to both NO_2^- and O_2.[52]

X-ray diffraction studies[53] of the structures of equimolar $NaNO_3$-

KNO_3 melts containing $AgNO_3$ indicate a preferred bidentate-like orientation of the nitrate groups around the Ag^+ ions with a closely bonded oxygen, r(Ag...O) = 245 pm, and a more distant oxygen, r(Ag...O) = 300 pm. Similar results[53] for melts containing both $AgNO_3$ and AgI indicate a non-random distribution of cations due to a preferential association of I^- with approximately four Ag^+ cations, irrespective of the total Ag^+ fraction in the melts.

The species present in molten Na_2CO_3 have been elucidated[54] from electrochemical studies (1173K) of sparged beds of Na_2CO_3 using mixtures of O_2, CO_2 and H_2O. A sequence of reactions (scheme 1) has been proposed to account for the observed solution species; the equilibrium constants quoted in scheme 1 are either estimated or calculated from JANAF data.[54]

	K_e
$Na_2CO_3 \rightleftharpoons Na_2O + CO_2$	9.7×10^{-8}
$Na_2O \rightleftharpoons 2Na + \frac{1}{2}O_2$	2.6×10^{-11}
$Na_2CO_3 + \frac{1}{2}O_2 \rightleftharpoons Na_2CO_4$	1.6×10^{-11}
$Na_2CO_4 \rightleftharpoons Na_2O_2 + CO_2$	1.8×10^{4}
$Na_2CO_4 + CO_2 \rightleftharpoons Na_2C_2O_6$	7.8×10^{1}
$Na_2O_2 + O_2 \rightleftharpoons 2NaO_2$	4.4×10^{-3}
$Na_2O_2 \rightleftharpoons Na_2O + \frac{1}{2}O_2$	3.4×10^{-1}

<u>Scheme 1</u>.

The solution chemistry of sulphur-containing moieties has been ascertained in both molten Na_2SO_4 (using cyclic voltammetry and chronopotentiometric methods)[55] and Li_2SO_4-Na_2SO_4-K_2SO_4 molten eutectic (using tga methods).[56] Electrochemical reduction of SO_3 in pure Na_2SO_4 melts[55] leads, via intermediate formation of $S_2O_7^{2-}$, SO_3^-, SO_3^{2-} and $S_2O_6^{2-}$ to products such as SO_2, O^{2-} and O_2^{2-} (Scheme 2). Under certain electrochemical conditions, SO_4^{2-} ions are also subject to decomposition. Thus, whereas at very positive potentials they evolve SO_3 and O_2 gases in addition to O_2^- ions and sulphites (equations 9-11), at very negative potentials they form S^{2-} and O_2^{2-} (equation 12).[55] Peroxide ions in pure Na_2SO_4 melts are also subject to electrochemical reduction

$$SO_3 + SO_4^{2-} \rightleftharpoons S_2O_7^{2-}$$

$$S_2O_7^{2-} + e \rightleftharpoons SO_4^{2-} + SO_3^-$$

$$SO_3^- + e \rightleftharpoons SO_3^{2-}$$

$$2SO_3^- \rightleftharpoons S_2O_6^{2-}$$

$$SO_3^{2-} \rightleftharpoons SO_2 + O^{2-}$$

$$S_2O_6^{2-} \rightleftharpoons 2SO_2 + O_2^{2-}$$

Scheme 2.

$$SO_4^{2-} \rightarrow SO_3 + \tfrac{1}{2}O_2 + 2e \qquad \ldots(9)$$

$$5SO_4^{2-} \rightarrow S_5O_{16}^{2-} + 2O_2^- + 6e \qquad \ldots(10)$$

$$12SO_4^{2-} \rightarrow 2S_6O_{19}^{2-} + 5O_2^- + 15e \qquad \ldots(11)$$

$$SO_4^{2-} + 4e \rightarrow S^{2-} + 2O_2^{2-} \qquad \ldots(12)$$

forming either O^{2-} or both O^{2-} and O_2^{2-} ions (equations 13,14).[55]

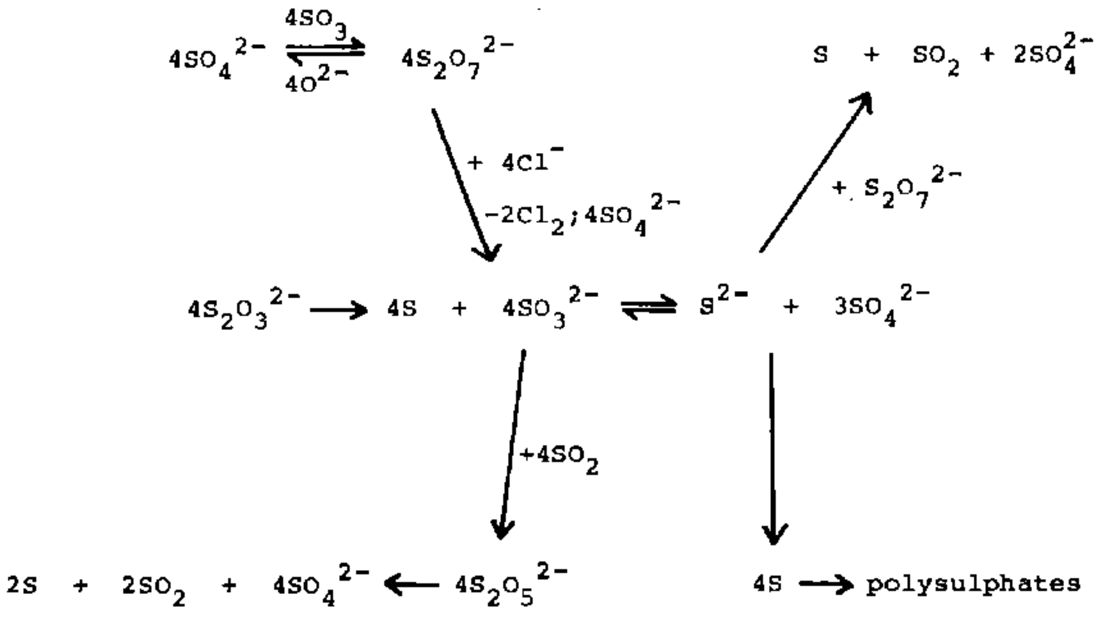
$$O_2^- + 3e \rightarrow 2O^{2-} \qquad \ldots(13)$$

$$2O_2^- + 4e \rightarrow 2O^{2-} + O_2^{2-} \qquad \ldots(14)$$

The reactions of sulphide anions and of the sulphur oxyanions, SO_3^{2-}, $S_2O_3^{2-}$, $S_2O_5^{2-}$ and $S_2O_7^{2-}$ have been investigated[56] in Li_2SO_4-Na_2SO_4-K_2SO_4 molten eutectic under nitrogen, air, SO_2, SO_3 or CO_2 atmospheres and in the presence of acidic, basic or reducing solutes (eg. O^{2-}, Cl^-). A general survey of the reactions of these sulphur-containing moieties under these conditions is given in Scheme 3; the major products were elemental sulphur and sulphate although sulphur oxides were sometimes evolved.[56]

1.4 SIMPLE COMPOUNDS OF THE ALKALI METALS

To qualify for abstraction and inclusion in this section, papers must describe a significant development in the chemistry of a binary or ternary compound containing an alkali metal. The



Scheme 3.

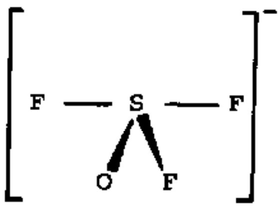
increase in communications dealing with the isolation and characterisation of ion pairs in low temperatures matrices and with the theoretical analysis of small molecules, principally containing lithium, first noted in the 1982 Review[57] has been maintained for the present Review. Consequently, the subsections traditionally included for the classical chemistry of the binary and ternary derivatives of the alkali metals are preceeded by two subsections in which these topically significant subjects are considered.

1.4.1 Ion Pairs

In a note of some significance, Ault[58] has pointed out that the salt/molecule reaction technique, which has proven useful in the synthesis, in low temperature matrices, of several unusual product anions through halide transfer to a suitable Lewis acid acceptor, has several drawbacks. Firstly, distortion of the product anions sometimes occurs leading to splitting of otherwise degenerate i.r. modes; in addition, some shifting of band position is noted as the cation is varied from Na^+ to Cs^+. Secondly, chloride salts are much less reactive than fluoride salts; for example CsF reacts with COF_2 to form $Cs[COF_3]$, but CsCl reacts with neither COF_2 nor

$COCl_2$. He rationalises these limitations by recognising that the alkali metal cation is itself a strong Lewis acid which will compete with the acceptor molecule for the halide ion thus giving rise to the phenomena of anion distortion and lack of reactivity.[58]

Ault[59] has also reported the results of an i.r. matrix isolation study of the products of the co-deposition of CsF with SO_2, SOF_2 and SO_2F_2, viz. the ion pairs $Cs[SO_2F]$, $Cs[SOF_3]$ and $Cs[SO_2F_3]$, respectively. The spectra of the novel anions $[SOF_3]^-$ and $[SO_2F_3]^-$ are consistent with structures of C_s (6) and C_{2v} (7) symmetry similar to those of $ClOF_3$ and ClO_2F_3, respectively.



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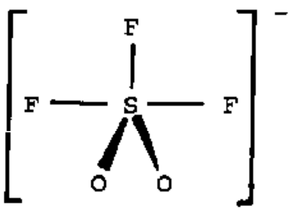
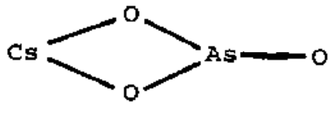


(7)

Infrared studies of $M[AsO_2]$ (M = K-Cs),[60] $M[AsO_3]$ (M = K-Cs),[60] $M[ClO_3]$ (M = K-Cs)[61] and $M[ReO_4]$ (M = K,Cs)[62] condensed into various cryogenic matrices from the vapour above the corresponding alkali metal arsenates,[60] chlorates[61] and perrhenates[62] have been reported by Ogden, Beattie et al. Detailed analysis of ^{18}O enrichment studies for $Cs[AsO_3]$,[60] $Cs[ClO_3]$[61] and $Cs[ReO_4]$[62] provide evidence for structures with C_{2v} (8), C_{3v} (9) and C_{2v} (10) symmetry, respectively. The observation of $M[AsO_2]$ in the matrices obtained from the alkali metal arsenates is construed as evidence for partial thermal decomposition during the vapourisation process.[60]



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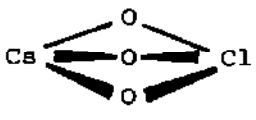

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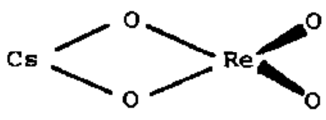
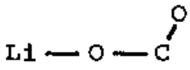


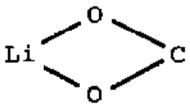
(10)

Margrave et al have published the results of their i.r. studies of the co-condensation of lithium atoms with CH_3NC or CH_3CN[63] and with CO_2[64] in solid argon or xenon matrices. Whereas the Li-CH_3CN reaction yields LiCN, the Li-CH_3NC reaction exclusively affords

LiNC, the more stable isomer.[63] Although concomitant photolysis during the Li-CH_3CN reaction gives a mixture of LiCN and LiNC, it has no effect on the Li-CH_3NC reaction. A reaction mechanism, in which the lithium atom attacks the organic molecule at the end opposite to the methyl group, is proposed.[63] Cocondensation of lithium atoms with CO_2 leads to the formation of five products;[64] viz, two geometrical isomers of Li[CO_2] with C_s (11) and C_{2v} (12) symmetry, Li_2[CO_2], Li[C_2O_4] and Li_2[C_2O_4]. The product yields

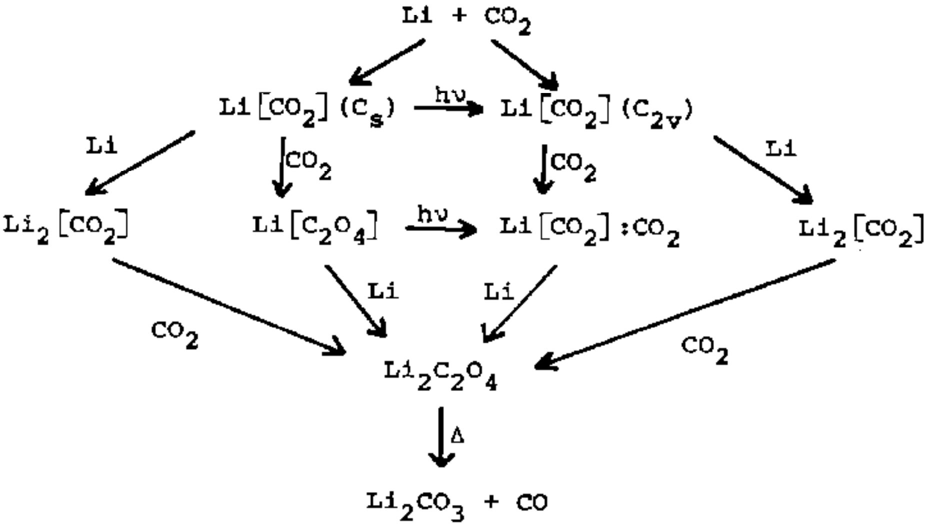


(11)



(12)

can be varied by changing the concentrations of the metal and/or CO_2 in the argon matrix (Scheme 4).[64]

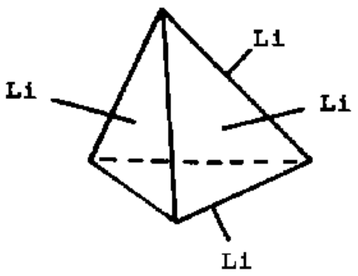


Scheme 4.

E.s.r. studies[65] of M[O_4] (M = Na-Cs) ion pairs obtained by reacting MO_2 and oxygen in various cryogenic matrices suggest a model $[O_2-O_2]^-$ structure in which a relatively weak bond connects two equivalent O_2 moieties. Calculations for Na[O_4] are consistent with $r(O_2...O_2) \geqslant 180$ pm. The e.s.r. spectra do not distinguish between cis- and trans-$[O_4]^-$ but symmetry restrictions may preclude formation of the cis isomer.[65]

1.4.2 Theoretical Treatment of Small Moieties

A substantial number of papers[66-78] describing theoretical analyses of lithium containing moieties has been published during the period of this Review. Although the majority originate from the schools of theoretical chemistry led by Schleyer and Pople several other authors are active in this field. Indeed, the recent (1978) assertion by Schleyer et al[79] that the face lithiated tetralithiotetrahedrane (13) lies at a minimum in the C_4Li_4 potential energy surface is contested by Richie.[66] Using programming and computer technology not then available to Schleyer



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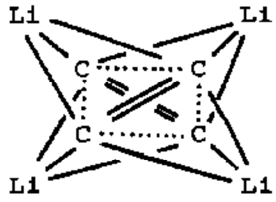


(14)

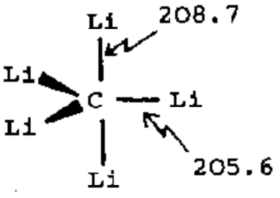
et al, Richie has undertaken a detailed analysis of the C_4Li_4 potential energy surface and of the vibrational frequencies of various isomers and concludes that (13) decomposes to a structure with D_{2d} symmetry (14).

Schleyer et al[67] have continued their ab initio computations on first row hypervalent molecules (i.e.,molecules in which the maximum stoichiometry expected on the basis of the octet rule is violated) showing that both trigonal bipyramidal CLi_5 (15, D_{3h}) and octahedral CLi_6 (19, O_h) are highly stable towards all possible dissociation reactions:

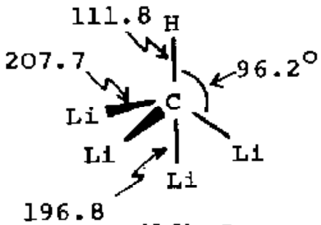
$$CLi_5(D_{3h}) \rightarrow CLi_4(T_d) + Li \qquad \Delta H = +226.4 \text{ kJ.mol}^{-1} \quad ...(15)$$

$$CLi_6(O_h) \rightarrow CLi_4(T_d) + 2Li \qquad \Delta H = +272.8 \text{ kJ.mol}^{-1} \quad ...(16)$$

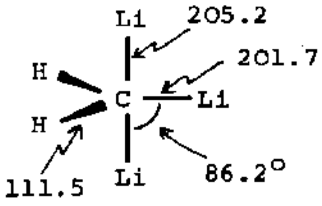
The related series of molecules $CLi_{5-n}H_n$ $(1 < n < 3)$, (16 - 18) and $CLi_{6-n}H_n$ $(1 < n < 4)$ (20 - 23) have been shown to behave similarly although CH_5 and CH_6 are only likely to exist as weak complexes between CH_4 and a hydrogen atom or a hydrogen molecule. A number of geometries were explored for all the hypervalent molecules considered; the lowest energy structures with bond lengths and angles are illustrated in (15)-(23).



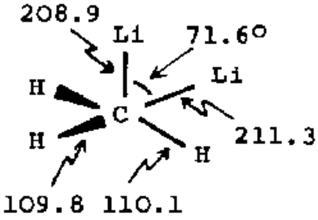
(15) D_{3h}



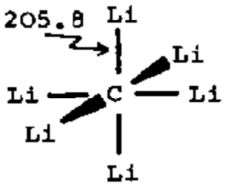
(16) C_{3v}



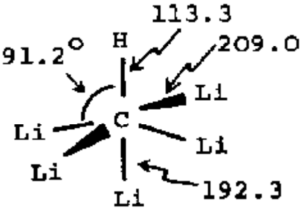
(17) C_{2v}



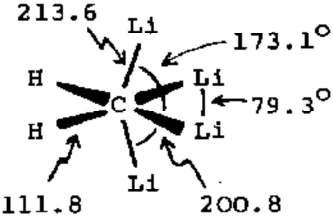
(18) C_s



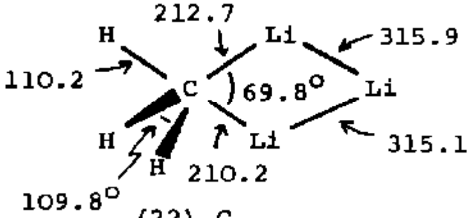
(19) (O_h)



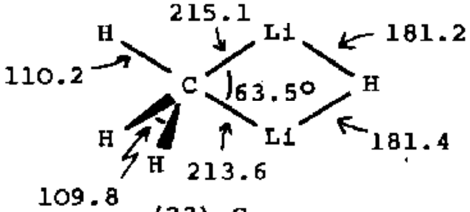
(20) C_{4v}



(21) C_{2v}



(22) C_s distances/pm.



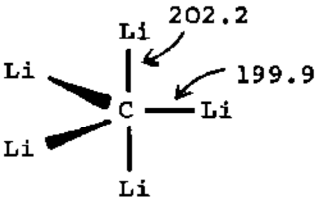
(23) C_s

Schleyer and Pople[68] have also shown, on the basis of ab initio molecular orbital calculations that all lithiated methanonium ions, $[CLi_{5-n}H_n]^+$, with the exception of $[CH_4Li]^+$ are highly stable species. In agreement with mass spectroscopic data for the ions, all possible dissociation reactions are highly endothermic (Table 2). Calculations for various geometries of the $[CLi_{5-n}H_n]^+$ $(0 \leq n \leq 4)$

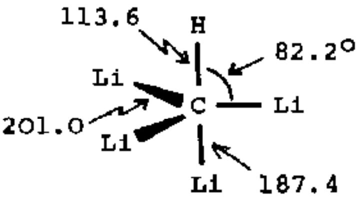
<u>Table 2</u> Dissociation energies of lithium stabilised methanonium ions, $[CLi_{5-n}H_n]^+$ $(0 \leq n \leq 4)$[68]

Dissociation products from $[CLi_{5-n}H_n]^+$	Dissociation energy / $kJ.mol^{-1}$ n = 0	n = 1	n = 2	n = 3	n = 4
$Li^+ + CLi_{4-n}H_n$	343.1	359.8	315.1	214.6	33.5
$H^+ + CLi_{5-n}H_{n-1}$	-	1333.4	1336.0	1280.3	1085.7
$H_2 + [CLi_{5-n}H_{n-2}]^+$	-	-	312.1	335.1	320.9
$LiH + [CLi_{4-n}H_{n-1}]^+$	-	321.3	355.6	451.0	590.8
$Li_2 + [CLi_{3-n}H_n]^+$	243.1	291.2	390.4	623.0	-

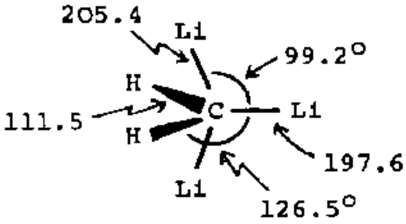
species indicated preferences for structures (<u>24</u> - <u>28</u>).



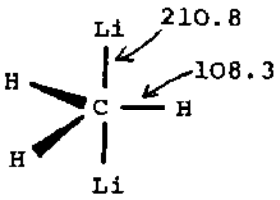
(<u>24</u>) D_{3h}



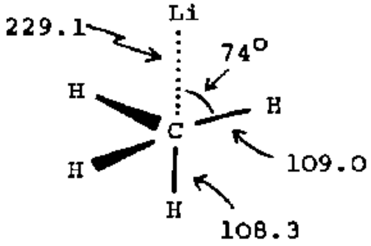
(<u>25</u>) C_{3v}



(<u>26</u>) C_{2v}



(<u>27</u>) D_{3h}

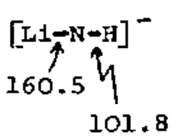


(<u>28</u>)

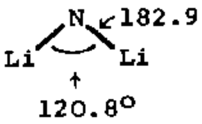
[All species (<u>24</u>) - (<u>28</u>) have a single positive charge]

distances/pm.

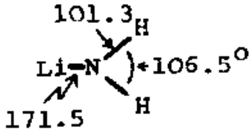
The results of a similar ab initio MO treatment of monomeric lithiated nitrogen species in anionic $[NLi_{2-n}H_n]^-$ $(0 \leq n \leq 1)$, neutral $NLi_{3-n}H_n$ $(0 \leq n \leq 2)$ and cationic $[NLi_{4-n}H_n]^+$ $(0 \leq n \leq 3)$ forms have been published by Schleyer and Pople.[69] Geometry optimisation showed that $[LiNH]^-$ is linear (29), $[Li_2N]^-$ is bent (30) and that the lithiated ammonias are planar (31-33). Although all four $[NLi_{4-n}H_n]^+$ ($0 \leq n \leq 3$) cations (34-37) retain the basic tetrahedral shape of $[NH_4]^+$, lithium substitution markedly reduces the



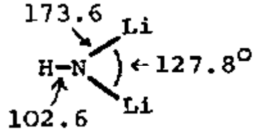
(29) $C_{\infty v}$



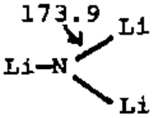
(30) C_{2v}



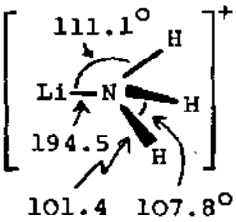
(31) C_{2v}



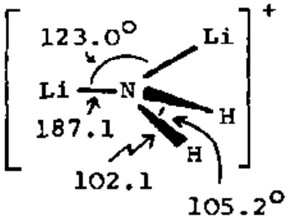
(32) C_{2v}



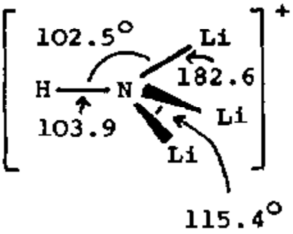
(33) D_{3h}



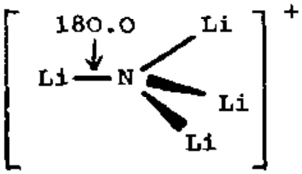
(34) C_{3v}



(35) C_{2v}



(36) C_{3v}

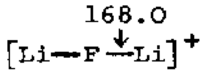


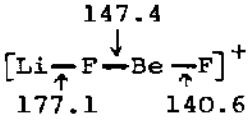
(37) T_d

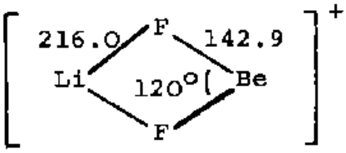
distances/pm.

preference for tetrahedral over planar geometries; the effect is, however, smaller than in the analogous carbon compounds. The nature of nitrogen-lithium bonding is complex. The ionic component (σ donation from lithium to nitrogen) may predominate but considerable π-bonding from nitrogen to lithium can take place giving these species some covalent character.[69]

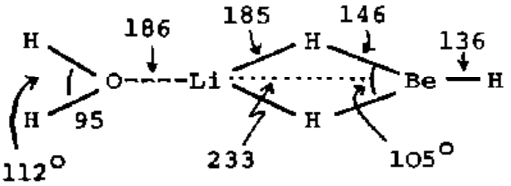
Russian authors[70,71] have completed ab initio calculations of the geometric structures, potential surfaces, force fields and vibrational frequencies of $[Li_2F]^+$, $[LiBeF_2]^+$ and $LiBeH_3.H_2O$. Both $[Li_2F]^+$ (38) and $[LiBeF_2]^+$ (39) have linear equilibrium configurations with $D_{\infty h}$ and $C_{\infty v}$ symmetry, respectively.[70] The cyclic C_{2v} structure of $[LiBeF_2]^+$ (40) is a saddle point on the potential surface of the ions. The results are compared with earlier data for the corresponding hydrides. The absolute







(38) $D_{\infty h}$ 39) $C_{\infty v}$ (40) C_{2v}

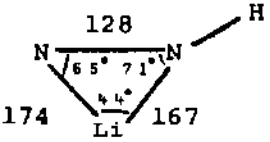


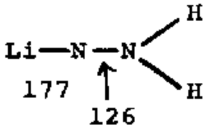
distances/pm.

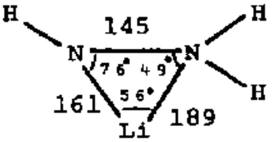
(41)

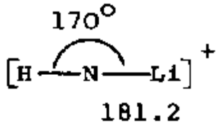
minimum on the potential surface of $LiBeH_3.H_2O$ corresponds to a structure (41) in which the $LiBeH_3$ molecule is in the ground state configuration and the water molecule is coordinated to the lithium cation in agreement with simple electrostatic concepts.[71]

An ab initio theoretical analysis[72] of a series of model lithium compounds, $Li\text{-}N_2H$, $Li\text{-}N_2H_2$, $Li\text{-}N_2H_3$ and $[Li{=}NH]^+$, which represent supposed intermediates in the protonation of dinitrogen when bound to transition metals has been effected. It is clear from the geometries of the optimised energy structures (42-45) that in cases such as $Li\text{-}N_2H$ and $Li\text{-}N_2H_3$ sideways bonding is preferable and that coulombic forces are at least as significant as π-bonding in determining the structures of the model systems.[72]









(42) (43) (44) (45)

distances/pm.

All NNH angles were maintained at 120° and N-H distances at 105pm.

An ab initio computational investigation of the reaction of the simplest carbenoid, $LiCH_2F$, with ethylene has been carried out by Schleyer et al[73] to ascertain the transition structure. Computed structures of the reactants, the carbenoid-ethylene complex and the transition structure are shown in Figure 2.

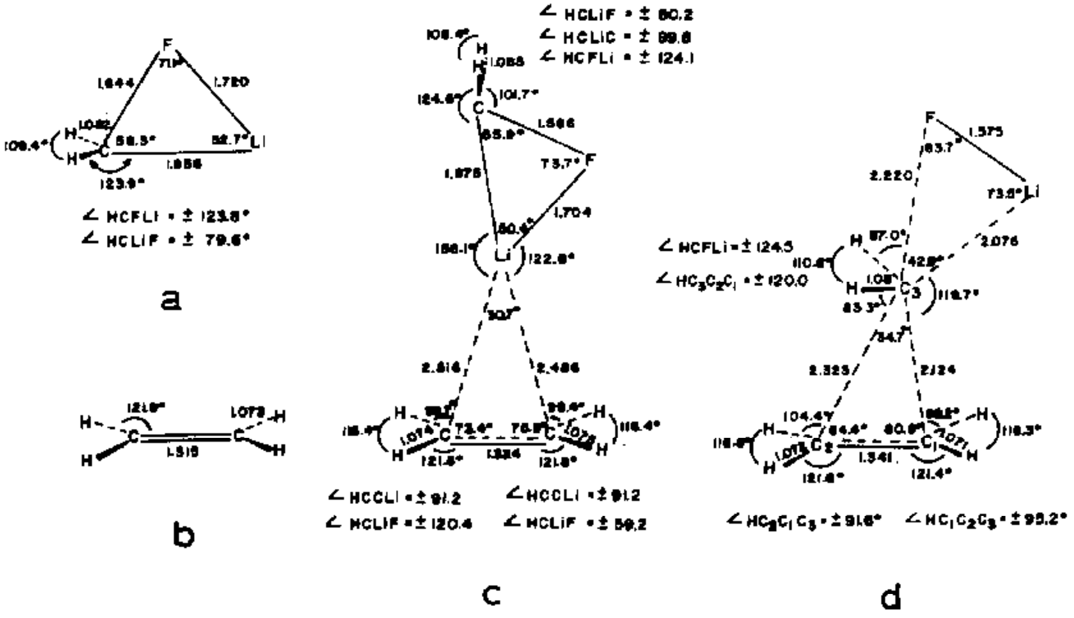
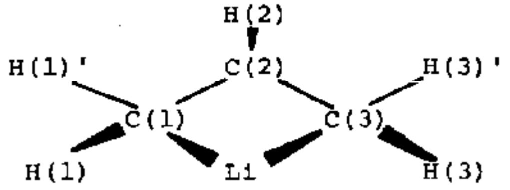
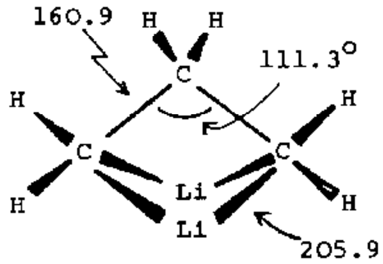


Figure 2. Computed structures of isolated $LiCH_2F$ (a), C_2H_4 (b), the carbenoid-ethylene complex (c) and the transition structure (d). (Reproduced by permission from J. Am. Chem. Soc., 105(1983)6997).

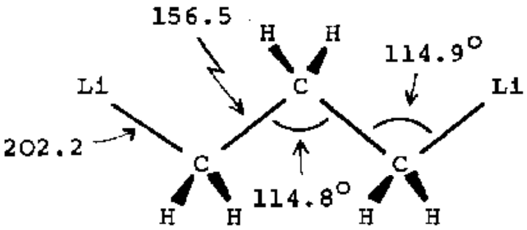
MNDO calculations, undertaken by Decker and Boche,[74] of the geometry optimised structure of allyllithium (46) confirm earlier ab initio results obtained by Schleyer et al;[80] the allyl moieties are considerably distorted from planarity, the inner hydrogen atoms H(1) and H(3) being strongly bent away from, and the central hydrogen atom H(2) being only slightly bent towards, the lithium atom. Similar geometries were derived for the solvated species, $C_3H_5Li,2H_2O$ and $C_3H_5Li,3H_2O$.[74] Relevant data are collated in Table 3.



(46)



(47) C_{2v}

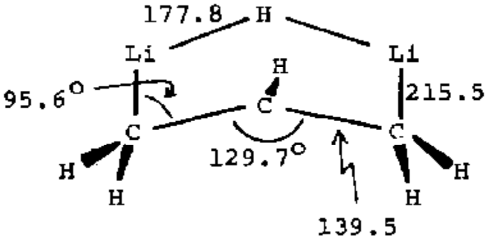


(48) C_{2v} distances/pm.

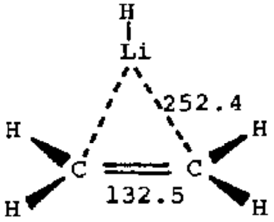
Table 3. Out of plane angles /° (+ve - above plane; -ve - below plane) for allyllithium and solvated allyllithium species

Angle	C_3H_5Li[74]	C_3H_5Li[80]	$C_3H_5Li.2H_2O$[74]	$C_3H_5Li.3H_2O$[74]
C(2)-H(2)	+7.4	+11.1	+6.6	+4.5
C(1)-H(1)'	+1.0	-3.0	0.0	-2.7
C(1)-H(1)	-29.9	-31.1	-27.1	-24.7
C(2)-Li	+39.4	+46.9	+43.8	+49.6

Schleyer et al[75] have established from ab initio calculations that a doubly lithium bridged structure (47) is the lowest energy configuration of 1,3-dilithiopropane. This form exerts considerable thermodynamic stability; rearrangement to an extended geometry (48) is endothermic by 102.9 $kJ.mol^{-1}$ and disproportion with propane into two molecules of n-propyllithium requires 81.2 $kJ.mol^{-1}$. On the other hand, elimination of LiH from 1,3-dilithiopropane (47) is more favourable than from primary alkyllithiums; conversion of (47) to an allyllithium-LiH complex (49) (a possible elimination intermediate) is exothermic by 121.3 kJ. mol^{-1} whereas the ethylene-LiH complex (50) is 30.1 $kJ.mol^{-1}$ less stable than ethyllithium.[75] 1,2-Dilithiopropane behaves similarly to the previously studied[81] 1,3-dilithioethane, which is 124.7 $kJ.mol^{-1}$ less stable than the corresponding vinyllithium complex.



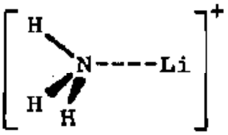
(49) C_s



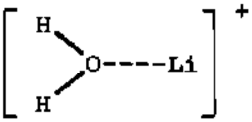
(50) C_{2v}

distances/pm.

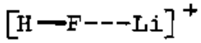
Theoretical calculations have been performed to investigate the structural and energetic properties of the complexes of Li^+ with the hydrides NH_3, H_2O and HF and with a series of closed shell bases, H_mABH_n (A,B = C,N,O or F)[76] and of the complexes of M^+ (M = Li,Na,Mg) with $(HF)_2$ and with $(HCl)_2$.[77] Association of Li^+ with the bases[76] normally occurs along a direction which corresponds to the negative end of the molecular dipole moment vector; thus $[H_3NLi]^+$, $[H_2OLi]^+$ and $[HFLi]^+$ have structures (51-53) with C_{3v}, C_{2v} and $C_{\infty v}$ symmetry, respectively. For bases with two atoms bearing lone pairs, Li^+ may take a bridging position;



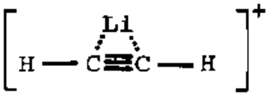
(51) C_{3v}



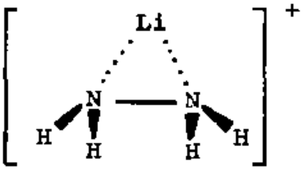
(52) C_{2v}



(53) $C_{\infty v}$

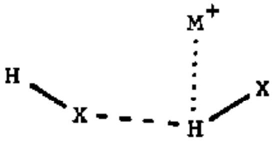


(54) C_{2v}

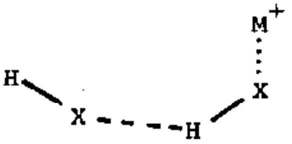


(55) C_{2v}

thus $[HC{\equiv}CHLi]^+$ and $[H_2N\text{-}NH_2Li]^+$ have structures (54,55) with C_{2v} symmetry. Although in general there appears to be only one stable structure for the complexes $[H_mABH_nLi]^+$, two isomers are found for complexes of the bases HN=NH, $H_2N\text{-}NH_2$ and $H_2N\text{-}OH$; the most stable structure is invariably the one which the Li^+ is located in a bridging position (cf. 54, 55). For $[COLi]^+$, two separate energy minima, corresponding to linear triatomic species with attachment of Li^+ at oxygen and carbon, are found.[76] Geometrical optimisation of three models of $[(HX)_2M]^+$ (M = Li,Na,Mg) (56-58) has been investigated to assess the influence of the presence of the cation on the properties and reactivities of hydrogen bonds. Location of the cation in a position perpendicular to the X....X line (56,57) reduces the strength of the hydrogen bond; location on an extension of the X....X line (58) results in a strengthening of the hydrogen bond.



(56)



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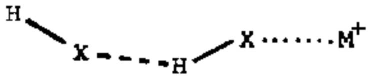


(58)

The X_α discrete variation method has been used[78] to investigate the electronic structures and hence calculate the ionisation potentials of the radicals M_2F, M_2Cl (M = Li,Na,Cs) M_3O, M_3S, M_4N, M_4P (M = Li,Na) using the equilibrium geometry of the singly charged cations. In all cases, the ionisation potentials are smaller than those of the constituent alkali metal atoms, thus justifying the classification of the resultant cations as 'superalkali' cations.[78]

1.4.3 Binary Compounds

There is a paucity of abstracted papers for this section. Those that have been deemed appropriate for inclusion describe either some aspect of the chemistry of gas phase species[82-86] or a novel synthetic route to a binary compound.[87,88]

Physicochemical parameters of gas phase alkali metal hydrides have been determined by three independent groups.[82-84] The thermodynamic properties of the isotopic lithium hydride molecules, $^{x}Li^{y}H$ (x = 6,7; y =1,2,3) have been computed ($100 < T/K < 2000$) from the latest spectroscopic data.[82] The binding energies and spectroscopic constants of the alkali metal hydride molecules, MH (M = Li-Cs) have been calculated using a number of different potential models;[83] the data so derived are compared with available experimental results. The ionic character of the M-H (M = Li-Cs) bond in the alkali metal hydride molecules has also been assessed together with that of the M-OH and M-X (M = Li-Cs; X = F-I) bonds in alkali metal hydroxide and halide molecules.[84] In general, bond ionicity fractions increase in the sequences:

$$Cs > Rb > K > Na > Li \; ; \; F > Cl > Br > I > OH > H$$

Anomalously large covalent contributions to the strength of Li-X bonds were not confirmed.[84]

The geometries and energetics of alkali metal halide dimer molecules, $(MX)_2$ (M = Li-Cs; X = F-I) have been calculated using the ionic Rittner model.[85] The interionic distances in the dimers, which are assumed to adopt a rhombohedral shape with D_{2h} symmetry, are ~20-30 pm. longer than in the corresponding monomers and ~20-30 pm smaller than in the corresponding alkali metal halide crystals. The calculated data are in good agreement with experimental results, where available, and with the results of other calculations.

SIMS data for the alkali metal halides, MX (M = Li-Cs, X = F-I) are consistent with the emission of intense $[M(MX)_n]^+$ cluster ions.[86] Anomalous ion intensity behaviour at n = 13-15, 22-24, 37-39 and 62-64 corresponds to the formation of stable 'cubic-like' structures. For salts with small anions (eg. for NaF) an inhanced ion intensity was also observed for n = 4, corresponding to a cluster ion with a square planar 3 x 3 x 1 structure.[86]

Sodium hydride has been produced[87] in high yield by thermal decomposition of sodium silyl formed by interaction (298K) of silane with a solution of sodium in 1,2-dimethoxyethane containing naphthalene; purification of the product was effected by washing with diethyl ether.

$$Na + SiH_4 \xrightarrow[\text{1,2-dme 298K}]{\text{naphthalene}} NaSiH_3 + \tfrac{1}{2}H_2 \qquad ...(17)$$

$$NaSiH_3 \xrightarrow{\Delta} NaH + \frac{1}{n}(SiH_2)_n \qquad ...(18)$$

Dilithium hexadecaphosphide has been obtained[88] as the thf solvate, $Li_2P_{16}.8thf$ by reaction of white phosphorus with lithium dihydrogenphosphide in the molar ratio 1.92:1 in refluxing thf.

$$23P_4 + 12LiPH_2 \rightarrow 6Li_2P_{16} + 8PH_3 \qquad \ldots(19)$$

1.4.4 Ternary Oxides and Chalcogenides

To avoid unnecessary duplication with other Chapters of this Review, the ternary compounds considered in this and the next subsection are restricted to those containing both an alkali metal and a transition metal, lanthanide or actinide. During the past three or four years, there has been a general increase in the number of papers devoted to ternary halides at the expense of those devoted to ternary oxides and chalcogenides. This trend has now developed to such an extent that on this occasion the former exceed the latter for the first time.

A limited number of papers have been published[89-91] in which some aspect of the chemistry of alkali metal vanadates(V) has been described. The equilibrium phases formed in the M_2O-V_2O_5 (M = K, Rb,Cs) systems - M_3VO_4, $M_4V_2O_7$, MVO_3 (M = K,Rb,Cs), $Cs_2V_4O_{11}$, $M_3V_5O_{14}$ (M = K,Rb) and $M_2V_8O_{21-x}$ (M = K,Rb) - have been characterised using X-ray diffraction, i.r. and microscopical techniques. The only novel compounds are $Cs_2V_4O_{11}$ and the ψ-type bronzes, $M_2V_8O_{21-x}$ (M = K,Rb); the conversion of stoichiometric $M_2V_8O_{21}$, obtained by heating (<723K) mixtures of KVO_3 and V_2O_5 in air, to the ψ-type bronze readily occurs at higher temperatures (>723K) and has been studied in detail using e.p.r. spectroscopic methods. In an independent study,[90] the structural characteristics of $Na_4V_2O_7$ have been determined; relevant data are included in Table 4.

Phase transformations have also been studied[91] in the $LiVO_3$-V_2O_5 system under an oxygen partial pressure of 1.0 Pa. Pressure-temperature diagrams for the vanadium oxide bronzes, $Li_xV_2O_5$ ($0 < x < 1$) have been constructed and the partial thermodynamic quantities for the vaporisation of oxygen from these materials determined.[91]

Alkali metal uranates(VI) have been studied by four independent groups of authors. The chemistry of lithium uranates(VI) has been clarified from the results of a reinvestigation of the Li_2O-UO_3 system ($p_{O_2} = 10^5$ Pa; $T \leq 1203K$) by Prins and Cordfunke[92] and from a novel study of the reactions between UO_2 or U_3O_8 and $LiNO_3$ or Li_2CO_3 ($923 < T/K < 1073$) by Fujino et al.[93] Although no novel lithium uranates(VI) were discovered in either study, Prins and Cordfunke[92] observed a phase transition in $Li_2U_3O_{10}$; the enthalpy of the transition was measured by d.s.c. and the powder pattern of β-$Li_2U_3O_{10}$ (the high temperature form) indexed (Table 4). Prins and Cordfunke[92] also showed that the lithium-rich uranate(VI) is $Li_{6.43}UO_{6.215}$ ($Li_2O.0{\cdot}311UO_3$) and not Li_6UO_6 as asserted previously; samples of $Li_2O:UO_3$ ratio 3:1 invariably contained significant quantities of Li_4UO_5. Fujino et al[93] concluded from their experiments at $LiNO_3:UO_2$ and $Li_2CO_3:UO_2$ ratios of 6:1 and 3:1 that Li_6UO_6 did not exist, there only being evidence for the presence of Li_4UO_5. Phase boundaries in the vicinity of α-$LiU_{0.83}O_3$ ($Li_2O.1{\cdot}60UO_3$), β-$LiU_{0.83}O_3$ ($Li_2O.1{\cdot}75UO_3$) and γ-$LiU_{0.83}O_3$ ($Li_2O.1{\cdot}67UO_3$) were determined more precisely by Prins and Cordfunke.[92]. The α- and β-compounds are two closely related structures which can coexist upto 1168K; at higher temperatures $Li_2O.1{\cdot}75UO_3$ is unstable with respect to $Li_2O.1{\cdot}60UO_3$. The γ-compound is really a hexagonal sub-cell of $Li_2O.1{\cdot}60UO_3$. Both groups of authors also recognised that the previously described $Li_2U_2O_7$ is in effect the α-compound ($Li_2O.1{\cdot}60\,UO_3$).[92,93]

A concurrent study by Fujino et al[93] of the sodium uranates(VI) formed in the reactions between UO_2 or U_3O_8 and $NaNO_3$ or Na_2CO_3 indicated that the previously described $Na_4U_5O_{17}$ and $Na_6U_7O_{24}$ were in actual fact the same material. Although $Na_2U_2O_7$ and Na_2UO_4 were also observed as reaction products, no evidence was found for Na_4UO_5.[93]

In a reinvestigation of the K_2O-UO_3 system, Dion and Noel[94] prepared four potassium uranates(VI) which they designate as K_2UO_4, $K_2U_2O_7$, $K_2U_4O_{13}$ and $K_2U_7O_{22}$. They have published novel structural data for the first three uranates and confirmed parameters reported earlier for the fourth uranate; relevant crystallographic data are collated in Table 4. Dion and Noel[94] also studied the K_2O-MoO_3 system and the UO_2MoO_4-K_2MoO_4-MoO_3 domain. For the former system all previously published data were confirmed and for the latter domain three new complex compounds $K_6UMo_4O_{18}$, $K_2UMo_2O_{10}$ and $K_2U_3Mo_4O_{22}$ were identified.[94]

A careful tgs study,[95] in a controlled gaseous environment, has shown that the thermal stability of the caesium uranate(VI), Cs_2UO_4, is sensitive to traces of moisture; addition of water

Table 4. Crystallographic parameters for diverse ternary oxides and chalcogenides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	β/°	Ref.
$Na_4V_2O_7$	monoclinic	C2/c	1537.6	575.7	3256.4	95.1	90
$Cs_3Nb_{5.96}O_{16.4}$	orthorhombic	Amam	1831.5	2450.6	729.6	-	99
K_2MoO_4 (Incommensurate phase)	orthorhombic	Ccmm	1093.3	631.2	794.4	-	102
$LiReO_4$	triclinic	$P\bar{1}$	965.2	845.5	692.8	-	103
			(101.5°)	(106.6°)	(97.2°)	-	
$LiFe_5O_8$ (disordered phase)	cubic	Fd3m	829.2	-	-	-	104
$LiFe_5O_8$ (ordered phase)	cubic	$P4_332$	831.4	-	-	-	104
CsCuO	orthorhombic	Ama2	508.6	1023.8	589.9	-	105
$M_3Cu_5O_4$ (M_3 = Cs_3, Rb_2K, RbK_2, K_3)*	monoclinic	-	1031.3	763.0	1475.0	106.5	106
β-$Li_2U_3O_{10}$	monoclinic	P2	680.5	1906.7	725.0	121.1	92
K_2UO_4	tetragonal	I4/mm	433.2	-	1318.5	-	94
$K_2U_2O_7$	monoclinic	$P2_1$	692.5	797.3	699.9	109.6	94
$K_2U_4O_{13}$	hexagonal	$P6_3/m$	1430.7	-	1399.8	-	94
$K_2U_7O_{22}$	orthorhombic	Pbam	694.5	1953.0	721.5	-	94

$MMoS_3$ (M = K,Rb,Cs)	hexagonal	$P6_3/m$	872.0	-	440.8	-	107
KFe_2S_3	orthorhombic	Cmcm	901.0	1098.0	540.0	-	108
Na_6CoS_4	hexagonal	$P6_3mc$	890.2	-	687.8	-	109
$Cs_7Fe_4Te_8$	monoclinic	C2/c	2056.9	930.6	1823.5	117.5	110

* Several isostructural compounds were prepared; the crystallographic data refer to the system listed first.

vapour to the system results in a decrease in the decomposition temperature from 1200K (in dry N_2) to 1000K (in N_2 containing 2.3 kPa water vapour).

Interest in the intercalation of alkali metals into solid state lamellar structures has been rekindled with the publication of a number of pertinent papers on this topic.[96-98] The kinetics of the electrochemical insertion of lithium into sodium tungsten bronzes, Na_xWO_3 ($0.4 < x < 0.7$) to form the mixed alkali metal bronzes $Li_yNa_xWO_3$ ($0.0 < y < 0.5$; $x + y < 0.93$) have been determined;[96] the diffusion coefficient of lithium in these materials decreases with increasing lithium and sodium concentrations until above $x \sim 0.7$ insignificant quantities of lithium can be intercalated in the structure.

Insertion of lithium into Nb_2O_5 and related compounds[97] and of sodium, potassium and rubidium into $MNbWO_6$ (M = Na-Rb)[98] has been demonstrated. Reaction of Nb_2O_5 and its derivatives with n-butyllithium at ambient temperatures leads to intercalate stoichiometries of 0.4 to 1.7 lithium atoms per host metal;[97] these data together with the associated volume increases are quoted in Table 5. Intercalation of sodium, potassium and rubidium into the $MNbWO_6$ (M = Na-Rb) defect pyrochlore structure leads to the limiting stoichiometry products M_2NbWO_6 (M = Na-Rb);[98] the corresponding reaction with caesium did not occur, presumably because the Cs^+ ion is too large to occupy the 16d site of the defect pyrochlore structure.

Detailed structural studies[99] of non-stoichiometric caesium niobate(V), $Cs_3Nb_{5.96}O_{16.4}$, have shown that although its composition is close to the stoichiometry $Cs_2O.2Nb_2O_5$, the deficiency of Nb_2O_5 results in a new structural type derived from $Cs_2Nb_4O_{11}$ and pyrochlore by the breaking of octahedral chains; relevant crystallographic parameters of $Cs_3Nb_{5.96}O_{16.4}$ are included in Table 4.

Standard free energies of formation (from the binary oxides) of the sodium tungstates(VI), $Na_2W_6O_{19}$, $Na_2W_4O_{13}$, $Na_2W_2O_7$ and Na_2WO_4 have been derived[100] from the results of an electrochemical study of the thermodynamic properties of Na_2O-WO_3 ($0.5 \leqslant x_{WO_3} \leqslant 0.84$; $1065 < T/K < 1239$). The data are collated in Table 6; those for $Na_2W_6O_{19}$ show that it is stable with respect to $Na_2W_4O_{13}$ and pure WO_3.[100]

Table 5. Intercalate stoichiometries and volume increases observed on insertion of lithium into Nb_2O_5 and related compounds.[97]

Substrate	$n^{\dagger}$	$m^{\ddagger}$	Volume Increase %	Substrate	$n^{\dagger}$	$m^{\ddagger}$	Volume Increase %
Nb_2O_5	1.9	0.95	5.9	$TiNb_{24}O_{62}$	15.7	0.63	5.5
$Nb_2O_5^{*}$	1.7	0.85	1.4	$WNb_{12}O_{33}$	10.7	0.82	4.9
$LiNb_{13}O_{33}$	11.0	0.79	6.7	$W_3Nb_{14}O_{44}$	16.3	0.96	6.2
VNb_9O_{25}	11.4	1.14	7.6	$W_8Nb_{18}O_{69}$	22.0	0.85	6.8
$GeNb_9O_{25}$	17.0	1.70	7.7	$WV_2O_{7.5}$	3.5	1.17	15.0
$TiNb_2O_7$	1.2	0.40	3.6	$W_{0.2}V_{2.8}O_7$	3.7	1.23	15.2
$Ti_2Nb_{10}O_{29}$	6.4	0.53	6.2				

† Number of atoms of lithium inserted per mole of substrate.

‡ Number of atoms of lithium inserted per atom of host metal.

* Nb_2O_5 stabilised by small quantities of fluorine.

Table 6. Standard free energies of formation (from the binary oxides) of a series of sodium tungstates(VI).[100]

Compound	T/K	ΔG_f^{o}/kJ.mol^{-1}
$Na_2W_6O_{19}$ (s)	1125-1175	-556.5 + 0.161T
$Na_2W_4O_{13}$ (s)	1015-1110	-463.5 + 0.094T
$Na_2W_2O_7$ (s)	913-1014	-406.2 + 0.060T
Na_2WO_4 (s)	921- 960	-293.2 + 0.014T

Theoretical group analyses of the i.r. spectra ($33 < \bar{\nu}/cm^{-1} < 1000$) of lithium isotope substituted $^{6,7}Li_2TiO_3$ have been effected[101] to assess the distribution of the Li^+ ions in the octahedral and tetrahedral sites of the structure; the conclusions reached agree quite well with the results of X-ray structure analysis.

Several investigations of ternary oxides,[102-106] sulphides,[107-109] and tellurides[110] have been undertaken in which the primary goal was the determination of structural information. The compounds studied are listed in Table 4 together with their unit cell parameters. Of particular interest are the structures of K_2MoO_4,[102] $LiFe_5O_8$[104] and KFe_2S_3.[108]

The results reported for K_2MoO_4 refer to the incommensurate phase which exists between the room temperature and the high temperature modifications ($593 < T/K < 733$).[102] The structure of this phase (Table 4) was elucidated using data collected with a 4-circle diffractometer and a multiply twinned spherical crystal (633K); the modulation consists of a periodic shift of K^+ ions in the z direction with a correlated flipping over of the MoO_4^{2-} ions.[102]

The structures of disordered and ordered $LiFe_5O_8$ have been refined to establish the cation distribution pattern.[104] In the disordered form, the Li atoms are distributed in statistical disorder with the Fe atoms over the 16d (O_h ; r(Fe,Li)...O = 202.5 pm) sites of the Fd3m structure; Fe atoms are also located in the 8a (T_d ; r(Fe...O) = 188.0 pm) sites. The oxygen atoms are sited in the 8c and 24e positions. In the ordered form, the Li atoms are located in the 4b (O_h ; r(Li...O) = 210.8 pm) sites of the $P4_332$ structure while the Fe atoms are located in the 8a (distorted Td ; r(Fe...O) = 191.5, 187.9 (x3) pm) and 12d (distorted O_h ; r(Fe...O) = 195.0 (x2), 201.1 (x2), 205.8 (x2) pm) positions. The oxygen atoms are sited in the 32e positions.[104]

The ^{57}Fe Mossbauer spectrum of KFe_2S_3 exhibits a single peak inferring that this material contains only one form of iron and not two as indicated by its formula;[108] the isomer shift of the peak is intermediate between values typical of pure ionic Fe^{2+} and Fe^{3+}. The spectrum is rationalised by invoking electron delocalisation involving the Fe^{2+} and Fe^{3+} ions in neighbouring crystallographically equivalent sites leading to an intermediate hyperfine interaction.[108]

1.4.5 Ternary Halides

Compounds considered in this subsection are restricted to anhydrous ternary halides containing both an alkali metal and a transition metal, lanthanide or actinide; hydrated materials are not considered. Topics of current interest in this field are phase relationships and structural parameters. The papers in which the former are discussed[111-115] are exclusively Russian; those in which the latter are discussed[116-133] primarily German, a major contribution being made by Hoppe[116,117,121-123,129,130] as he turns his attention from ternary oxides to ternary halides.

Phase relationships in the NaF-YbF_3,[111] NaCl-$RhCl_3$,[112] NaCl-$PdCl_2$,[113] KCl-$PdCl_2$,[113] NaBr-$TbBr_3$,[114] KBr-$TbBr_3$,[114] NaI-YbI_2[115] and CsI-YbI_2[115] systems have been established by d.t.a., X-ray diffraction and crystal-optical methods. Three phases were discovered in the NaF-YbF_3 system.[111] At high temperatures (>1073K) the only stable phase is a congruently melting (1227K) phase of variable composition ($0.35 < x_{NaF} < 0.51$) with a fluorite-type structure, the cubic cell parameter of which increased linearly from a_o = 544.0 pm for x_{NaF} = 0.50 to a_o = 548.5 pm for x_{NaF} = 0.35. At lower temperatures (<823K), the homogeneity range of this phase is reduced ($0.38 < x_{NaF} < 0.40$), $NaYbF_4$ and $NaYb_2F_7$ being formed in solid phase transformation reactions at temperatures of 873K and 1033K, respectively. Crystallographic parameters for the latter two fluorides[111] are included in Table 7.

The NaCl-$RhCl_3$ system[112] exhibits two ternary chlorides; Na_3RhCl_6 which exists over a narrow temperature range forming in a

Table 7. Crystallographic parameters for a number of ternary halides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	$\beta/^{o}$	Ref.
$CsLiCl_2$	tetragonal	P4/nmm	492.4	-	950.0	-	116
$CsAgCl_2$ (≤443K)	orthorhombic	Cmcm	437.4	1919.9	568.5	-	117
KMF_3 (M = Mn,Fe,Ni)*	cubic	Pm3m	418.89	-	-	-	118,119
$CsCdF_3$	cubic	Pm3m	446.6	-	-	-	120
$CsLnF_3$ (Ln = Eu,Yb)*	cubic	Pm3m	477.7	-	-	-	121,122
$RbYbF_3$	cubic	Pm3m	453.0	-	-	-	121,122
$NaYbF_4$	hexagonal	-	595.3	-	347.3	-	111
β-$BaNiF_6$	hexagonal	-	732	-	713	-	123
$LiDy_2Cl_5$	monoclinic	C2/c	1545.6	659.2	728.7	95.8	124
LiV_2F_6	tetragonal	$P4_2$/mnm	469.7	-	928.9	-	125
$NaYb_2F_7$	hexagonal	-	391.5	-	947	-	111
$NaNp_3F_{13}$	hexagonal	$P6_3$/mmc	802.2	-	1651.3	-	126
Rb_2ZnCl_4	orthorhombic	Pnma	926.4	728.6	1271.9	-	127
K_2PrCl_5	orthorhombic	Pnma	1263.1	875.6	797.3	-	129
M_2UCl_5 (M = K,Rb)*	orthorhombic	Pnma	1271.9	880.2	799.5	-	130
Na_2HfCl_6	tetragonal	-	1599	-	1321	-	131
M_2HfCl_6 (M = K,Cs)*	cubic	Fm3m	1003.6	-	-	-	131
$K_2ReBr_nCl_{6-n}$ $(0 \leq n \leq 6)$†	cubic	Fm3m	984.0/1038.6	-	-	-	132
$K_2OsBr_nCl_{6-n}$ $(0 \leq n \leq 6)$†	cubic	Fm3m	979.4/1033.7	-	-	-	132
K_2PtI_6	tetragonal	P4/mnc	771.7	-	1145.4	-	133
M_2PtI_6 (M = Rb,Cs)	cubic	Fm3m	1127.4	-	-	-	133

* Several isostructural compounds were prepared; the crystallographic data refer to the element listed first.

† A series of solid solutions were prepared; the crystallographic data refer to the two end members of the series.

peritectic reaction at 949K and decomposing in a peritectoid reaction at 788K to give the other ternary chloride, $NaRhCl_4$.[112] The $MCl-PdCl_2$ (M = Na,K) systems[113] are similar. They both contain a single ternary chloride of stoichiometry M_2PdCl_4 which melts congruently; Na_2PdCl_4 melts at 703K, K_2PdCl_4 at 807K.

The $MBr-TbBr_3$ (M = Na,K) systems[114] are also very similar. They both contain two phases of stoichiometry M_3TbBr_6 and $M_3Tb_2Br_9$; whereas the former undergoes phase transformations (673K for Na_3TbBr_6, 693K for K_3TbBr_6) before decomposing in peritectic reactions (933K for Na_3TbBr_6, 898K for K_3TbBr_6), the latter simply decompose in peritectoid reactions (733K for $Na_3Tb_2Br_9$, 573K for $K_3Tb_2Br_9$).[114]

Although no compounds are formed in the $NaI-YbI_2$ system, a single ternary iodide has been observed in the $CsI-YbI_2$ system.[115] The former system is a simple eutectic with restricted solid solubility based on the two components; at ambient temperatures, the solubility of NaI in YbI_2 is ~15%, that of YbI_2 in NaI is ~10%. The ternary iodide found in the $CsI-YbI_2$ system, $CsYbI_3$, melts congruently (995K) after undergoing a transformation (857K).[115]

A relatively large number of ternary halides have been prepared and characterised by crystallographic methods;[116-133] they are listed in Table 7 together with pertinent structural data. Diverse synthetic techniques were used to procure these materials. By far the most popular was the classical solid state method; it accounts for the preparation of all the chlorides and bromides with the exception of $LiDy_2Cl_5$ which was obtained by reduction of $DyCl_3$ using liquid lithium:[124]

$$2Li + 2DyCl_3 \rightarrow LiDy_2Cl_5 + LiCl \qquad ...(20)$$

A similar method, involving reduction of LnF_3 (Ln = Eu,Yb) by liquid rubidium or caesium, was used for the synthesis of $CsLnF_3$ (Ln = Eu,Yb) and $RbYbF_3$.[122] Although the majority of the other ternary fluorides were prepared by high pressure fluorination reactions, novel synthetic methods have been reported for K_2FeF_4,[134] β-Cs_2MnF_4[134] and Cs_3LnF_7 (Ln = Ce,Pr,Tb,Nd,Dy,Er).[135] K_2FeF_4[134] has been produced by thermal treatment (1073K; 30 mins) of $KFeF_3$ (obtained from freshly prepared $FeCl_2$ solution by addition of KF under a hydrogen atmosphere) with KHF_2 in stoichiometric amounts. β-Cs_2MnF_4[134] has been prepared by thermal treatment (898K; 150 mins) of CsF and MnF_2 under a hydrogen atmosphere followed by rapid quenching to ambient temperature. The rate of quenching was critical, slow cooling giving mixtures of α- and β-Cs_2MnF_4.[134] The fluorolanthanates(III), Cs_3LnF_7 (Ln = Ce, Pr,Tb,Nd,Dy,Er) have been prepared by reaction of Cs_3LnF_6 with XeF_2 in a specially prepared nickel thermal analysis cell;[135] the reaction temperatures corresponding to the formation of Cs_3LnF_7 were found to increase regularly from 388K to 655K in the series:

Ce < Tb < Pr < Dy < Nd

Synthesis of the ternary iodides included in Table 7, M_2PtI_6 (M = K,Rb,Cs) was effected by thermal treatment (433K; 24 hours) of highly concentrated aqueous solutions containing both MI (M = K, Rb,Cs) and either PtI_4 or H_2PtCl_6 in the presence of trace amounts of HI and I_2.[133]

The results of diverse studies of the structural chemistry of several ternary fluorides with the perovskite structure, viz., $KMnF_3$,[118,136] $KFeF_3$,[119] $KNiF_3$,[118,137] $CsCdF_3$,[120] $RbYbF_3$,[121,122] and $CsLnF_3$ (Ln = Eu,Yb)[121,122] have been published. Of particular interest are those describing the electronic structures of KMF_3 (M = Mn,Fe,Ni). The electron density distributions in the cubic crystals of $KMnF_3$[118], $KFeF_3$[119] and $KNiF_3$[118] have been determined using X-ray diffraction data collected at 293K. Refinement with spherical scattering factors for the 3d orbitals revealed that the electronic configurations for the three transition metals are $(t_{2g})^{3.0}$ $(e_g)^{2.0}$, $(t_{2g})^{3.9}$ $(e_g)^{2.1}$, $(t_{2g})^{5.7}$ $(e_g)^{2.3}$, respectively. These results are in broad agreement with the angle resolved X-ray (Mg K_α) photoelectron spectra of single crystals of $KMnF_3$[136] and $KNiF_3$[137] which have been satisfactorily interpreted using SCF X_α calculations assuming the presence of the O_h species, $[MnF_6]^{4-}$ and $[NiF_6]^{4-}$, respectively. The corresponding spectrum of K_2FeF_5[138] was similarly rationalised assuming the presence of O_h species, $[FeF_6]^{3-}$.

A temperature dependent study of the lattice parameters of $CsCdF_3$ has shown that it increases from 446.6 pm (at 301K) to 449.6 pm (at 723K).[120]

Phase transformations in the ternary chlorides, $MCrCl_3$ (M = Rb, Cs) have been studied by adiabatic calorimetric ($6 < T/K < 350$) and d.s.c. ($300 < T/K < 500$) methods.[139] Although $CsCrCl_3$ simply exhibits a first order transition at 171.1K, $RbCrCl_3$ exhibits a transition with thermal hysteresis at 193.3K together with a continuous transition at 440±10K. The latter is thought to be a second order transition which can be associated with the ($\beta\rightarrow\alpha$) phase change located, according to X-ray diffraction data, at 470K. Enthalpy and entropy data for these transitions are collected in Table 8 together with similar data for the phase transformations exhibited by Rb_2ZnCl_4 at 74.6, 195.2 and 303.2K. The structural chemistry of Rb_2ZnCl_4 has been elucidated from single crystal X-ray[127] and neutron[128] diffraction and detailed heat capacity[140] studies; the data quoted in Table 8 were derived from the latter study.[140]

Table 8. Thermodynamic parameters for phase transformations in $RbCrCl_3$,[139] $CsCrCl_3$[139] and Rb_2ZnCl_4.[140]

Compound	Transition temperature/K	$\Delta H/J.mol^{-1}$	$\Delta S/JK^{-1}.mol^{-1}$
$RbCrCl_3$	193.3±0.1	1.43±0.07	0.007±0.0004
$CsCrCl_3$	171.1±0.1	4.42±0.07	0.026±0.0004
Rb_2ZnCl_4	74.6±0.15	30±1	0.42 ±0.01
	195.2±0.05	6.2 ±0.9	0.032±0.005
	303.2±0.3	222.7	0.66 ±0.14

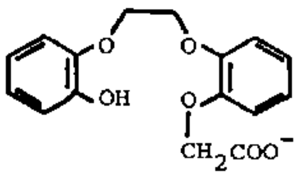
Finally, the spectroscopic properties (i.r., Raman, u.v.-visible and e.s.r.) of $RbUF_6$ have been measured and rationalised.[141]

1.5 COMPOUNDS OF THE ALKALI METALS CONTAINING ORGANIC MOLECULES OR COMPLEX IONS.

Rather than consider the recently published chemistry of the compounds element by element, the majority of the papers abstracted for this section are discussed in a number of subsections devoted to specialised subjects of current interest and importance. Although the majority of these are all the same as those for the 1982 Review,[142] three novel subsections dealing with complexes formed between alkali metals and lariat ethers, between alkali metals and macrocyclic imines and with heterobimetallic complexes containing both an alkali metal (generally lithium) and a transition metal have been included in the present Review. It is inevitable that some abstracted papers cannot be assigned to one of these subsections. These papers are considered in subsections for the individual alkali metals; when data pertinent to several alkali metals are reported, they are discussed once only in the subsection for the lightest element concerned.

1.5.1 Complexes of Acyclic Lipophilic Ionophores

This subsection, previously devoted exclusively to acyclic polyether complexes, has been expanded to allow for the recent diversification in acyclic complexing agents for alkali metal cations. Single crystal X-ray diffraction studies have been undertaken on the novel neutral trinuclear Rb-Co-Rb complex $[Co[(\underline{59})_2Rb]_2]$;[143] the resultant structure is compared to that of the corresponding potassium complex $[Co[(\underline{59})_2K]_2]$ discussed in the 1982 Review.[142] The similarity in the two complexes is obvious



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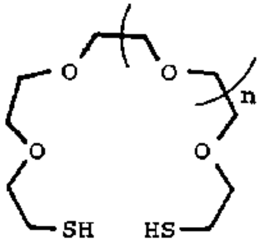
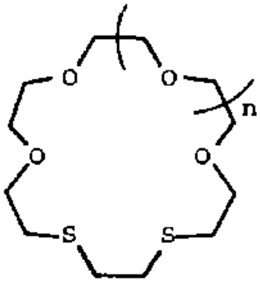


n=1 (60)
n=2 (61)



n=1 (62)
n=2 (63)

from a consideration of Figure 3. Each of the four ligands is bonded through a carboxylate oxygen atom to the central Co atom, $r(Co...O)_{av}$ = 194.9 pm (Rb^+ complex), 195.5 (K^+ complex). The ligands are arranged in two pairs which sandwich each of the alkali metal cations, coordination being effected via the five oxygen heteroatoms. The only differences in the structure are minor; they arise from the absence in the Rb^+ complex of the crystallographic two-fold axis present in the K^+ complex. Thus, the pentagonal antiprismatic arrangement for the crystallographically equivalent K^+ ions, $r(K...O)$ = 270.5 - 293.1 pm is more regular than that for the crystallographically distinct Rb^+ ions,

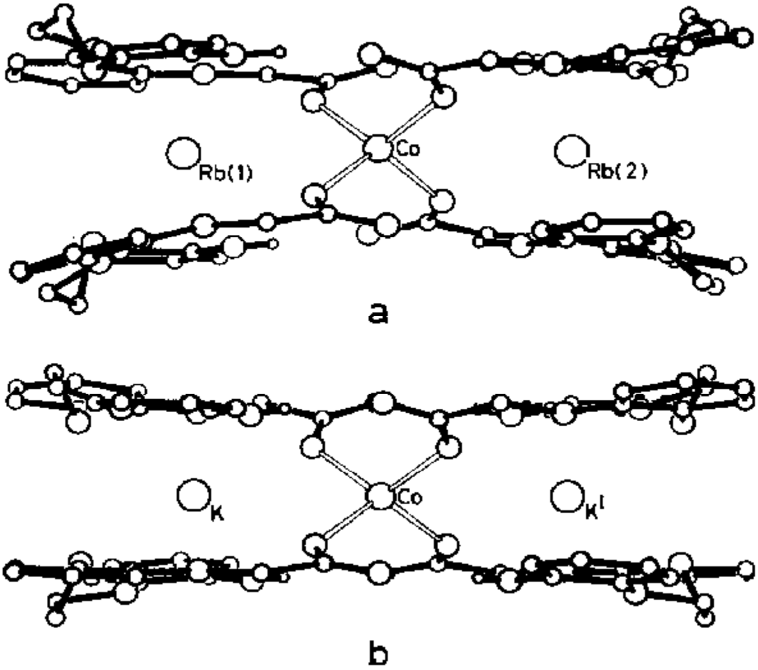
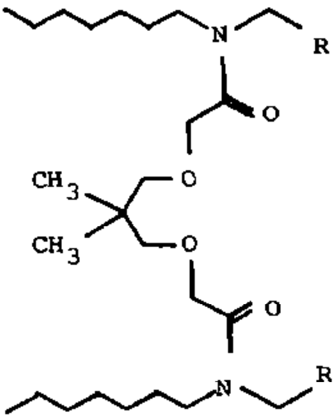


Figure 3. Views of the complexes $[Co[(\underline{59})_2Rb]_2]$ and $[Co[(\underline{59})_2K]_2]$ perpendicular to the (100) and (001) planes respectively (reproduced by permission from J. Chem. Soc., Dalton Trans., (1983)915).

r(Rb(1)...O) = 289.1 - 304.4 pm, r(Rb(2)...O) = 287.3 - 304.1 pm, and the ligand planes in the Rb^+ complex are distorted rather more from parallel formations than in the K^+ complex.[143]

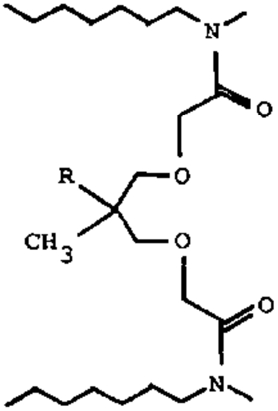
Extraction of alkali metal (Li-K) picrates from aqueous solution into dichloromethane by the novel acyclic α,ω-dithiols (60,61) and their cyclic analogues (62,63) has been assessed and compared with that of more conventional ionophores.[144] For all the alkali metal cations studied, the disulphide crown ether (62,63) is a better ionophore than the corresponding acyclic compounds (60,61). In comparison with hexaethyleneglycol or DB18C6, however, the novel compounds were less effective.[144]

The selectivity of the newly prepared acyclic lipophilic ionophores (64-80) for the alkali metal cations has been elucidated.[145-148] The most efficient of the hexafunctional dioxa diamide derivatives (64-67) as a Li^+ ion carrier is (66);[145] it



(64)-(67)

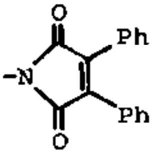
(64) R = CH_2COOH
(65) R = $CH_2COOC_2H_5$
(66) R = $CH_2OC_2H_5$
(67) R = $CH_2CON(C_2H_5)_2$

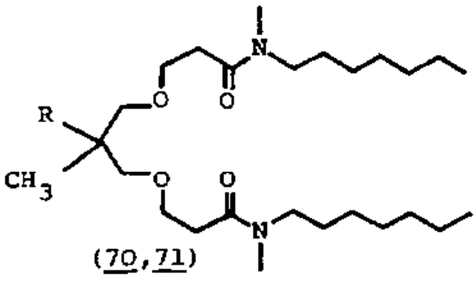


(68,69)

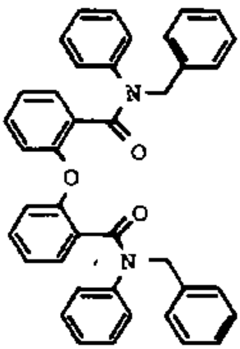
(68,70) R = Me

(69,71) R =





(70,71)



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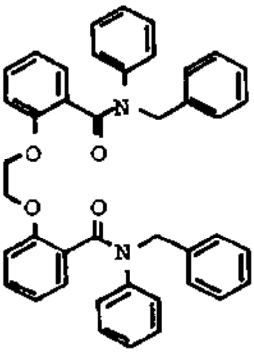

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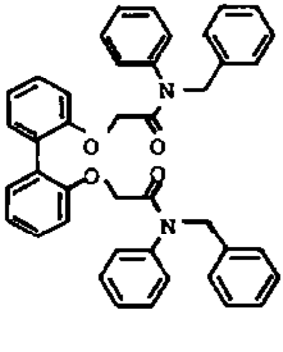

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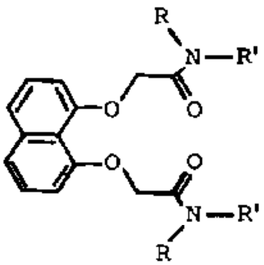
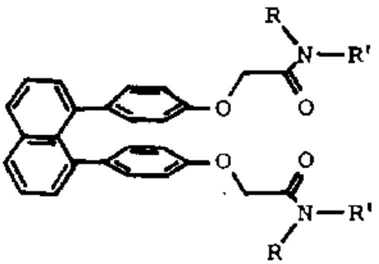
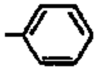
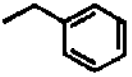


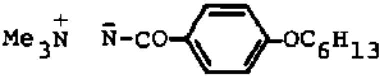
(74,75)



(76,77)

(74,76) R =  , R' = 

(75,77) R = R' = 



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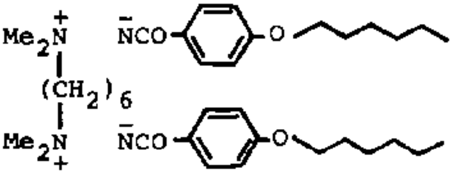
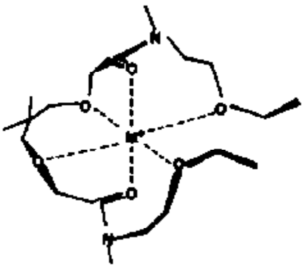


(80)

transports Li^+ ions as effectively as valinomycin transports K^+ ions. The ligand is thought to wrap around the Li^+ ion in a pseudo-octahedral arrangement using six binding sites, thus forming a lipophilic envelope of aliphatic residues (81).[145]



(81)

Diphenylmaleimide substitution in the related dioxadiamide ligands (68,70) to form (69,71) has very little effect on the Li^+ ion selectivity of these ionophores;[146] when incorporated into polyvinylchloride membranes, the substituted ionophores (69,71) induce the same ion selectivity (and ion transport behaviour) as the unsubstituted ligands (68,70). In similar membranes, the series of ionophores (72-78) induce selectivities of Na^+ ions over K^+ ions by a factor of upto 20.[147]

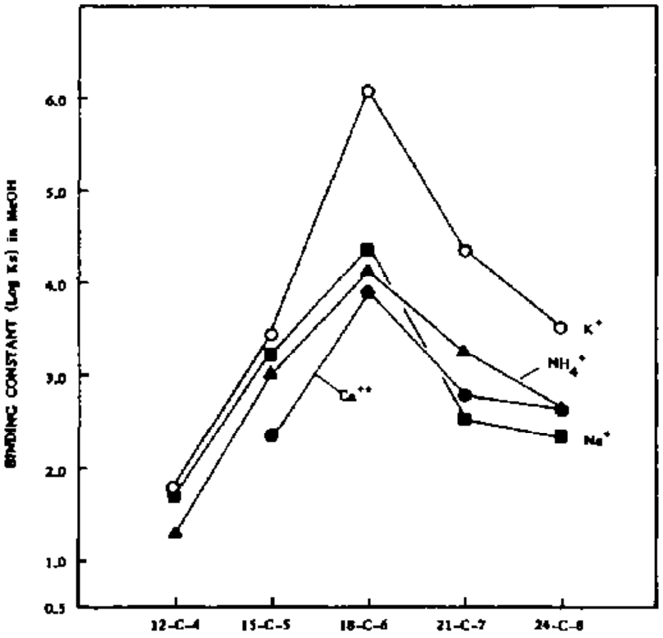
The efficiency of the aminimides (79,80) as ionophores for K^+ ion transport has been assessed;[148] that of (79) is markedly lower than that of (80). With (80), the results exhibited a pH dependence which was thought to indicate that it transports potassium picrate against its own concentration gradient possibly because of the degree of interaction between the quaternary nitrogen of the ionophore and the anionic oxygen of the picrate.[148]

1.5.2 Crown Complexes

The continuing high level of interest shown in alkali and alkaline earth metal complexes of crown and related macrocyclic ligands is such that this topic has been divided into three subsections in which complexes formed by (i) 'classical' crown compounds and their substituted derivatives (ii) bis(crown ethers) and lariat ethers and (iii) novel macrocyclic ligands of unusual design are considered.

The hole-size cation-diameter relationship in crown complexes has been reassessed by Gokel et al[149] from equilibrium stability constant data for the homologous series of crown ethers ranging from 12C4 to 24C8 with Na^+, K^+, NH_4^+ and Ca^{2+} ions, determined in anhydrous methanol (Figure 4). The key observation is that the widely recounted 'hole-size-selectivity' principle is not applicable to this series of simple macrocycles. Instead, as shown in Figure 4, the K^+ ion is bound most strongly by all of these macrocycles and the strongest binding for all of the cations occurs with 18C6.[149]

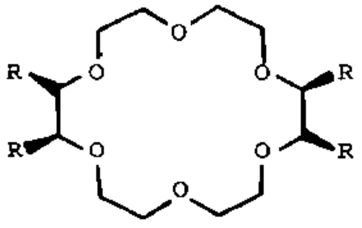
In a further communication on the chemistry of caesium 18C6 compounds, Dye et al[150] have resolved their earlier dichotomy over the identity of the compound of stoichiometry Cs(18C6) as discussed in the 1982 Review.[151] Whilst characterising a newly synthesised compound of stoichiometry $Cs(18C6)_2$ as a crystalline electride $[(18C6)_2Cs]^+e^-$ it became obvious that the earlier product was a ceside $[(18C6)_2Cs]^+.Cs^-$ and not an electride $[(18C6)Cs]^+.e^-$. The two compounds were prepared in identical fashion (reaction of caesium with 18C6 in a 2-aminopropane diethyl ether mixture in the presence of dissolved lithium) using 1:1 and 1:2 reaction stoichiometries. Definitive proof that one is a ceside and the other an electride was obtained from ^{133}Cs n.m.r. solid state studies using magic angle sample spinning techniques; contributory



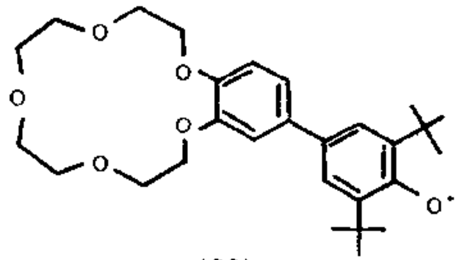
<u>Figure 4</u>. Equilibrium stability constants for binding of Na^+, K^+, $NH_4{}^+$ and Ca^{2+} by simple crown ethers (reproduced by permission from J. Am. Chem. Soc., 105(1983)6786).

evidence was provided by optical spectroscopy, magnetic measurements and electrical conductivity data.[150]

Single crystal X-ray diffraction studies have been effected for $[B13C4.Li]^+ SCN^-$,[152] $[DB14C4.Li]^+ SCN^-$,[153] $[18C6.Na(thf)_2]^+ [Nb\{(o\text{-}CH_2C_6H_4)_2(\eta\text{-}C_5H_5)_2\}]^-$,[154] and $[\{(\underline{82})K\}_2]^{2+}[KBr_3(H_2O)_4]^{2-}$,-$3H_2O$.[155] The coordination spheres of the Li^+ ions in the B13C4[152] and DB14C4[153] complexes are very similar; they are generated by the four heteroatoms of the crown ether ring and the nitrogen atom of the anion in a distorted square based pyramidal geometry with the cation being located ~80 pm above the plane of the four oxygen atoms. The interatomic distances in the B13C4 complex, r(Li...O) = 201-216 pm, r(Li...N) = 194.5 pm,[152] are almost identical to those in the DB14C4 complex, r(Li...O) = 203.3, 205.4



(<u>82</u>); R = $CONMe_2$

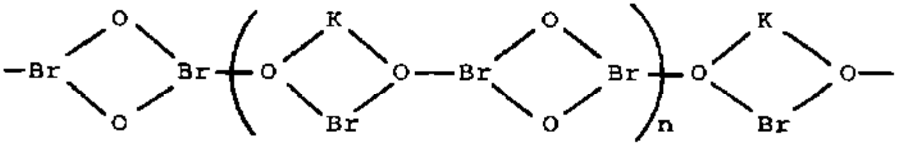


(<u>83</u>)

pm, r(Li...N) = 196 pm.[153] The data for $[B13C4.Li]^+$ SCN^- refute the earlier suggestion,[156] based on solution data, that the Li^+ ion fits almost exactly into the B13C4 cavity.

The structure of $[18C6.Na(thf)_2]^+[Nb\{(o\text{-}CH_2C_6H_4)_2(\eta\text{-}C_5H_5)_2\}]^-$ contains two crystallographically independent cations both of which lie on inversion centres.[154] The Na^+ environments of these cations are hexagonal bipyramidal; the heteroatoms of the polyether ring form the equatorial plane, r(Na...O) = 268-280 pm and the thf oxygen atoms occupy the apical positions, r(Na...O) = 228-232pm.[154]

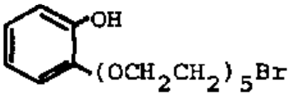
The heptahydrate 3:2 KBr complex of (<u>82</u>) consists of hydrated polymeric chains formed by repetition of the unit $[\{(\underline{82})K\}_2]^{2+}$ $[KBr_3(H_2O)_4]^{2-}$,$3H_2O$ along the 110 axis.[155] The two K^+ ions in the dimeric cationic unit are located in distinctly different bonding environments. Whereas K(1) lies at the centre of a macrocyclic ring and is coordinated to all six heteroatoms, r(K(1)...O) = 273-284 pm, K(2) lies 112 pm above the plane of the six heteroatoms of a macrocyclic ring and is only coordinated to three of them, r(K(2)...O) = 275.8-290.8 pm. The approximately hexagonal pyramidal coordination sphere of K(1) is completed by an oxygen atom of an amide residue, r(K(1)...O) = 277 pm; the distorted octahedral coordination sphere of K(2) is completed by two oxygen atoms from amide residues, r(K(2)...O) = 269,289 pm, and a single water oxygen, r(K(2)...O) = 283 pm. The third K^+ ion forms part of the anionic chain:



with average K(3)...O distances of 319 pm.[155]

Complex formation between the spin labelled crown ether (<u>83</u>) and the alkali (Li-Rb) and alkaline earth (Mg-Ba) metal salts has been studied in frozen ethanol solutions by the e.s.r. technique.[15] Two 2:1 complexes and a 1:1 complex co-exist in all the solutions studied. Structural information for the two kinds of 2:1 complexes was deduced from a detailed analysis of the e.s.r. spectra for the K^+ ion complex. In both structures the K^+ ion is sandwiched between two parallel crown ether derivatives, the difference being the angle (70^o or 30^o) between the two parallel aryloxyl groups; whereas there is no overlap between the two aryloxyl groups in the former conformation, some overlap (and hence interaction) occurs in the latter conformation.[157]

The template effect of alkali and alkaline earth metal cations on the kinetics of the cyclisation of (84) to B18C6 in methanol[158]



(84)

and 99% dmso[159] has been investigated. A rationale for the template effect involving (rate enhancing) proximity effects and (rate retarding) chemical effects arising from interaction of the cations with the nucleophilic site of the substrate is presented.[158,159]

Complex formation between Li^+, Na^+ or K^+ and 12C4 in methanol[160] and between Na^+, K^+, Rb^+ or Cs^+ and DB24C8 in acetonitrile[161] has been studied using ^{13}C n.m.r. and conductivity methods, respectively. The stability constants of the 12C4 complexes[160] were obtained by a computerised iterative least squares method. Whereas Na^+ and K^+ form both 1:1 and 1:2 complexes, Li^+ is complexed but weakly. Although the 1:1 complexes are of comparable stability, Na^+ forms a much more stable 2:1 sandwich complex than K^+. The stability constants of the DB24C8 complexes[161] decrease in the sequence:

$$Na^+ > Cs^+ > K^+ \approx Rb^+$$

DB24C8 showing no remarkable selectivity for the alkali metals in acetonitrile.

The kinetics of the complexation of K^+ by 18C6 have been determined in a variety of non-aqueous solvents (methanol, dioxolane, acetone, and acetone-dioxane and acetone-thf mixtures) using ^{39}K n.m.r. techniques.[162] In dioxolane exchange of K^+ between sites is thought to occur via the bimolecular exchange process (equation 21) rather than the dissociative mechanism (equation 22) favoured by aqueous systems; the most likely

$$^{*}K^{+} + [18C6.K]^{+} \rightleftharpoons [18C6.^{*}K]^{+} + K^{+} \qquad ...(21)$$

$$K^{+} + 18C6 \rightleftharpoons [18C6.K]^{+} \qquad ...(22)$$

transition state for the former process involves the symmetrical dicationic complex, $[K..18C6..K]^{2+}$.[162]

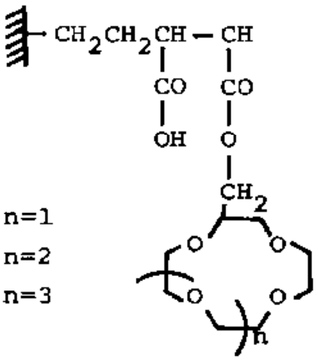
The extraction of alkali metal picrates from aqueous solution into organic solvents in the presence of crown ethers has been described by both Russian[163] and Japanese[164,165] authors. Spectrophotometrically determined extraction constants[163] for the extraction of Na^+-Cs^+ into $CHCl_3$ in the presence of 15C5 decrease with increasing cationic radii; that for Li^+, however, is very much smaller than those for any of the other alkali metals. Although a similar sequence of extraction constants is observed in benzene, their absolute magnitude is lowered by a factor of ~100.[163] Both enthalpy and entropy data for the extraction of Na^+ or K^+ into benzene in the presence of B15C5 are large and negative.[164] When combined, however, they give a small negative value for the free energy of the extraction process and a relatively low preference of Na^+ over K^+.[164] The synergistic extraction of Rb^+ or Cs^+ into benzene in the presence of mixtures of a crown ether (12C4, 15C5, B15C5) and a neutral donor solvent (tributylphosphate-TBP; trioctylphosphine oxide-TOPO) has been studied (298K).[165] All the extracted complexes had the stoichiometric composition M^+ : crown ether : neutral donor solvent : picrate ion = 1:1:1:1. The TOPO complexes are more readily extracted than the corresponding TBP complexes; similarly, the Rb^+ complexes are more readily extracted than the corresponding Cs^+ complexes. For both TOPO and TBP, the adduct formation constants for Rb^+ and Cs^+ decrease in the sequences:

B15C5 > 12C4 > 15C5 and 12C4 > B15C5 > 15C5

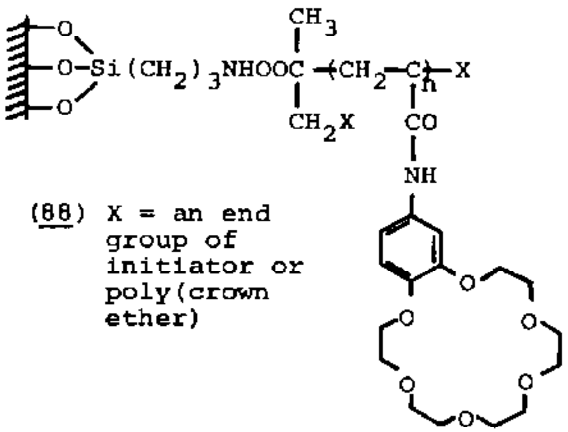
respectively.[165]

Limiting ionic molar conductivities ($\lambda^o/\Omega^{-1}cm^2mol^{-1}$) of $[18C6.K]^+$ and $[DB18C6.K]^+$ complexes in both protic and aprotic solvents have been determined (298K) and compared with corresponding data for tetraalkylammonium ions.[166] In general the mobility of $[18C6.K]^+$ is similar to that of $[(n-C_4H_9)_4N]^+$; this is not surprising since the two cations have nearly identical crystalline ionic radii. A consistent trend in the relative magnitudes of the mobilities of these two ions is observed from protic to aprotic solvents. Whereas $[18C6.K]^+$ ($\lambda^o = 25.0\Omega^{-1}cm^2 mol^{-1}$) is more mobile than $[(n-C_4H_9)_4N]^+$ (19.3) in water, the latter (61.4) is more mobile than the former (59.0) in acetonitrile; the two ions have almost identical mobilities (39.0; 38.9) in methanol solutions. This trend is thought to suggest that, unlike $[(n-C_4H_9)_4N]^+$, $[18C6.K]^+$ does not enforce a hydrogen-bonded structure on a protic solvent. Similar results were observed for $[DB18C6.K]^+$ and $[(n-C_5H_{11})_4N]^+$.[166]

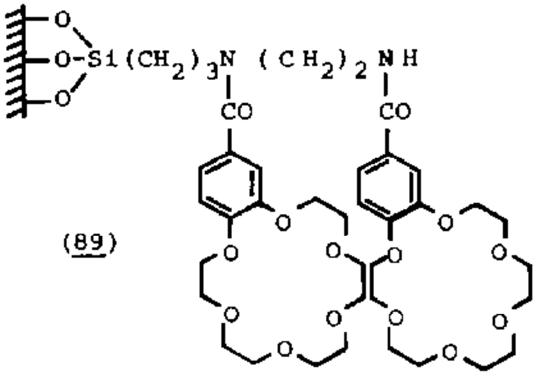
A small number of papers, in which the complexing ability of crown ethers anchored to polymeric membranes or resins is discussed have been published[167-170] during the period of the Review. Complex formation between Li^+-Cs^+ and B18C6 incorporated in polyvinylalcohol has been studied spectrophotometrically in aqueous dioxane and thf.[167] The variation of the apparent complex formation constants with solvent composition are interpreted in terms of the activity of water in the solvent mixtures. The process of complex formation liberates approximately three molecules of water from the vicinity of the cations.[167]



(85) n=1
(86) n=2
(87) n=3



(88) X = an end group of initiator or poly(crown ether)



(<u>89</u>)

Membranes fabricated from poly(ethylene-CO-maleic anhydride) modified by a crown ether moiety (<u>85</u>-<u>87</u>) exhibit efficient proton driven cation (Na^+, K^+, Cs^+) transport properties;[168] they do show, however, distinctly different ion selectivities, the 12C4 (<u>85</u>), 15C5 (<u>86</u>) and 18C6 (<u>87</u>) derivatives binding Na^+, K^+ and Cs^+ respectively. The chromatographic properties of poly (B18C6) modified silica (<u>88</u>) and bis(B18C6) modified silica (<u>89</u>) have been assessed[169] using water or aqueous methanol as the mobile phase; they both separate the alkali metal cations, retention times increasing in the sequence:

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

The alkaline earth metal cations could also be separated using the modified silicas (<u>88</u>) and (<u>89</u>) as stationary phases.[169]

The feasibility of determining quantitative data on the complexation of Na^+ or K^+ (as picrates) by soluble crown ethers in dioxane or toluene by studying the competition equilibrium:

$$[\text{Poly-Cr.M}]^+\text{Picrate}^- + \text{Cr} \rightleftharpoons [\text{Cr.M}]^+ \text{Picrate}^- + \text{Poly-Cr} \qquad \ldots(24)$$

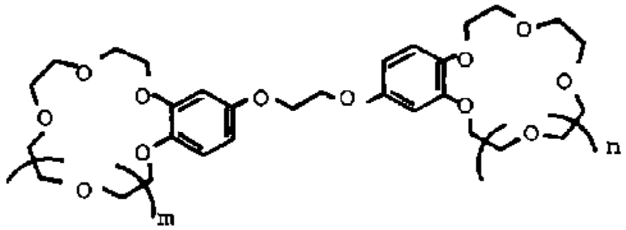
where Cr is a soluble crown ether and Poly-Cr is a crown ether attached to a cross-linked polystyrene resin, using spectrophotometric methods has been demonstrated.[170]

The kinetics and mechanism of the interaction of $K_2S_2O_8$ and 18C6 in basic aqueous media have been elucidated.[171] The oxidation of 18C6 occurs via a radical chain mechanism; the rate of the reaction is markedly enhanced vis-vis the oxidation of simple ethers by a Coulombic attraction between a cation complexed crown radical and the $S_2O_8^{2-}$ anion.

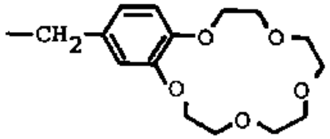
1.5.3 Complexes of Bis(crown ethers) and of Lariat Ethers

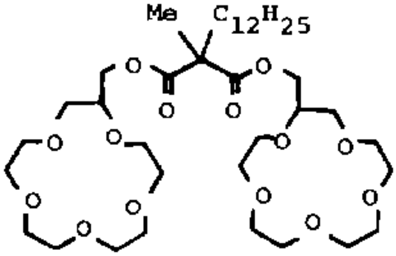
The rapidly increasing numbers of communications on the chemistry of alkali and alkaline earth metal complexes of bis(crown ether) derivatives,[172-174] of so-called lariat ethers,[175-178] and of phosphorus donor-crown ether ligands[179-182] (which generate similar coordination environments to lariat ethers) has necessitated the inclusion of a subsection to cover these topics.

Japanese authors[172-174] have reported on the alkali metal cation selectivities of the bis(crown ether) derivatives (90-97). Ikeda et al[172] have determined the efficacy of the novel bis(benzocrown ethers)(90-92) in extracting alkali metal picrates from water into CH_2Cl_2. The unsymmetrical derivative (90) selectively complexed Rb^+ in the presence of all the other alkali metal cations. The K^+ ion selectivities of the lipophilic bis(15C5) derivative (93) and of the series of bis(15C5) derivatives (94-97) of cyclohexane

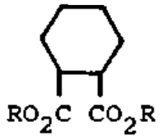


(90) m = 2, n = 1
(91) m = 1, n = 1
(92) m = 2, n = 2

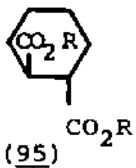
R= 



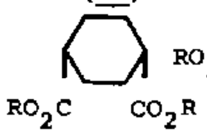
(93)



(94)



(95)

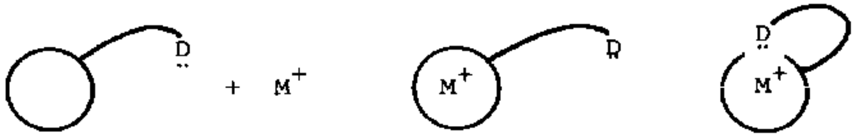


(96)

(97)

dicarboxylic acid and benzene dicarboxylic acid have been assessed by Kimura et al.[173,174] The lipophilic bis(crown ether) (93) is highly selective for K^+ ion;[173] indeed, in its preference for K^+ over Rb^+ and Cs^+ it is superior to valinomycin. Of the bis(crown ether) derivatives (94-97) of the dicarboxylic acids, the cis-1,2-cyclohexanedicarboxylic acid derivative was found to be outstandingly K^+ ion selective.[174]

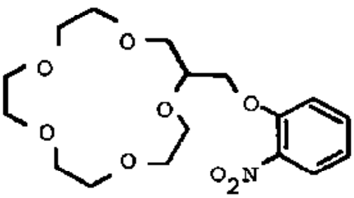
Gokel et al[175-177] have synthesised a large number of crown ethers bearing flexible side arms containing one or more neutral donor group and assessed their cation binding ability. The proposed binding concept (Scheme 5) illustrates the derivation of the name 'lariat ethers' used to describe these compounds.



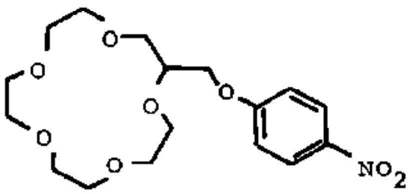
Scheme 5

Although the presence of the donor groups often enhanced the cation binding ability of the ether, the increases in stability constant were but minimal.[175] The conformation of the side chain is critical. Thus, electrochemical studies of the stability constants of complexes formed between Na^+ and the nitrobenzene substituted lariat ethers (98,99) in acetonitrile indicate that whereas (98) exhibits a strongly enhanced intramolecular cation binding by the NO_2 group, (99) interacts much more weakly owing to the inappropriate siting of the NO_2 group.[176]

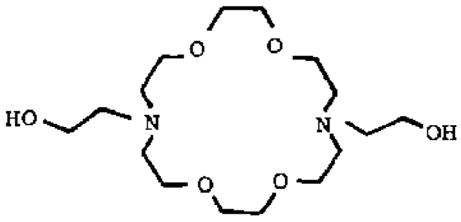
Unequivocal evidence for side arm participation in these complexes has been obtained from a single crystal X-ray diffraction study of the structures of the NaI complex of (100)



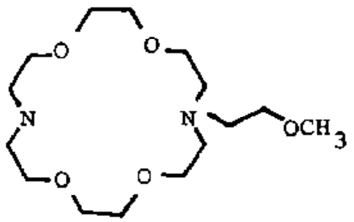
(98)



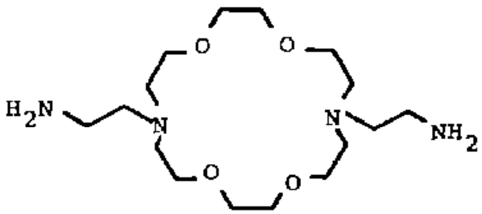
(99)



(100)



(101)



(102)

and of the KI complex of (101).[177] Ortep drawings of the two complexes plus skeletal drawings of the cation coordination spheres are shown in Figure 5. In the Na^+ complex (Figure 5(a)), the macroring donor atoms are arranged in a twist-boat structure, r(Na...O) = 243.7-261.1 pm, r(Na...N) = 263.0, 263.7 pm; the oxygen atom in each side arm occupying a 'flagpole' position, r(Na...O) = 242.6, 258.8 pm. In the K^+ complex (Figure 5(b)), the macroring donor atoms are disposed in a chair conformation with the K^+ ion distinctly above the plane of four ring oxygen atoms, r(K...O) = 278.6-290.8, r(K...N) = 295.7 pm; the side arm oxygen is located underneath the plane in an apical position of the coordination sphere, r(K...O) = 290.9 pm and iodide occupies the opposite apical position, r(K...I) = 343.4 pm.[177]

Not all complexes containing lariat ethers adopt this conformation; in the monohydrate complex formed between RbI and (102), the two side arms of the lariat ether act not intra- but inter-molecularly.[178] Thus the 9-fold coordination sphere of the Rb^+ ion is composed of the four oxygen atoms, r(Rb...O) = 283.1-293.6 pm, and two nitrogen atoms, r(Rb...N) = 316.5, 324.5 pm, of the macrocyclic ring, the nitrogen atoms of the side arms of two symmetry related macrocyclic rings, r(Rb...N) = 333.7, 335.8 pm and a water molecule, r(Rb...O) = 314.6 pm. The geometry of the

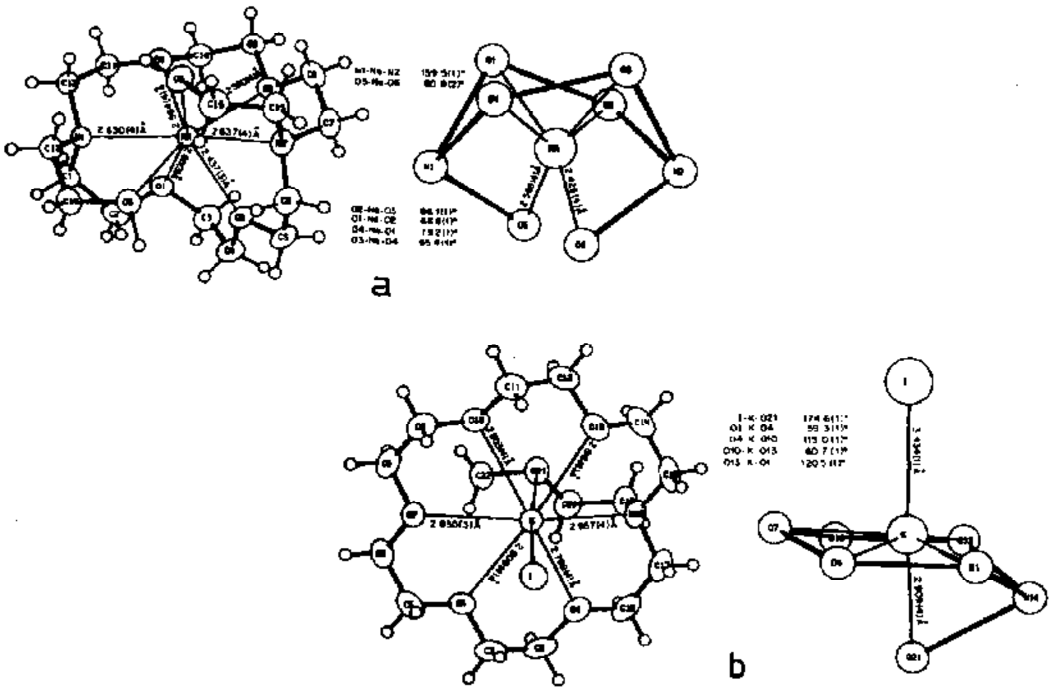
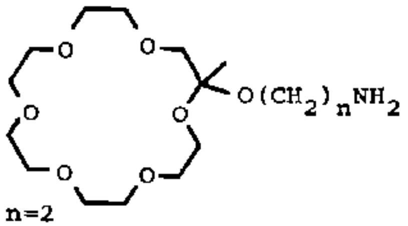


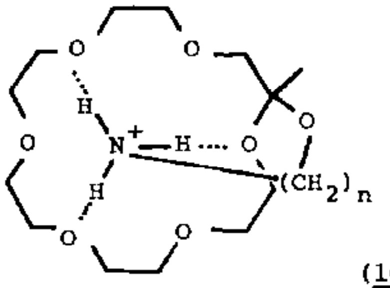
Figure 5. Molecular structure and cation coordination sphere of (a) the NaI complex of (100) and (b) the KI complex of (101) (reproduced by permission from J. Am. Chem. Soc., 105(1983)6717).

coordination sphere is highly distorted; the heteroatoms of the ring occupy one hemisphere and the side arm nitrogen atoms and the water molecule occupy the other.[178]

The lariat ethers (103,104) have been prepared by a group of Japanese authors.[179] They exhibit both an excellent selectivity for K^+ in the presence of Na^+ and an ability to transport K^+ across a liquid membrane; this latter transport process, which is acid-base driven, involves the reversible intramolecular complexation of the crown ring and the side arm protonated amino group forming (105,106).[179]

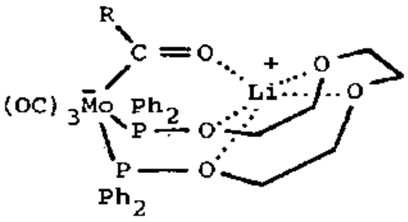


(103) n=2
(104) n=5

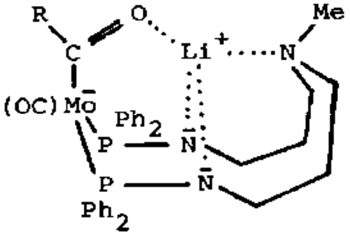


(105) n=2
(106) n=5

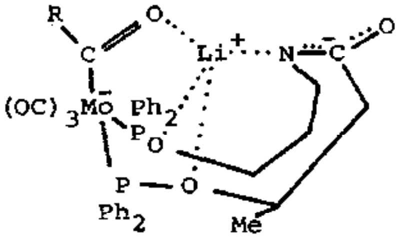
Powell et al[180-182] have synthesised a series of Li^+ complexes of phosphorus donor crown ether ligands containing molybdenum or tungsten carbonyl fragments bearing acylate or benzoylate moieties (107-111). The stability of the complexes arises from the strong



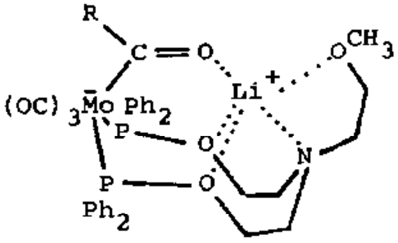
(107)



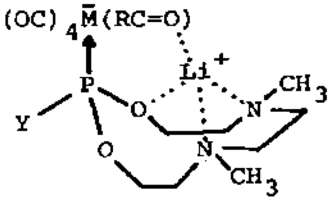
(108)



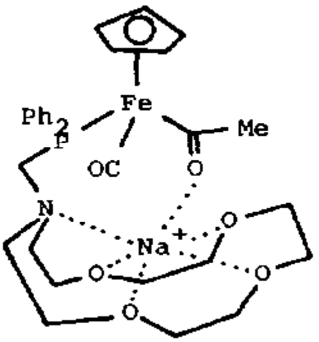
(109)



(110)



(111)



(112)

binding of the acylate/benzoylate residue for the Li^+ ion coordinated by the heteroatoms of the macroring. Single crystal X-ray diffraction studies have been completed on two complexes, (110) and (111); their molecular structures are compared in Figure 6. Whereas (110) adopts a 'lariat' ether complex conformation with an intramolecular (PhCO)-Li$^+$ interaction (Figure 6a), (III) is a dimeric species the two benzoylate complexes being joined via two intermolecular (PhCO)-Li$^+$ interactions (Figure 6b). In the monomer (Figure 6a), the Li$^+$ ion adopts a distorted trigonal bipyramidal coordination sphere composed of the four heteroatoms of the macroring, r(Li$^+$...O) = 201-209 pm, r(Li$^+$...N)= 223 pm and the oxygen atom of the benzoylate residue, r(Li....O) = 192 pm.[181] In the dimer (Figure 6b), the Li$^+$ ion is tetrahedrally coordinated by three heteroatoms of the macroring, r(Li...O) = 193 pm, r(Li...N) = 210,212 pm and the oxygen atom of the bridging benzoylate moiety, r(Li...O) = 188 pm.[182]

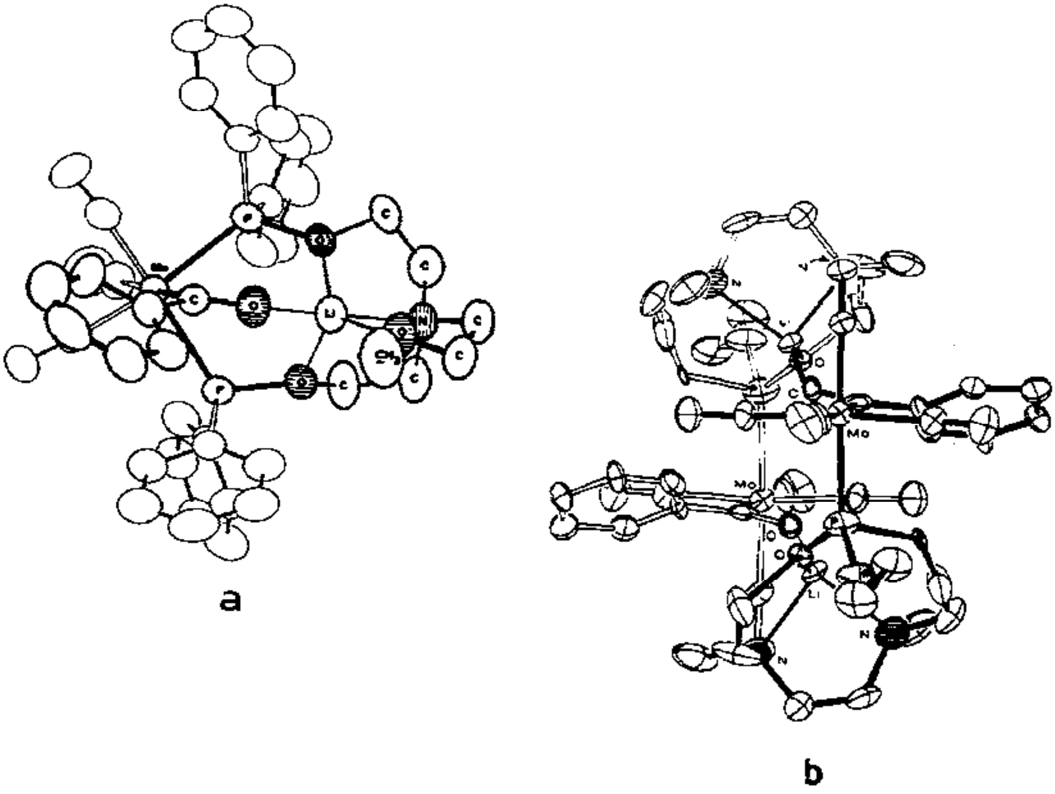
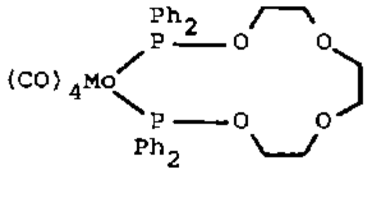
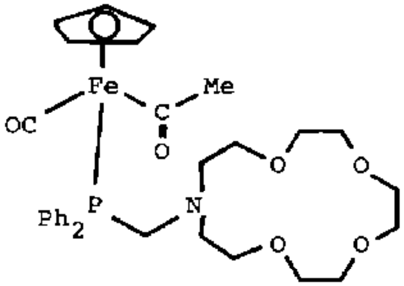


Figure 6. Molecular geometries of (a) monomeric $(CO)_3Mo(PhCOLi)$-$(Ph_2POCH_2CH_2)_2NCH_2CH_2OCH_3)$ and (b) dimeric [cis$(CO)_4Mo$-$(PhCOLi)(EtOP\{OCH_2CH_2N(CH_3)CH_2\}_2)$] (reproduced by permission from (a) Inorg. Chim. Acta, 76(1983)L75 and (b) J. Organomet. Chem., 243(1983)C1).

A similar Na^+ complex (112) has been isolated by McLain.[183] Whereas the preparative route chosen by Powell et al[180-182] involves reaction of phenyllithium with the appropriate substrate (eg. (113) affords (107)) in thf, McLain's synthesis of (112)



(113)



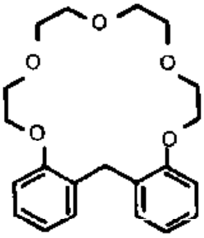
(114)

involves addition of $NaPF_6$ to CH_2Cl_2 solutions of (114) obtained by reaction of diphenylphosphine and monoaza 15C5 with aqueous formaldehyde followed by thermal treatment with $(\eta^5\text{-}C_5H_5)Fe(CO)_2Me$.[183]

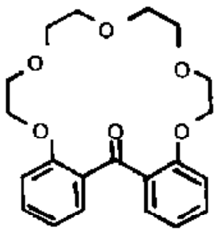
1.5.4 Complexes of Macrocyclic Polyethers of Novel Design

With the inclusion in this Review of subsections devoted to complexes of lariat ethers (1.5.3) and of nitrogen contining heterocycles (1.5.6), this subsection has diminished in length when compared with earlier Reviews. The majority of the papers abstracted[184-190] describe the results of structural studies undertaken by either Weber[184-186] or Owen.[187,188]

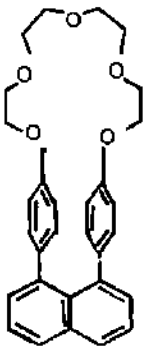
Weber has determined the molecular structures of $[(115)Na]^+NCS^-$,[184] $[(116)K]^+NCS^-$[185] and $[(117)K]^+NCS^-$;[186] whereas that of $[(115)Na]^+NCS^-$ is monomeric and that of $[(117)K]^+NCS^-$ dimeric, $[(116)K]^+NCS^-$ contains two independent ion pairs per asymmetric unit one of which is monomeric, the other dimeric. In the NaNCS complex of (115),[184] the Na^+ ion is coordinated by the five heteroatoms of the macrocyclic ring, r(Na...O) = 237.5-254.6 pm, and the nitrogen atom of the anion, r(Na...N) = 233.8 pm in a distorted pentagonal pyramidal arrangement. In the monomeric fragment of the structure of the complex of KNCS with (116),[185] the K^+ ion has three strong (r(K...O) = 269-276 pm) and two weak (r(K...O) = 307.0,321.1) contacts with the heteroatoms of the ring together with a very strong carbonyl oxygen contact (r(K...O) = 258.7 pm); the K^+ ion coordination sphere is completed by the



(<u>115</u>)

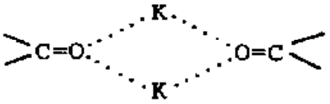


(<u>116</u>)

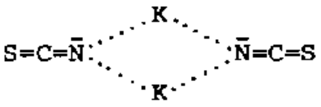


(<u>117</u>)

nitrogen atom of the anion, r(K...N) = 271.4 pm. In the dimeric fragment,[185] the K^+ ion is attached to the five heteroatoms of the ring, r(K...O) = 275.8-308.7 pm, to the carbonyl oxygen, r(K...O)= 304.9 pm and to a symmetry related carbonyl oxygen, r(K...O) = 284.6 pm, giving a dimeric structure via



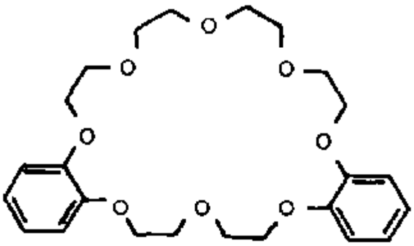
linkages; the K^+ coordination sphere is completed by the nitrogen atom of the anion which lies in the space between the two macrocyclic rings, r(K...N) = 273.6 pm. In the dimeric structure of the complex of KNCS with (<u>117</u>),[186] the two macrocyclic rings are held together via



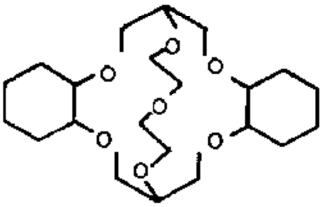
linkages. The K^+ ion coordination sphere is composed of four of the five oxygen atoms of one of the polyether rings, r(K...O) = 280.1-291.6 pm (the fifth oxygen is somewhat more remote, r(K...O) = 325.4 pm) and the nitrogen atoms of two symmetry related anions, r(K...N) = 290.5, 292.9 pm.

Owen has described the geometries of the cationic species present in [(<u>118</u>)Na]$^+ClO_4^-$[187] and [(<u>119</u>)Mg]$^{2+}(ClO_4)_2 \cdot H_2O$.[188] Asymmetric DB24C8 (<u>118</u>) wraps around the Na^+ ion, its eight oxygen atoms forming a distorted square antiprismatic coordination sphere.[187] Seven oxygen atoms are fairly close to the cation, r(Na...O) = 244.7 - 260.5 pm; the eigth, however, is somewhat more remote, r(Na...O) = 271.8 pm. The anion is not coordinated to the cation in agreement with the i.r. spectra.[187] The asymmetric unit of $[(\underline{119})Mg]^{2+}(ClO_4)_2.H_2O$[188] contains two crystallographically independent molecules each of which contains a Mg^{2+} ion coordinated to a water molecule, r(Mg(1)...O) = 205.6, r(Mg(2)...O) = 204.5 pm, and to the seven oxygen atoms of the macrocycle; as for the asymmetric DB24C8 derivative, one of these oxygen atoms is somewhat more remote than the others, r(Mg(1)...O) = 212.3-225.9,249.1; r(Mg(2)...O) = 212.5-224.7, 258.1 pm.[188]

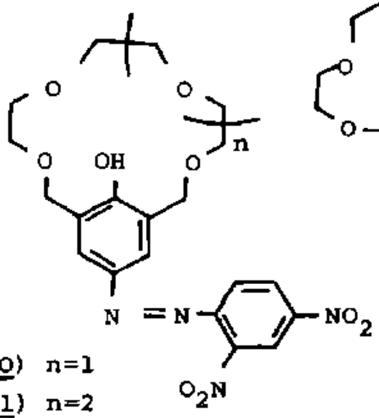
Spectroscopic studies of the complexation of alkali and alkaline earth metal cations by (<u>120</u>,<u>121</u>) in $CHCl_3$, CH_3OH and $(C_2H_5)_3N$ have been undertaken.[189] Linear relationships between $r_{M^{n+}}$ (M^+ = Li-Cs; M^{2+} = Mg-Ba) and both the position of the absorption maximum and the molar absorption coefficients of the resulting complexes were established. The possibility of the colourimetric determination of Rb^+ and Cs^+ by (<u>120</u>) was also demonstrated.[189]



(<u>118</u>)

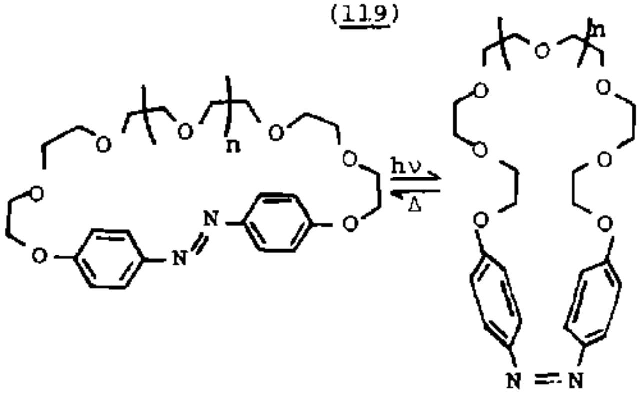


(<u>119</u>)



(<u>120</u>) n=1

(<u>121</u>) n=2



(<u>122</u>) n=1

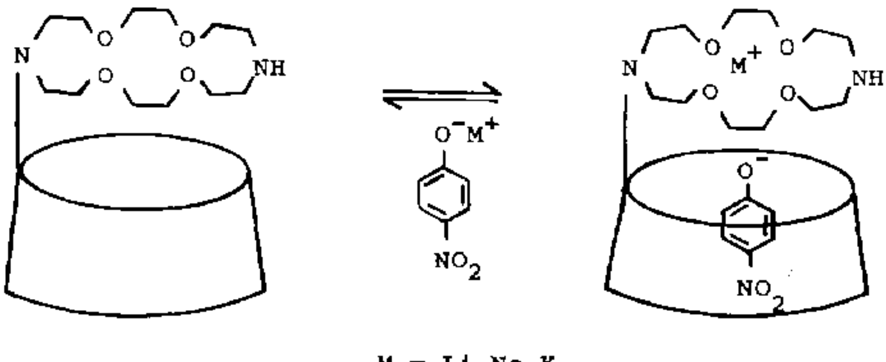
(<u>123</u>) n=2

(<u>124</u>) n=3

Three novel photoresponsive azobenzeneophane-type crown ethers (122-124) in which the 4,4' positions of the azobenzene residue are linked by a polyoxyethylene chain have been synthesised.[190] Whereas the trans-cis isomerisation was effected by u.v. light, the cis-trans isomerisation was brought about either thermally or by visible light; the interconversion was completely reversible. Although the trans isomers totally lack affinity for alkali metal cations, the cis isomers are capable of binding considerable amounts. The latter also exhibit selectivity in the binding of alkali metal cations; (122) for Na^+, (123) for K^+ and (124) for Rb^+.[190]

1.5.5 Cryptates and Related Complexes

The novel diaza-crown ether capped cyclodextrin (125) has been synthesised by Willner and Goren;[191] it provides a molecular assembly with two recognition receptor sites, which cooperate in the association of alkali metal p-nitrophenolates as substrates. Thus, insertion of the anion in the hydrophobic cavity of β-CD assists the binding of the cation to the crown component and coordination of the cation with the crown receptor provides an electrostatic anchoring site for the anion in the β-CD cavity (126). The binding of the alkali metal p-nitrophenolates to (125) is substantially better than that to either of the separate host components, β-CD and diaza-crown ether.[191]



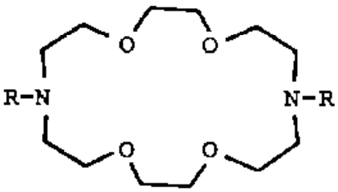
(125) M = Li,Na,K (126)

Reaction of the third stage intercalation compound $C_{36}K$ with C222 in a neutral non-polar solvent yields, after some considerable time (~6 weeks) the first stage intercalation compound of composition $C_{36}[C222K]_{0.85}$ with interlayer spacing of 1550pm.[192]

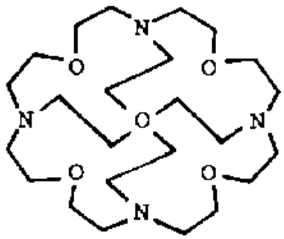
The K^+ ions are thought to lie inside the cryptand cage within the graphite layers, although direct evidence confirming the presence of the cage is, as yet, lacking.[192]

Structural analyses of the $[C222K]^+$ salt of bis(4-methylimidazolato)(tetraphenylphosphinato)iron(III)[193] and of the ethylenediamine adduct of the $[C222Ba]^{2+}Se_4^{2-}$ salt[194] have been completed. In the former complex,[193] the K^+ ion is simply coordinated by the six oxygen atoms of the cryptand, r(K...O) = 275.6-286.6 pm. In the latter complex,[194] the coordination sphere of the Ba^{2+} ion is composed of the eight heteroatoms of the cryptand, r(Ba...O) = 275.3-288.7, r(Ba...N) = 297.2, 298.1 pm, a selenium atom of the Se_4^{2-} anion, r(Ba...Se) = 343.2 pm, and a nitrogen atom of the ethylenediamine molecule, r(Ba...N) = 307.7 pm.

Several groups have investigated kinetic and thermodynamic aspects of the complexation of alkali and alkaline earth metal cations by cryptands and related species in a variety of aqueous and non-aqueous solvents.[195-200] Cox et al[195-197] have reported data for $[C222.K]^+$ in aqueous CH_3CN solutions,[195] for $[C2_B22.Ca]^{2+}$ and $[C2_B2_B2.Ca]^{2+}$ in methanol[196] and for $[(\underline{127}).M]^{2+}$ (M = Ca-Ba) and $[(\underline{128}).M]^{2+}$ (M = Ca-Ba) in methanol.[197] Lacoste and Schue[198]



(127) R = H
(128) R = Me

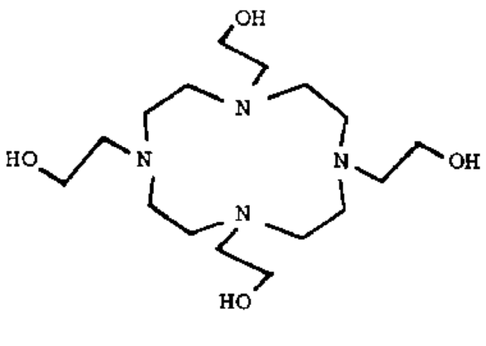


(129)

have used spectroscopic methods to study the kinetics of the dissolution of alkali metals in thf containing C222, C221 and (129).[198] Pizer and Selzer[199] have used similar techniques to determine stability constants for alkaline earth metal cryptate formation between C222, C221 and C211 and Ca^{2+}, Sr^{2+} and Ba^{2+} in dmso. Similar cation specificity to that observed in water is displayed; the magnitude of the stability constants measured in dmso, however, are less than those in water by a factor of at least 100.[199] Multinuclear (^{13}C and ^{1}H) n.m.r. and calorimetric measurements have been accrued by Popov et al[200] to study interactions of C221 with Na^+ and K^+ ions in a variety of non-aqueous solvents. The n.m.r. spectra of the two complexes in solution are quite different, indicating that the ligand exists in different conformations, as in the crystalline state. Calorimetric measurements show that C221 forms a more stable complex with Na^+ than with K^+. The Na^+/K^+ selectivity is extremely sensitive to the solvent and is particularly pronounced in CH_3NO_2 solutions.[200]

1.5.6 Complexes of Macrocyclic Polyimine Ligands

Structural data for complexes of alkali and alkaline metal cations with the tetrapodand macrocyclic tetraimine (130) have been elucidated both in the solid state[201,202] and in solution.[203] Groth has determined (at 123K) the crystal and molecular structures of the 2:1 complex between LiCl and (130)[201] and of the 1:1 complexes between NaNCS or KNCS and (130).[202] As the size of the alkali metal cation increases the coordination environment offered by the tetraimine ligand (130) expands from 5-coordinate (for Li^+), through 7-coordinate (for Na^+) to 8-coordinate (for K^+) as the number of ligating side arm oxygen atoms increases from one through three to a maximum of four. Of the two crystallographically distinct Li^+ ions in the $[(130),2Li(H_2O)_2]^{2+}2Cl^-$ complex, one adopts this type of configuration being coordinated by the four heteroatoms of the macrocycle, r(Li...N) = 207.9-234.7 pm as well as the oxygen atom of a gauche oriented side chain, r(Li...O) = 194.8 pm. The other Li^+ ion lies in a completely different environment being coordinated by the oxygen atoms from three anti-oriented side chains of different symmetry related ligands, r(Li...O) = 192.2-194.3 pm and by a single water molecule, r(Li...O) = 192.7pm.[201]



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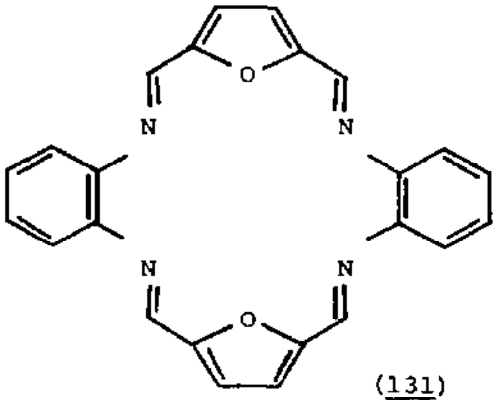

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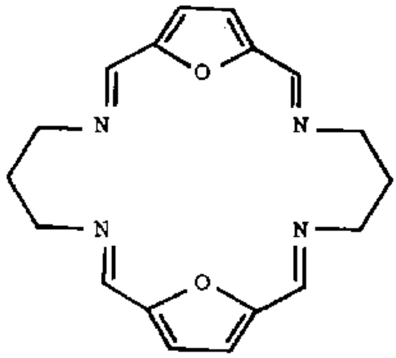


(132)

The Na^+ ion in $[(130)Na]^+NCS^-$, is located in the cavity formed by the four heteroatoms of the macrocyclic ring, r(Na...N) = 256.9-264.3 pm and by the oxygen atoms of three gauche oriented side chains, r(Na...O) = 238.8-252.6 pm. Two crystallographically independent K^+ ions appear in $[(130)K]^+NCS^-$. They have very similar coordination spheres being surrounded by the oxygen atoms of all four side chains, r(K(1)...O) = 265.9-287.4, r(K(2)...O) = 272.6-282.4 pm, together with the four nitrogen atoms of the tetraimine ring, r(K(1)...N) = 286.8-288.9, r(K(2)...N) = 283.3-291.0 pm.

The solution structures of the complexes formed by (130) with alkali (Li-K) and alkaline earth (Mg-Ba) metal cations have been investigated by Grace and Krane[203] using ^{13}C n.m.r. longtitudinal relaxation time measurements. It is concluded that the number of side arms involved in cation binding in solution differs from that in the solid state. Thus, whereas Li^+ binds one, Na^+ binds three and K^+ binds four side arms in the solid state, the solution n.m.r. data indicate that whereas Na^+ binds three side arms, both Li^+ and K^+ bind between two and three.[203]

Drew et al[204,205] have investigated the template synthesis of complexes of the 18- and 20-membered macrocyclic tetraimines (131, 132). Cyclic condensation of 2,5-diformylfuran with o-phenylenediamine in methanol in the presence of K^+, Ca^{2+} or Ba^{2+} ions yields complexes of (131);[204] reaction of 2,5-diformylfuran with 1,3-diaminopropane in methanol in the presence of Ca^{2+}, Sr^{2+} or Ba^{2+}, but not Mg^{2+}, gives complexes of (132) in very high yield.[205] The complexes all have a 1:1 ligand:metal stoichiometry except those of the Ba^{2+} ion which contain two macrocyclic ligands per cation.[204,205] The structures of $[(131)_2Ba][BPh_4]_2$[204] and

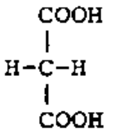
$[(\underline{132})_2Ba(H_2O)_2][Co(NCS)_4]$[205] have been determined. The $[(\underline{131})_2Ba]^{2+}$ ion has imposed C_2 symmetry; the Ba atom, which is located between two almost parallel N_4 planes separated by ca. 260 pm, is 12-coordinate being bonded to the four nitrogen, r(Ba...N) = 296-308pm, and two oxygen atoms, r(Ba...O) = 291-302pm of each ring.[204] The Ba atom of the $[(\underline{132})_2Ba(H_2O)_2]^{2+}$ cation is bonded to all six heteroatoms of one macrocycle, r(Ba...N) = 301.6-310.9, r(Ba...O) = 285.9, 286.1 pm, but only to a single furan di-imine moiety of the second macrocycle, r(Ba...N) = 308.4, 309.7, r(Ba...O) = 286.1 pm. The 11-fold coordination sphere of the Ba atom is completed by two water molecules, r(Ba...O) = 276.7, 299.7 pm.[205] Temperature dependent ^{1}H-n.m.r. studies of the analogous complex, $[(\underline{132})_2Ba(MeCN)_2][BPh_4]_2$ in CD_3CN indicate that the hexahapto-trihapto coordination observed in the solid state is retained in solution.[205]

1.5.7 Salts of Carboxylic Acids

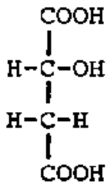
As for the 1982 Review, the majority of papers abstracted for this subsection report novel structural data for these materials.[206-213] Neutron diffraction studies of potassium hydrogen diformate, the structure of which has been determined previously in an X-ray diffraction investigation, have been undertaken at 120 and 295K to elucidate further the hydrogen bonding in this salt.[206] The K^+ ion is surrounded by eight oxygen atoms from one bidentate and six monodentate formate anions; increase in temperature results in a marked increase in the length of K-O contacts of between 1.7 and 7.2 pm (r(K...O) =275.4-301.7 pm at 120K; r(K...O) = 278.2-306.8 pm at 295K).[206]

Anhydrous sodium acetate, as crystallised from aqueous solutions at temperatures above 371K, the decomposition temperature of the more familiar trihydrate, exists in two forms both of which are orthorhombic (Form I: a = 1785.0, b = 998.2, c = 606.8 pm; Form II: a = 595.1, b = 2021.3, c = 590.2 pm).[207] The space group for form I can be unambiguously defined as Pcca; that for form II, however, is more difficult to determine since the structure is characterised by stacking faults in the molecular layers perpendicular to b giving rise to domains belonging to space group Pcca with halved b axis and hence space group Icab (standard Ibca). The unit cells of the two forms are related by $a_{II}=a_I/3$; $b_{II}\sim 2b_I$; $c_{II}\sim c_I$. Each of the two crystallographically independent Na^+ ions in form I is surrounded by six oxygen atoms provided by one bidentate and four monodentate anions, r(Na...O) = 235-267 pm.[207]

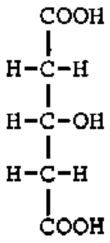
The asymmetric units of dilithium malonate and of disodium malonate trihydrate contain two and four crystallographically distinct cations, respectively.[208] Both Li^+ ions are tetrahedrally coordinated by four carboxylate oxygen atoms. All four of the Na^+ ions are located in approximately octahedral coordination spheres; those of Na(1) and Na(2) are composed of four carboxylate oxygen atoms and two water molecules, those of Na(3) and Na(4) by five



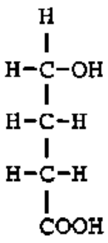
Malonic Acid



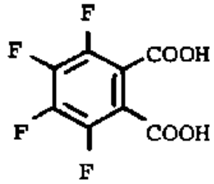
Malic Acid



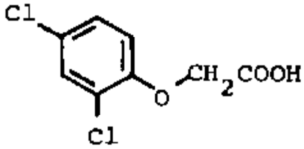
Citric Acid



Succinic Acid



Tetrafluorophthalic Acid



2,4-Dichlorophenoxy Acetic Acid

carboxylate oxygen atoms and a single water molecule. Precise details of the coordination geometries (interatomic distances and angles) are not quoted.[208]

An interesting observation made by Lenstra et al[209,210] is that the cation coordination number (7) in racemic sodium hydrogen-l-malate[209] appears to be larger than that (6) in racemic potassium hydrogen-l-malate monohydrate.[210] The two crystallographically independent Na^+ ions in the former salt are coordinated by seven oxygen atoms in the form of a highly distorted monocapped octahedron, r(Na(1)...O) = 238-266 pm (from three anions), r(Na(2)...O) = 239-271 pm (from four anions).[209] The K^+ ion in the latter salt is coordinated by four oxygen atoms from three different anions, r(K...O) = 262.6-286.8 pm, and two water molecules, r(K...O) = 284.3, 285.2 pm. A seventh long range coulombic interaction, however, links the K^+ ion to a more remote oxygen atom of a neighbouring anion, r(K...O) = 321.6 pm.[210]

The structure of trilithium citrate pentahydrate[211] contains four crystallographically independent Li^+ ions (two of these lie at special positions with 50% occupancy per asymmetric unit). Three Li^+ ions are four-coordinate; the fourth is six-coordinate. The coordination distances vary markedly, r(Li...O) = 188.3-222.2 pm, the longest being observed in the case of the octahedrally coordinated Li^+ ion.[211]

Refinement of the structure of dipotassium tetrafluorophthalate[212] has resulted in improved interatomic distances and angles. The K^+ ion is coordinated by one fluorine atom, r(K...F)= 288.0 pm, four oxygen atoms from monodentate carboxylate anions, r(K...O) = 269.0-278.8 pm and two oxygen atoms from a bidentate carboxylate anion, r(K...O) = 286.5, 294.4 pm. The two oxygen atoms of the bidentate carboxylate anion are symmetrically arranged opposite the fluorine atom to give a pseudo-octahedral coordination geometry.[212]

The 9-fold K^+ ion coordination sphere in the molecular structure of potassium 2,4-dichlorophenoxyacetate hemihydrate[213] is composed of a single chlorine atom, r(K...Cl) = 326.2 pm, and eight oxygen atoms afforded by two water molecules, r(K...O) = 282.8, 332.2 pm, and by one phenoxy, r(K...O) = 316.7 pm, and five carboxylate moieties, r(K...O) = 269.0-311.6 pm, of the anions.[213]

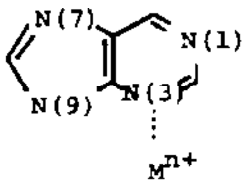
The molecular structure of the 1:1 adduct of CsF with succinic acid has also been determined from single crystal X-ray diffraction data. Although the hydrogen bonding within this adduct is the feature of prime interest to the authors, they do report the Cs^+ coordination geometry. The cation is surrounded by two fluorine atoms, r(Cs...F) = 295.8; 313.4 pm, and four oxygen atoms, r(Cs...O) = 308.3-312.2 pm, with a fifth, somewhat more remote, oxygen atom, r(Cs...O) = 346.2 pm.[214]

The far i.r. and Raman spectra of polycrystalline lithium formate monohydrate and the Rayleigh wing scattering of its aqueous solutions have been reported;[215] several new bands have been identified and assigned.

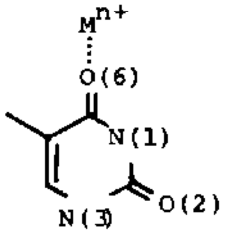
The alkali metal thiocarboxylates, RCOSM (M = Li-Cs), have been conveniently prepared[216] in high yield by reaction of the appropriate thiocarboxylic acids with either the metal hydrides, MH (M = Li-K), or the metal acetates, CH_3COOM (M = Rb,Cs); the products were characterised spectroscopically as well as chemically.

1.5.8 Complexes of Nucleotides and Related Species

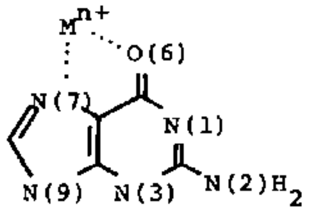
The binding of alkali and alkaline earth metal cations to nucleotides has been studied both theoretically[217] and experimentally.[218,219] Sagarik and Rode[217] have considered interactions between various metal cations and the bases, adenine, guanine, thymine and cytosine using ab initio MO SCF calculations with minimal GLO basis set. Their results indicate that alkali and alkaline earth metal cations prefer to bind at N(3) of adenine (rather than at either of the other two reactive sites, N(1) or N(7)), simultaneously at N(7) and O(6) of guanine (rather than N(3)) at O(6) of thymine (rather than O(2)) and simultaneously at N(1) and O(2) of cytosine.[217]



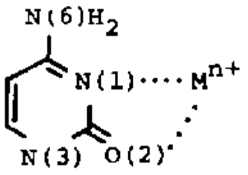
Adenine



Thymine



Guanine



Cytosine

Multinuclear n.m.r. (^{1}H, ^{7}Li, ^{31}P, ^{35}Cl and ^{81}Br) experiments[218] in acetone and thf have shown that LiX (X = F,Cl,Br) and $LiClO_4$ binding to phosphates involves complexation of the phosphonyl oxygen atom by the Li^+ ion with the concomitant formation of 1:1 salt-phosphate complexes. Single crystal X-ray diffraction studies of disodium deoxycytidine-5'-monophosphate heptahydrate[219] have shown that neither sodium atom interacts with the anion; they are both completely surrounded by water molecules. Whereas Na(1) has a near octahedral 6-fold coordination, r(Na(1)...O) = 237.4-257.9 pm, Na(2) has a highly distorted five coordinate geometry, r(Na(2)...O) = 230.8-254.2 pm.[219]

Sodium ion release from DNA, caused both by intercalating drugs (eg., ethidium bromide) and by denaturation has been studied using ^{23}Na n.m.r. techniques;[220] the efficacy of the techniques for monitoring DNA conformational changes and binding interactions is established.

1.5.9 Heterobimetallic Complexes containing Alkali Metals

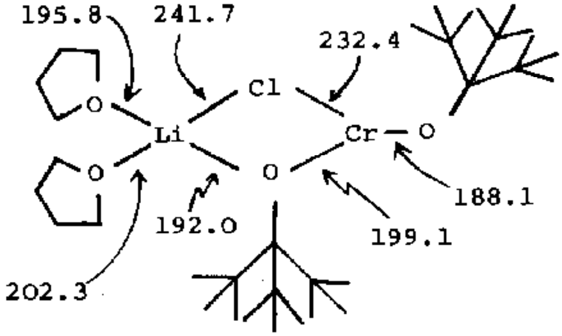
The dearth of papers on this subject during 1982 which resulted in the omission of this subsection in the previous Review was but temporary. The syntheses of a significant number of heterobimetallic complexes containing lithium[221-226] and sodium[227-229] have been reported during 1983; most of the complexes have been fully characterised by single crystal X-ray diffraction methods.

The Li-Cr(II) derivative, $[Cr(OCBu^t{}_3)_2.LiCl(thf)_2]$[221] (<u>133</u>) has been crystallised from the solution formed by addition of a slurry of $CrCl_3$ in thf to a 1:1 mixture of n-butyllithium in n-hexane and t-butylalcohol in ether. Interaction of $FeCl_3$ with either naphthyl-lithium or phenyl-lithium in dry ether under an inert atmosphere affords the Li-Fe(II) complex, $[Fe(C_{10}H_7)_4.\{Li(Et_2O)\}_2]$,[222] (<u>134</u>), or the Li-Fe($\bar{0}$) complex, $[Fe(C_6H_5)_4.\{Li(Et_2O)\}_4]$,[223] (<u>135</u>) respectively. The phenyl complex, but not the naphthyl complex, is able to reduce dinitrogen. The exceedingly complicated Li-Fe($\bar{0}$) derivative, $[\{(\eta^5-C_5H_4Li)Fe(\eta^5-C_5H_3LiCH(Me)NMe_2)\}_4\{LiOEt\}_2\{tmeda\}_2]$ (tmeda = $Me_2NCH_2CH_2NMe_2$),[224] (<u>136</u>) was serendipitously discovered as a crystalline by-product of the preparation of the dilithio-α-N,N-dimethylaminoethylferrocene - tmeda adduct. Under argon at 273K, finely dispersed lithium reduces a pentane solution of $[(\eta^2-C_2H_4)Co(PMe_3)_3]$ to give an orange-brown solution which, on slow evaporation, yields orange crystals of the Li-Co($\bar{0}$) complex, $[(\eta^2-C_2H_4)Co(PMe_3)_3.Li]$[225] (<u>137</u>). The Li-Ni($\bar{0}$) complex, $[(\eta^2-C_2H_4)_2Ni(CO.NMe_2)Li(pmdeta)]$ (pmdeta = $Me_2NCH_2CH_2N(Me)CH_2CH_2$-$NMe_2$),[226] (<u>138</u>) has been prepared by reaction of ethene with an ether solution containing a mixture of $[(cdt)Ni(CO)]$ (cdt = trans, trans, trans-1,5,9-cyclododecatriene) and $[LiNMe_2(pmdeta)]$ at 263K. As a 16-electron compound it is quite reactive and is readily converted into the 18-electron compound, $[Ni(CO)_3.(CONMe_2).Li$-

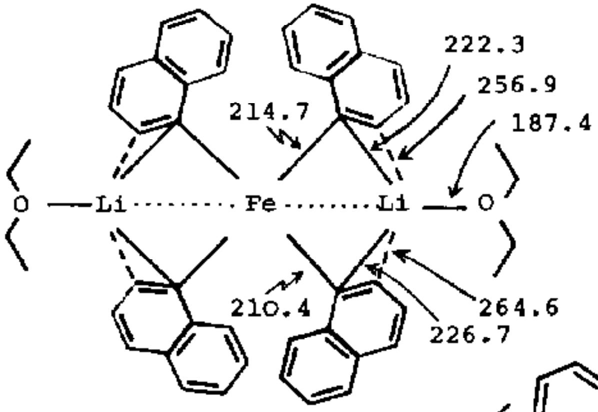
(pmdeta)] (139) by reaction with CO in ether in the temperature range $195 < T/K < 273$.

With the sole exception of (139), schematic representations of the structures of these heterobimetallic derivatives are included in Figure 7. The coordination geometry of the Li^+ ion in (133)[221] is severely distorted from tetrahedral owing to steric effects; it is composed of the bridging chlorine, r(Li...Cl) = 241.7 pm and oxygen (of a tri-tert-butylmethoxide ligand) atoms, r(Li...O) = 192.0 pm, together with the oxygen atoms of the two thf molecules, r(Li...O) = 195.8, 202.3 pm.[221] The Li^+ ion environments in (134)[222] and (135)[223] are similar. That in (134) lies between two naphthyl cycles on the straight line connecting the iron and ether oxygen atoms. It has short contacts with the ether oxygen atoms, r(Li...O) = 187.4 pm and two α-carbon and two β-carbon atoms of the naphthyl anions, r(Li...αC) = 222.3, 226.7, r(Li...βC) = 256.9, 264.6 pm. The iron atom is too remote for a bonding interaction, r(Li...Fe) = 279.7 pm. The Li^+ ion in (135) also lies on the straight line connecting the iron, r(Li...Fe) = 250 pm, and the ether oxygen atoms, r(Li...O) = 194.0 pm; in this case, however, it is located between two symmetry related phenyl anions, r(Li...αC) = 214, r(Li...βC) = 224 pm. Each of the five symmetry independent Li^+ ions in (136)[224] achieves a distorted environment in a different way; full details are shown in Figure 7. The structure of (137)[225] consists of trimeric units, in each of which the monomers are constructed in the form of an equilateral triangle. Each Li^+ ion interacts with one $[(\eta^2\text{-}C_2H_4)(PMe_3)_3]$ moiety in a 'side-on' fashion and additionally 'end-on' with the neighbouring complex via its ethene ligand; full details are given in Figure 7. The structure of (138)[226] contains a planar bis(ethene) nickel moiety linked to a planar carbamoyl moiety via a short nickel-carbon bond. The Li^+ ion is bonded to the carbonyl group, r(Li...O) = 184.1 pm via a free electron pair (∠C-O-Li = 128.2°); its distorted tetrahedral coordination sphere is completed by the three nitrogen atoms of the pmdeta molecule, r(Li...N) = 210.9-216.1 pm.

Heterobimetallic complexes containing sodium are generally much less complex than those containing lithium, the Na^+ ion normally being found in a discrete cationic moiety. Thus the tmeda adduct of sodium μ-hydridotetrakis(ethene)dinickelate($\bar{0}$),[227] prepared in the reaction:



(133)



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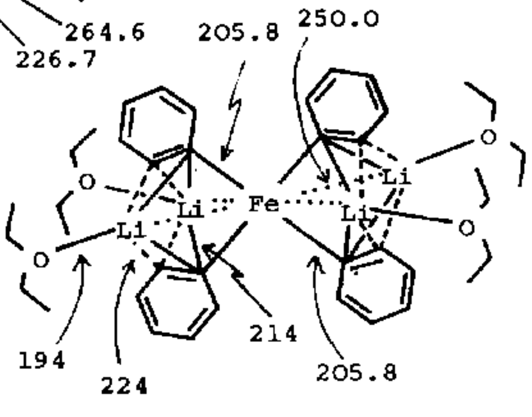
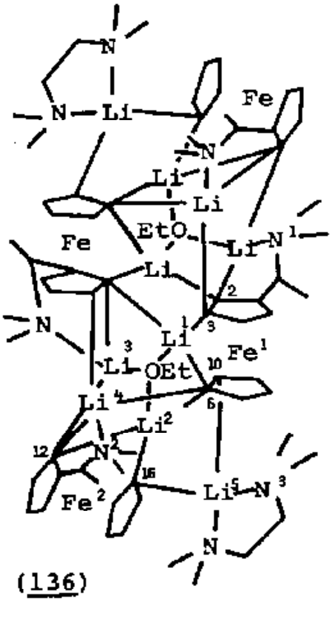


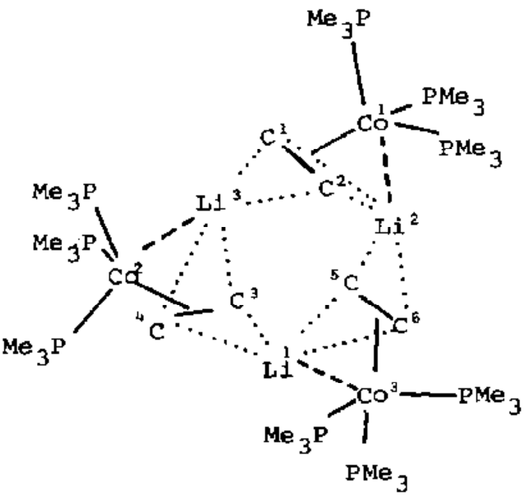
(135)



(136)

Bond distances/pm in (136)

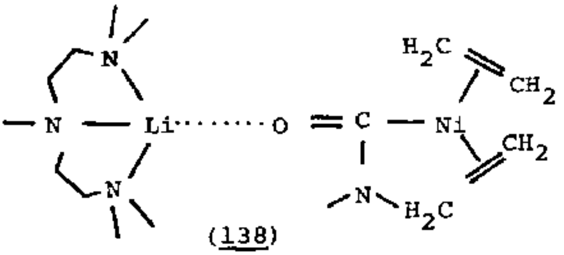
From:	Li^1		Li^2		Li^3		Li^4		Li^5	
To:	O	190	O	193	O	190	N^2	210	N^3	225
	C^2	228	C^6	236	N^1	221	C^3	251	N^4	218
	C^2	236	C^{12}	226	C^2	235	C^6	224	C^{10}	256
	C^6	222	C^{16}	228	C^{12}	220	C^{12}	218	C^{16}	204



(137)

Bond distances/pm in (137)

From:	Li^1		Li^2		Li^3	
To:	Co^3	238	Co^1	240	Co^2	240
	C^3	231	C^1	259	C^1	230
	C^4	223	C^2	251	C^2	230
	C^5	243	C^5	230	C^3	236
	C^6	261	C^6	221	C^4	268



(138)

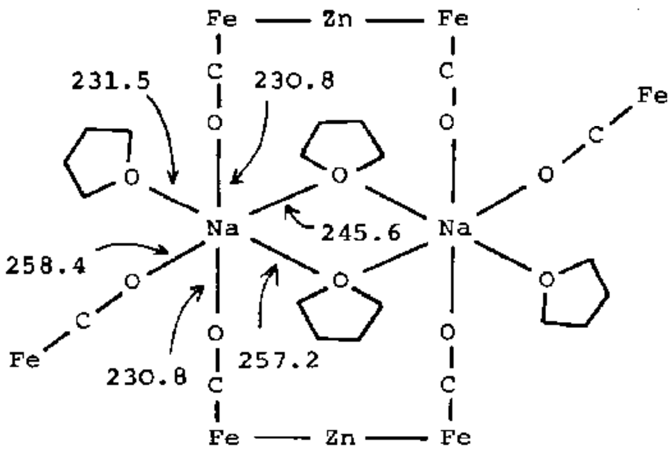
distances/pm.

Figure 7. Schematic representations of the molecular structures of six heterobimetallic complexes containing lithium.

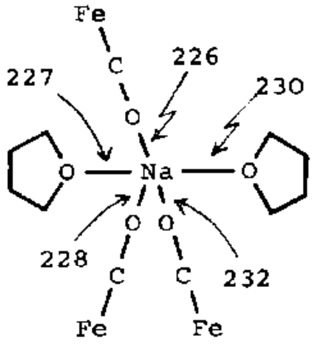
$$2Ni(C_2H_4)_3 + NaHAlR_3 \xrightarrow[\text{tmeda}\ 233K]{Et_2O} [Na(tmeda)_2]^+[HNi_2(C_2H_4)_4]^- + 2C_2H_4 + AlR_3.solv \qquad ...(23)$$

contains the $[Na(tmeda)_2]^+$ cation in which the Na atom is surrounded by the four nitrogen atoms of the two tmeda molecules, r(Na...N) = 251.1-260.4 pm, in a distorted tetrahedral geometry. A lithium complex of identical molecular formula has been prepared but its structure has not been ascertained.[227]

Sosinsky et al[228,229] have prepared and structurally characterised a series of complexes of molecular formula $[Na(thf)_2]_2^+[M(Fe(CO)_4)_2]^{2-}$ (M = Zn,Cd,Hg). A surprising feature of these compounds is the distinctly different structural chemistry exhibited by the cations of the Zinc and Mercury derivatives. For the zinc complex, the Na^+ counterion occurs in an unusual dimeric structure containing Na^+ ions in distorted



(140)



(141)

octahedral coordination spheres (140), while for the mercury complex, monomeric Na^+ counterions with distorted trigonal bipyramidal geometry are observed (141).[228,229]

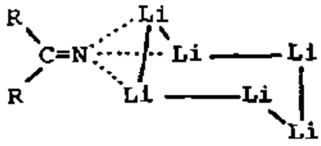
1.5.10 Lithium Derivatives

Interest in the inorganic chemistry of lithium is rapidly expanding. Not only have more papers been abstracted for this subsection than in previous years but there has also been a substantial increase of effort in the experimental study of heterobimetallic complexes containing lithium (1.5.9) and in the theoretical investigation of low molecular weight species containing lithium (1.4.2).

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

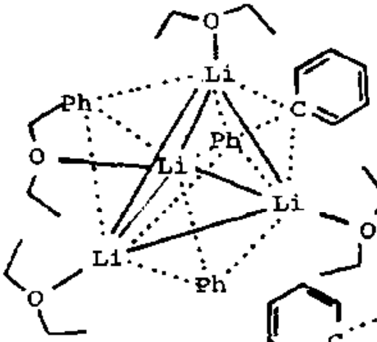
Single crystal X-ray diffraction studies have been completed on a significant number of lithium derivatives; hexameric,[230] tetrameric,[231-236] dimeric,[221,232,236-241] monomeric[242-244] and polymeric[245] structures have all been observed; significant features of these structures are shown schematically in Figure 8. The lithioketmine $Li(N{=}CBu^t{}_2)$ (142) and lithioguanidine $Li[N{=}C(NMe_2)_2]$ (143) have remarkably similar hexameric structures $[\{Li(N{=}CR_2)\}_6]$ (R = Bu^t or NMe_2) based on slightly folded chair shaped Li_6 rings held together by triply-bridging methyleneamino-groups, $N{=}CR_2$ (Figure 8).[230] In the Li_6 rings, $r(Li...Li)_{av}$ = 235 pm (in 142) or 244.5 pm (in 143) and the mean dihedral angles between Li_6 chair seats and backs are 85° and 78°, respectively. The nitrogen atoms of the bridging methyleneamino groups are approximately equidistant from the three bridged lithium atoms, $r(Li...N)_{av}$ = 206 pm (in 140) or 200 pm (in 141).

The two compounds, $[(PhLi.Et_2O)_4]$ (144) and $[(PhLi.Et_2O)_3.LiBr]$ (145) exhibit the same basic tetrameric architecture.[231] A core consists of four lithium atoms arranged at the corners of a tetrahedron, r(Li...Li) = 250-270 pm (in 144) or 250-300 pm (in 145). Negative ions (Ph^- or Br^-) are situated above each of the faces bridging three lithium atoms; in (144), an ether molecule is attached to each lithium atom, whereas in (145) the lithium atom opposite the Br^- ion does not carry an ether molecule. Although the Li...C distances are nearly equal in (144), $r(Li...C)_{av}$ = 233 pm, in (145) there are two groups of Li...C distances; ether free $r(Li...C)_{av}$ = 215 pm and ether complexed $r(Li...C)_{av}$ = 228 pm. The Li...O distances also vary in the two compounds; r(Li...O) = 205 pm (in 144) or 195 pm (in 145).[231] A similar core structure to that of (144) is found for $[(PhC{\equiv}CLi)_4(tmhda)_2]$ (tmhda = $Me_2N(CH_2)_6NMe_2$) (146).[232] The four ethyne residues lie along the 3-fold axes of the Li_4 tetrahedron, $r(Li...Li)_{av}$ = 272 pm, bridging three lithium atoms, r(Li...C) = 220 pm; the distorted tetrahedral coordination sphere of the lithium atom is completed by a nitrogen atom of a bidentate bridging tmhda molecule, $r(Li...N)_{av}$ = 211 pm. The complex, $[\{(\eta^1\text{-}C_3H_5)Li\}_2\{LiBr\}_2\{Et_2O\}_4]$ (147)[233] has a structure reminiscent of that of (145). It is based on a Li_4 skeleton in the form of a distorted tetrahedron, r(Li...Li) = 256-321 pm. The four faces of the tetrahedron are capped by two Br^- ions, r(Li..Br) = 257-260 pm, and by two cyclopropyl anions, r(Li...C) = 220-230 pm which adopt an eclipsed orientation relative to their corresponding Li_3 face. Each lithium atom is also coordinated by the oxygen atom of an ether molecule located on the C_3 axis of the tetrahedron, r(Li...O) = 196,197 pm.[233] The structure of $[(CH_3OCH_2CH_2CHLiCH_3)_4]$ (148)[234] is quite interesting in that the



(142) R = Bu^t

(143) R = NMe_2



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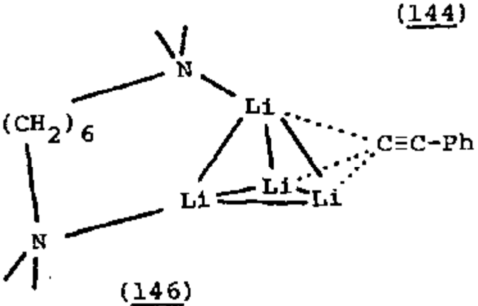

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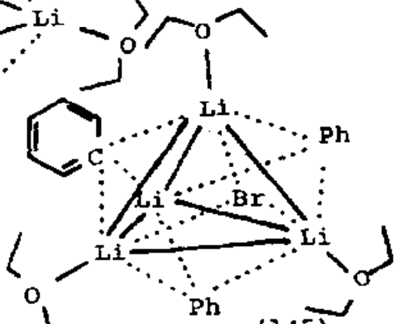

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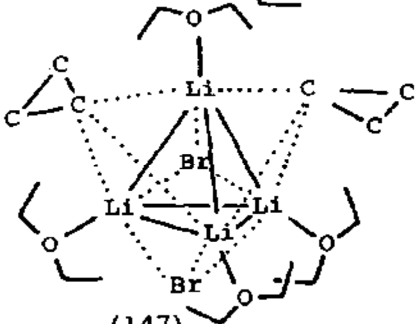

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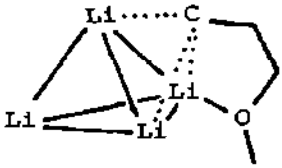

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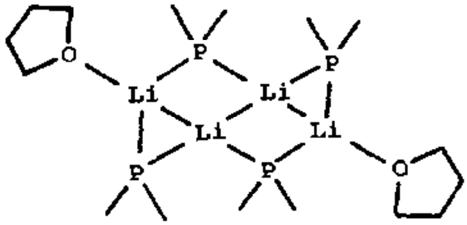

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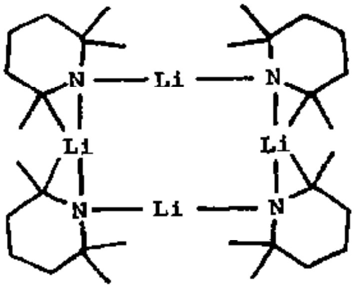


(150)

Figure 8. Schematic representations of the significant features of (142 - 150).

anion provides both the carbon atom to bridge the three lithium atoms on the faces of the Li_4 tetrahedra, r(Li...C) = 228.8-236.2 pm, as well as the oxygen atom to lie on the C_3 axes of the tetrahedron and hence complete the tetrahedral coordination of the lithium atoms, r(Li...O) = 192.3 pm. As for the other tetramers discussed thus far, the Li_4 geometry is distorted tetrahedral, r(Li...Li) = 247.4-250.6 pm.[234]

Low temperature (T < 190K) ^{13}C n.m.r. studies[246] of $Bu^tC{\equiv}CLi$ in thf indicate that it exists as a non-fluxional solvated cubic tetramer similar to those described above. Thus, each ethyne anion bridges three lithium atoms of the Li_4 tetrahedron, the coordination geometry of the lithium atom being completed by the oxygen atom of a thf molecule.[246]

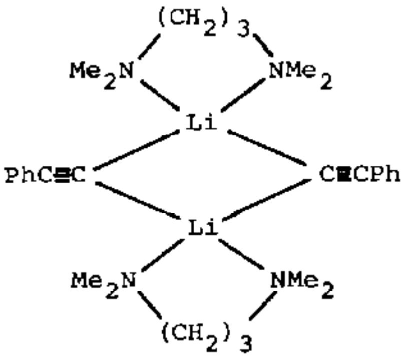
A staggered planar Li_4 unit has been observed in the structure of $[(LiPBu^t_2.thf)_4]$ (149).[235] The four lithium atoms, all of which have virtually planar coordination geometries, are part of a planar Li_4P_4 framework; the Li-Li distances (302.5, 306.5 pm) suggest that direct Li-Li bonding is relatively unimportant. Two of the phosphide groups are triply bridging to three lithium atoms, r(Li...P) = 258.6-266.9 pm, while the other two bridge only two lithium atoms, r(Li...P) = 247.6, 249.8 pm. The two terminal lithium atoms each bear a coordinated thf molecule, r(Li...O) = 192.3 pm.[235]

A third type of tetrameric conformation is exhibited by $[\{\overline{CMe_2(CH_2)_3CMe_2N}Li\}]$ (150).[236] It is a planar eight membered $(LiN)_4$ ring in which the lithium atoms bridge the nitrogen atoms of the piperidine rings, $r(Li...N)_{av}$ = 200 pm. The latter adopt a chair conformation and are arranged in staggered relationship to each other providing an inversion centre.[236]

Most of the dimeric molecules which have been structurally characterised contain a Li_2X_2 bridging unit where the second atom X can be carbon,[232,237,238] nitrogen,[236,239] oxygen,[221] or bromine;[240] schematic representations of the structures of these materials (151-155) are included in Figure 9.

The crystal structures of $[(PhC{\equiv}CLi.tmpda)_2]$ (tmpda = $Me_2N(CH_2)_3NMe_2$) (151),[232,237] which is isostructural with $[(PhLi.tmeda)_2]$, and of $[(8\text{-}Me_2NC_{10}H_6Li.Et_2O)_2]$ (152),[238] contain a Li_2C_2 linkage. In (151) the lithium atoms are located in a distorted tetrahedral environment being coordinated by two 'end-on' bonded bridging ethyne groups, r(Li...C) = 213,216 pm, and by the

Figure 9.



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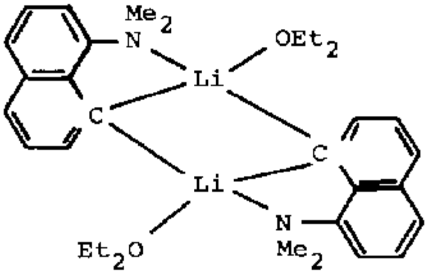

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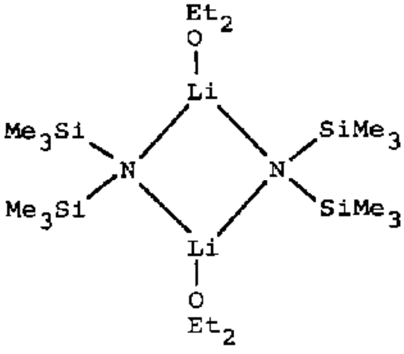

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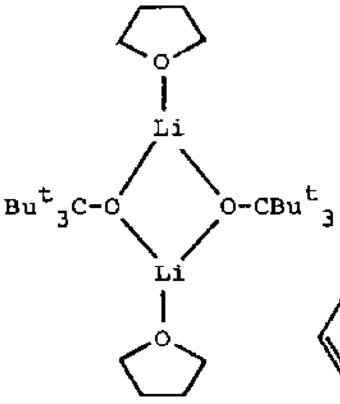

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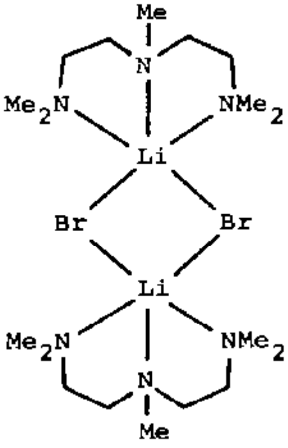

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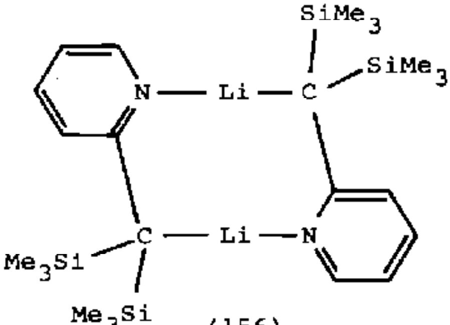

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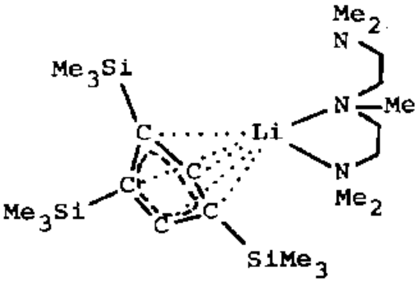

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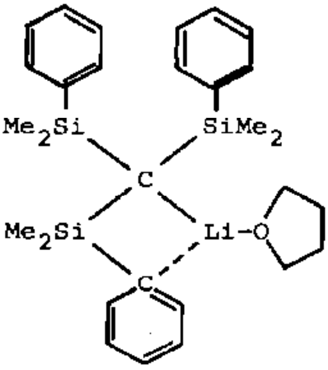

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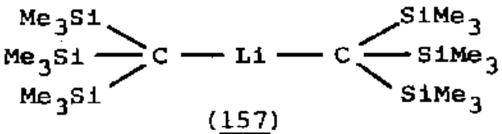


(157)

two nitrogen atoms of the tmpda molecule, r(Li...N) = 211, 212 pm.[232,237] A similar pseudo tetrahedral coordination geometry pertains for the lithium atoms in (152); it comprises the C(1) atoms of bridging naphthyl anions, r(Li...C) = 222.4, 223.2 pm, the amino nitrogen atom, r(Li...N) = 213.6 pm and an ether oxygen atom, r(Li...O) = 196.9 pm. In ether solution, multinuclear (^1H, ^7Li) n.m.r. experiments indicate that an equilibrium exists between the solid state structure (152) and the ether-free species [$(8\text{-}Me_2NC_{10}H_6Li)_n$] for which a tetranuclear conformation is proposed.[238]

The molecular structure of [$\{(SiMe_3)_2NLi.Et_2O\}_2$], (153), which contains a Li_2N_2 linkage has been reported by two independent groups of authors;[236,239] the two determinations are in excellent agreement. The lithium atoms in (153) are in an unusual three coordinate geometry provided by the bridging nitrogen atoms of the silazane groups, r(Li...N) = 205.5 pm, and the ether oxygen atom, r(Li...O) = 194.3 pm.[239] A similar coordination geometry is found for the lithium atoms in the structure of [$\{(Bu^t{}_3CO)Li.thf\}_2$] (154),[221] which has a Li_2O_2 linkage. The three atoms surrounding the lithium atoms are the bridging oxygen atoms of the tri-tert-butylmethoxide ligand, r(Li...O) = 183.0-185.2 pm, and the oxygen atom of the thf molecule, r(Li...O) = 196.3,200.9 pm.[221]

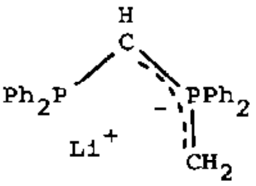
The structure of [$\{LiBr(pmdeta)\}_2$] (155)[240] contains a pair of dimeric aggregates both of which possess Li_2Br_2 linkages; the metal-halogen bonds within each centrosymmetric aggregate are unsymmetric, r(Li(1)...Br) = 251,320 pm or r(Li(2)...Br) = 257,287 pm. The environments about each of the crystallographically distinct lithium atoms are very similar; three contacts to the nitrogen atoms of the pmdeta molecule, r(Li(1)...N) = 216-228, r(Li(2)...N) = 219-231 pm and the two contacts to the bridging bromine atoms provide a trigonal bipyramidal angular geometry.[240]

A somewhat different dimeric conformation is adopted by [$\{2\text{-}(Me_3Si)_2C(Li)C_5H_4N\}_2$] (156);[241] the lithium atoms form part of a Li-C-C-N-Li-C-C-N ring, being coordinated by the nitrogen atom of the pyridine ring; r(Li...N) = 193.6 pm, and the carbon atom of the $C(SiMe_3)_2$ fragment, r(Li...C) = 221.3 pm in a near linear disposition (∠NLiC = 146.9°).

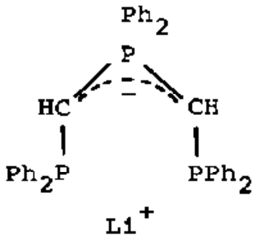
The four monomeric complexes, $[Li(thf)_4]^+[Li\{C(SiMe_3)_3\}_2]^-$,[242] [$Li\{C(SiMe_2Ph)_3\}(thf)$],[243] [$\{\eta^5\text{-}2,4,5\text{-}(SiMe_3)_3C_5H_2\}Li.tmeda$][244] and [$\{\eta^5\text{-}2,4,5\text{-}(SiMe_3)_3C_5H_2\}Li.pmdeta$][244] have been structurally characterised. The asymmetric unit of the first complex[242] contains two $[Li(thf)_4]^+$ cations related by an inversion centre and two crystallographically distinct $[Li\{C(SiMe_3)_3\}_2]^-$ anions. The cation consists of a lithium atom tetrahedrally coordinated by the oxygen atoms of the four thf molecules, $r(Li...O)_{av}$ = 196 pm. The two anions, each of which lies across an inversion centre, have essentially similar geometries (157); they are based on linear CLiC linkages, the two Li-C bond lengths being nearly identical, r(Li(1)...C) = 216 pm, r(Li(2)...C) = 220 pm.[242] In the second complex (158),[243] the lithium atom is covalently bonded to the oxygen atom of the thf molecule, r(Li...O) = 185 pm, and to the central carbon atom of the $(Me_2PhSi)_3C$ fragment, r(Li...C) = 212 pm; it also interacts strongly with the *ipso* carbon atom of one of the phenyl groups, r(Li...C) = 240 pm, without significantly distorting the hybridisation at that atom. The geometry around the lithium atom is almost planar, with the lithium atom only 14pm out of the plane defined by the coordinating atoms.[243] The third and fourth complexes,[244] are very similar since the potentially tridentate pmdeta ligand only uses two nitrogen atoms to coordinate the lithium atom in an almost identical fashion to the bidentate tmeda ligand. The structure of the pmdeta adduct (159) is included in Figure 9. The lithium atom, as well as being attached to two of the three nitrogen atoms of the pmdeta ligand, r(Li...N) = 217.3, 221.8 pm, is η^5-bonded by the cyclopentadiene ring, r(Li...C) = 230.4-235.0 pm.[244]

The structure of the 1:1 dme adduct of lithium bis(trimethylsilyl)bismuthide[245] is composed of chains of alternating lithium and bismuth atoms, r(Li...Bi) = 292 pm, the pseudotetrahedral coordination geometry of the two atoms being completed either by silicon atoms of two Me_3Si moieties, r(Bi...Si) = 263.3 pm, or by the two oxygen atoms of the dme molecule, r(Li...O) = 210 pm.[245]

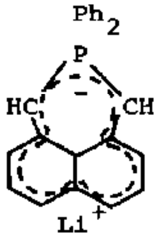
A limited number of papers[247-251] have been published on other diverse aspects of lithium chemistry. The preparation of the lithium ylide complexes (160-163) by metallation of the appropriate ylide with $LiCH_3$ has been reported;[247,248] they were studied primarily by multinuclear (^1H, ^{31}P) n.m.r. techniques. Sodium and potassium ylide complexes, analogous to (160) and (161) have also been synthesised and characterised.[247] An independent multinuclear (^1H, ^7Li, ^{13}C, ^{17}O and ^{35}Cl) n.m.r. study[249] of the solvation of $LiClO_4$ by the radical (164) in thf, CH_3CN or CH_3NO_2



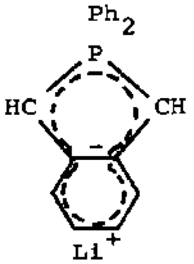
(160)



(161)



(162)

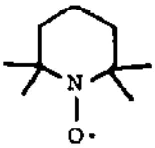


(163)

indicates that the ability of solvent or radical to compete for solvation of the $LiClO_4$ increases in the order:

$CH_3NO_2 < CH_3CN <$ (164) $<$ thf

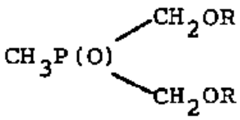
The enthalpy of formation of the complex containing both Li^+ and the radical was found to be 4.6±0.2 kJ.mol^{-1} in thf and -3.3±0.8 kJ.mol^{-1} in CH_3CN.[249] The formation constants of the complexes,

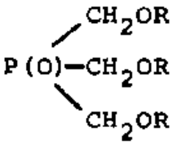


(164)

(165) ROR

(166) $ROCH_3CH_2OR$

(167) 

(168) 

(165-168) $R = Me_2P(O)CH_2$-

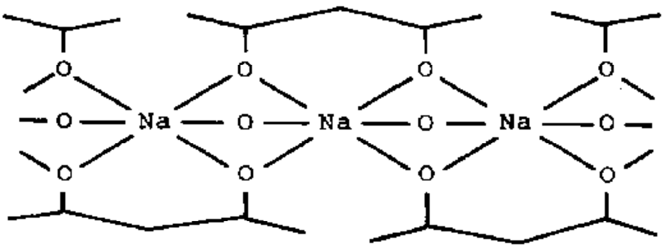
$(M^+L)X$, between lithium or sodium 2,4-dinitrophenolates (MX) and the phosphoryl containing ligands (L; 165-168) have been determined spectrophotometrically in thf/$CHCl_3$ (4:1) and CH_3CN/$CHCl_3$ (1:1) mixtures;[250] the results are compared with similar data obtained from electrical conductivity experiments.

The thermal decomposition of the alkali metal cyanurates, $MH_2C_3N_3O_3$, $M_2HC_3N_3O_3$ and $M_3C_3N_3O_3$ (M = Li-Cs) has been studied by thermal analysis methods;[251] the products have been investigated by chemical analysis and i.r. spectroscopy. Decomposition of the dihydrogen and monohydrogen cyanurates gives free cyanuric acid and the normal cyanurates which subsequently decompose to the corresponding alkali metal cyanates; the thermal stability of the normal cyanurates increases with increasing charge density of the cation (i.e. from Cs^+ to Li^+).[251]

1.5.11 Sodium Derivatives

As for the 1982 Review, most of the papers abstracted for this subsection deal with structural aspects of these materials. The crystal and molecular structures of methyl sodium,[252] sodium acetylacetonate monohydrate,[253] sodium dimethyldithiocarbamate dihydrate,[254] sodium di-isopropyldithiocarbamate pentahydrate[255] and the disodium salt of octamethyldisilatriazine[256] have been elucidated. Methyl sodium has been prepared[252] by reaction of methyllithium with sodium tert-butoxide; depending on reaction conditions, the products contain variable amounts of methyllithium (Na:Li varies from 36:1 to 3:1). All the products have a cubic unit cell with a_o = 2020 pm, space group $F\bar{4}3c$ and twenty-four $(CH_3M)_4$ units. Their geometry is analogous to that of $(CH_3Li)_4$ with r(Na...Na) = 312, 318 pm and r(Na...C) = 258, 264 pm. Owing to their mutual arrangement, eight large cavities are formed which can accommodate $(CH_3Li)_4$ units upto a maximum Na:Li ratio of 3:1. The bonding within the $(CH_3Na)_4$ tetramers resembles that of the corresponding lithium compound with more strongly polarised Na_3C 4-centre bonds.[252]

The coordination geometry about the Na^+ ion in the acetylacetonate derivative (169) is distorted octahedral.[253] Two trans-located water molecules act as symmetrical bridges between adjacent Na^+ ions, r(Na...O) = 242.2,242.3 pm. Each acetylacetonate anion forms a chelate ring with one sodium atom, r(Na...O) =



(169)

231.8,232.5 pm, and has additional contacts to the two neighbouring Na^+ ions, r(Na...O) = 238.2,238.7 pm. The Na^+ ions form a zig-zag chain parallel to (010) with r(Na...Na) = 305.7 pm and an Na-Na-Na angle of 164.4°.[253]

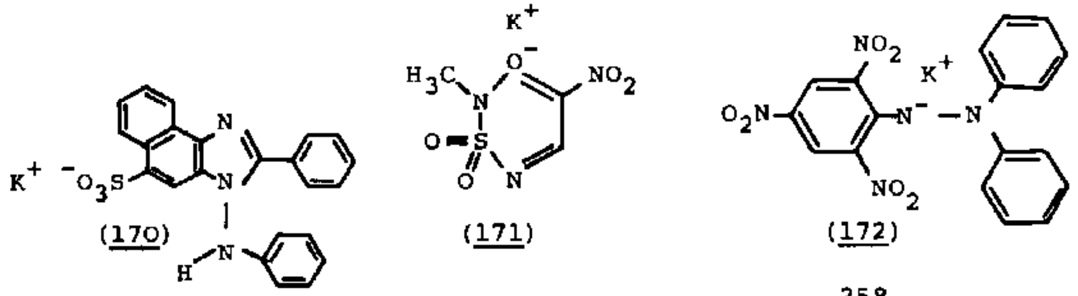
The two dithiocarbamate derivatives[254,255] have markedly different Na^+ ion coordination environments. The Na^+ ion in $Na[S_2CN(CH_3)_2].2H_2O$ is coordinated by four water molecules, r(Na...O) = 233.0-246.6 pm and two sulphur atoms from different anions, r(Na...S) = 299.2,301.5 pm, in a distorted octahedral geometry.[254] That in $Na[S_2CN(C_3H_7)_2].5H_2O$ is surrounded solely by six water molecules in a distorted octahedral arrangement, r(Na...O) = 239.2-245.4 pm, there being no direct interaction between cation and anion.[255] Pairs of these octahedra edge share to generate $[Na_2(H_2O)_{10}]^{2+}$ polyhedra which are connected to form layers parallel to (001) by O-H...O and O-H...S hydrogen bonding.[255]

Alkali metal derivatives, $[(Me_3SiNM)_2SiMe_2]$ (M = Na-Cs) of octamethyldisilatriazine have been synthesised by reaction of $(Me_3SiNH)_2SiMe_2$ with MNH_2 (M = Na,K,Cs) or with the metal in the presence of styrene (M = K,Rb) or with elemental caesium;[256] a monosodium derivative has also been prepared. Although dimeric in benzene solution, the disodium derivative is trimeric in the solid state. The trimers possess a cluster of six Na^+ ions which are bridged by the nitrogen atoms of the anions. If only Na-N bonds are considered, the Na^+ ions have coordination numbers of 2, 3 and 4. Very short Na-C contacts, $r(Na...C)_{min}$ = 265.6 pm, comparable to the longest Na-N bonds, r(Na...N) = 230.4-260.1 pm, exist in the structure infering that metal-alkyl interactions also occur in the crystal.[256]

The hydrogen bonds formed between alkali metal fluorides (MF; M = Na-Cs) and aliphatic diols or acids have been studied in solutions of concentration $\geqslant$0.5 mol.kg^{-1} at 303K using ^{19}F n.m.r. techniques;[257] the enthalpies of association of KF with ethene-1,2-diol and methanoic acid have been determined from variable temperature n.m.r. studies.

1.5.12 Potassium, Rubidium and Caesium Derivatives

Although a small number of papers describing the chemistry of potassium derivatives have been abstracted for this subsection, none pertaining to rubidium or caesium derivatives were found in the literature search. The structures of three unrelated potassium compounds have been reported;[258-260] although the coordination environments of the K^+ ions in potassium 3-anilino-2-phenyl-3H-naphtho[1,2-d]imidazole-5-sulphonate (170)[258] and in the monopotassium salt of 3-hydroxy-2-methyl-4-nitro-2H-1,2,6-thiadiazine-1,1-dioxide (171)[259] are straightforward distorted 6-fold and 7-fold geometries, respectively, that of the K^+ ion in potassium 1-(N,N-diphenylhydrazono)-2,4,6-trinitrobenzenide (172)[260] is unusual. Whereas the K^+ ions in (170) are surrounded by six oxygen atoms of four adjacent sulphate residues, r(K...O) =



(170) (171) (172)

269-299 pm, in a distorted octahedral arrangement,[258] those in (171) are coordinated by seven oxygen atoms of six anions, r(K...O) = 270-289 pm, in a rectangularly capped trigonal prismatic geometry.[259] The K^+ ion coordination in (172) is best considered as a combination of two hemispheres. The first comprises seven oxygen atoms from two bidentate and three monodentate nitrate groups of five separate anions, r(K...O) = 287.5-317.4 pm, and the negatively charged nitrogen atom of the hydrazine linkage, r(K...N) = 290.8 pm; the second contains a phenyl ring with two particularly short K-C contacts, r(K...C) = 321.3,327.9 pm.[260]

In a letter[261] referring to a paper by Emsley et al[262] on the adduct [$KF\text{-}CH_2(CO_2H)_2$], Truter contends that the conclusion that the adduct structure contains F-H distances as short as 70 pm should be treated with caution, not only because of the relatively high final R value (0.116) but also because the structure contains K-H distances shorter than 320 pm; such distances are very short for ions of like charge and certainly have not been found previously near K^+ ions. In their reply, Emsley et al[263] note Truter's suggestions but reiterate their basic premise that the system contains very short O...H...F bonds, r(O...F) = 241-249 pm. Emsley et al[264] have also reported novel data derived from ab initio calculations and spectroscopic investigations on hydrogen bonding interactions between KF and phosphorous acid, HPO_3H_2, in aqueous solution. Crystals of the adduct, [$KF.HPO_3H_2$], have been grown from aqueous solution; they differ from those grown from CH_3OH, which are known to be strongly hydrogen bonded.[264]

REFERENCES

1 P.Hubberstey, Coord. Chem. Rev., 56(1984)1.
2 Various articles in J. Phys. F, Metal Phys., 13(1983).
3 Various articles in J. Nucl. Mater., 114-118(1983).
4 Various articles in J. Electrochem. Soc., 130(1983).
5 Y.C.Chan and W.C.Stwalley, J. Chem. Thermodyn., 15(1983)989.
6 C.H.Wu, J. Phys. Chem., 87(1983)1534.
7 D.Plavsic, J.Koutecky, G.Pacchioni and V.Bonacic-Koutecky, J. Phys. Chem., 87(1983)1096.
8 O.K.Chopra, J. Nucl. Mater., 115(1983)223.
9 K.Natesan, J. Nucl. Mater., 115(1983)251.
10 R.J.Pulham and P.Hubberstey, J. Nucl. Mater., 115(1983)239.
11 M.G.Barker, P.Hubberstey, A.T.Dadd and S.A.Frankham, J. Nucl. Mater., 114(1983)143.
12 E.Ruedl and T.Sasaki, J. Nucl. Mater., 116(1983)112.
13 S.P.Awasthi and H.U.Borgstedt, J. Nucl. Mater., 116(1983)103.
14 R.H.Fairlie and D.A.Greenwood, J. Phys. F., Metal Phys., 13(1983)1645.
15 R.G.Taylor and R.Thompson, J. Nucl. Mater., 115(1983)25.
16 M.A.Mignanelli and P.E.Potter, J. Nucl. Mater., 114(1983)168.
17 M.A.Mignanelli and P.E.Potter, J. Nucl. Mater., 118(1983)150.
18 P.Kozoulia, J.P.Bros and M. Gaune-Escard, J. Chem. Thermodyn., 15(1983)757.
19 C.H.Wu, J. Nucl. Mater., 114(1983)30.
20 P.Lamparter, W.Martin, S.Steeb and W.Freyland, Z. Naturforsch., Teil A, 38(1983)329.
21 B.P.Alblas, W. van der Lugt, J.Dijkstra, W.Geertsma and C. van Dijk, J. Phys. F., Metal Phys., 13(1983)2465.
22 S.Matsunaga, T.Ishiguro and S.Tamaki, J. Phys. F., Metal Phys., 13(1983)587.
23 W.F.Calaway and M.-L.Saboungi, J. Phys. F., Metal Phys., 13(1983)1213.
24 K.Hoshino, J. Phys. F., Metal Phys., 13(1983)1981.
25 K.Hoshino, J. Phys. F., Metal Phys., 13(1983)L189.
26 A.P.Copestake, R.Evans, H.Ruppersberg and W.Schirmacher, J. Phys. F., Metal Phys., 13(1983)1993.
27 T.Ishiguro and S.Tamaki, J. Phys. F., Metal Phys., 13(1983)51.
28 M.Iwamatsu, R.A.Moore and S.Wang, J. Phys. F., Metal Phys., 13(1983)503.
29 M.Iwamatsu, S.K.Lai, R.A.Moore and S.Wang, J. Phys. F., Metal Phys., 13(1983)1027.
30 M.G.Adamson and J.E.Leighty, J. Nucl. Mater., 114(1983)327.
31 J.Llanos, R.Nesper and H.G. von Schnering, Angew. Chem. Int. Ed. Engl., 22(1983)998.
32 P.Hubberstey, Coord. Chem. Rev., 56(1984)15.
33 M.Miyake, T.Suzuki, H.Morikawa, H.Ohno and K.Furukawa, J. Chem. Soc., Faraday Trans. I, 79(1983)2997.
34 H.Ohno, K.Furukawa, R.Takagi, K.Igarashi and J.Mochinaga, J. Chem. Soc., Faraday Trans. II, 79(1983)463.
35 M.Miyake, K.Okada, S.Iwai, H.Ohno and K.Furukawa, J. Chem. Soc., Faraday Trans. I, 75(1979)1169.
36 P.Hubberstey, Coord. Chem. Rev., 34(1981)10.
37 B.D.Antonov, Zh. Strukt. Khim., 16(1975)501.
38 R.Fehrmann, N.H.Hansen and N.J.Bjerrum, Inorg. Chem., 22(1983)4009.
39 T.Sasamoto, M.Itoh and T.Sata, Bull. Chem. Soc. Jpn., 56(1983)2415.
40 O.Waernes, F.Palmisano and T.Ostwald, Acta Chem. Scand., Ser. A, 37(1983)207.

41 O.Waernes and T.Ostwald, Acta Chem. Scand., Ser. A, 37(1983)293.
42 A.L.Novozhilov and Y.S.Zhoglik, Russ. J. Inorg. Chem., 28(1983)1376.
43 N.Q.Minh and N.-P.Yao, J. Electrochem. Soc., 130(1983)1025.
44 D.Warin, Z.Tomczuk and D.R.Vissers, J. Electrochem. Soc., 130(1983)64.
45 V.A.Maroni and Z.Tomczuk, J. Electrochem. Soc., 130(1983)864.
46 F.L.Delnick and D.K.McCarthy, J. Electrochem. Soc., 130(1983)1875.
47 W.C.Child and G.N.Papatheodorou, J. Phys. Chem., 87(1983)271.
48 M.Blander and Z.Nagy, Z. Naturforsch., Teil A, 38(1983)116.
49 K.Tanemoto, G.Mamantov and G.M.Begun, Inorg. Chim. Acta, 76(1983)L79.
50 J.P.Collman, J.I.Brauman, G.Tustin and G.S.Wann, J. Am. Chem. Soc., 105(1983)3913.
51 R.W.Berg and N.J.Bjerrum, Polyhedron, 2(1983)179.
52 D.A.Nissen and D.E.Meeker, Inorg. Chem., 22(1983)716.
53 B.Holmberg and G.Johansson, Acta Chem. Scand., Ser. A, 37(1983)367.
54 G.B.Dunks and D.Stelman, Inorg. Chem., 22(1983)2168.
55 W.C.Fang and R.A.Rapp, J. Electrochem. Soc., 130(1983)2335.
56 R.I.Dearnaley, D.H.Kerridge and D.J.Rogers, Inorg. Chem., 22(1983)3242.
57 P.Hubberstey, Coord. Chem. Rev., 56(1984)22.
58 B.S.Ault, Inorg. Chem., 22(1983)2221.
59 K.Garber and B.S.Ault, Inorg. Chem., 22(1983)2509.
60 J.S.Ogden, T.J.Sibley and S.J.Williams, J. Chem. Soc., Dalton Trans., (1983)851.
61 I.R.Beattie and J.E.Parkinson, J. Chem. Soc., Dalton Trans., (1983)1185.
62 S.A.Arthers, I.R.Beattie, R.A.Gomme, P.J.Jones and J.S.Ogden, J. Chem. Soc., Dalton Trans., (1983)1461.
63 Z.A.Kafafi, R.H.Hauge and J.L.Margrave, Polyhedron, 2(1983)167.
64 Z.H.Kafafi, R.H.Hauge, W.E.Billups and J.L.Margrave, J. Am. Chem. Soc., 105(1983)3886.
65 D.M.Lindsay, D.R.Herschbach and A.L.Kwiram, J. Phys. Chem., 87(1983)2113.
66 J.P.Richie, J. Am. Chem. Soc., 105(1983)2083.
67 P. von R.Schleyer, E.-U.Wurthwein, E.Kaufmann, T.Clark and J.A.Pople, J. Am. Chem. Soc., 105(1983)5930.
68 P. von R.Schleyer, B.Tidor, E.D.Jemmis, J.Chandrasekhar, E.-U.Wurthwein, A.J.Kos, B.T.Luke and J.A.Pople, J. Am. Chem. Soc., 105(1983)484.
69 E.-U.Wurthwein, K.D.Sen, J.A.Pople and P. von R.Schleyer, Inorg. Chem., 22(1983)496.
70 V.M.Ozerova and V.G.Solomonik, Russ. J. Inorg. Chem., 28(1983)1408.
71 A.I.Boldyrev, Russ. J. Inorg. Chem., 28(1983)1571.
72 J.R.Dilworth, A.Garcia-Rodriguez, G.J.Leigh and J.N.Murrell, J. Chem. Soc., Dalton Trans., (1983)455.
73 J.Mareda, N.G.Rondan, K.N.Houk, T.Clark and P. von R. Schleyer, J. Am. Chem. Soc., 105(1983)6997.
74 G.Decher and G.Boche, J. Organomet. Chem., 259(1983)31.
75 P. von R.Schleyer, A.J.Kos and E.Kaufmann, J. Am. Chem. Soc., 105(1983)7617.
76 J.E.Del Bene, M.J.Frisch, K.Raghavachari, J.A.Pople and P. von R.Schleyer, J. Phys. Chem., 87(1983)73.
77 P.Hobza, H.-J.Hofmann and R.Zahradnik, J. Phys. Chem., 87(1983)573.

78 G.L.Gutsev and A.I.Boldyrev, Russ. J. Inorg. Chem., 28(1983)1237.
79 G.Rauscher, T.Clark, D.Poppinger, P. von R.Schleyer, Angew. Chem., Int. Ed. Engl., 17(1978)276.
80 T.Clark, E.D.Jemmis, P. von R.Schleyer, J.S.Binkley and J.A.Pople, J. Organomet. Chem., 150(1978)1.
81 A.J.Kos, E.D.Jemmis, P. von R.Schleyer, R.Gleiter, U.Fischbach and J.A.Pople, J. Am. Chem. Soc., 103(1981)4996.
82 Y.C.Chan and W.C.Stwalley, J. Chem. Thermodyn., 15(1983)995.
83 A.J.Kaur, P.C.Jain, P.S.Bakhshi and J.Shanker, Indian J. Chem., Sect. A, 22(1983)595.
84 R.S.Tsekhanskii, Russ. J. Inorg. Chem., 28(1983)474.
85 B.T.Gowda and S.W.Benson, J. Chem. Soc., Faraday Trans. II, 79(1983)663.
86 T.M.Barlak, J.E.Campana, J.R.Wyatt and R.J.Colton, J. Phys. Chem., 87(1983)3441.
87 A.V.Dubrovin, A.S.Dubrovina and S.A.Petrov, Russ. J. Inorg. Chem., 28(1983)158.
88 M.Baudler and O.Exner, Chem. Ber., 116(1983)1268.
89 V.N.Krasil'nikov, M.P.Glazyrin, A.A.Ivakin, L.A.Perelyaeva and A.P.Palkin, Russ. J. Inorg. Chem., 28(1983)417.
90 K.Kato and E.Takayama, Acta Crystallogr., C39(1983)1480.
91 V.L.Volkov, Russ. J. Inorg. Chem., 28(1983)265.
92 G.Prins and E.H.P.Cordfunke, J. Less-Common Met., 91(1983)177.
93 T.Fujino, K.Ouchi, T.Yamashita and H.Nateume, J. Nucl. Mater., 116(1983)157.
94 C.Dion and A.Noel, Bull. Soc. Chim. Fr., (1983)I-257.
95 S.Bharadwaj, S.R.Dharwadkar, G.Chattopadhyay and M.S. Chandrasekharaiah, J. Nucl. Mater., 114(1983)344.
96 A.J.Mark, I.D.Raistrick and R.A.Huggins, J. Electrochem. Soc., 130(1983)776.
97 R.J.Cava, D.W.Murphy and S.M.Zahurak, J. Electrochem. Soc., 130(1983)2345.
98 D.W.Murphy, J.L.Dye and S.M.Zahurak, Inorg. Chem., 22(1983)3679.
99 M.-C.Saine and M.Gasperin, Acta Crystallogr., C39(1983)1153.
100 R.Y.Lin and J.F.Elliott, Metall. Trans., 14A(1983)1713.
101 N.V.Porotnikov, N.G.Chaban and K.I.Petrov, Russ. J. Inorg. Chem., 28(1983)1402.
102 A.J. van der Berg, H.Overeijnder and F.Tuinstra, Acta Crystallogr., C39(1983)678.
103 T.Betz and R.Hoppe, Z. Anorg. Allg. Chem., 500(1983)23.
104 A.Tomas, P.Laruelle, J.L.Dormann and M.Nogues, Acta Crystallogr., C39(1983)1615.
105 H.Klassen and R.Hoppe, Z. Anorg. Allg. Chem., 497(1983)70.
106 R.Hoppe and W.Losert, Z. Anorg. Allg. Chem., 504(1983)60.
107 J.Huster, G.Schippers and W.Bronger, J. Less-Common Met., 91(1983)333.
108 G.Amthauer and K.Bente, Naturwissenschaften, 70(1983)146.
109 K.Klepp and W.Bronger, Z. Naturforsch., Teil B, 38(1983)12.
110 W.Bronger, M.Kimpel and D.Schmitz, Acta Crystallogr., B39(1983)235.
111 P.P.Fedorov, A.V.Rappo, F.M.Spiridonov and B.P.Sobolev, Russ. J. Inorg. Chem., 28(1983)420.
112 V.V.Krylov, M.P.Danilov, N.N.Steparava and Y.A.Kotlyar, Russ. J. Inorg. Chem., 28(1983)1230.
113 V.V.Safonov and V.A.Mireev, Russ. J. Inorg. Chem., 28(1983)1004.
114 A.G.Dudareva, A.B.Streckachinskii, G.Tamerat, O.V.Polyanskaya and A.I.Ezhov, Russ. J. Inorg. Chem., 28(1983)610.

115 A.K.Molodkin, A.M.Karagodina, A.G.Dudareva and V.A.Krokhin, Russ. J. Inorg. Chem., 28(1983)1693.
116 H.-Ch. Gaebell, G.Meyer and R.Hoppe, Z. Anorg. Allg. Chem., 498(1983)94.
117 H.-Ch.Gaebell, G.Meyer and R.Hoppe, Z. Anorg. Allg. Chem., 497(1983)199.
118 N.Kijima, K.Tanaka and F.Marumo, Acta Crystallogr., B39(1983)557.
119 N.Miyata, K.Tanaka and F.Marumo, Acta Crystallogr., B39(1983)561.
120 K.D.Reddy, P.Kistaiah and L.Iyengar, J. Less-Common Met., 92(1983)81.
121 G.Wu and R.Hoppe, J. Less-Common Met., 93(1983)452.
122 G.-Q.Wu and R.Hoppe, Z. Anorg. Allg. Chem., 504(1983)55.
123 B.G.Muller and R.Hoppe, Z. Anorg. Allg. Chem., 498(1983)128.
124 G.Meyer, Z. Anorg. Allg. Chem., 507(1983)111.
125 R.M.Metzger, N.E.Heimer, C.S.Kuo, R.F.Williamson and W.O.J.Boo, Inorg. Chem., 22(1983)1060.
126 A.Cousson, H.Abazli, M.Pages and M.Gasperin, Acta Crystallogr., C39(1983)318.
127 A.S.Secco and J.Trotter, Acta Crystallogr., C39(1983)317.
128 M.Quilichini and J.Pannetier, Acta Crystallogr., B39(1983)657.
129 G.Meyer and E.Huttl, Z. Anorg. Allg. Chem., 497(1983)191.
130 G.Meyer, H.-C.Gaebell and R.Hoppe, J. Less-Common Met., 93(1983)347.
131 G.J.Kipouros and S.N.Flengas, Can. J. Chem., 61(1983)2183.
132 H.Muller, P.Bekk and I.Hagenlocher, Z. Anorg. Allg. Chem., 503(1983)15.
133 G.Thiele, C.Mrozek, D.Kammerer and K.Wittmann, Z. Naturforsch. Teil B, 38(1983)905.
134 A.A.Majmudar, Y.W.Gokhale and G.S.Rao, Indian J. Chem., Sect. A, 22(1983)145.
135 M.Kiselev, S.A.Goryachenkov and L.I.Martynenko, Russ. J. Inorg. Chem., 28(1983)651.
136 K.Broomfield and P.M.A.Sherwood, J. Chem. Soc., Faraday Trans. II, 79(1983)785.
137 K.Broomfield and P.M.A.Sherwood, J. Chem. Soc., Faraday Trans. II, 79(1983)799.
138 K.Broomfield and P.M.A.Sherwood, J. Chem. Soc., Faraday Trans. II, 79(1983)1321.
139 J.Garcia, J.Bartolome, D.Gonzalez, R.Navarro and W.J.Crama, J. Chem. Thermodyn., 15(1983)1109.
140 T.Atake, K.Nomoto, B.K.Chaudhuri and H.Chihara, J. Chem. Thermodyn., 15(1983)339.
141 H.-D.Amberger, W.Grape and E.Stumpp, J. Less-Common Met., 95(1983)181.
142 P.Hubberstey, Coord. Chem. Rev., 56(1984)37.
143 D.L.Hughes and J.N.Wingfield, J. Chem. Soc., Dalton Trans., (1983)915.
144 M.Raban, J.Greenblatt and F.Kandil, J. Chem. Soc., Chem. Commun., (1983)1409.
145 A.Shanzer, D.Samuel and R.Korenstein, J. Am. Chem. Soc., 105(1983)3815.
146 A.Villager, W.E.Morf and W.Simon, Helv. Chim Acta, 66(1983)1078.
147 F.Vogtle, T.Kleiner, R.Leppkes, M.W.Laubli, D.Ammann and W.Simon, Chem. Ber., 116(1983)2028.
148 S.Tsuchiya, Y.Yamada and M.Seno, J. Chem. Soc., Chem. Commun., (1983)995.

149 G.W.Gokel, D.M.Goli, C.Minganti and L.Echegoyan, J. Am. Chem. Soc., 105(1983)6786.
150 A.Ellaboudy, J.L.Dye and P.B.Smith, J. Am. Chem. Soc., 105(1983)6490.
151 P.Hubberstey, Coord. Chem. Rev., 56(1984)40.
152 G.Shoham, W.N.Lipscomb and U.Olsher, J. Am. Chem. Soc., 105(1983)1247.
153 G.Shoham, W.N.Lipscomb and U.Olsher, J. Chem. Soc., Chem. Commun., (1983)208.
154 L.M.Engelhardt, W.-P.Leung, C.L.Raston and A.H.White, J. Chem. Soc., Chem. Commun., (1983)386.
155 A.-C.Dock, D.Moras, J.-P.Behr and J.-M.Lehn, Acta Crystallogr., C39(1983)1001.
156 U.Olsher and J.Jagur-Grodzinski, J. Chem. Soc., Dalton Trans., (1981)501.
157 K.Mukai, M.Yamashita, K.Ueda, K.Tajima and K.Ishizu, J. Phys. Chem., 87(1983)1338.
158 G.Ercolani, L.Mandolini and B.Masci, J. Am. Chem. Soc., 105(1983)6146.
159 G.Illuminati, L.Mandolini and B.Masci, J. Am. Chem. Soc., 105(1983)555.
160 E.Amble and E.Amble, Polyhedron, 2(1983)1063.
161 Y.Takeda, Bull. Chem. Soc. Jpn., 56(1983)3600.
162 E.Schmidt and A.I.Popov, J. Am. Chem. Soc., 105(1983)1873.
163 A.Y.Nazarenko, I.V.Pyatnitskii and Z.Z.Nizhnik, Russ. J. Inorg. Chem., 28(1983)1637.
164 Y.Takeda, Bull. Chem. Soc. Jpn., 56(1983)931.
165 Y.Takeda, Bull. Chem. Soc. Jpn., 56(1983)2589.
166 Y.Takeda, Bull. Chem. Soc. Jpn., 56(1983)866.
167 J.M.Kim, M.Ozeki, J.Komiyama and T.Iijima, J. Chem. Soc., Faraday Trans. I, 79(1983)2153.
168 K.Kimura, H.Sakamoto, M.Yoshinaga and T.Shono, J. Chem. Soc., Chem. Commun., (1983)978.
169 M.Nakajima, K.Kimura and T.Shono, Bull. Chem. Soc. Jpn., 56(1983)3052.
170 R.Sinta, P.S.Rose and J.Smid, J. Am. Chem. Soc., 105(1983) 4337.
171 J.K.Rasmussen, S.M.Heilmann, P.E.Toren, A.V.Pocius and T.A.Kotnour, J. Am. Chem. Soc., 105(1983)6845.
172 T.Ikeda, A.Abe, K.Kikukawa and T.Matsuda, Chem. Letters, (1983)369.
173 K.Kimura, H.Tamura and T.Shono, J. Chem. Soc., Chem. Commun., (1983)492.
174 K.Kimura, A.Ishikawa, H.Tamura and T.Shono, Bull. Chem. Soc. Jpn., 56(1983)1859.
175 D.M.Dishong, C.J.Diamond, M.I.Cinoman and G.W.Gokel, J. Am. Chem. Soc., 105(1983)586.
176 A.Kaifer, L.Echegoyen, D.A.Gustowski, D.M.Goli and G.W.Gokel, J. Am. Chem. Soc., 105(1983)7168.
177 F.R.Fronczek, V.J.Gatto, R.A.Schultz, S.J.Jungk, W.J.Colucci, R.D.Gandour and G.W.Gokel, J. Am. Chem. Soc., 105(1983)6717.
178 G.Weber, W.Saenger, K.Muller, W.Wehner and F.Vogtle, Inorg. Chim. Acta, 77(1983)L199.
179 Y.Nakatsuji, H.Kobayashi and M.Okahara, J. Chem. Soc., Chem. Commun., (1983)800.
180 J.Powell, M.Gregg, A.Kuksis and P.Meindl, J. Am. Chem. Soc., 105(1983)1064.
181 J.Powell, S.C.Nyburg and S.J.Smith, Inorg. Chim. Acta, 76(1983)L75.
182 J.Powell, K.S.Ng, W.W.Ng and S.C.Nyburg, J. Organomet. Chem., 243(1983)C1.

183 S.J.McLain, J. Am. Chem. Soc., 105(1983)6355.
184 F.-A. von Itter, F.Vogtle, G.Weber and G.M.Sheldrick, Z. Naturforsch., Teil B, 38(1983)262.
185 G.Weber, Inorg. Chim. Acta, 74(1983)55.
186 G.Weber, Inorg. Chim. Acta, 76(1983)L279.
187 J.D.Owen, Acta Crystallogr., C39(1983)861.
188 J.D.Owen, Acta Crystallogr., C39(1983)579.
189 K.Nakashima, Y.Yamawaki, S.Nakatsuji, S.Akiyama, T.Kaneda and S.Misumi, Chem. Letters, (1983)1415.
190 S.Shinkai, T.Minami, Y.Kusano and O.Manabe, J. Am. Chem. Soc., 105(1983)1851.
191 I.Willner and Z.Goren, J. Chem. Soc., Chem. Commun., (1983) 1469.
192 R.Setton, F.Beguin, L.Facchini, M.F.Quinton, A.P.Legrand, B.Ruisinger and H.P.Boehm, J. Chem. Soc., Chem. Commun., (1983)36.
193 R.Quinn, C.E.Strouse and J.S.Valentine, Inorg. Chem., 22(1983)3934.
194 T.Konig, B.Eisenmann and H.Schafer, Z. Anorg. Allg. Chem., 498(1983)99.
195 B.G.Cox, C.Guminski, P.Firman and H.Schneider, J. Phys. Chem., 87(1983)1357.
196 B.G.Cox, N. Van Truong, J. Garcia-Rosas and H. Schneider, Inorg. Chim. Acta, 77(1983)L155.
197 B.G.Cox, P.Firman and H.Schneider, Inorg. Chim. Acta, 69(1983)161.
198 J.Lacoste and F.Schue, Bull. Chem. Soc. Jpn., 56(1983)3491.
199 R.Pizer and R.Selzer, Inorg. Chem., 22(1983)1359.
200 E.Schmidt, J.-M.Tremillion, J.-P.Kintzinger and A.I.Popov, J. Am. Chem. Soc., 105(1983)7563.
201 P.Groth, Acta Chem. Scand., Ser. A, 37(1983)71.
202 P.Groth, Acta Chem. Scand., Ser. A, 37(1983)283.
203 D.S.B.Grace and J.Krane, J. Chem. Res. (S), (1983)162.
204 S.M.Nelson, F.S.Esho and M.G.B.Drew, J. Chem. Soc., Dalton Trans., (1983)1857.
205 M.G.B.Drew, F.S.Esho and S.M.Nelson, J. Chem. Soc., Dalton Trans., (1983)1653.
206 K.Hermansson, R.Tellgren and M.S.Lehmann, Acta Crystallogr., C39(1983)1507.
207 L.-Y.Hsu and C.E.Nordman, Acta Crystallogr., C39(1983)690.
208 M.Soriano-Garcia and S.N.Rao, Acta Crystallogr., C39(1983)850.
209 H.M.Doesburg and A.T.H.Lenstra, Bull. Soc. Chim. Belg., 92(1983)249.
210 H.J.Geise, J.F.J. von Loock and A.T.H.Lenstra, Acta Crystallogr., C39(1983)69.
211 M.Rossi, L.F.Rickles and J.P.Glusker, Acta Crystallogr., C39(1983)987.
212 D.S.S.Gowda and R.Rudman, Acta Crystallogr., C39(1983)582.
213 C.H.L.Kennard, G.Smith and E.J.O'Reilly, Inorg. Chim. Acta, 77(1983)L181.
214 J.Emsley, D.J.Jones and R.Kuroda, Acta Crystallogr., C39(1983)729.
215 A.Agarwal, D.P.Khandelwal and H.D.Bist, Can. J. Chem., 61(1983)2282.
216 S.Kato, M.Oguri and M.Ishida, Z. Naturforsch., Teil B, 38(1983)1583.
217 K.P.Sagarik and B.M.Rode, Inorg. Chim. Acta, 76(1983)L209.
218 J.J.C. van Lier, L.J.M. van de Ven, J.W. de Haan and H.M.Buck, J. Phys. Chem., 87(1983)3501.

219 J.Pandit, T.P.Seshadri and M.A.Viswamitra, Acta Crystallogr., C39(1983)342.
220 Y.H.Mariam and W.D.Wilson, J. Am. Chem. Soc., 105(1983)627.
221 J.Hvorslef, H.Hope, B.D.Murray and P.P.Power, J. Chem. Soc., Chem. Commun., (1983)1438.
222 T.A.Bazhenova, R.M.Lobkovskaya, R.P.Shibaeva, A.K.Shilova, M.Gruselle, G.Leny and E.Deschamps, J. Organomet. Chem., 244(1983)375.
223 T.A.Bazhenova, R.M.Lobkovskaya, R.P.Shibaeva, A.E.Shilov, A.K.Shilova, M.Gruselle, G.Leny and B.Tchoubar, J. Organomet. Chem., 244(1983)265.
224 I.R.Butler, W.R.Cullen, J.Reglinski and S.J.Rettig, J. Organomet. Chem., 249(1983)183.
225 H.F.Klein, H.Witty and U.Schubert, J. Chem. Soc., Chem. Commun., (1983)231.
226 K.Porschke, G.Wilke and C.Kruger, Angew. Chem., Int. Ed. Engl., 22(1983)547.
227 K.R.Porschke, W.Kleimann, G.Wilke, K.H.Claus and C.Kruger, Angew. Chem., Int. Ed. Engl., 22(1983)991.
228 B.A.Sosinsky, R.G.Shong, B.J.Fitzgerald, N.Norem and C.O'Rourke, Inorg. Chem., 22(1983)3124.
229 R.G.Shong, C.G.Pierpont and B.A.Sosinsky, Inorg. Chem., 21(1982)3247.
230 W.Clegg, R.Snaith, H.M.M.Shearer, K.Wade and G.Whitehead, J. Chem. Soc., Dalton Trans., (1983)1309.
231 H.Hope and P.P.Power, J. Am. Chem. Soc., 105(1983)5320.
232 B.Schubert and E.Weiss, Angew, Chem., Int. Ed. Engl., 22(1983)496.
233 H.Schmidbaur, A.Schier and U.Schubert, Chem. Ber., 116(1983)1938.
234 G.W.Klumpp, P.J.A.Geurink, A.L.Spek and A.J.M.Duisenberg, J. Chem. Soc., Chem. Commun., (1983)814.
235 R.A.Jones, A.L.Stuart and T.C.Wright, J. Am. Chem. Soc., 105(1983)7459.
236 M.F.Lappert, M.J.Slade,A.Singh, J.L.Atwood, R.D.Rogers and R.Shakir, J. Am. Chem. Soc., 105(1983)302.
237 B.Schubert and E.Weiss, Chem. Ber., 116(1983)3212.
238 J.T.B.H.Jastrzebski, G. van Koten, K.Goubitz, C.Arlen and M.Pfeffer, J. Organomet. Chem., 246(1983)c75.
239 L.M.Engelhardt, A.S.May, C.L.Raston and A.H.White, J. Chem. Soc., Dalton Trans., (1983)1671.
240 S.R.Hall, C.L.Raston, B.W.Skelton and A.H.White, Inorg. Chem. 22(1983)4070.
241 R.A.Papasergio, C.L.Raston and A.H.White, J. Chem. Soc., Chem. Commun., (1983)1419.
242 C.Eaborn, P.B.Hitchcock, J.D.Smith and A.C.Sullivan, J. Chem. Soc., Chem. Commun., (1983)827.
243 C.Eaborn, P.B.Hitchcock, J.D.Smith and A.C.Sullivan, J. Chem. Soc., Chem. Commun., (1983)1390.
244 P.Jutzi, E.Schluter, C.Kruger and S.Pohl, Angew. Chem., Int. Ed. Engl., 22(1983)994.
245 O.Mundt, G.Becker, M.Rossler and C.Witthauer, Z. Anorg. Allg. Chem., 506(1983)42.
246 G.Fraenkel and P.Pramanik, J. Chem. Soc., Chem. Commun., (1983)1527.
247 H.Schmidbaur and U.Deschler, Chem. Ber., 116(1983)1386.
248 H.Schmidbaur and A.Mortl, J. Organomet. Chem., 250(1983)171.
249 W.Kolodziejski and G.E.Maciel, J. Phys. Chem., 87(1983)4694.
250 K.B.Yatsimirskii, E.I.Sinyavskaya, L.V.Tsymbal, E.N.Tsvetkov, and T.E.Kron, Russ. J. Inorg. Chem., 28(1983)795.

251 G.B.Seifer and Z.A.Tarasova, Russ. J. Inorg. Chem., 28(1983)799.
252 E.Weiss, G.Sauermann and G.Thirase, Chem. Ber., 116(1983)74.
253 J.J.Sahbari and M.M.Olmstead, Acta Crystallogr., C39(1983)1037.
254 A.Oskarsson and I.Ymen, Acta Crystallogr., C39(1983)66.
255 I.Ymen, Acta Crystallogr., C39(1983)874.
256 D.J.Brauer, H.Burger, W.Geschwandtner, G.R.Liewald and C.Kruger, J. Organomet. Chem., 248(1983)1.
257 J.M.Miller, R.K.Kanippayoor and J.H.Clark, J. Chem. Soc., Dalton Trans., (1983)683.
258 M.R.Ciajolo, M.Parrilli, P.A.Temussi and A.Tuzi, Acta Crystallogr., C39(1983)983.
259 C.Esteban-Calderon, M.Martinez-Ripoll and S.Garcia-Blanco, Acta Crystallogr., C39(1983)440.
260 R.Gopal, B.E.Robertson and J.A.Weil, Can. J. Chem., 61(1983)2735.
261 M.R.Truter, J. Chem. Soc., Dalton Trans., (1983)187.
262 J.Emsley, D.J.Jones and R.Kuroda, J. Chem. Soc., Dalton Trans., (1982)1179.
263 J.Emsley, D.J.Jones and R.Kuroda, J. Chem. Soc., Dalton Trans., (1983)187.
264 J.Emsley, J.Lucas, R.J.Parker and R.E.Overill, Polyhedron, 2(1983)19.