

# Chapter 1

## ELEMENTS OF GROUP 1

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## 1.1 INTRODUCTION

Since the principal research interests in alkali and alkaline earth metal chemistry have changed little in recent years, the format adopted for this review of the Jan. 1986-June 1987 literature mirrors those of the 1985[1] and earlier reviews. Thus the majority of the abstracted papers are discussed in sections covering topics of current importance and significance rather than individual elements; only a limited number of papers describing diverse and unconnected subjects are considered on the latter basis. For certain topics, notably complexes of crowns, cryptates and related complexants, the chemistry of the two groups of metals is so similar that, to avoid repetition, it is only considered in the pertinent section of this Chapter. The organometallic chemistry of both groups of metals, is not reviewed here as it is discussed in detail elsewhere.

Alkalides and electrides have been pursued by three independent groups.[2-6] Dye et al.[2] have described the first crystal structure of an electride, viz.,  $[(18C6)_2Cs]^+e^-$ , which was crystallised from dimethylether-trimethylamine mixtures as black shiny platelets. The electron is trapped in a nearly spherical, otherwise empty, cavity of radius 240pm surrounded by eight  $[(18C6)_2Cs]^+$  cations, the geometries of which are unremarkable.[2] Evidence that the electrons are trapped at anionic sites remote from  $Cs^+$  and that they interact with all eight cationic neighbours and are not preferentially localised on any one has also been provided by Dye et al.[3] from  $^{133}Cs$ -mas n.m.r. spectral data for  $[(18C6)_2Cs]^+e^-_{1-x}Na^-_x$  ( $x = 0.0, 0.2, 0.8, 1.0$ ). Dye et al.[3] have also reported  $^{133}Cs$ -mas n.m.r. spectral data for the alkalides  $[(18C6)_2Cs]^+M^-$  ( $M = Na-Cs$ ) and  $[(15C5)_2Cs]^+M^-$  ( $M = Na-Rb$ ). The chemical shifts of the  $Cs^+$  ions are independent of the alkalide ( $\delta = -60 \pm 2ppm$  for  $[(18C6)_2Cs]^+$  and  $\delta = +27 \pm 3ppm$  for  $[(15C5)_2Cs]^+$ ), except for  $[(18C6)_2Cs]^+Cs^-$  which shows temperature dependent chemical shifts, ( $\delta = -40$  to  $-50ppm$  for  $[(18C6)_2Cs]^+$  and  $\delta = -205$  to  $-240ppm$  for  $Cs^-$ ).

Edwards et al. have shown that the alkali metals ( $M = Na-Cs$ ) dissolve in 12C4[4] and 15C5[5] to give intense blue solutions. Spectroscopic studies (optical, e.s.r. and n.m.r.) revealed the presence of alkali metal cations and anions, electrons and

cation-electron pairs. The anions had characteristic optical bands ( $\lambda_{max}/nm$ : Na -  $670 \pm 10$ ; K -  $840 \pm 20$ ; Rb -  $890 \pm 20$ ; Cs -  $990 \pm 20$ ). Although  $^{23}Na^-$  and  $^{87}Rb^-$  gave singlet n.m.r. peaks at high field ( $\delta = -61.8 \pm 0.1$  ppm,  $\Delta\nu_{1/2} = 10$  Hz for  $Na^-$ ;  $\delta = -191 \pm 2$  ppm,  $\Delta\nu_{1/2} = 1000$  Hz for  $Rb^-$ ) resonances due to  $^{39}K^-$  and  $^{133}Cs^-$  were not observed. Two e.s.r. signals attributable to solvated electrons and cation-electron pairs were detected in frozen solution; on melting the resonances merged to give a single time averaged signal.

Optical spectroscopic studies of saturated solutions of sodium in hmpa-thf mixtures ( $0.061 < x_{hmpa} < 0.390$ ) effected by Saji et al.[6] indicate that  $Na^-$  is the only anionic species present and that three hmpa molecules solvate a single  $Na^-$  ion.

Three communications describing aspects of the cocatalytic function of alkali metal cation promoters in carbonate[7] and oxide[8,9] catalysts have been published; doping with  $M^+$  ( $M = Li-Rb$ ) improves the activity and selectivity of  $MCO_3$  ( $M = Sr, Ba$ ) as catalysts for the oxidative dimerisation of methane;[7] addition of  $Cs^+$  to  $Cu/ZnO$  catalysts greatly increases the rate of syngas ( $CO + H_2$ ) conversion to methanol;[8] and doping of  $Ru/Al_2O_3$  catalysts with  $K^+$  stabilises the formyl intermediates formed in syngas conversion.[9]

Solid state  $^{23}Na$ -mas n.m.r. spectra of a comprehensive mixture of sodium salts, solvates and complexes have been determined.[10] The  $^{23}Na$  chemical shifts were measured relative to 1M aqueous  $NaCl$  solution and where necessary were corrected for quadrupole coupling effects; whereas for the salts they varied with the anion (from  $\delta \sim 8$  ppm for  $NaF$  or  $NaCl$  to  $\delta = -52$  ppm for  $NaBPh_4$ ), for the solvates and complexes they were independent of the counter-ion, differing only with the ligand molecule and the  $Na...O$  interatomic distances.[10]

## 1.2 THE ELEMENTS

Presumably for the reasons outlined in the 1985 review[1] interest in the elements has declined such that the number of papers abstracted no longer warrants the retention of a separate section. Those which have been abstracted will be considered, as appropriate, in other subsections of the review; the majority,

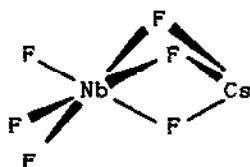
associated with the chemistry of intermetallic compounds, will be incorporated in the section dealing with simple compounds of the alkali metals.

### 1.3 SIMPLE COMPOUNDS OF THE ALKALI METALS

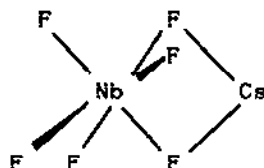
Experimental investigations of ion pairs containing alkali metal cations and theoretical studies of small molecules containing lithium have been maintained at levels that ensure the inclusion of subsections to cater for these topics. Following the demise of the section on the elements, the subsection devoted to the chemistry of intermetallic compounds has been transferred here to complement those catering for binary and ternary derivatives. Finally, increasing interest in the chemistry of alkali metal intercalates has necessitated the addition of a new subsection to cover this subject.

#### 1.3.1 Ion Pairs

Matrix isolation i.r. studies[11] of a series of alkali metal salts of hexafluoroanions,  $AMF_6$  ( $A = K-Cs$ ;  $M = Nb, Ta, U, As$ ), have shown that the geometry of the condensed species is dependent on the magnitude of the host-guest interaction. As the latter increases from Ne or Ar to CO or  $N_2$ , the coordination of the metal changes from a tridentate (face) interaction (1) to a bidentate (edge) interaction (2). The strength of host-guest interactions

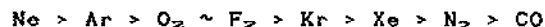


(1)



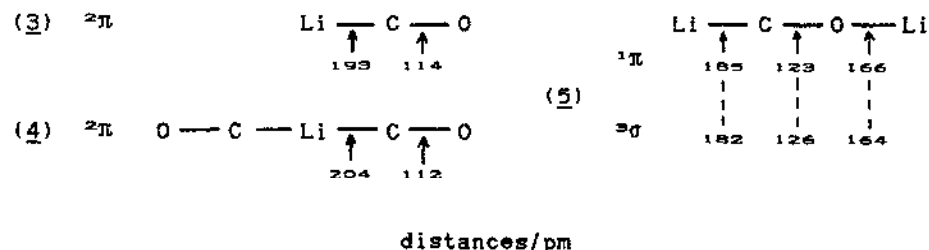
(2)

has been correlated with the separation between terminal and bridging  $\nu(\text{C}\dots\text{O})$  in matrix isolated  $\text{CsClO}_4$ ; [11] the given sequence of decreasing frequency separation is assumed to correlate with increasing host-guest interaction

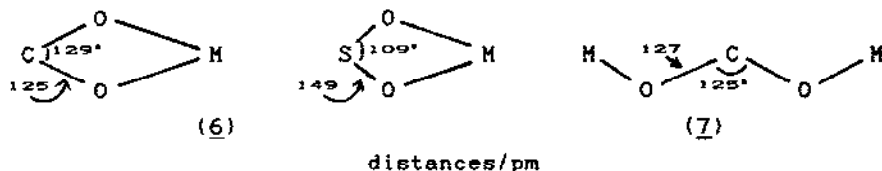


The complexes formed during the codeposition of alkali metal atoms and  $\text{NH}_3$ , [12]  $\text{CO}$ , [13]  $\text{CO}_2$  [14] and  $\text{SO}_2$  [15] in low temperature matrices have been studied by vibrational (i.r. and Raman) spectroscopic techniques. The 1:1 complexes formed between  $\text{M}(\text{Li-K,Cs})$  and  $\text{NH}_3$  [12] exhibit weak charge transfer, Li and Na appearing to act as Lewis acids, K and Cs possibly acting as Lewis bases; the strongest interaction undoubtedly occurs in the  $\text{Li-NH}_3$  complex.

The products of the codeposition of Li and  $\text{CO}$  [13] include (i) four mononuclear species  $\text{Li}(\text{CO})_n$  ( $n = 1-4$ ) which are closely related to transition metal carbonyls, (ii) species with several Li atoms and one or two  $\text{CO}$  molecules in which the carbonyl groups are only weakly coupled and (iii) species in which true chemical bonds are formed between carbonyls. Ab initio calculations, [16] using 4-31G and 6-31G<sup>+</sup> basis sets, of the electronic structures and equilibrium geometries of the simpler lithium carbonyl species formed in these experiments suggest that  $\text{Li}(\text{CO})$  (3) and  $\text{Li}(\text{CO})_2$  (4) exist in the  $^2\pi$  state and that  $\text{Li}_2(\text{CO})$  (5) adopts two inequivalent geometries with  $^1\pi$  and  $^3\sigma$  states. [16]



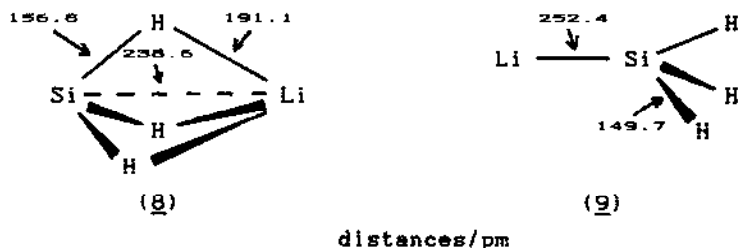
1:1  $\text{M}:\text{CO}_2$  [14] and  $\text{M}:\text{SO}_2$  [15] and 1:2  $\text{M}:\text{CO}_2$  [15] ( $\text{M} = \text{Na}, \text{K}, \text{Cs}$ ) species are formed on codeposition of alkali metals with  $\text{CO}_2$  and  $\text{SO}_2$ . Whereas  $\text{M}(\text{CO}_2)$  and  $\text{M}(\text{SO}_2)$  have planar ring symmetry (6)  $\text{M}_2(\text{CO}_2)$  adopts both a W-shape structure with  $\text{C}_{2v}$  symmetry (7) and a  $\text{C}_\infty$  symmetry structure of uncertain geometry.



### 1.3.2 Theoretical Treatment of Small Moieties

The number of papers abstracted for this subsection is markedly reduced. They can, however, still be considered under one of the three headings used in the earlier reviews: low molecular weight inorganic species:[17-21] organometallic compounds:[22-28] and reaction intermediates.[29,30] Lithium derivatives predominate, moieties containing heavier alkali metals being restricted to  $\text{MBO}_2$  ( $\text{M} = \text{Na}, \text{K}$ ), [21]  $\text{NaCH}_2\text{CN}$  [26] and  $\text{NaCHO}$ . [27]

Ab initio calculations of the interaction of  $\text{Li}^+$  with  $\text{NH}_3$  indicate that the ion-molecule interaction is mainly electrostatic in character. [17] Monte Carlo simulations of  $\text{Li}(\text{H}_2\text{O})_n^+:\text{NO}_2^-$  clusters ( $1 \leq n \leq 28$ ) suggest that the affinity to form an ion pair decreases as more  $\text{H}_2\text{O}$  molecules are added; [18] for the larger clusters, solvent separated ion pairs are more stable than intimate ion pairs by  $87 \text{ kJ} \cdot \text{mol}^{-1}$ . Owing to the more favourable electrostatic interactions in the ion pair  $\text{SiH}_3^-\text{Li}^+$ , the inverted  $\text{C}_{2v}$  geometry (8) of  $\text{LiSiH}_3$  is calculated, using a 6-31G<sup>\*</sup> basis set, to be more stable than the classical  $\text{C}_{2v}$  isomer (9) by  $10.0 \text{ kJ} \cdot \text{mol}^{-1}$ ; [19] the energy barrier separating (8) and (9) ( $56.5 \text{ kJ} \cdot \text{mol}^{-1}$ ) involves movement of  $\text{Li}^+$  from one side of the  $\text{SiH}_3^-$  moiety to the other. Calculations based on SCEP and CISD

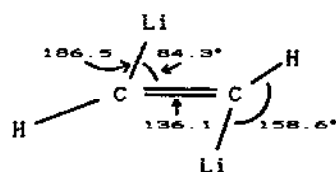


methods suggest that the ground states of  $\text{LiMgH}_3$  and  $\text{LiAlH}_4$  have bidentate ( $\text{C}_{2v}$ ) geometries. [20] Although these conclusions contrast, in part, with earlier data for  $\text{LiBH}_3$  and  $\text{LiBH}_4$  which show

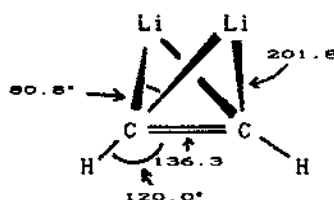
ground state configurations with bidentate ( $C_{2v}$ ) and tridentate ( $C_{3v}$ ) geometries, respectively, the energy differences between the bidentate and tridentate geometries for both  $LiBH_4$  and  $LiAlH_4$  are extremely small (within  $8.5\text{--}25.1\text{ kJ mol}^{-1}$ ). [20] The experimentally observed increase in the dissociation energies of the  $M\text{--}BO_2$  ( $M = Li, Na, K$ ) bonds from 478 and  $480\text{ kJ mol}^{-1}$  for  $M = Na$  and  $K$ , respectively, to  $560\text{ kJ mol}^{-1}$  for  $M = Li$ , has been shown by calculations based on the extended HMO method, to be due to the introduction of p-orbitals into the MO bonding for  $Li\text{--}BO_2$ . [21] In a separate study, the ionic character of the  $M\text{--}BO_2$  bond has been found to decrease from 49% (for  $K$ ) through 46% (for  $Na$ ) to 43% (for  $Li$ ). [21]

Schleyer's [22,23,25-27] and Streitwieser's [24,27-29] groups have almost monopolised the theoretical analysis of organometallic molecules and reaction intermediates; the sole exception is a paper published by McKee on the mechanism of the deprotonation of ethanol by  $LiNH_2$ . [30]

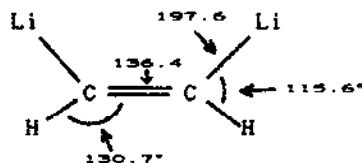
1,2-dilithioethene [22] and 2,3-dilithiopropene [23] have been studied, the former for the second time, the latter for the first time, using ab initio methods. Reoptimisation of the structures of 1,2-dilithioethene [22] using more sophisticated basis sets



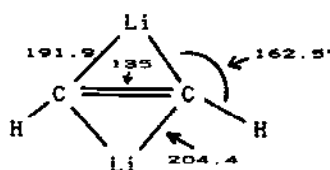
(10)



(11)



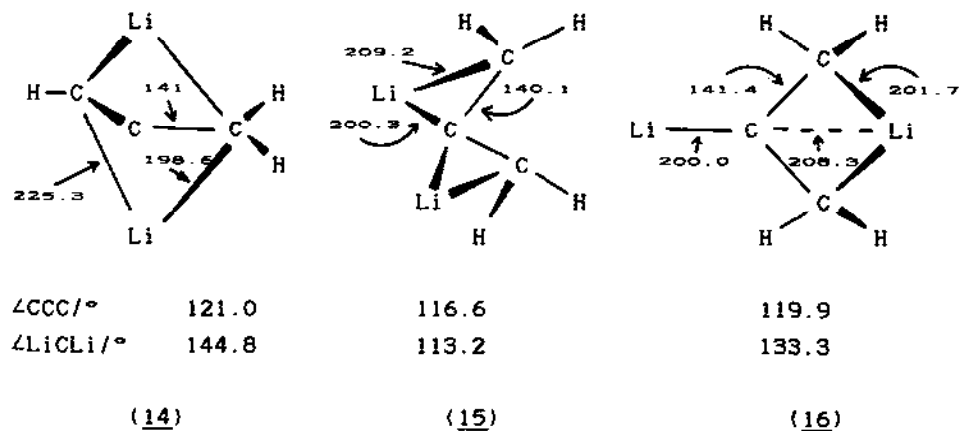
(12)



(13)

distances/pm

indicate that the trans-isomer (10) is more stable than either of the two cis-isomers (11,12) in agreement with recent experimental findings[31] but contrary to the earlier theoretical conclusions.[32] Furthermore, although (10) and (11) were found to be minima, (12) was found to be a transition state structure. The most favourable pathway for transportation of (11) into (10) does not involve rotation about the carbon-carbon double bond but in-plane inversion of one of the CH groups, the first step in the process being rearrangement of (11) into another doubly bridged cis isomer (13) in which both lithiums are in the molecular plane.[22] The analysis of the potential surface of 2,3-dilithiopropene[23] revealed two minima and a single transition state structure. The former, which have  $C_{2v}$  symmetry (14) and  $C_2$  symmetry (15) structures lie 10.3 and 25.4 kJ.mol<sup>-1</sup> above the latter which possesses a 2-lithioallyllithium structure (16) in which both lithiums lie on the  $C_{\infty}$  plane with one lithium bridging the terminal carbons and the other adjacent to the central carbon.[23]



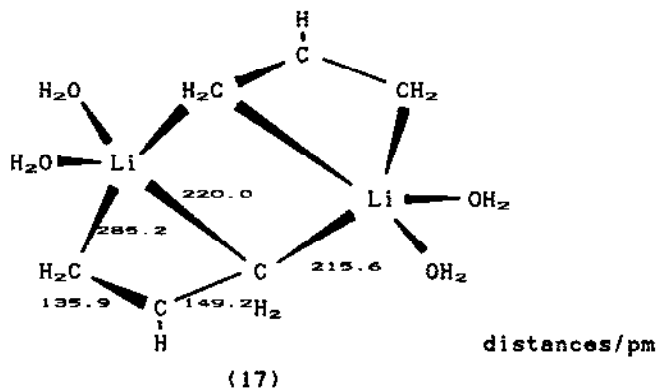
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MNDO calculations of various symmetrical and unsymmetrical dimeric structures of 3-lithiopropene (allyllithium) have been undertaken[24] to rationalise the results of a series of cryoscopic measurements and variable temperature <sup>13</sup>C-n.m.r. studies which show that whereas allylsodium and allylpotassium are



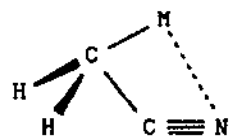
monomeric in thf, allyllithium exists as an unsymmetrical dimer. The theoretical analysis showed geometry (17) to be lowest in energy.[24]

Ab initio calculations reveal a significant kinetic acceleration of methyl radical addition to ethene on complexation of the alkene

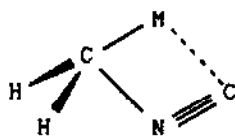


with the lithium cation;[25] the calculated activation energies in the absence and presence of  $\text{Li}^+$  are 60.2 and 25.1  $\text{kJ}\cdot\text{mol}^{-1}$ , respectively. It is suggested that the effect should be general for alkyl radical addition to alkene-metal complexes.[25]

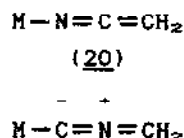
Extended ab initio examination[26] of the Li, Na derivatives of the  $\text{CH}_2\text{CN}^-$ ,  $\text{CH}_2\text{NC}^-$  and isomeric anions found lithium bridged and, to a lesser extent, sodium bridged geometries (18) and (19) to be favoured; the metallated ketenimine forms (20) are next lowest in energy with the metallated nitrile ylides (21) somewhat higher in energy. Aggregation and solvation



(18)



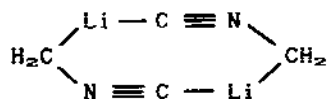
(19)



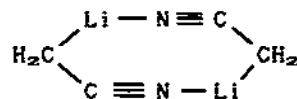
(21)

effects of the lithium compounds were probed by MNDO calculations.[26] The most stable unsolvated dimers of both  $\text{LiCH}_2\text{CN}$  and  $\text{LiCH}_2\text{NC}$  have 8-membered ring structures (22). Solvation, however, favours the formation of the alternative

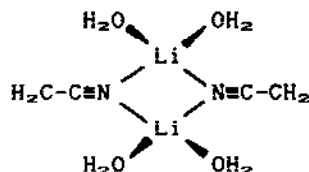
4-membered ring N-lithiated ketenimine dimer (23).[26]



(22a)



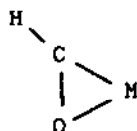
(22b)



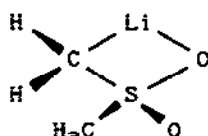
(23)

Ground state metal bridged geometries (24) are also predicted for the formyl complexes MCHO ( $M = \text{Li}, \text{Na}$ ) from *ab initio* calculations.[27] Such  $\eta^2$ -coordination, which is favoured by large electronegativity differences between metal and carbon, is characterised by rather long C-O bonds, significant alkoxy-carbene

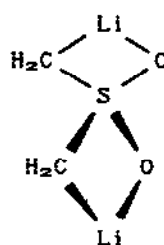
	LiCHO	NaCHO
$r(\text{H}\dots\text{C})/\text{pm}$	110.4	-
$r(\text{C}\dots\text{O})/\text{pm}$	124.3	123.9
$r(\text{C}\dots\text{M})/\text{pm}$	190.2	224.3
$r(\text{H}\dots\text{O})/\text{pm}$	178.2	216.5
$\angle\text{OCH}/^\circ$	65.1°	70.3°



(24)



(25)

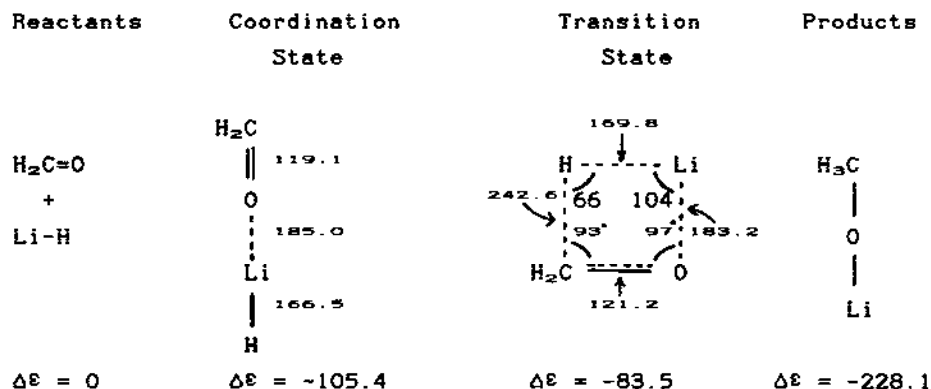


(26)

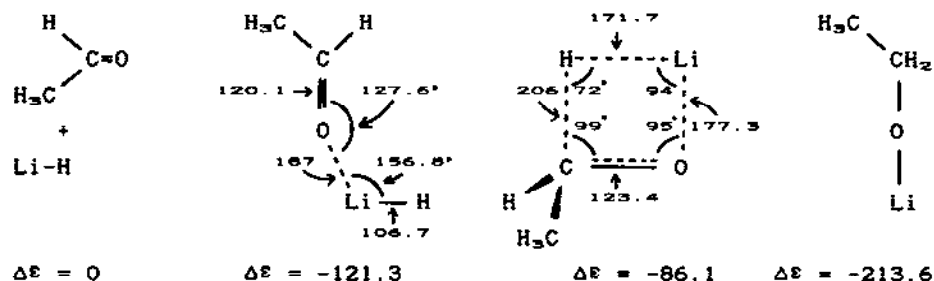
character in the formyl group and predominantly ionic M-C interactions.[27]

Optimisation of the geometry of the monolithium salt of dimethylsulphone[28] resulted in a ground state structure (25) in which the lithium is clearly associated with the carbon and only one oxygen. Similar calculations for the corresponding dilithium salt[28] gave a ground state structure (26) in which each lithium is associated with one carbon and one oxygen. In both compounds the interaction is primarily ionic in character ( $\text{Li}^+ \dots \text{CH}_2\text{SO}_2\text{CH}_3$  and  $\text{Li}^+ \dots \text{CH}_2\text{SO}_2\text{CH}_2 \dots \text{Li}^+$ ). [28]

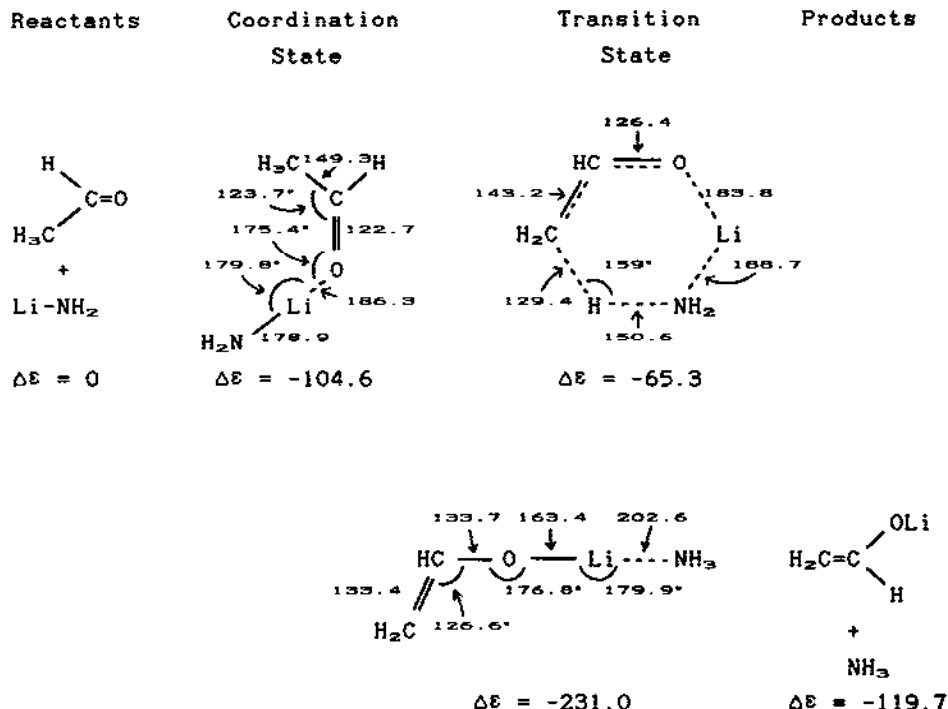
Theoretical analyses of the reaction of LiH with methanol and ethanol (3-21G" basis set)[29] and of  $\text{LiNH}_2$  with ethanol (3-21+G basis set)[30] predict the mechanisms given in schemes 1 - 3.



Scheme 1



Scheme 2



Scheme 3

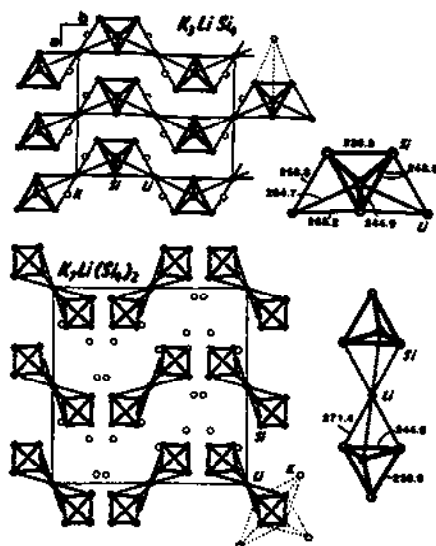
(Distances/pm: Energies/kJ.mol<sup>-1</sup> are quoted relative to that of the reactants)

For all three reactions, the transition state is predicted to be very similar in character to the reactants.[29,30] Indeed, integrated population analysis of Schemes (1) and (2) indicate that Li carries a charge of +0.85 in the transition state, almost the same as in ground state organolithium compounds.[29]

### 1.3.3 Intermetallic Compounds

Reaction of Li+K mixtures with silicon (sealed Nb ampoule in a quartz ampoule; 4h heating to 1073K; 4h annealing at 1073K; slow cooling over 12h) results in the formation of red transparent silicides which are flammable in air and which form flammable silanes with protic solvents.[33] The products formed, K<sub>3</sub>LiSi<sub>4</sub> or K<sub>7</sub>Li(Si<sub>4</sub>)<sub>2</sub>, depend on the reactant molar ratios. Their structures

are shown in Figure 1. In  $K_3LiSi_4$ , the  $Si_4^{4-}$  tetrahedra are linked by the lithiums to form infinite chains  $\infty^1[Li(Si_4)]^{3-}$ . Each lithium thus acts as a  $\mu_3$ -ligand bridging two faces of separate tetrahedra and hence bonds to six silicons (258.8-294.7pm; mean 272.9pm). In  $K_7Li(Si_4)_2$ , the two  $Si_4^{4-}$  tetrahedra are linked by the lithium atom to generate a centrosymmetric dumb-bell shaped  $[Li(Si_4)_2]^{7-}$  unit located on a 3-fold symmetry axis. Again the lithium is surrounded by six silicons from two separate tetrahedra (271.4pm). Whereas in  $K_3LiSi_4$  only one potassium caps a tetrahedral face, six act as  $\mu_3$ -ligands in  $K_7Li(Si_4)_2$ ; the remaining potassiums either bridge edges or coordinate corners of the  $Si_4$  tetrahedra (Figure 1). [33] Vibrational spectroscopic



**Figure 1.** Crystal structures of  $K_3LiSi_4$  and  $K_7Li(Si_4)_2$  showing the polymeric  $[Li(Si_4)]^{3-}$  chain and the dumb-bell shaped  $[Li(Si_4)_2]^{7-}$  unit. In both structures, the  $\mu_3$ -coordinated potassiums are shown using hatched lines (reproduced by permission from Angew. Chem., Int. Ed. Engl., 25(1986)566).

studies have been completed for  $K_3LiSi_4$  and  $K_7Li(Si_4)_2$ : [34] the  $A_1$  (Raman active),  $E$  (Raman active) and  $T_2$  (infrared and Raman active)

bands predicted for the  $\text{Si}_4^{4-}$  anion (symmetry  $\bar{4}3m-T_d$ ) were observed at 482, 285 and  $356\text{cm}^{-1}$  respectively.

The normal pressure modification of LiGe is obtained by fusion of equimolar quantities of lithium and germanium under argon at 923K in a molybdenum crucible.[35] Conversion to the high pressure modification is achieved by treatment at 4GPa and 773K for 10 minutes in BN or iron crucibles followed by quenching to ambient conditions.[35] The normal pressure phase (tetragonal; space group  $I4_1/a$ ;  $a = 975$ ,  $c = 578$  pm) is a Zintl phase. The high pressure modification (tetragonal; space group  $I4_1/amd$ ;  $a = 405.3$ ,  $c = 2328.2$  pm), however, crystallises in a novel structural type which shows similarities to the structures of LiSn and LiPb.[35]

Reaction of sodium and tellurium (1:3 molar ratio) in liquid ammonia at ~223K yields  $\text{NaTe}_3$ . [36] Single crystals can be obtained by heat-treatment of the crude product (corundum crucible in sealed glass ampoule; 1h heating at 773K; 120h annealing at 653K). Its structure (trigonal; space group  $P\bar{3}c1$ ;  $a = 903.3$ ,  $c = 2193\text{pm}$ ) contains three crystallographically independent 6-coordinate sodiums each of which lies on a 3-fold symmetry axis ( $\text{Na}(1) \dots \text{Te} = 307.0, 331.4\text{pm}$ ;  $\text{Na}(2) \dots \text{Te} = 316.1, 324.0\text{pm}$ ;  $\text{Na}(3) \dots \text{Te} = 316.9, 319.4\text{pm}$ ). [36]

$^{197}\text{Au}$ -Mossbauer spectra of  $\text{MAu}$  ( $M = \text{Li-Cs}$ ) intermetallics and of  $[\text{C222M}]^-\text{Au}^-$  ( $M = \text{K-Cs}$ ) [37] are consistent with a cubic environment for the Au atom in all three complexes,  $[\text{C222M}]^-\text{Au}^-$  ( $M = \text{K-Cs}$ ), but only two intermetallics,  $\text{RbAu}$  and  $\text{CsAu}$ . For the other two intermetallics,  $\text{NaAu}$  and  $\text{KAu}$ , the spectra indicate the presence of sizeable electric field gradients at the Au atoms. [37]

#### 1.3.4 Binary Compounds

Since the papers abstracted for this section are limited in number and fragmented in nature, they are considered as a group starting with hydrides, proceeding through nitrides and phosphides, oxides and sulphides, and halides, and finishing with amides, hydroxides and bifluorides.

Schleyer et al. [38] have reported the preparation of extremely active LiH, NaH and KH "superbase" reagents under mild conditions. Finely suspended LiH, capable of instantly metalating dibenzylketone and 1,1,2,2-tetraphenylacetone at room temperature, was produced by hydrogenating BuLi in hexane in the presence of tmeda. Hydrogenation of BuNa and BuK, previously prepared by reaction of

$\text{NaO}^t\text{Bu}$  or  $\text{KO}^t\text{Bu}$  with  $\text{BuLi}$  in hexane/tmeda solutions gave highly reactive  $\text{NaNH}$  and  $\text{KH}$  in suspension. Whereas the latter instantaneously metalated  $^t\text{BuCOCH}_3$  at 253K, the former was less vigorous, completion of enolate formation requiring 20 minutes at 273-293K. [38]

The use of  $\text{Li}_3\text{N}$  as a reducing agent has been demonstrated. [39] Stoichiometric reactions of  $\text{Cp}_2\text{TiCl}_2$  or  $\text{CpTiCl}_3$  with  $\text{Li}_3\text{N}$  (in various molar ratios) in thf result in reduction to  $(\text{Cp}_2\text{TiCl}_2)_2$ ,  $(\text{CpTiCl}_2)_n$  and  $(\text{CpTiCl})_4$ . Further reduction produces hexanuclear nitrido titanium clusters  $\text{Cp}_6\text{Ti}_6\text{N}$  and  $\text{Cp}_6\text{Ti}_6\text{N}_3$  characterised from mass spectrometric evidence.  $\text{Cp}_2\text{Ti}(\text{CO})_2$  is formed by the reaction between  $\text{Cp}_2\text{TiCl}_2$  and  $\text{Li}_3\text{N}$  in thf in the presence of  $\text{CO}$ . [39]

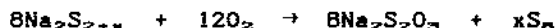
As part of a comprehensive review of polyphosphorus compounds, Baudler [40] has considered the chemistry of both alkali metal polyphosphides and alkali metal hydrogen polyphosphides; specific emphasis is placed on structure determination using single crystal xrd and  $^{31}\text{P}$ -n.m.r. techniques. Baudler [41-44] has also reported the preparation of  $\text{MP}_5$  ( $\text{M} = \text{Li}, \text{Na}$ ), [41]  $\text{M}_3\text{P}_{19}$  ( $\text{M} = \text{Li}-\text{K}$ ), [42] and  $\text{Na}_2\text{P}_{16}$ . [43, 44] Lithium pentaphosphacyclopentadienide ( $\text{LiP}_5$ ) was obtained by reaction of  $\text{LiPH}_2$  with white phosphorus (1:5 molar ratio) in dry thf; [41] sodium pentaphosphacyclopentadienide ( $\text{NaP}_5$ ) was formed, together with sodium tetraphosphacyclopentadienide ( $\text{NaP}_4\text{CH}$ ) and sodium triphosphacyclobutadienide ( $\text{NaP}_3\text{CH}_2$ ), by nucleophilic cleavage of white phosphorus by metallic sodium in diglyme. [41] All three anions are rings with unsubstituted phosphorus atoms of coordination number 2 that are stabilised by mesomerism. The nonadecaphosphides,  $\text{M}_3\text{P}_{19}$  ( $\text{M} = \text{Li}-\text{K}$ ) were prepared by nucleophilic cleavage of white phosphorus with  $\text{LiPH}_2$  sodium or potassium, as appropriate. [42]  $\text{Li}_3\text{P}_{19}$  also results from the reaction of  $\text{Li}_3\text{P}_7$  with white phosphorus or iodine or 1,2-dibromoethane as well as from the degradation of  $\text{Li}_2\text{P}_{16}$  with  $\text{LiPH}_2$ . [42] Reaction of white phosphorus with sodium (molar ratio 3:1) in boiling thf or monoglyme in the presence of 18C6 gives sodium hexadecaphosphide  $\text{Na}_2\text{P}_{16}$  as a solvated adduct  $\text{Na}_2\text{P}_{16} \cdot (18\text{C}6)_3 \cdot 2\text{thf}$ . [43] In liquid ammonia, as well as  $\text{Na}_2\text{P}_{16}$ , the products of the reaction (molar ratio 2:1, 1.5:1) include 1,3-diaminotriphosphane. [44]

Single crystal xrd structural analysis of lithium heptaphosphide ( $\text{Li}_3\text{P}_7$ ), prepared by reaction of the elements at 870K in sealed Nb or Ta crucibles, has revealed a new structure type (orthorhombic

symmetry; space group  $P2_12_12_1$ ;  $a = 974.2$ ,  $b = 1053.5$ ,  $c = 759.6\text{pm}$ ).[45]

The interalkali metal sulphide,  $\text{KNaS}$ , has been crystallised by annealing a mixture of  $\text{Na}_2\text{S}$  and  $\text{K}_2\text{S}$  (sealed corundum tube under argon; 6 days heating at  $873\text{K}$ );[46] it is isostructural with  $\text{PbCl}_2$  (orthorhombic; space group  $\text{Pnma}$ ;  $a = 770.3$ ,  $b = 460.4$ ,  $c = 829.3\text{pm}$ ).

The degradation of sodium sulphide in the solid phase (as  $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ )[47] and in aqueous solution[48] and of sodium polysulphides[49] has been considered. A two step dehydration pathway involving loss of initially three and then two water molecules was proposed to rationalise the results of tga and xrd studies of the thermal decomposition of  $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ :[47] a topotactic process was put forward to account for the structural transformation mechanisms. U.v. irradiation ( $\lambda = 248\text{nm}$ ) of  $\text{Na}_2\text{S}$  in aqueous solution leads to hydrogen and  $\text{Na}_2\text{S}_x$  ( $\Phi(\text{H}_2) = 0.34$  at  $\lambda = 254\text{nm}$ );[48] light adsorption occurs via  $\text{HS}^-$ , which is produced by hydrolysis of  $\text{Na}_2\text{S}$ , affording the solvated electron and the  $\text{HS}^\cdot$  radical. In the presence of formate anions, hydrogen evolution becomes catalytic with respect to  $\text{HS}^-$  ( $\Phi(\text{H}_2) = 0.12$  at  $\lambda = 254\text{nm}$ ).[48] Aqueous sodium polysulphide ( $\text{Na}_2\text{S}_x$ ;  $2 < x < 4.6$ ) undergoes autoxidation by either air or pure oxygen according to the equation:[49]



Iodometric determination, vibrational spectroscopy and ion-pair chromatography showed that neither  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$  nor polythionates are formed and that the sulphur consists of  $\text{S}_8$  (>99%).[49]

Single crystals of  $\text{RbO}_3$  have been synthesised by repeated ozonisation of  $\text{RbO}_2$  at  $298\text{K}$  followed by extraction using liquid ammonia.[50] The packing of the ions within the structure (monoclinic; space group  $\text{P}2_1/\text{c}$ ;  $a = 645.2$ ,  $b = 602.2$ ,  $c = 876.3\text{pm}$ ;  $\beta = 122.34^\circ$ ) strongly resembles the  $\text{CsCl}$ -type structure, with nine  $\text{Rb}\cdots\text{O}$  interatomic distances varying from  $293.2$  to  $319.1\text{pm}$  and a tenth more remote  $342.1\text{pm}$  contact.[50]

A linear relationship has been noted between the dissociation energy of the alkali metal halides ( $\text{MX}$ ;  $\text{M} = \text{Na}-\text{Cs}$ ,  $\text{X} = \text{Cl}-\text{I}$ ) and the magnetic shielding constants of the alkali metal ( $^{23}\text{Na}$ ,  $^{39}\text{K}$ ,  $^{87}\text{Rb}$ ,  $^{133}\text{Cs}$ ) and halogen ( $^{35}\text{Cl}$ ,  $^{79}\text{Br}$ ,  $^{127}\text{I}$ ) nuclei.[51] A similar



relationship has also been observed between the dissociation energy of the alkali metal and alkaline earth metal fluorides and the  $^{19}\text{F}$ -n.m.r. chemical shift.[51]

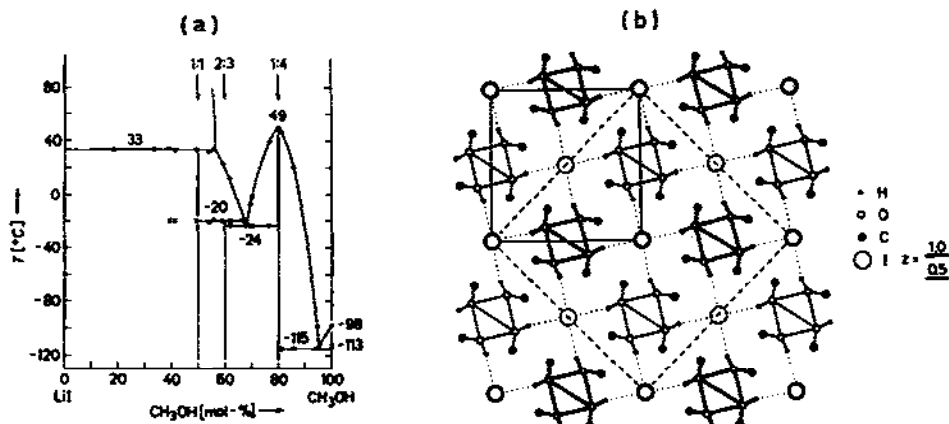
The solution structure of alkali metal halides has been probed in water,[52,53] various aprotic solvents[54] and in the n-butylpyridinium chloride- $\text{AlCl}_3$  ambient temperature molten salt.[55] The solvation structure[52] and dynamics[53] of a sodium chloride ion-pair in water have been computer simulated. The  $\text{Na}^+$  ion attempts to maintain an octahedral geometry at all separations. As a stable contact ion-pair the coordination shell comprises five water molecules and the  $\text{Cl}^-$  ion. As the ions are separated an unstable octahedron is generated. At further separations the  $\text{Cl}^-$  ion is replaced by a sixth water molecule to form a stable solvent-separated ion-pair. For the two stable structures, the coordinated water molecules are strongly hydrogen bonded to those in the outer spheres; for the distorted octahedral structure this hydrogen bonding is weakened owing to rotation of the five coordinated water molecules.[52,53]

Dimeric aggregates between  $\text{LiX}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and  $\text{LiSCN}$  have been observed using FTIR spectroscopic techniques in thf, 1,4-dioxane, 1,3-dioxolane, cyclopentanone, dimethylcarbonate, isopropylacetate, and diethylcarbonate;[54] no aggregates were observed in dmf, turea or propylene carbonate. No aggregates involving  $\text{LiI}$  were noted in any of these solvents.[54] Tetrameric aggregates of stoichiometry  $\text{Li}_4\text{Br}_2(\text{NCS})_2$  were seen in diethylether;[54] the corresponding chloride aggregates were not accessible owing to the insolubility of  $\text{LiCl}$  in ethers. In some ethers (di-n-butylether, s-butylethylether and i-propyl-n-propylether), however, mixed tetramers of stoichiometry  $\text{Li}_4\text{I}_n(\text{NCS})_{4-n}$  are formed between  $\text{LiI}$  and  $\text{LiSCN}$ . [54]

$^7\text{Li}$ -n.m.r. and potentiometric studies of lithium salts ( $\text{LiX}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{ClO}_4^-, \text{AsF}_6^-, \text{NO}_3^-$ ) dissolved in the n-butylpyridinium chloride- $\text{AlCl}_3$  ambient temperature molten salt indicate the presence of  $\text{LiCl}_2^-$  monomers and  $\text{Li}_2\text{Cl}_4^{2-}$  dimers in a fast two site exchange mechanism.[55]

As part of a search for fast solid  $\text{Li}^+$  ion conductors, Rabenau et al.[56] have reinvestigated the phase diagram of the  $\text{LiI}-\text{CH}_3\text{OH}$  system and the crystal structure of the highest conducting phase,  $\text{LiI} \cdot 4\text{CH}_3\text{OH}$ . Unlike earlier phase diagrams, which showed the formation of  $\text{LiI} \cdot \text{CH}_3\text{OH}$  adducts of stoichiometry 1:1, 1:3 and 1:4,

the modified diagram (Figure 2(a)) contains three adducts of stoichiometry 1:1, 2:3 and 1:4; [56] whereas  $\text{LiI} \cdot 4\text{CH}_3\text{OH}$  melts congruently 322K.  $\text{LiI} \cdot \text{CH}_3\text{OH}$  and  $2\text{LiI} \cdot 3\text{CH}_3\text{OH}$  undergo peritectic decomposition reactions at 253K and 249K, respectively (Figure 2(a)). In the structure of  $\text{LiI} \cdot 4\text{CH}_3\text{OH}$  (Figure 2(b)), the  $\text{Li}^+$  ions



**Figure 2.** (a) Phase relationships in the  $\text{LiI}-\text{CH}_3\text{OH}$  system and (b) projection of the crystal structure of  $[\text{Li}(\text{CH}_3\text{OH})_4]^+ \text{I}^-$  viewed along (001). (The  $\text{Li}^+$  ions in the centres of the tetrahedra are omitted. The centres of the tetrahedra are located on the  $z = 0.75$  (thick) and  $z = 0.25$  (thin) layers; the  $\text{I}^-$  ions are located on the  $z = 0.0$  (thick) and  $z = 0.5$  (thin) layers.) (reproduced by permission from Angew Chem., Int. Ed. Engl., 25(1986)1087).

are surrounded tetrahedrally by oxygen atoms with formation of  $[\text{Li}(\text{CH}_3\text{OH})_4]^+$  units ( $\text{Li} \cdots \text{O} = 191.9\text{pm}$ ); [56] the arrangement of the  $[\text{Li}(\text{CH}_3\text{OH})_4]^+$  and  $\text{I}^-$  ions in the structure is similar to that in zinc blende (the corresponding unit cell is shown by broken lines in Figure 2(b)).

The complex adduct,  $2\text{NaI} \cdot 3\text{CH}_3\text{CN} \cdot 3\text{H}_2\text{O}$ , crystallises with hexagonal symmetry. [57] Each  $\text{Na}^+$  ion is located on a 3-fold symmetry axis and is octahedrally coordinated to three water ( $\text{Na} \cdots \text{O} = 241.6\text{pm}$ ) and three acetonitrile molecules ( $\text{Na} \cdots \text{N} = 252.3\text{pm}$ ). The sodium

centered octahedra share opposite faces with two adjacent octahedra to form continuous  $[\text{Na}(\text{H}_2\text{O})_3(\text{CH}_3\text{CN})_3]_\infty$  chains; the shared faces contain either three nitrogens or three oxygens alternately along the chain.[57]

The structure of  $\text{RbI}_3$  (orthorhombic; space group  $\text{Pnma}$ ;  $a = 1090.8$ ,  $b = 665.5$ ,  $c = 971.1\text{pm}$ ) is isotypic with that of  $\text{CsI}_3$ . [58] The  $\text{I}_3^-$  ions are asymmetric and slightly bent ( $\text{I} \dots \text{I} = 283.3$ ,  $305.1\text{pm}$ ;  $\angle \text{III} = 178.11^\circ$ ); the  $\text{Rb}^+$  ions are surrounded by seven iodine atoms in an irregular geometry ( $\text{Rb} \dots \text{I} = 363.4\text{--}415.8\text{pm}$ ). [58]

Jacobs et al. [59-61] have completed a detailed structural study of the polymorphism of a series of alkali metal amides [59] and hydroxides; [60,61] pertinent crystallographic data are summarised in Table 1. The interalkali metal amides,  $\text{CsLi}(\text{NH}_2)_2$  and  $\text{CsLi}_2(\text{NH}_2)_3$ , were obtained by reaction of the metals with ammonia in high pressure autoclaves. [59] The structure of the hexagonal modification of  $\text{CsLi}(\text{NH}_2)_2$ , including the hydrogens, was established from single crystal xrd data. [59] The Li atoms occupy distorted nitrogen tetrahedra ( $\text{Li} \dots \text{N} = 211\text{pm}$ ) which are connected by trans-located edges along (001) to generate an infinite  $[\text{Li}(\text{NH}_2)_2]^-$  chain ( $\text{Li} \dots \text{Li} = 280.3\text{pm}$ ); the Cs atoms combine the chains with ten amide anions surrounding each Cs atom ( $\text{Cs} \dots \text{N} = 342.3$ ,  $353.7$ ,  $390.4\text{pm}$ ). [59] For the hydroxides, the influence of the asymmetric charge distribution of the anion decreases with increasing temperature. [60,61] In the low temperature TII-variants, the anions are hydrogen bonded forming infinite chains. On warming the hydrogen bonds break giving more mobile hydroxide anions; intermediate phase transformations are associated with the discontinuous expansion of the rocking vibrations of the anions. In the high temperature NaCl-variants, the anions rotate quasi-freely. [60,61]

The lattice energies of the alkali metal bifluorides have been improved using revised auxiliary thermodynamic data. [62] The new data (Table 2) are such that the lattice energies of the bifluorides exceed those calculated by classical ionic models and the difference between the lattice energies of the fluorides and bifluorides decreases steadily with cation radius in accordance with crude ionic models. [62]

Single crystal xrd studies of  $\text{KF} \cdot 2.5\text{HF}$  and  $\text{KF} \cdot 3\text{HF}$  have revealed the structural formulae  $\text{K}_2[\text{H}_2\text{F}_3][\text{H}_3\text{F}_4]$  and  $\text{K}[\text{H}_3\text{F}_4]$ . [63] Full details of the structures of the  $[\text{H}_n\text{F}_{n+1}]^-$  anions are given.

**Table 1.** Crystallographic parameters for various polymorphs of  $\text{CsLi}(\text{NH}_2)_2$ , [59]  $\text{CsLi}_2(\text{NH}_2)_3$ , [59]  $\text{RbOH}$ , [60]  $\text{RbOD}$ , [60]  $\text{CsOH}$  [61] and  $\text{CsOD}$ . [61]

Compound	Temp. Range	Symmetry	Space Group	Z	a/pm	b/pm	c/pm	$\beta/^\circ$
$\text{CsLi}(\text{NH}_2)_2$		monoclinic	$C2/c$	-	656.4	1166.5	577.0	117.4
		hexagonal	$P6_222$	-	633.4	-	840.9	-
$\text{CsLi}_2(\text{NH}_2)_3$		orthorhombic	$Cmcm$	-	875.1	1118.4	545.0	-
$\text{RbOH}$	15-265	orthorhombic	$Cmc2_1$	4	412.4	1117.6	421.1	-
	265-367	monoclinic-I	$P2_1/m$	2	415.1	424.5	603.0	104.5
	367-511	monoclinic-II	$P2_1/m$	2	415.8	427.6	605.4	103.7
	511-m.p	cubic	$Fm3m$	4	608.0	-	-	-
$\text{RbOD}$	15-300	orthorhombic	$Cmc2_1$	4	412.5	1109.9	421.3	-
	300-369	monoclinic-I	$P2_1/m$	2	414.7	424.1	600.6	105.1
	369-451	monoclinic-II	$P2_1/m$	2	415.5	426.6	603.1	104.2
	451-513	modification with random arrangement of atoms						
	513-m.p	cubic	$Fm3m$	4	607.5	-	-	-
$\text{CsOH}$	200-498	orthorhombic	$Cmcm$	4	435.0	1199.2	451.6	-
	498-m.p	cubic	$Fm3m$	4	642.7	-	-	-
$\text{CsOD}$	23-230	ortho-rhombic-I	$P2_12_12_1$	4	431.9	1153.8	446.9	-
	230-460	ortho-rhombic-II	$CmCm$	4	435.2	1189.6	451.2	-
	460-m.p	cubic	$Fm3m$	4	645.7	-	-	-

The coordination of the K atoms is square antiprismatic in  $\text{KF}, 2.5\text{HF}$  with an additional fluorine above a square face of one of the two independent polyhedra and cube-like in  $\text{KF}, 3\text{HF}$  with  $\text{K}\cdots\text{F}$  contact distances in the range 269.9-313.7pm. [63]

### 1.3.5 Ternary germanides and pnictides

To avoid unnecessary duplication with other Chapters of this

**Table 2.** Revised thermodynamic data for alkali metal bifluorides and fluorides.[62]

	Li	Na	K	Rb	Cs
$-\Delta H_f^\circ(\text{MHF}_2(\text{s}))/\text{kJ.mol}^{-1}$	942.3	920.3	927.7	922.6	923.8
$U_L(\text{MHF}_2(\text{s}))/\text{kJ.mol}^{-1}$	939	841	753	724	693
$-\Delta H_f^\circ(\text{MF}(\text{s}))/\text{kJ.mol}^{-1}$	616.0	573.6	567.3	557.7	553.5
$U_L(\text{MF}(\text{s}))/\text{kJ.mol}^{-1}$	1047	928	827	793	756

review the ternary compounds considered in this and subsequent subsections are restricted to those containing both an alkali metal and a transition metal. Although a plethora of papers mainly dealing with structural properties have been abstracted for oxides, chalcogenides and halides, only five have been discovered for this subsection. Schuster has prepared and characterised both germanides[64,65] and pnictides.[65-67] Synthesis usually involved prolonged heat treatment of the constituent elements in the appropriate molar ratios in sealed crucibles. Characterisation was normally based on single crystal or powder xrd methods; exceptionally neutron diffraction techniques[66] were used. Pertinent crystallographic data are summarised in Table 3. The dimorphism of  $\text{Li}_2\text{ZnGe}$  was investigated using both xrd and tga methods;[64] the  $\alpha \rightarrow \beta$  transition temperature was found to be 780(5)K.

During an attempted synthesis of  $\text{Rb}_3\text{As}_7$  in a sealed niobium tube, rubidium was added in excess; the reaction product, clearly not  $\text{Rb}_3\text{As}_7$ , was dissolved in a solution of C222 in ethylenediamine from which red crystals of  $[\text{C222Rb}]_x[\text{Rb}(\text{NbAs}_6)]$  (27) crystallised.[68] In (27), only two of the three Rb atoms are enclosed in the C222 molecules. The third forms a one dimensional  $[\text{Rb}(\text{NbAs}_6)]^{2-}$  chain with the complex anion  $[\text{NbAs}_6]^{3-}$ . Evidently the  $\text{Rb} \dots \text{As}$  interactions in the chains are able to compete not only with those between  $\text{Rb}^+$  and ethylenediamine but also with those between  $\text{Rb}^+$  and C222. This surprising observation has been probed using INDO calculational methods to study the electronic structure of  $[\text{VAs}_6]^{3-}$  and  $[\text{K}(\text{VAs}_6)]^{2-}$ . Although Rb and Nb had to be replaced by K and V for technical reasons, the changes were not thought to alter significantly the

derived energy level diagram, which revealed that the coupling of the  $3a_1$  ( $As, 4p$ ) state with  $Rb(ns, np_z)$  functions is a important feature of the bonding As-Rb interactions along the chain.[68]

Table 3. Crystallographic parameters for diverse germanides and pnictides prepared by Schuster et al.

	Structure Type	Symmetry	Space Group	a/pm	c/pm	Ref
$\alpha$ - $Li_2ZnGe$	$Na_3As$	hexagonal	-	432.6	828.6	64
$\beta$ - $Li_2ZnGe$	$Li_3Bi$	cubic	-	614.0	-	64
$LiLnGe$ ( $Ln=Pr, Tb, Dy, Yb$ ) <sup>*</sup>	$Fe_2P$	hexagonal	$P6_2m$	731.6	437.3	65
$LiYbBi$	$LiYSn$	hexagonal	-	959.5	763.5	65
$NaMnX$ ( $X=P, As, Sb, Bi$ ) <sup>*</sup>	-	tetragonal	$P4/nmm$	408.7	687.6	66
$MMnX$ ( $M=Li, K$ ) <sup>*</sup>	-	tetragonal	$P4/ncc$	426.7	617.8	66
$NaCu_4X_2$ ( $X=As, Sb$ ) <sup>*</sup>	$CaCu_4P_2$	rhombohedral	$R\bar{3}m$	410.0	2389.3	67
$KCu_4X_2$ ( $X=As, Sb$ ) <sup>*</sup>	$CaCu_4P_2$	rhombohedral	$R\bar{3}m$	412.0	2595.6	67

<sup>\*</sup> The crystallographic data refer to the element listed first.

### 1.3.6 Ternary oxides and chalcogenides

Following their initial studies reviewed in the 1985 Review,[1] Hoppe et al.[69-74] have maintained their interest in oxides containing two alkali metals reporting the synthesis and characterisation of six novel compounds. Three preparative routes were employed. The two more common methods involved prolonged heat-treatment in sealed capsules of either mixtures of the constituent binary oxides ( $Na_3Li_3Mn_3O_9$ , [69]  $Rb_7NaZn_2O_6$ , [70]  $Cs_2K_2Cd_3O_5$  [71]) or mixtures containing a ternary oxide and the appropriate alkali metal oxide ( $KLi_6IrO_6$ , [72]  $Rb_2Li_{14}Tb_3O_{14}$  [73]); the third method, used to produce  $KNa_2AuO_2$ , [74] involved controlled oxidation of the intermetallic  $NaAu$  using  $Na_2O_2$  and  $K_2O_2$ . Preparative details are summarised in Table 4. All six compounds were characterised using xrd methods; pertinent structural information is collected in Table 5.

**Table 4.** Experimental details reported by Hoppe et al. for the synthesis of diverse ternary oxides.

Product	Reagents	Molar Ratio	Temp K	Anneal time/d	Vessel	Ref
$\text{Na}_3\text{Li}_5\text{Mn}_5\text{O}_9$	$\text{Na}_2\text{O}:\text{Li}_2\text{O}:\text{MnO}$	1:2:2	973	14	Ni	69
$\text{KLi}_6\text{IrO}_6$	$\text{Li}_2\text{O}:\text{K}_4\text{IrO}_4$	3:1	1023	30	Ag	72
$\text{Rb}_2\text{Li}_{14}\text{Tb}_3\text{O}_{14}$	$\text{Rb}_2\text{O}:\text{Li}_6\text{TbO}_6$	2:1	973	27	Au	73
$\text{KNa}_2\text{AuO}_2$	$\text{K}_2\text{O}_2:\text{Na}_2\text{O}_2:\text{NaAu}$	1:1:2	703	6	Ag	74
$\text{Rb}_7\text{NaZn}_2\text{O}_6$	$\text{Rb}_2\text{O}:\text{Na}_2\text{O}:\text{ZnO}$	1.2:1.2:1	1223	36	Pt	70
$\text{Cs}_2\text{K}_2\text{Cd}_3\text{O}_5$	$\text{Cs}_2\text{O}:\text{K}_2\text{O}:\text{CdO}$	1:1:1	823	17	Ag	71
$\text{Li}_6\text{CoO}_4$	$\text{Na}_2\text{O}:\text{Li}_2\text{O}:\text{CoO}$	1.3:1.3:2	853	22	Co	80
$\text{B-LiRhO}_2$	$\text{Na}_2\text{O}:\text{Li}_2\text{O}:\text{Rh}_2\text{O}_3$	1.45:2.91:1	1223	18	Pd	81
$\text{Li}_6\text{IrO}_6$	$\text{Li}_2\text{O}:\text{IrO}_2$	5:1	1098	30	Ag	75
$\text{Li}_6\text{IrO}_6$	$\text{Li}_2\text{O}:\text{Na}_2\text{IrO}_3$	5:1	1098	40	Ag	75
$\text{Li}_2\text{PdO}_2$	$\text{Na}_2\text{O}:\text{Li}_2\text{O}_2:\text{Tb}_4\text{O}_7$	1:3:1	1373	7	Pd	82
$\text{Li}_6\text{PtO}_6$	$\text{Li}_2\text{O}:\text{Na}_3\text{LiPt}_2\text{O}_6$	10:1	1098	100	Au	75
$\text{Li}_6\text{CeO}_6$	$\text{Li}_2\text{O}_2:\text{KCeO}_2$	4.5:1	923	63	Ag	75
$\text{Li}_6\text{Tb}_2\text{O}_7$	$\text{Li}_2\text{O}_2:\text{Tb}_4\text{O}_7$	6.8:1	1023	13	Au	73
$\text{Li}_6\text{Tb}_2\text{O}_7$	$\text{Rb}_2\text{Li}_{14}\text{Tb}_3\text{O}_{14}$	-	1123	25	Au	73
$\text{Na}_4\text{CrO}_4$	$\text{Na}_2\text{O}:\text{Cr}_2\text{O}_3$	4:1	1273	30	Ni	76
$\text{Na}_3\text{AuO}_2$	$\text{Na}_2\text{O}_2:\text{NaAu}$	1:1	703	6	Ag	77
$\text{NaPrO}_2$	$\text{K}_2\text{O}:\text{Na}_2\text{O}:\text{PrO}_{1.66}$	1.1:1.2:1	1273	2	Ni	78
$\text{NaTbO}_2$	$\text{Na}_2\text{TbO}_3$	-	1273	10	Ni	78
$\text{K}_4\text{ZnO}_3$	$\text{K}_2\text{O}:\text{ZnO}$	2.1:1	873	30	Pt	70
$\text{K}_4\text{ZnO}_3$	$\text{K}_2\text{O}:\text{K}_2\text{ZnO}_2$	1:1	823	14	Ag	70
$\text{Cs}_{14}\text{Cd}_9\text{O}_{16}$	$\text{Cs}_2\text{O}:\text{CdO}$	~2:1	773	20	Ag	79

Hoppe et al. [70,73,75-82] have also made a very significant contribution to the chemistry of regular ternary oxides, describing the preparation and structural characterisation of 13 materials. Although many of these oxides were synthesised from mixtures containing just one alkali metal oxide ( $\text{Li}_6\text{IrO}_6$ , [75]  $\text{Li}_6\text{Tb}_2\text{O}_7$ , [73]  $\text{Na}_4\text{CrO}_4$ , [76]  $\text{Na}_3\text{AuO}_2$ , [77]  $\text{NaTbO}_2$ , [78]  $\text{K}_4\text{ZnO}_3$ , [70]  $\text{Cs}_{14}\text{Cd}_9\text{O}_{16}$  [79]),

several were obtained from reaction systems containing two alkali metal oxides ( $\text{Li}_6\text{CoO}_4$ , [80]  $\beta\text{-LiRhO}_2$ , [81]  $\text{Li}_6\text{IrO}_6$ , [75]  $\text{Li}_2\text{PdO}_2$ , [82]  $\text{Li}_6\text{PtO}_6$ , [75]  $\text{Li}_6\text{CeO}_6$ , [75]  $\text{NaPrO}_2$  [78]). In general, similar preparative routes to those described above were used. Others, worthy of comment, involved thermal decomposition of higher ternary oxides ( $\text{NaTbO}_2$  [78]) or mixed alkali metal oxides ( $\text{Li}_6\text{Tb}_2\text{O}_7$  [73]), and oxidation of metals ( $\text{Li}_2\text{PdO}_2$  [82]), intermetallic compounds ( $\text{Na}_3\text{AuO}_2$  [77]), binary oxides ( $\text{Li}_6\text{Tb}_2\text{O}_7$  [73]) or ternary oxides ( $\text{Li}_6\text{CeO}_6$  [75]); experimental details are collected in Table 4. The oxides were structurally characterised using single crystal or powder xrd methods; pertinent data are included in Table 5.

Further structural information for ternary oxides has been published by Russian authors; [83-86] full details are given in Table 5. A novel (fourth) modification of  $\text{LiFeO}_2$  prepared from  $\alpha\text{-NaFeO}_2$  by ion exchange methods has been described; [83] the two oxides are isostructural and have rhombohedral layer structures. A non-stoichiometric cubic phase of approximate composition  $\text{K}_2\text{Fe}_{4.0}$  has been observed in a study of the kinetics of the reaction of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{K}_2\text{CO}_3$ ; [84] it is thought to be produced by interaction of  $\alpha\text{-Fe}_2\text{O}_3$  with the initially formed  $\text{KFeO}_2$ . Xrd, dta and electrical conductivity studies of the  $\text{Li}_2\text{O-RuO}_2$  system [85] have revealed the formation of  $\text{Li}_6\text{RuO}_6$ ,  $\text{Li}_2\text{RuO}_3$  and bronzes of variable composition  $\text{Li}_{2x}\text{RuO}_{2+x}$  ( $0.05 < x < 0.15$ ). All three compositions are stable to 1773K.  $\text{Li}_6\text{RuO}_6$  exists in two structural modifications depending on the method of synthesis; whereas heating the mixture of binary oxides to 1023K for 25 hours followed by 1173K for 5 hours gives  $\text{Li}_6\text{RuO}_6\text{-I}$ , heating it to 1273K for 20 to 30 hours yields  $\text{Li}_6\text{RuO}_6\text{-II}$ . Similar studies of the  $\text{K}_2\text{O-RuO}_2$  system [86] indicate the formation of  $\text{K}_4\text{RuO}_4$  and  $\text{K}_2\text{RuO}_3$ , both of which decompose in peritectic reactions at 1238 and 1323K, respectively. Russian authors [87] have also reported the  $\text{KVO}_3\text{-V}_2\text{O}_5$  phase diagram which is a complex section of the  $\text{K}_2\text{O-V}_2\text{O}_5\text{-VO}_2$  system. Four compounds are formed, all of which undergo peritectic decomposition reactions,  $\text{KV}_3\text{O}_{13-x}$  (828K),  $\text{K}_2\text{V}_6\text{O}_{21}$  (803K),  $\text{KV}_3\text{O}_9$  (773K) and  $\text{K}_3\text{V}_5\text{O}_{14}$  (691K), together with the vanadium bronze  $\text{K}_x\text{V}_2\text{O}_5$ . [87]

Spectroscopic methods have been used to probe the structural chemistry of  $\text{Li}_2\text{TiO}_3$ , [88]  $\text{Li}_2\text{ZrO}_3$  [89] and  $\text{Li}_2\text{HfO}_3$ . [89] The  $^7\text{Li}$ -n.m.r. spectra of  $\text{Li}_2\text{TiO}_3$  ( $300 < T/K < 520$ ) [88] indicate that  $\text{Li}_2\text{TiO}_3$  contains two  $\text{Li}^+$  ions with differing environments; that in the lower symmetry environment is responsible for a quadrupole



**Table 5.** Crystallographic parameters for diverse ternary oxides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	$\beta/^\circ$	Ref
$\text{Na}_3\text{Li}_5\text{Mn}_5\text{O}_9$	Trigonal	$\bar{R}3m$	335.6	-	2612.0	-	69
$\text{KLiIrO}_6$	Trigonal	$\bar{R}3m$	819.6	-	710.0	-	72
$\text{Rb}_2\text{Li}_{1.4}\text{Tb}_3\text{O}_{3.4}$	Orthorhombic	Immm	1283.1	790.9	736.9	-	73
$\text{KNa}_2\text{AuO}_2$	Orthorhombic	Pnmm	1025.6	547.2	400.0	-	74
$\text{Rb}_7\text{NaZn}_2\text{O}_6$	Triclinic	$\bar{P}1$	1128.3	974.5	711.8	-	70
			(114.1°	88.5°	106.4°)		
$\text{Cs}_2\text{K}_2\text{Cd}_3\text{O}_5$	Triclinic	$\bar{P}1$	983.2	918.0	653.5	-	71
			(108.3°	113.7°	99.9°)		
$\text{LiFeO}_2$	Hexagonal	-	295.6	-	1457	-	83
$\text{Li}_6\text{RuO}_6\text{-I}$	Tetragonal	-	537.2	-	1488	-	85
$\text{Li}_6\text{RuO}_6\text{-II}$	Tetragonal	-	617.2	-	1162	-	85
$\text{Li}_2\text{RuO}_3$	Monoclinic	-	507.8	875.5	984.5	99.9	85
$\text{Li}_6\text{CoO}_4$	Tetragonal	$\text{P}4_2/\text{nmc}$	653.6	-	465.4	-	80
$\beta\text{-LiRhO}_2$	Cubic	$\text{F}4_32$	841.3	-	-	-	81
$\text{Li}_6\text{IrO}_6$	Trigonal	$\bar{R}3$	541.5	-	1505.3	-	75
$\text{Li}_2\text{PdO}_2$	Orthorhombic	Immm	375.3	298.2	931.6	-	82
$\text{Li}_6\text{PtO}_6$	Trigonal	$\bar{R}3$	541.5	-	1501.4	-	75
$\text{Li}_6\text{CeO}_6$	Trigonal	$\bar{R}3$	564.3	-	1620.7	-	75
$\text{Li}_6\text{Tb}_2\text{O}_7$	Monoclinic	$\text{P}2_1/\text{a}$	1056.3	613.5	546.6	109.7	73
$\text{Na}_4\text{CrO}_4$	Triclinic	$\bar{P}1$	859.7	569.8	640.0	-	76
			(124.0°	98.4°	98.9°)		
$\text{Na}_3\text{AuO}_2$	Tetragonal	$\text{P}4_2/\text{mnm}$	970.5	-	457.8	-	77
$\text{NaPrO}_2$	Tetragonal	$\text{I}4_1/\text{amd}$	476.2	-	1096.1	-	78
$\text{NaTbO}_2$	Tetragonal	$\text{I}4_1/\text{amd}$	463.1	-	1037.4	-	78
$\text{K}_2\text{Fe}_4\text{O}_7$	Cubic	-	1681	-	-	-	84
$\text{K}_4\text{RuO}_4$	Tetragonal	-	1158	-	767.0	-	86
$\text{K}_2\text{RuO}_3$	Orthorhombic	-	1029	705.4	566.8	-	86
$\text{K}_4\text{ZnO}_3$	Triclinic	$\bar{P}1$	1103.3	881.3	698.2	-	70
			(109.7°	89.6°	102.4°)		
$\text{Cs}_{1.4}\text{Cd}_9\text{O}_{1.6}$	Monoclinic	$\text{C}2/\text{c}$	2087.2	674.4	2583.8	94.6	79

triplet and that in the higher symmetry environment gives rise to a dipole singlet (relative contribution 1:3). [88] A group theoretical analysis of the vibrational spectra of  $\text{Li}_2\text{ZrO}_3$  and  $\text{Li}_2\text{HfO}_3$  [89] indicates, that of the two space groups (C2/c, Cc) proposed for these oxides in a previous structural analysis, [90] the centrosymmetric C2/c space group is the more appropriate.

**Table 6.** A selection of metallocthermic reductions of lanthanide(III) halides with alkali metals. [93]

Reactants	Reactant ratio	T/K	Time/d	Products
$\text{NdCl}_3, \text{Li}$	1:1	1123	7	$\text{NdCl}_2, \text{LiCl}$
$\text{DyCl}_3, \text{Li}$	2:2	973	7	$\text{LiDy}_2\text{Cl}_5, \text{LiCl}$
$\text{SmCl}_3, \text{Na}$	1:1	1173	3	$\text{SmCl}_2, \text{NaCl}$
$\text{NdCl}_3, \text{K}$	2:2	1123	5	$\text{KNd}_2\text{Cl}_5, \text{KCl}$
$\text{TmCl}_3, \text{Cs}$	1:1	873	7	$\text{CsTmCl}_3$
$\text{YbBr}_3, \text{Rb}$	1:1	1023	7	$\text{RbYbBr}_3$
$\text{YbCl}_3, \text{Li}$	1:1	1173	3	$\text{Yb}_4\text{OCl}_6, \text{YbCl}_2, \text{LiCl}$
$\text{SmCl}_3, \text{Sm}_2\text{O}_3, \text{Li}$	10:1:12	1173	4	$\text{Sm}_4\text{OCl}_6, \text{LiCl}$
$\text{EuBr}_3, \text{Eu}_2\text{O}_3, \text{Li}$	6:1:8	1123	7	$\text{Eu}_4\text{OBr}_6, \text{LiBr}, \text{Li}_2\text{O}$
$\text{NdCl}_3, \text{Na}$	1:1	1123	7	$\text{NdOCl}$
$\text{PrBr}_3, \text{Li}$	1:1	1123	10	$\text{Pr}_2\text{Br}_3, \text{LiBr}$
$\text{GdCl}_3, \text{Li}$	1:1	973	6	$\text{LiGdCl}_4, \text{Gd}$
$\text{GdCl}_3, \text{Na}$	1:1	973	3	$\text{Na}_3\text{GdCl}_6, \text{Gd}$
$\text{ErCl}_3, \text{Na}$	1:1	973	9	$\text{Na}_3\text{ErCl}_6, \text{Er}$
$\text{GdCl}_3, \text{K}$	1:1	973	10	$\text{KGd}_2\text{Cl}_7, \text{K}_2\text{GdCl}_5, \text{Gd}$
$\text{LuCl}_3, \text{Li}$	1:1	1223	30	$\text{Li}_3\text{LuCl}_6, \text{Lu}$
$\text{CsLu}_2\text{Cl}_7, \text{Li}$	1:1	773	19	$\text{Cs}_2\text{LiLuCl}_6, \text{Lu}$
$\text{KGd}_2\text{Cl}_7, \text{Li}$	1:1	773	20	$\text{Li}_2\text{GdClH}_x^*, \text{K}_2\text{GdCl}_5$
$\text{LuCl}_3, \text{Cs}$	2:1	973	7	$\text{LuClH}_x^*, \text{Cs}_3\text{Lu}_2\text{Cl}_9, \text{Cs}_2\text{Lu}_7\text{Cl}_{18}\text{C}^*$

\* The interstitials (H or C) arise from impurities in either the reactants or the containers.

Two novel ternary chalcogenides have been reported by Klepp et

al.[91,92] Reaction of a stoichiometric mixture of  $\text{Na}_2\text{S}$ , Fe and S at 970K for 2 days in a corundum vessel gave  $\text{Na}_5\text{FeS}_4$  (orthorhombic; space group Pbca;  $a = 1194.7$ ,  $b = 709.1$ ,  $c = 2154\text{pm}$ ).[91] Similarly, reaction of  $\text{Na}_2\text{Te}_2$ , Cu and Te in a 1:6:2 molar ratio at 973K for 2 days in a corundum vessel, yielded  $\text{NaCu}_3\text{Te}_2$  (rhombohedral; space group R3m;  $a = 427.6$ ,  $c = 2378\text{pm}$ ).[92]

### 1.3.7 Ternary halides

As noted in earlier Reviews, interest in these compounds revolves around their phase relationships, structural chemistry and spectroscopic properties. Each of these topics will be considered in turn for the simple ternary halides; solvated materials are not covered.

Meyer and Schleid[93] have drawn attention to the synthetic potential of so-called "metallothermic reductions" involving the action of highly electropositive metals (alkali metals) on metal (lanthanide) halides. A systematic investigation of reactions between binary or ternary lanthanide halides  $\text{MX}_3$  ( $X = \text{Cl}, \text{Br}$ ) or  $\text{A}_x\text{M}_y\text{X}_z$  (e.g.  $\text{KGd}_2\text{Cl}_7$ ) and alkali metals (Li-Cs) in tantalum (or other refractory metal) containers under strictly dry and anaerobic conditions have produced the products listed in Table 6.

Phase relationships have been studied in the  $\text{KCl-IrCl}_3$ , [94]  $\text{RbCl-CeCl}_3$  [95] and  $\text{CsCl-FeCl}_3$  [96] systems using a variety of dta, tga, xrd and spectroscopic methods. Only one compound  $\text{K}_3\text{IrCl}_6$  was found in the  $\text{KCl-IrCl}_3$  system; [94] the previously observed  $\text{K}_4\text{Ir}_2\text{Cl}_{10}$  could not be detected.  $\text{K}_3\text{IrCl}_6$  is polymorphic, changing phase at 693K, before decomposing at temperatures above 1123K to give  $\text{K}_2\text{IrCl}_6$ . [94] Three compounds were discovered in the  $\text{RbCl-CeCl}_3$  system; [95]  $\text{RbCeCl}_6$  which melts congruently at 1019K,  $\text{Rb}_2\text{CeCl}_5$  and  $\text{RbCe}_2\text{Cl}_7$  which decompose in peritectic reactions at 881 and 889K, respectively. Dta, tga, xrd and spectroscopic data for the thermal decomposition of  $\text{CsFeCl}_4$ ,  $\text{Cs}_2\text{FeCl}_5 \cdot \text{H}_2\text{O}$  and  $\text{Cs}_3\text{FeCl}_6 \cdot \text{H}_2\text{O}$  have been used to revise the  $\text{CsCl-FeCl}_3$  phase diagram. [96] Two ternary chlorides exist:  $\text{CsFeCl}_4$  which melts congruently at 656K and  $\text{Cs}_3\text{Fe}_2\text{Cl}_9$  which decomposes in a peritectic reaction at 543K; anhydrous  $\text{Cs}_2\text{FeCl}_5$  does not exist and anhydrous  $\text{Cs}_3\text{FeCl}_6$  is metastable upto 553K. [96]

Safonov and Mireev[97] have completed a review of phase equilibria in a number of chloride systems including the  $\text{MCl-PdCl}_2$  ( $M = \text{Li-Cs}$ ) systems. Two compounds occur in the  $\text{MCl-PdCl}_2$  ( $M =$

Na-Cs) systems;  $M_2PdCl_4$  is formed for  $M = Na-Cs$  and  $MPd_3Cl_7$  is produced for  $M = Rb, Cs$ . No compounds exist in the  $LiCl-PdCl_2$  system. [97]

Table 7. Alkali metal lanthanide iodides.

Compound	Systems								
Lanthanum(III)									
M <sub>7</sub> LnI <sub>10</sub>	Na-Gd	Na-Er							
M <sub>4</sub> LnI <sub>7</sub>	Li-Sm	Rb-Sm							
M <sub>3</sub> LnI <sub>6</sub>	Li-Gd	Na-Sm	K-Pr	K-Dy	Rb-Ce	Cs-La	Cs-Gd	Cs-Tm	
	Li-Dy	Na-Gd	K-Nd	K-Ho	Rb-Gd	Cs-Pr	Cs-Dy		
	Li-Ho		K-Sm	K-Er	Rb-Dy	Cs-Nd	Cs-Ho		
			K-Gd		Rb-Ho	Cs-Sm	Cs-Er		
M <sub>7</sub> Ln <sub>3</sub> I <sub>16</sub>	Na-Nd	Na-Dy							
M <sub>2</sub> LnI <sub>5</sub>	K-La	K-Pr	K-Nd						
M <sub>3</sub> Ln <sub>2</sub> I <sub>9</sub>	Li-Sm	Rb-Ce	Cs-Pr	Cs-Sm	Cs-Ho	Cs-Tm			
		Rb-Sm	Cs-Nd	Cs-Gd	Cs-Er				
MLnI <sub>4</sub>	K-Sm	K-Ho	Rb-Ho						
MLn <sub>2</sub> I <sub>7</sub>	Rb-Ce	Rb-Dy							
MLn <sub>4</sub> I <sub>13</sub>	Cs-Nd								
MLn <sub>5</sub> I <sub>28</sub>	Cs-La	Cs-Pr							
Lanthanum(II)									
M <sub>3</sub> YbI <sub>5</sub>	Li-Yb								
MYbI <sub>3</sub>	Na-Yb	Rb-Yb	K-Yb	Cs-Yb					
MYb <sub>2</sub> I <sub>5</sub>	Li-Yb	K-Yb							

Molodkin and Dudareva have produced several original papers[98-100] and have completed a comprehensive review[101] on the alkali metal lanthanide iodides; the compounds known to be formed in the MI-LnI<sub>3</sub> and MI-YbI<sub>2</sub> systems are summarised in Table 7. Gromov et al.[95] have reported the phase diagram of the RbI-CeI<sub>3</sub> system; it contains three compounds, of which two melt congruently, Rb<sub>3</sub>CeI<sub>6</sub> (879K) and RbCe<sub>2</sub>I<sub>7</sub> (771K), and one decomposes in a peritectic reaction, Rb<sub>3</sub>Ce<sub>2</sub>I<sub>9</sub> (777K).

Twelve novel ternary halides have been synthesised and structurally characterised using X-ray[102-110] or neutron[111] diffraction methods; pertinent crystallographic data are included in Table 8. The majority of the ternary halides were produced by heat-treatment either of the appropriate binary halides (Li<sub>2</sub>Ml<sub>6</sub> (M = Zr, Hf), [102] Na<sub>3</sub>CrCl<sub>6</sub>, [103] Rb<sub>3</sub>V<sub>2</sub>Br<sub>9</sub>, [111] Cs<sub>3</sub>V<sub>2</sub>Cl<sub>9</sub> [111]) or of a ternary halide/binary halide mixture (NaMn<sub>3</sub>F<sub>10</sub> [104]). Using

**Table 8.** Crystallographic parameters for diverse ternary halides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	$\beta/^\circ$	Ref
Li <sub>2</sub> ZrI <sub>6</sub>	cubic	Im3m <sup>*</sup>	1358				102
Li <sub>2</sub> HfI <sub>6</sub>	cubic	Im3m <sup>*</sup>	1357				102
LiMnF <sub>4</sub>	monoclinic	P2 <sub>1</sub> /c	541.4	462.9	569.4	113.2	107
Na <sub>3</sub> CrCl <sub>6</sub>	trigonal	P $\bar{3}$ 1c	682.0		1203.4		103
Na <sub>2</sub> MnF <sub>3</sub>	monoclinic	P2 <sub>1</sub> /c	771.9	523.6	1086.2	109.0	109
NaMn <sub>3</sub> F <sub>10</sub>	orthorhombic	Fdd2	1318.1	1561.8	730.9		104
KCrF <sub>4</sub>	orthorhombic	Pnma	1576	743	1838		105
KCrF <sub>4</sub>	orthorhombic	Pnma	1573.2	743.2	1833.1		106
K <sub>4</sub> CdCl <sub>6</sub>	trigonal	R $\bar{3}$ c	1210.5		1490.9		110
Rb <sub>3</sub> V <sub>2</sub> Br <sub>9</sub>	hexagonal	P6 <sub>3</sub> /mmc	736.1		1853		111
Rb <sub>4</sub> CdCl <sub>6</sub>	trigonal	R $\bar{3}$ c	1243.9		1557.0		110
Cs <sub>3</sub> V <sub>2</sub> Cl <sub>9</sub>	hexagonal	P6 <sub>3</sub> /mmc	724.0		1795		111
Cs <sub>2</sub> CuF <sub>4</sub>	tetragonal	I4/mmm	440.3		1403.2		108

\* Alternative space groups are I432 and I $\bar{4}3m$ .

similar heat-treatment methods, two groups independently produced  $\text{KCrF}_4$ ; whereas Dewan et al. [105] heated a mixture of  $\text{KHF}_2$ ,  $\text{CrF}_3$  and  $\text{PbCl}_2$  to 1203K followed by slow cooling ( $6\text{K h}^{-1}$ ) to 623K. Hoppe et al. [106] annealed a mixture of  $\text{KF}$ ,  $\text{CuF}_2$  and  $\text{CrF}_3$  in a gold tube at 1023K for 60 days. Several other interesting preparative routes were employed: these included thermal decomposition either of a higher ternary halide ( $\text{LiMnF}_4$  [107]) or of a mixed alkali metal halide ( $\text{Cs}_2\text{CuF}_4$  [108]), and crystallisation from aqueous solution ( $\text{Na}_2\text{MnF}_5$ , [109]  $\text{M}_4\text{CdCl}_6$  ( $\text{M} = \text{K}, \text{Rb}$ ) [110]). The synthetic route to  $\text{Cs}_3\text{IrI}_6$ , which has been the subject of a vibrational analysis, is also worthy of note; [112] it was prepared by repeated iodination of  $\text{Cs}_3\text{IrBr}_6$  with  $\text{NaI}$  at 433K with intermediate regrinding and repressing. Vibrational spectroscopic analyses have also been completed [113] for  $\text{M}_3\text{Mo}_2\text{X}_9$  ( $\text{M} = \text{K}$ ,  $\text{X} = \text{Cl}$ ;  $\text{M} = \text{Rb}$ ,  $\text{X} = \text{Cl}$ ;  $\text{M} = \text{Cs}$ ,  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ). The temperature dependences of  $^{81}\text{Br}$  n.q.r. frequencies and quadrupolar relaxation times of  $\text{Cs}_2\text{ZnBr}_4$  have been measured. [114] Single crystal luminescence and absorption spectra as well as luminescence decay times of  $\text{CsMg}_{1-x}\text{Ni}_x\text{X}_3$  ( $\text{X} = \text{Cl}, \text{Br}$ ) have been determined ( $10 \leq T/\text{K} \leq 273$ ); [115] the presence of excitation energy transfer was established in  $\text{CsNiCl}_3$  and  $\text{CsNiBr}_3$ .

Five mixed alkali metal halides with cubic ( $\text{Fm}\bar{3}\text{m}$ ) structures have been reported. Cubic  $\text{Rb}_2\text{LiFeF}_6$  ( $a = 824.4\text{pm}$ ) [112] and  $\text{Cs}_2\text{NaFeF}_6$  ( $a = 873.9\text{pm}$ ) [116] are metastable high pressure phases obtained by heating the normal pressure variants, previously prepared from the binary fluorides, to 523K at  $30 \times 10^8 \text{ Nm}^{-2}$  for 2h. in a platinum vessel. Cubic  $\text{Cs}_2\text{LiLuCl}_6$  ( $a = 1040.9\text{pm}$ ) [117] and  $\text{Cs}_2\text{KScCl}_6$  ( $a = 1087.3\text{pm}$ ) [117] were prepared by reaction of  $\text{CsLu}_2\text{Cl}_7$  with lithium and of  $\text{Cs}_3\text{Sc}_2\text{Cl}_9$  with potassium in arc welded tantalum vessels at 773K; the former product is metastable at room temperature. Single crystals of cubic  $\text{Cs}_2\text{KCuF}_6$  ( $a = 889.4\text{pm}$ ) [118] were obtained by annealing powders, manufactured by heating a  $\text{CsCl}:\text{KCl}:\text{CuO}$  mixture (2:1:1 molar ratio) in a fluorine atmosphere at 653K for 12 days, followed by annealing under argon at 713K for 100 days in copper vessels.

Halogen ordering in  $\text{Cs}_3\text{Cr}_2\text{Br}_3\text{Cl}_6$  has been investigated using single crystal xrd and spectroscopic (optical, vibrational) methods. [119,120] Its structure is based on closest packing of  $\text{Cs}(\text{Cl}, \text{Br})_3$  layers with chromium atoms ordered in octahedral sites to form isolated pairs of face-shared octahedra (i.e. binuclear  $\text{Cr}_2\text{Cl}_6\text{Br}_3^{3-}$  units) of which bromine selectively occupies the

terminal halogen positions at one end only.

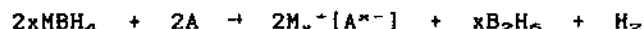
Very small quantities of  $K_2Cr_3Cl_2F_6$  (monoclinic, space group  $P2_1/c$ ,  $a = 672.6$ ,  $b = 1115.7$ ,  $c = 739.1$  pm,  $\beta = 125.3^\circ$ ) were obtained, together with the principal products,  $KCrF_4$  and  $K_2CrF_5$ , on heating  $KHF_2$ ,  $CrF_3$ ,  $PbCl_2$  mixtures to 1203K. [105]

The Curie temperatures of  $Rb_2CrCl_3Br$  (55.0K) and  $Rb_2CrCl_2Br_2$  (57.0K) are comparable to that of  $Rb_2CrCl_4$  (52.4K); [121] the optical spectra of both compounds are dominated by two magnon annihilation side bands which almost vanish at low temperature.

### 1.3.8 Intercalates

Owing to their importance in high-density energy storage devices, a rapid increase in the number of papers devoted to the chemistry of alkali metal intercalates can be perceived; hence the need for a separate subsection to cover this topic.

A convenient straightforward method for intercalating alkali metal cations into layered solid matrices using  $MBH_4$  ( $M = Li-K$ ) reagents has been published; [122] the  $BH_4^-$  anion acts as the reducing agent and cation intercalation occurs with concomitant formation of  $B_2H_6$  and  $H_2$ :



In the majority of cases, the reaction proceeds clearly without undesirable byproducts; a list of intercalates, and the conditions under which they were obtained, is given in Table 9.

Theoretical [123] and experimental [124,125] studies of molybdenum [123] and tungsten [124,125] bronzes have been completed. The band electronic structure of  $Mo_{0.30}MoO_3$  ( $M = K, Rb$ ) has been examined by performing tight-binding band calculations on a number of model chains and slabs; [123] when normalised to  $M_3Mo_{10}O_{30}$  (i.e. half unit cell) the derived band structure readily rationalises the fact that the material is a pseudo-one dimensional conductor. The structure of  $K_{0.26}WO_3$  has been shown to be hexagonal, space group  $P6_3$  with unit cell parameters  $a = 738.9$ ,  $c = 750.8$  pm from time-of-flight single crystal neutron X-ray diffraction data. The mixed alkali metal tungsten bronzes,  $M_xK_yWO_3$  ( $M = Li, Na$ ) have been prepared [125] from binary oxide mixtures in closed vessels ( $773 < T/K < 1123$ ) and characterised by xrd and sem methods. Products containing significant amounts of lithium or sodium could

not be prepared. A hexagonal phase forms with lithium for  $x > 0.19$  and  $(x+y) < 0.33$ ; the corresponding sodium derivative could not be prepared. A tetragonal phase was obtained with both lithium and sodium for  $x > 0.45$  and  $(x+y) < 0.60$ . [125]

Four distinct rhombohedral phases ( $\text{Li}_x\text{Mo}_6\text{X}_8$ ;  $\text{X} = \text{S, Se}$ ;  $x = 1, 3, 3.8$  and  $4$ ) have been identified [126] as a result of the electrochemical intercalation of lithium into the  $\text{Mo}_6\text{X}_8$  ( $\text{X} = \text{S, Se}$ )

**Table 9.** Intercalated products synthesised using  $\text{NBH}_4$  ( $\text{M} = \text{Li-K}$ ) reagents. [122]

Compound $\text{M}_x[\text{A}^{n-}]$	Solvent	$[\text{A}]:[\text{BH}_4^-]$ ratio	Time	T/K	Color
$\text{Li}_{0.76}\text{MoO}_3$	ether	1:0.80	12h	298	dark blue
$\text{Na}_{0.55}\text{MoO}_3$	i-PrOH	1:1	5h	338	blue
$\text{Na}_{0.82}(\text{H}_2\text{O})_{1.23}\text{MoO}_3$	wet EtOH	1:11	6h	333	blue
$\text{K}_{0.41}\text{MoO}_3$	i-PrOH	1:1	12h	338	blue
$\text{Li}_{0.88}\text{V}_2\text{O}_5$	ether	1:1	4h	298	dark green
$\text{Li}_{0.47}\text{V}_2\text{O}_5$	ether	1:1	3h	298	dark green
$\text{Li}(\text{H}_2\text{O})_3\text{FeOCl}$	wet ether	1:13	2h	298	black
$\text{Na}_{0.6}(\text{MeOH})_{0.3}\text{FeOCl}$	MeOH	1:1	2h	298	black
$\text{K}_{0.26}\text{FeOCl}$	MeOH	1:0.9	2h	298	black
$\text{Li}_{0.08}\text{TaS}_2$	pyridine	1:1.9	6h	338	metallic gray
$\text{Li}_{0.21}\text{TaS}_2$	pyridine	1:5	10h	338	metallic gray
$\text{Li}_{0.17}(\text{H}_2\text{O})_{0.4}\text{TaS}_2$	wet MeOH	1:3.5	12h	298	metallic gray
$\text{Na}_{0.40}\text{TaS}_2$	pyridine	1:1.4	22h	338	metallic gray
$\text{Na}_{0.4}(\text{H}_2\text{O})_4\text{TaS}_2$	wet pyridine	1:1.4	22h	338	metallic gray
$\text{Li}_x\text{TiS}_2$	EtOH	1:1	22h	338	metallic gray

host lattices by cathodic reduction in the galvanic cell:

$\text{Li}/\text{LiClO}_4, \text{propylene carbonate}/\text{Mo}_6\text{X}_8$  ( $\text{X} = \text{S, Se}$ ).



The results are closely similar for the two systems.  $^7\text{Li}$ -n.m.r. data indicate that partial charge transfer occurs in  $\text{Li}_x\text{Mo}_6\text{S}_8$  with formation of triangular  $(\text{Li}_3)^{2+}$  clusters suggesting the formulation,  $\text{Li}_3^{2+}[\text{Mo}_6\text{S}_8]^{2-}$ ; [126] the  $\text{Li}^+$  ions appear to be "normal" in the other intercalates. A similar rhombohedral phase,  $\text{Li}_{3.5}\text{Mo}_6\text{Te}_8$ , has been produced by reaction of  $\text{Mo}_6\text{Te}_8$  with n-butyllithium in evacuated Schlenk tubes at 298K for 5 days. [127] Crystallographic parameters for the  $\text{Li}_x\text{Mo}_6\text{X}_8$  intercalates [126,127] are collected in Table 10.

**Table 10.** Rhombohedral lattice parameters of lithium intercalates,  $\text{Li}_x\text{Mo}_6\text{X}_8$  (X = S, Se, Te).

x	1	3	3.8	4	1	3	4	3.5
X	S	S	S	S	Se	Se	Se	Te
a/pm	646.7	663.8	659.6	664.7	672.4	691.5	692.3	706.2
$\alpha/^\circ$	92.55	94.29	94.23	94.52	92.23	94.43	94.40	92.52

The intercalates  $\text{A}_x\text{MXH}_x$  and their host lattices  $\text{MXH}_x$  (A = Li-K; M = Sc, Y, Gd; X = Cl, Br; x = 0.6-0.7) have been synthesised [128] by stoichiometric reaction of  $\text{MX}_3$ ,  $\text{MH}_2$  (or  $\text{H}_2$ ), M and AX in sealed tantalum or niobium vessels at 1023-1173K. Although the intercalates adopt the ZrBr-type heavy atom structure, the host lattices have either the ZrCl- or ZrBr-type heavy atom structures.

Lithium insertion into  $\text{AM}_2\text{P}_3\text{O}_{12}$  (A = Li, Na; M = Ti, Zr) and  $\text{NbTiP}_3\text{O}_{12}$  could only be achieved for those phases containing chemically reducible species; [129] singly and doubly lithiated phases were prepared from  $\text{ATi}_2\text{P}_3\text{O}_{12}$  (A = Li, Na) and  $\text{NbTiP}_3\text{O}_{12}$  but  $\text{AZr}_2\text{P}_3\text{O}_{12}$  (A = Li, Na) were unreactive (Ti(IV) and Nb(V) can be reduced but Zr(IV) is inert).

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

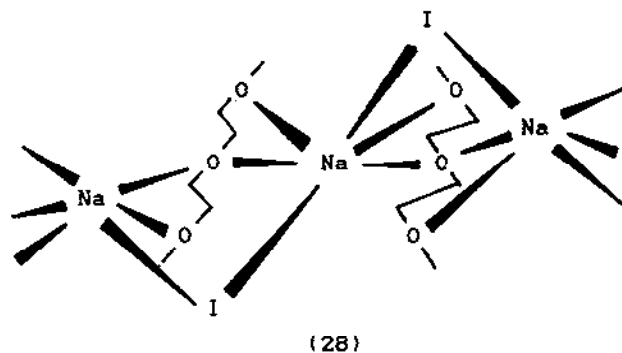
To provide a logical format for the presentation of the data abstracted for this section, the majority are reviewed in sub-divisions devoted to specialised subjects of current interest and importance; the remainder, which cannot be thus categorised, are considered in sub-divisions associated with the individual alkali metals. Since there has been but little change in

priorities during the past eighteen months, the sequence of subsections is identical to that adopted for the 1985 review.[1]

#### 1.4.1 Complexes of Acyclic Lipophilic Ionophores

The Raman spectra of liquid complexes of polyethyleneglycols with alkali metal salts are characterised by an intense polarised band near  $860\text{cm}^{-1}$ . [130] This band, which can be used as a useful monitor of complex formation, indicates a nearly symmetric ordering of the polyethylene chain around the alkali metal cation.

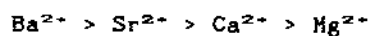
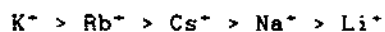
The molecular structure of the 1:1 adduct of NaI with diglyme consists of polymeric chains of NaI.diglyme units built up in a zig-zag arrangement (28). [131] The sodium atoms, which are



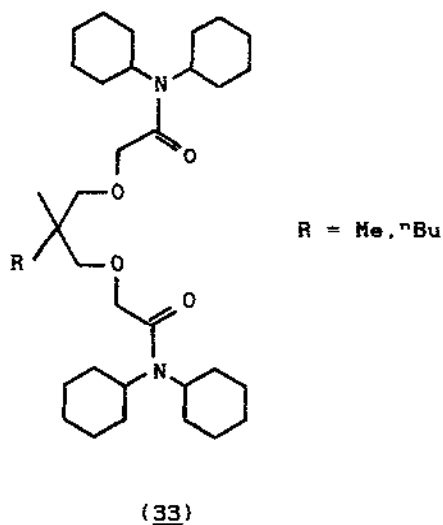
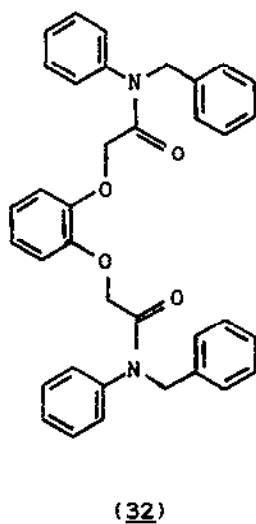
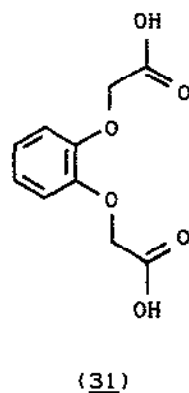
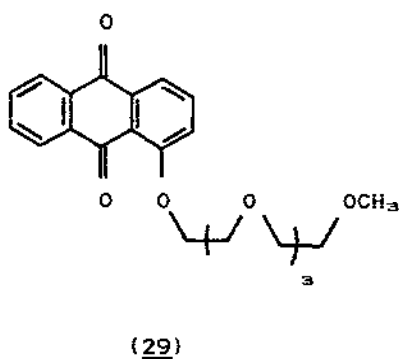
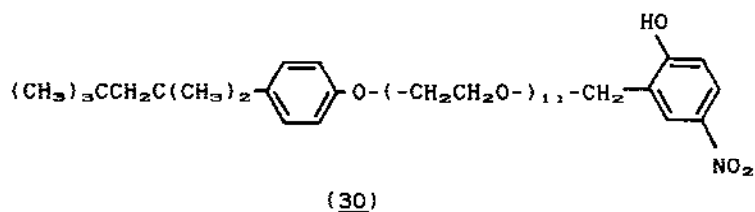
located on 2-fold axes are bridged by both the iodine ( $\text{Na}\dots\text{I} = 316.4\text{pm}$ ) and two of the oxygens of the diglyme molecules ( $\text{Na}\dots\text{O} = 242.7, 271.4\text{pm}$ ) in a distorted octahedral arrangement. The retention of the  $\text{Na}\dots\text{I}$  bonds is surprising since complexation with chelating ligands such as diglyme normally results in "solvent separated" ion pair formation. [131]

Enhanced binding and transport of alkali metal cations through an organic model membrane ( $0.1\text{M } n\text{-Bu}_4\text{NClO}_4$  in  $\text{CH}_2\text{Cl}_2$ ) via a novel electrochemical switching mechanism has been demonstrated. [132] Whereas the neutral anthraquinone podand (29) has very limited ability to transport  $\text{Li}^+$  across the membrane, the corresponding radical anion  $(29)^{\cdot-}$ , obtained by electrochemical reduction, exhibits much higher  $\text{Li}^+$  transport rates. [132]

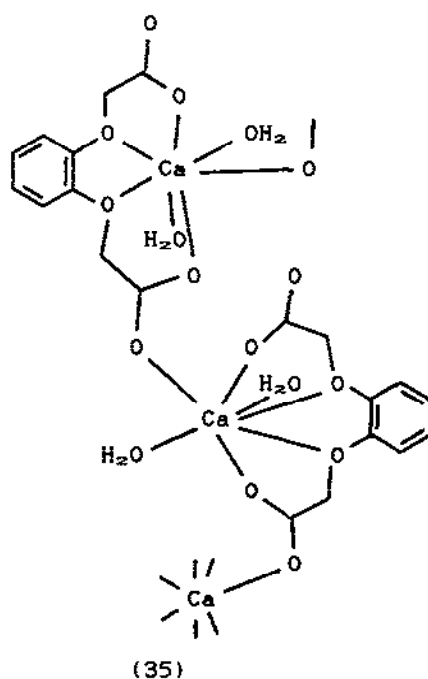
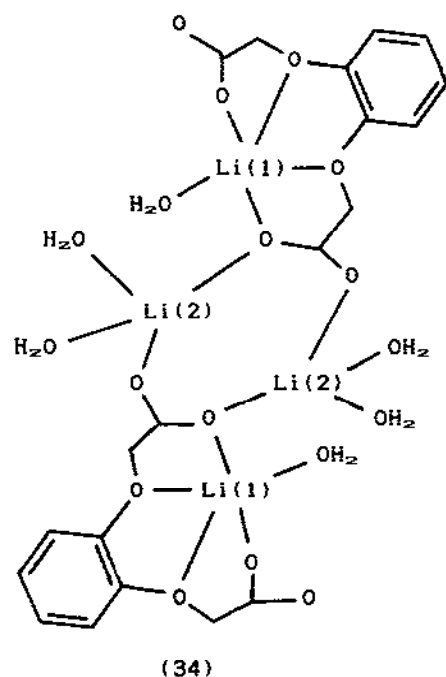
The extraction of  $\text{M}^+$  ( $\text{M} = \text{Li}-\text{Cs}$ ) and  $\text{M}^{2+}$  ( $\text{M} = \text{Mg}-\text{Ba}$ ) as halides from water into dichloroethane using (30) has been studied spectrophotometrically; [133] the observed extraction sequences are



Structural data have been published for the lithium[134] and



calcium[135] salts of benzene-1,2-dioxydiacetic acid (31). The lithium salt,  $[(31)_2Li_4] \cdot 6H_2O$  (34), [134] which is a centrosymmetric dimer, contains two independent Li atoms; whereas Li(1) is located in a square pyramidal coordination geometry comprising four equatorial oxygens of a chelating ligand ( $Li...O = 205.4pm$ ) and an axial water molecule ( $Li...O = 196.7pm$ ), Li(2) is tetrahedrally coordinated by two oxygens from separate ligands ( $Li...O = 193.1, 198.4pm$ ) and two water molecules ( $Li...O = 194.5, 197.7pm$ ). [134] The calcium salt,  $[(31)_2Ca_2] \cdot 4H_2O$  (35), [135] which is polymeric, is isomorphous and isostructural with the manganese salt. The Ca atom is positioned in a pentagonal bipyramidal coordination sphere provided by four equatorial oxygens of a chelating ligand ( $Ca...O = 230.8-252.1pm$ ), a fifth equatorial oxygen from a second ligand ( $Ca...O = 245.1pm$ ) and two axial water molecules ( $Ca...O = 233.4, 239.8pm$ ).



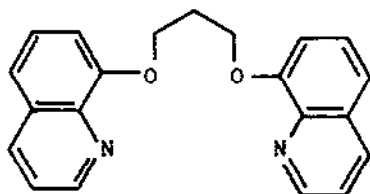
A series of ionophores, based on (32) have been prepared by substitution of the aromatic ring carrying the ether oxygens. [136] None of the substituents, despite their widely varying electronegativities ( $-CH_3$ ,  $-OCH_3$ ,  $-CHO$ ,  $-CN$ ,  $-NO_2$ ,  $-Br$ ) have a

discernible effect on the selectivity of the ionophores for  $M^+$  ( $M = \text{Li}-\text{Cs}$ ) and  $M^{2+}$  ( $M = \text{Mg}-\text{Ba}$ ) which vary in the sequences:

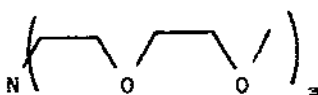


The ionophores (33) exhibit remarkable selectivity for  $\text{Li}^+$  in the presence of  $\text{Na}^+$  in highly lipophilic liquid membranes.[137] The crystal structure of  $[(33)\text{Li}]^+\text{NCS}^-$  (methyl version) shows the Li atom to be coordinated by the four oxygens of a chelating ligand ( $\text{Li}\dots\text{O} = 195.0, 197.9, 208.5, 222.9\text{pm}$ ) and the nitrogen of the anion ( $\text{Li}\dots\text{N} = 203.2\text{pm}$ ) in a square pyramidal arrangement; the Li atom lies 76pm above the plane of the four oxygens of the ionophore.[137]

The flexibility of this type of ionophore obviously favours coordination of the small Li atom. As well as  $[(31)_2\text{Li}_4]\cdot 6\text{H}_2\text{O}$  and  $[(33)\text{Li}]^+\text{NCS}^-$ ,  $[(36)\text{Li}]^+\text{ClO}_4^-$  has been structurally analysed.[138] Again a five-coordinate Li atom occurs, its square pyramidal geometry comprising the four heteroatoms of the ionophore ( $\text{Li}\dots\text{O} = 217$ ;  $\text{Li}\dots\text{N} = 121\text{pm}$ ) and an oxygen of the anion ( $\text{Li}\dots\text{O} = 200\text{pm}$ ).



(36)



(37)

Complexation of  $M^+$  ( $M = \text{Li}-\text{Cs}$ ) by (37) has been examined by fast atom bombardment mass spectroscopy.[139] It binds  $\text{Li}^+$  most strongly followed by  $\text{K}^+$  and  $\text{Na}^+$ ; it binds  $\text{Rb}^+$  and  $\text{Cs}^+$  but weakly. Competitive complexation experiments, between (37) and a series of crown ethers (12C4, 15C5, 18C6), for these cations, indicate that (37), is capable of complexing cations of a much wider range of sizes than the crown ethers;[139] the versatility of (37) can be attributed to its flexibility.

#### 1.4.2 Crown Complexes

As in previous years, many publications which describe aspects of the chemistry of alkali and alkaline earth metal complexes of crown ethers and related macrocyclic ionophores have been abstracted for this review. Consequently the topic has been split into four subsections in which complexes of (i) 'classical' crown ethers and their substituted derivatives, (ii) lariat ethers, (iii) novel macrocyclic ligands of unusual design, and (iv) natural product ionophores are discussed.

Cram[140] has written an extensive review of the complexation of cations by designed synthetic organic molecules in which he particularly emphasises the role of molecular preorganisation in the complexation process. Structure-bonding relationships involving the alkali metal cations are covered in detail.[140]

The synthesis of a variety of complexes containing Na<sup>+</sup> and K<sup>+</sup> and 18C6, DB18C6 or DCH18C6 from ethereal solvents has been described.[141] Although in the absence of the macrocycles both sodium and potassium salts (phenoxides, thiocyanates, oximates) are aggregated in solution, there is but little tendency for the sodium complexes and virtually no tendency for the potassium complexes isolated from the solutions containing the macrocycles to have host:guest ratios greater than 1:1. Host:guest ratios of 1:2 are observed for 18C6 and DCH18C6 with NaNCS, for DB18C6 and DCH18C6 with NaOPh and for DCH18C6 with KOPh; a host:guest ratio of 1:3 is observed for 18C6 with NaOPh. All other isolated complexes have host:guest ratios of 1:1; for DB18C6 with NaNCS a 1:1:1 complex involving incorporation of a solvent molecule (dme, thf, 1:3-dioxolane) is obtained.[141]

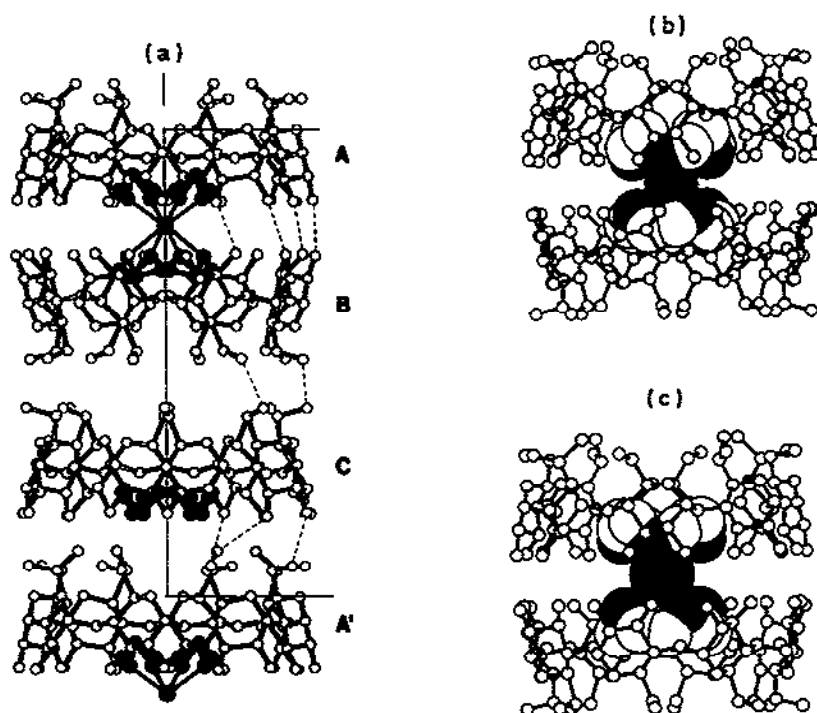
Structural analysis of the complexation of alkali and alkaline earth metals by crown ethers has been effected using both vibrational spectroscopic[142-144] and single crystal xrd methods.[144-148] The conformational changes which occur in 12C4[142] and 18C6[143] on complexation with M<sup>+</sup> (M = Li-K) have been studied by Russian authors using i.r. and Raman spectroscopy. When free, both ligands adopt conformations with C<sub>2</sub> symmetry; when complexed, 12C4 forms conformations with C<sub>4</sub> or D<sub>4</sub> symmetry and 18C6 adopts forms conformations with D<sub>3d</sub>, C<sub>3v</sub> or C<sub>1</sub> symmetry. Fourier transform infrared spectroscopic studies[144] of the solution (CHCl<sub>3</sub>) and solid state structure of the KNO<sub>3</sub> complex of

the 2,6-dimethyl derivative of 18C6 indicate that the structure is similar in the two phases. A single crystal xrd analysis[144] of the solid state structure shows it to contain two crystallographically distinct complexes. The K atoms in the two complexes, which are structurally very similar, are located above (K(1), 66; K(2) 64pm) and coordinated to the coplanar heteratoms (K(1)...O = 276.6-286.8; K(2)...O = 276.0-309.8pm) of the ligand which has  $D_{3d}$  symmetry (ignoring the methyl substituents); the 8-fold coordination spheres of the K atoms are completed by two oxygens of a bidentate nitrate anion (K(1)...O = 278.6, 279.8; K(2)...O = 272.8, 285.5pm).[144]

The isomorphous crystal structures of the macrocyclic inclusion complexes,  $\gamma$ -cyclodextrin.12C4.LiSCN.H<sub>2</sub>O (3:3:1:23) and  $\gamma$ -cyclodextrin.12C4.KCl.H<sub>2</sub>O (3:3:1:27) have been determined by xrd analyses.[145] Three  $\gamma$ -cyclodextrin molecules each of which includes a 12C4 molecule with similar orientation, are stacked along the 4-fold rotation axis forming a channel type structure (Fig. 3(a)). All three 12C4 molecules have the same  $C_4$  ring conformation; two of them form a 2:1 sandwich structure complex with the cation, [(12C4)<sub>2</sub>M]<sup>+</sup> (M = Li, K) (Fig. 3(b,c)) which is included in the hydrophobic channel formed by the two  $\gamma$ -cyclodextrin molecules, while the third is free of cation.[145]

Single crystal xrd structural analysis[146] of [18C6Sr]<sup>2+</sup>[(BuO)<sub>2</sub>PO<sub>2</sub>]<sub>2</sub><sup>-</sup>.H<sub>2</sub>O has revealed the presence of two crystallographically independent, but structurally similar, molecules. The Sr atoms are coordinated by the six oxygens of the crown ether (Sr(1)...O = 267-281; Sr(2)...O = 273-281pm), by two oxygens of monodentate dibutylphosphato anions (Sr(1)...O = 241, 247; Sr(2)...O = 243, 250pm) one on each side of the crown ether ring, and a water molecule (Sr(1)...O = 262; Sr(2)...O = 261pm). The heteroatoms of the 18C6 ring adopt a pseudo-boat conformation with the Sr atoms ~60pm from the base and with opposite ends tilted towards the Sr atom.[146] The structure [18C6Li]<sup>+</sup>[18C6Li(thf)]<sup>+</sup>[FePc]<sup>2-</sup> (Pc = phthalocyanine) has been reported in a letter;[147] no details of the structure of the cations are provided.

The crystal structure of [DB18C6K]<sup>+</sup>NCS<sup>-</sup> contains two crystallographically independent yet structurally similar molecular units.[148] In both molecules the K atoms lie above (K(1), 18; K(2), 7pm) and are coordinated to the six coplanar



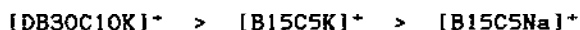
**Figure 3.** The channel-type structure (a) of  $\gamma$ -cyclodextrin.-12C4.LiSCN (3:3:1) inclusion complex ( $\text{Li}^+$  and 12C4 molecules are shown by full circles;  $\text{SCN}^-$  anions are omitted for clarity, and the structures of  $\gamma$ -cyclodextrin.12C4. $\text{Li}^+$  (b) and  $\gamma$ -cyclodextrin.-12C4. $\text{K}^+$  (c) (2:2:1) complexes ( $\text{M}^+$  and 12C4 molecules are plotted in the space filling mode, indicated by full and hatched circles, respectively)(reproduced by permission from J. Am. Chem. Soc., 109(1987) 2409).

oxygen of the ether ring ( $\text{K}(1) \dots \text{O} = 262\text{--}283$ ;  $\text{K}(2) \dots \text{O} = 266\text{--}283\text{pm}$ ). The hexagonal pyramidal coordination geometries of the K atoms are completed by the nitrogens of the anion ( $\text{K}(1) \dots \text{N} = 280$ ;  $\text{K}(2) \dots \text{N} = 269\text{pm}$ ). [148] The thermal stabilities of  $[\text{DB18C6K}]^+\text{X}^-$  ( $\text{X} = \text{NCS}, \text{Br}, \text{I}, \text{NO}_3$ ) and of some of their adducts with  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{CHCl}_3$  have been determined by dsc methods. Whereas  $[\text{DB18C6K}]^+\text{NCS}^-$  melts congruently,  $[\text{DB18C6K}]^+\text{X}^-$  ( $\text{X} = \text{I}, \text{NO}_3$ ) when melting undergo partial dissociation into their components. Of



the adducts,  $[\text{DB18C6K}]^+ \text{I}^- \cdot \text{C}_2\text{H}_5\text{OH}$  loses the ethanol without dissociation, but  $[\text{DB18C6K}]^+ \text{Br}^- \cdot 3\text{CHCl}_3$  dissociates into its components on heating.[148]

U.v.-visible[149;150] and n.m.r.[151-154] spectroscopic techniques have been used to determine thermodynamic parameters for the complexation of  $\text{M}^+$  and  $\text{M}^{2+}$  cations by crown ethers. From u.v.-visible spectral data, Gholivand et al. have shown that the stability sequence of the 1:1 complexes of  $\text{M}^+$  ( $\text{M} = \text{Na}, \text{K}$ ) with B15C5 or DB30C10 in  $\text{CH}_3\text{CN}-\text{H}_2\text{O}$  mixtures:[149]



does not differ with solvent concentration, and that the stability sequence of the 1:1 complexes of  $\text{M}^{2+}$  ( $\text{M} = \text{Ca}-\text{Ba}$ ) with DB30C10 in  $\text{CH}_3\text{OH}$ , dmf and dmsO:[150]



is independent of solvent.

$^{39}\text{K}$ -n.m.r. data have been used to calculate the formation constant of the 2:1 complex of  $\text{K}^+$  with B30C10 in nitrobenzene:[151] similar studies have shown that the 2:1 complex of  $\text{K}^+$  with DB30C10 coexists with the 1:1 complex in nitromethane.

Popov et al. have applied  $^{133}\text{Cs}$  n.m.r. spectroscopic methods to investigate the complexation of  $\text{Cs}^+$  by DB21C7,[152] DB24C8[152,153] and DB27C9[153] in binary solvent systems. Monotonic changes in formation constants were observed for all the solvent systems studied (dmsO with acetone, acetonitrile, propylene carbonate, pyridine or hmpa[152] and dmf with acetonitrile[153]) with the exception of the pyridine-methanol system[152] for which the observed variation is attributed to a change in the structure of the solvent with composition. Popov et al.[154] have also reported the simultaneous determination of the formation constants of  $\text{M}^+$  ( $\text{M} = \text{Li}-\text{Cs}$ ) and  $\text{Ba}^{2+}$  with 18C6, 1,10-diaza-18C6 and C222 in acetone, acetonitrile and propylene carbonate solutions containing two cations and a single anion using competitive n.m.r. methods. The results are discussed with respect to the size and charge of cation, the solvating ability of solvent and the nature of the ligand binding groups.[154]

Several authors[155-161] have considered diverse aspects of the

extraction of alkali and alkaline earth metal cations from aqueous solution into organic solvents containing crown ethers. A theoretical method has been described[155] for the estimation of two phase extraction constants from stability constants for complexation of  $M^+$  ( $M = \text{Li-Cs}$ ) by crown ethers and cryptands. The method gives satisfactory agreement with a variety of published extraction constants and can be used predictively. Extraction constants have been experimentally determined for  $M^{2+}$  ( $M = \text{Ca-Ba}$ ) in  $\text{H}_2\text{O-CH}_2\text{Cl}_2$  systems in the presence of diverse crown ether (15C5, B15C5, 18C6, DCH24C8, DB30C10) and cryptand (C221, C222) complexing agents,[156] for  $M^+$  ( $M = \text{Na-Cs}$ ) in  $\text{H}_2\text{O-CHCl}_3$  systems in the presence of 18C6[157] and for  $M^+$  ( $M = \text{Li-Cs}$ ) and  $M^{2+}$  ( $M = \text{Ca-Ba}$ ) in  $\text{H}_2\text{O-CHCl}_3$  systems containing various ring expanded crown ethers (DB16C5, DB-6-hydroxy-16C5 (38) and DB-6-hydroxy-19C6 (39)).[158] In the latter study,[158] the introduction of the hydroxyl group into the DB16C5 and DB19C6 polyether rings at the 6 position results in a sharp increase in the selectivity of the extraction. Both (38) and (39), unlike DB16C5 (and 18C6) selectively extract  $\text{K}^+$  in the presence of  $\text{Na}^+$ ; separation of  $\text{Li}^+$  from  $\text{Na}^+$  (using (38) or (39)), of  $\text{K}^+$  from  $\text{Rb}^+$  (using (38)) and of  $\text{Sr}^{2+}$  from  $\text{Ca}^{2+}$  and  $\text{Ba}^{2+}$  (using (39)) can also be effected.[158]

The mechanism of  $M^+$  ( $M = \text{Li-Cs}$ ) transport through a liquid membrane (1,1,2,2-tetrachloroethane) containing DB18C6 as carrier has been elucidated[159] from salt flux distribution coefficient and membrane potential measurements. The selectivity of the cation transport is controlled mainly by the size of the crown ring:[159] the salt flux, however, is determined by the hydrophobicity of the cation (the flux of weakly hydrated cations was high) and by the degree of hydration of the anions (the flux correlated well with the lyotropic number of the anions).

The relationship between the extractability of  $\text{K}^+$  (as picrate) from water into  $\text{CHCl}_3$  containing 18C6, DCH18C6 or DB18C6, and its rate of transfer across a  $\text{H}_2\text{O/CHCl}_3$  interface in the presence of these macrocyclic ligands has been assessed[160] from experimentally determined liquid-liquid extraction constants and from measured rates of ion uptake, ion release and ion transport. It was concluded that the macrocyclic ligands which are more preferable as mobile carriers in liquid membrane systems are those which are less hydrophobic and which form a more stable complex

with the cation.[160]

AC polarographic studies[161] of the kinetics of the transfer of  $\text{Na}^+$  across a  $\text{H}_2\text{O}/\text{C}_6\text{H}_5\text{NO}_2$  interface in the presence of DB18C6 have suggested that of the three possible sites for ionophore-ion complex formation (in the aqueous phase, in the organic phase, at the interface) the most probable is the interface between the two phases.

The extraction of the alkali and alkaline earth metal cations from aqueous solution onto 3-D matrices containing pendant crown ethers is receiving increasing attention.[162-164]

Chromatographic separation of  $\text{M}^+$  ( $\text{M} = \text{Li}-\text{Cs}$ ) and  $\text{M}^{2+}$  ( $\text{M} = \text{Mg}-\text{Ba}$ ) has been achieved on crown ether (B15C5, B18C6, B21C7) modified silica gels and resins using water as the mobile phase.[162] The two sets of matrices showed similar retention sequences:

B15C5       $\text{Li}^+ < \text{Na}^+ \sim \text{Cs}^+ < \text{Rb}^+ < \text{K}^+$

B18C6       $\text{Li}^+ < \text{Na}^+ < \text{Rb}^+ < \text{Cs}^+ < \text{K}^+$  ;     $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+}$

B21C7       $\text{Li}^+ \sim \text{Na}^+ < \text{K}^+ < \text{Rb}^+ \sim \text{Cs}^+$

but the resin based columns were inferior in their separation ability to the silica based ones.[162] Using DB18C6 modified resins, the extraction of  $\text{M}^+$  ( $\text{M} = \text{Na}-\text{Cs}$ ) from aqueous solution has been shown to be extremely sensitive to the anion:[163] for example, the extraction constants for  $\text{K}^+$  are increased by factors of  $\sim 1.5 \times 10^4$ ,  $8.9 \times 10^3$ ,  $2.1 \times 10^3$  and  $1.5 \times 10^3$  when chloride, bromide, iodide and thiocyanate are replaced by picrate.

Alkali metal cation ( $\text{Li}-\text{Cs}$ ) binding at the air-water interface has been studied using poly(4'-vinyl B18C6) spread on the surface of both pure water and aqueous solutions of the alkali metal salts.[164] At the interface the polymer is in highly extended conformation and cooperative binding between adjacent pendant groups is precluded. Hence, the affinity of the polymer for  $\text{M}^+$  at the interface mirrors that of B18C6 in solution.[164]

The distribution of  $\text{M}^+$  ( $\text{M} = \text{Li}-\text{Cs}$ ) as picrates between water and polyester-based polyurethane foam in the presence of DCH18C6 can be considered as an ion pair extraction of  $[\text{DCH18C6M}]^+\text{X}^-$  by an organic solvent:[165] as for more conventional systems, the sequence of extraction constants is governed by the ratio of

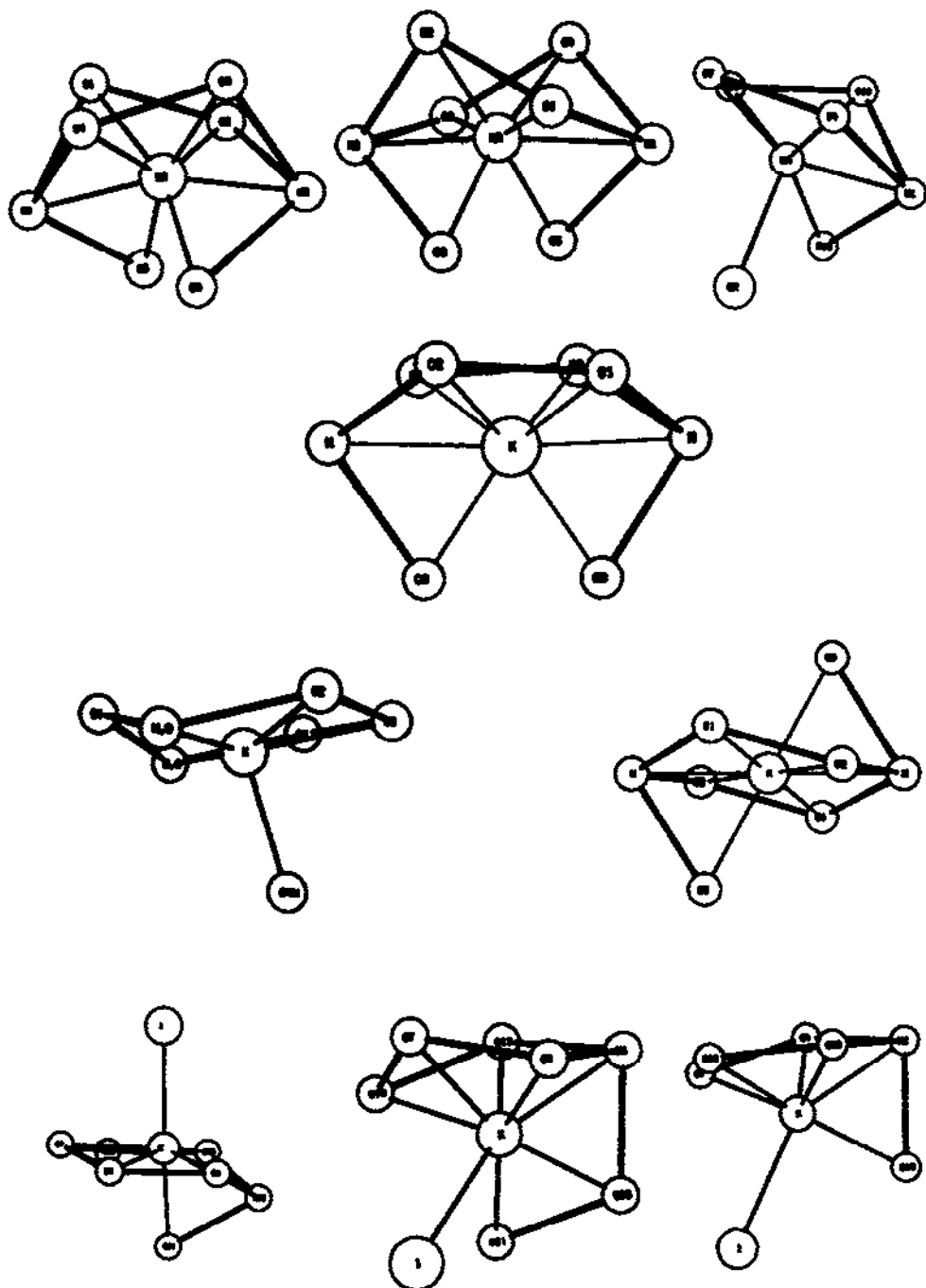
cation to crown ether size.

#### 1.4.3 Complexes of Lariat Ethers

Gokel et al.[166-167] have presented single crystal xrd structural data for an extensive range of mono- and bi-bracchial lariat ether complexes of sodium and potassium cations. The structurally characterised complexes are listed in Scheme 4 which also gives skeletal or framework drawings illustrating donor atoms, connectivities and complexed metal cations. Comparisons made between these structures and complexes of coronands and cryptands show that neither "hole size" nor "cavity size" concepts provide satisfactory explanations for the data. Instead, experimentally determined metal ion-to-donor distances coincide with the effective ionic radius defined by Shannon for various ions of differing coordination numbers. For these flexible ligands, the guest cation organises the host's donor group array (Scheme 4).[166] Solution thermodynamic data, obtained using ion selective electrode techniques, have been determined[167] for the  $\text{Na}^+$  and  $\text{K}^+$  complexes of N,N'-n-propyl-, N,N'-2-hydroxyethyl-, and N,N'-2-methoxyethyl-4,13-diaza-18-crown-6, four of which were also structurally analysed (Scheme 4); they are complicated but the complexation process can be described as enthalpy driven.

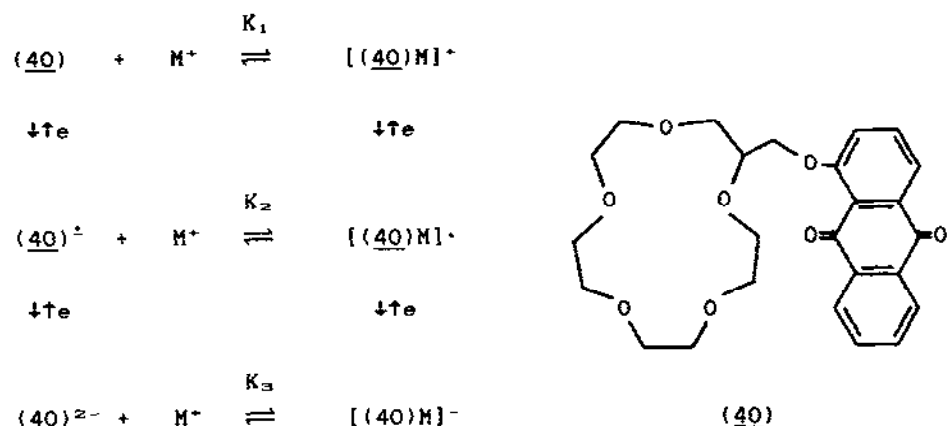
Gokel et al.[168] have gained direct evidence for  $\text{Na}^+$  selective intramolecular ion pairing in redox-switched nitrogen pivot lariat ethers from e.s.r. studies of solutions containing alkali metal cations in the presence of electrochemically reduced N-(2-nitrobenzyl)aza-15-crown-5; changes in the e.s.r. spectra occur on addition of  $\text{Li}^+$ ,  $\text{Na}^+$  or  $\text{K}^+$ , but the changes are most marked for  $\text{Na}^+$ . The radical anion sidearm complexes are thought to be relatively rigid species since the strongest side-arm interaction is observed for  $\text{Na}^+$  which is closest in size to the cavity formed by cooperating macrocycle and side-arm.[168]

Using cyclic voltammetric methods, Gokel et al.[169] have also observed enhanced cation binding for the C-pivot lariat ether (40) when electrochemically reduced according to Scheme 5. For  $\text{Li}^+$ , the reduction induced binding enhancements are  $K_2/K_1 = 2.4 \times 10^3$  (for one electron transfer) and  $K_3/K_2 = 7.7 \times 10^3$  (for two electron transfer). For  $\text{Na}^+$ , only the first reduction induced binding enhancement,  $K_2/K_1 = 2.3 \times 10^2$  could be determined, the redox couple for reduction of  $[(40)\text{Na}]$  to  $[(40)\text{Na}]^-$  not being



Scheme 4

observed. [169]

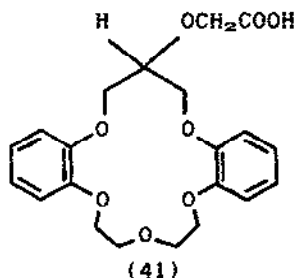
Scheme 5

By attaching an ionisable pendant group to a crown ether (41), Chang et al. [170] have shown that it is possible to tune the selectivity of the ligand towards  $M^+$  ( $M = Na, K$ ) and  $Ca^{2+}$  binding by adjusting the pH of the medium. It is suggested this mechanism may be important in biological ion transport through membranes with ionisable ionophores such as monensin and nigericin. The formation constants in pure methanol of the complexed cations for the neutral form of the ligand increase in the sequence:

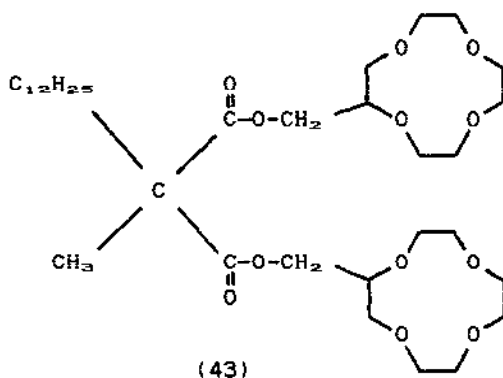
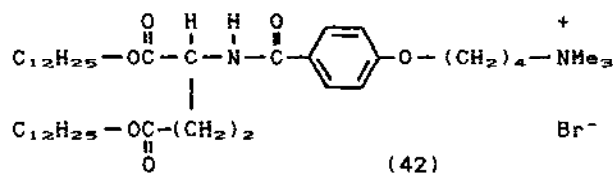
$$(41) \log K_{MHL} \quad Ca^{2+}(2.34) < Na^+(2.75) < K^+(2.78)$$

Those of the deprotonated ligand exhibited completely reversed behaviour:

$$(41-H)^- \log K_{ML} \quad Ca^{2+}(4.10) > Na^+(4.02) > K^+(3.72)$$



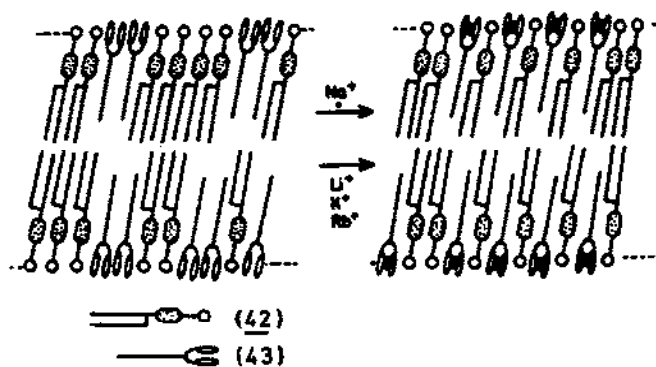
The selective discrimination of alkali metal cations has been achieved in a mixed bilayer system comprising the double chain amphiphile (42) and the bis(12C4) derivative (43). [171] The



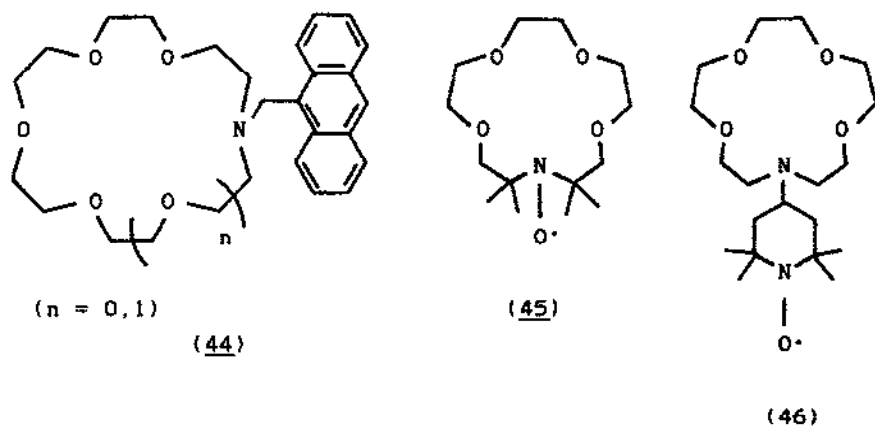
chiral bilayer (42) shows marked enhancement of circular dichroism due to strong exciton coupling of the chromophores. Addition of very small amounts of  $\text{Na}^+$  to the mixed bilayer system suppresses the c.d. intensity; similar suppression of the c.d. intensity by  $\text{K}^+$  requires concentrations increased by a factor of  $\sim 10^3$ . This difference is attributed to the specific binding of  $\text{Na}^+$  to the crown moiety (43), which results in an ordering of the bilayers as shown schematically in Figure 4.[169]

Addition of  $\text{Na}^+$  or  $\text{K}^+$ , but not  $\text{Li}^+$ , to a methanol solution of the N-pivot lariat ethers (44) results in the enhancement of the fluorescence quantum yield ( $\Phi_F$ ) of (44) by factors of 647.[172] It is suggested that this perturbation of the fluorescence may lead to quantitative remote signalling of the presence of  $\text{M}^+$  ( $\text{M} = \text{Na}, \text{K}$ ) in biological environments.

E.p.r. and endor studies of the N-substituted azacrown ethers (45) and (46) and of their complexes with  $\text{Na}^+$  indicate the presence of an interaction between the  $\text{Na}^+$  ion and the nitroxyl moiety in (45) but not in (46). [173]

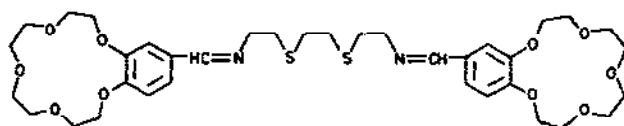


**Figure 4.** Schematic illustration of the suppression of c.d. intensity in an amphiphile-crown ether bilayer (reproduced by permission from J. Chem. Soc., Chem. Commun., (1987)617).

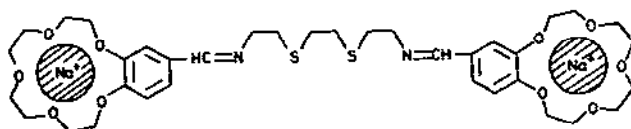


Beer[174] has shown that the complexation of alkali metal cations ( $\text{Na}^+$ ,  $\text{K}^+$ ) by the novel Schiff base bis(crown ether) ligand (47) is modified by the presence of transition metals ( $\text{Ag}^+$ ,  $\text{Cu}^{2+}$ ). In the absence of transition metals, the two B15C5 units of (47) act independently to complex two  $\text{Na}^+$  ions giving (48) and cooperatively to complex one  $\text{K}^+$  ion giving (49). In the presence of  $\text{Ag}^+$ , which prefers tetrahedral coordination by the  $\text{N}_2\text{S}_2$  chromophore, the 1:1 intramolecular sandwich complex type is no longer available for  $\text{K}^+$ ; instead a 2:1 complex (50) similar to

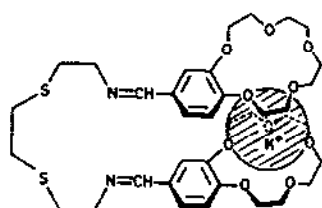




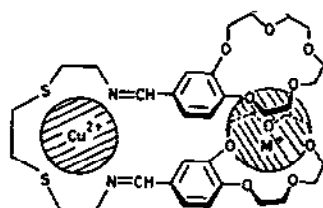
(47)



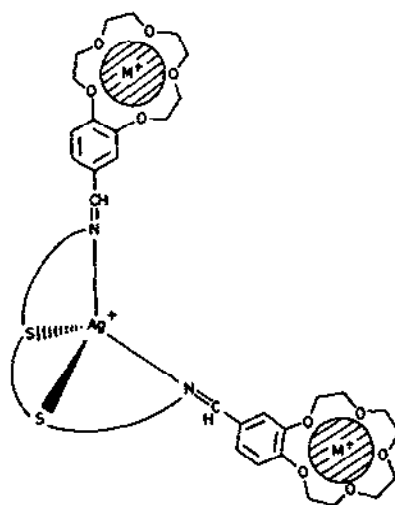
(48)



(49)



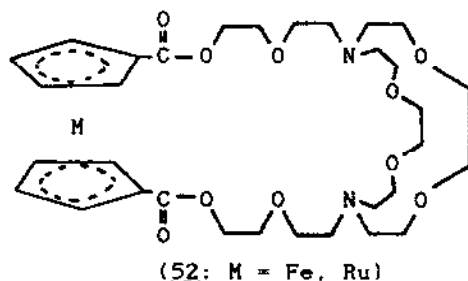
(51)



(50)

that formed by  $\text{Na}^+$  (50) is formed. In the presence of  $\text{Cu}^{2+}$ , however, which prefers square planar coordination by the  $\text{N}_2\text{S}_2$  chromophore, the formation of the 1:1 intramolecular sandwich complex type can occur giving (51); with  $\text{Na}^+$ , however, the stoichiometry of the complex (50) is unaltered at 2:1.[174]

Using f.a.b.m.s. techniques, Beer et al.[175] have shown that the novel metallocene cryptand molecules (52), essentially bibracchial lariat ethers with intramolecularly sandwiched arms, exhibit selective complexation of  $\text{K}^+$  to the exclusion of  $\text{Li}^+$ ,  $\text{Na}^+$  and  $\text{Cs}^+$ .



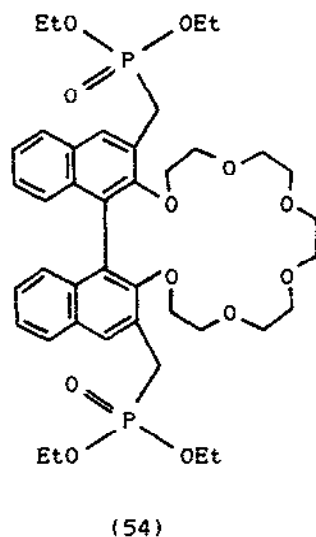
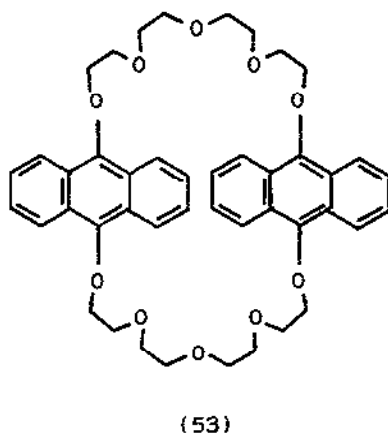
Alkali metal cations ( $\text{Na}^+$ ,  $\text{K}^+$ ) bound to 18C6 with a pendant thiazolium ion have been found to increase the rate of the oxidative decarboxylation of pyruvic acid in ethanol by binding the substrate and acting as the catalytic centre.[176]

#### 1.4.4 Complexes of Macrocyclic Polyethers of Novel Design

Compared with earlier reviews, a reduced number of papers have been abstracted for this subsection. Of these, the majority describe the synthesis and complexation characteristics of traditionally designed macrocyclic polyethers;[177-183] the others report similar data for calixarenes.[184-185]

Single crystal xrd structural analyses have been completed for [(53) $\text{Na}_2$ ] $^{2+}$ ( $\text{ClO}_4^-$ ) $_2$ [177] and [(54) $\text{K}$ ] $^+$  $\text{SCN}^-$ . $\text{CHCl}_3$ . [178] In the centrosymmetric structure of [(53) $\text{Na}_2$ ] $^{2+}$ ( $\text{ClO}_4^-$ ) $_2$ , [177] each Na atom is located in a pentagonal bipyramidal coordination sphere comprising (equatorially) five adjacent oxygens of the polyether ring ( $\text{Na}\cdots\text{O} = 245.5\text{-}255.9\text{pm}$ ) and (axially) two oxygens of separate anions ( $\text{Na}\cdots\text{O} = 243.6, 246.5\text{pm}$ ); the two anthracene rings are aligned forming a slightly staggered sandwich with an interplanar distance of 340pm. This conformation differs from

that of the free complexant giving sandwich excimer as opposed

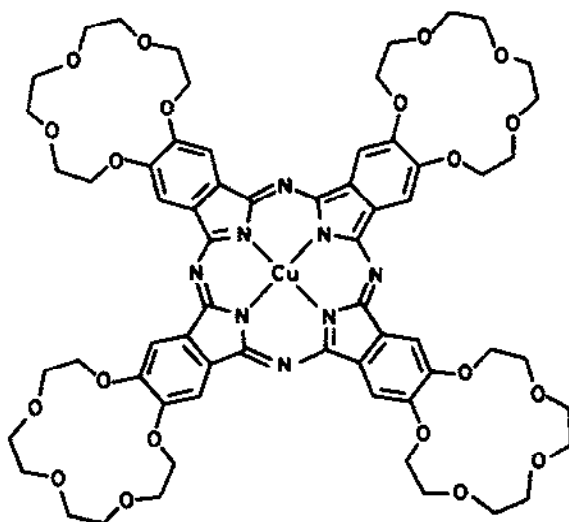


to monomer fluorescence emissions.[179] In the structure of [(54)K]<sup>+</sup>SCN<sup>-</sup>·CHCl<sub>3</sub>[178] the K atom lies on a crystallographic 2-fold symmetry axis and is surrounded by (equatorially) the six oxygens of the polyether ring (K...O = 272.3, 272.9, 281.8pm) and (axially) two oxygens from separate phosphonate groups (K...O = 270.2pm) in a hexagonal bipyramidal arrangement; the thiocyanate anion is remote from the cation.

The novel cylindrical crown ether, tridecalino-18C6[180] exhibits higher complexing selectivity for K<sup>+</sup> over Na<sup>+</sup>, as well as a higher intrinsic complexing ability for K<sup>+</sup> than either DCH18C6 or didecalino-18C6. The stability of the complex of K<sup>+</sup> with tridecalino-18C6 is ascribed to the fact that the cation is deeply buried in the lipophilic cylinder provided by the decalin moieties and hence is well shielded from attack by solvent in the decomplexation process.[180] The stability constants of the 1:1 complex of M<sup>+</sup> (M = Na, K, Cs) with 2-methoxy-1,3-xylyl-15C4 (55), 2-methoxy-1,3-xylyl-18C5 (56), 2-hydroxy-1,3-xylyl-15C4 (57) and 2-hydroxy-1,3-xylyl-18C5 (58), measured in CH<sub>3</sub>OH by calorimetric titration methods, increase in the sequence:[181]

(55) $\log K_{ML}$	$Na^+ (1.14) < Cs^+ (1.81) < K^+ (1.97)$
(56) $\log K_{ML}$	$Na^+ (2.30) < Cs^+ (2.76) < K^+ (3.52)$
(57) $\log K_{ML}$	$Na^+ (0.8) < K^+ (1.26) < Cs^+ (1.30)$
(58) $\log K_{ML}$	$Na^+ (2.25) < Cs^+ (2.62) < K^+ (3.18)$

Dutch[182] and Japanese[183] chemists have independently synthesised the polytopic ligand system (59) by refluxing 4,5-dibromo-B15C5, obtained by bromination of B15C5 (Fe-Br<sub>2</sub>; solvent CH<sub>2</sub>Cl<sub>2</sub>) with CuCN in dmf for 20h. The Dutch group[182] report that (59) has a high affinity for M<sup>+</sup> (M = Na-Cs) but a relatively low affinity for Li<sup>+</sup>. They also note[182] that K<sup>+</sup> ions induce dimerisation forming a complex of 4:2 stoichiometry, but that Li<sup>+</sup> ions form a monomeric complex of 4:1 stoichiometry; presumably the K<sup>+</sup> ions bind two 15C5 residues, whereas Li<sup>+</sup> ions are satisfactorily complexed by a single 15C5 moiety. The



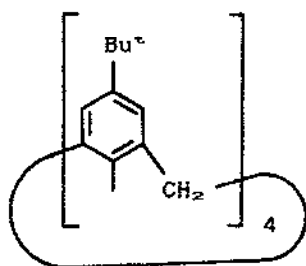
(59)

Japanese authors[183] also comment on the high tendency of (59) towards aggregation, especially K<sup>+</sup>-induced aggregation and suggest that this may enable the phthalocyanine to be used as a

colourimetric reagent.

The crystal and molecular structures of two alkali metal complexes based on calixarenes have been reported.[184,185] In [(60)Na.C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>]<sup>+</sup>[C<sub>6</sub>H<sub>5</sub>COO(AlMe<sub>2</sub>)<sub>2</sub>OAlMe<sub>3</sub>]<sup>-</sup>, [184] the Na atom lies above the plane of (44pm) and strongly interacts with the four oxygens of the methoxy groups (Na...O = 230pm), its square pyramidal geometry being remotely filled by a carbon atom of the aluminoxane anion (Na...C = 264pm). The toluene molecule is

located in the apolar cavity of the calixarene.[184] In [(61)K.CH<sub>3</sub>OH]<sup>+</sup>SCN<sup>-</sup>, [185] the K atom is completely encapsulated by the eight oxygens provided by the ether and amide fragments of the calixarene (K...O = 270.8, 274pm) in a square antiprismatic geometry. The methanol molecule resides in the apolar cavity of the calixarene.[185]



(60) R = OMe

(61) R = OCH<sub>2</sub>CONEt<sub>2</sub>

#### 1.4.5 Natural Product Ionophores

Pangborn et al. have reinvestigated the molecular structure of the Na<sup>+</sup> complex of the monocarboxylic acid polycyclic polyether antibiotic A204A (acetone adduct), [186] and have determined, for the first time, that of the K<sup>+</sup> complex monensin A (dihydrate). [187] The only difference between the two structural analyses of the former complex lies in the precise location of the Na atom. Previously Jones et al. [188] had located the Na atom close to the centre of the ring of heteroatoms giving six anomalously long Na...O contacts (271.3-297.0; average 279pm) and two fairly remote Na...O contacts (312.2, 316.7pm). Now, Pangborn et al. [186] prefer an asymmetric location in the ring of heteroatoms giving six normal Na...O contacts (233.9-294.9; average 257pm) and two extremely remote Na...O contacts (342.5, 371.8pm). Pangborn et al. [186] considered that Jones et al. [188] may have misidentified the cation, it being in reality, K<sup>+</sup> and have obtained preliminary results (only alluded to in this paper) on the corresponding K<sup>+</sup> complex confirming this suggestion.

As a result of their structural analysis of the  $K^+$  complex of monensin A (dihydrate), Pangborn et al.[187] discovered that the conformation of the ionophore in this complex is markedly different from that of the ionophore in the corresponding  $Na^+$  complex and concluded that the selectivity exhibited by monensin A for  $Na^+$  over  $K^+$  is due to the energetic cost of distorting the geometry of the ionophore to accommodate the  $K^+$  ion. The distorted 7-fold coordination geometry of the K atom is provided by seven oxygens of the encapsulating ionophore ( $K...O = 265.0-279.6pm$ ). [187]

Lactonisation of monensin and esterification of the carboxy-group of ionomycin have yielded two  $Li^+$ -selective ionophores. macrocyclic monensin monoacetate and ionomycinmethyl ester.[189] The selectivity factors for these ligands are compared with those of other natural products in Figure 5; it is clear that relatively small changes in the ionophores can result in relatively large modification of the ion selectivity order.

$^{23}Na$  n.m.r. spectra of complexes of  $Na^+$  with naturally occurring and synthetic ionophores have been recorded in  $CHCl_3$  and  $CH_3OH$ . [190] Comparison of the derived  $^{23}Na$  n.m.r. chemical shifts with those obtained in the solid state shows the complexes of  $Na^+$  with monensin and tetranactin adopt similar configurations in  $CHCl_3$  and the solid state. For the other systems, however, the  $^{23}Na$  n.m.r. signals indicate the existence of either conformational fluctuation of the ionophores or interaction of the  $Na^+$  ions with solvent or anion molecules.[190]

#### 1.4.6 Cryptates and Related Complexes

The complexation of  $Li^+$  by C22B,[191] of  $Li^+$ [192] and  $Na^+$ [193-195] by C21C<sub>3</sub>, of  $Na^+$  by C211,[193-195] of  $K^+$  [196-198] and  $Cs^+$ [199] by C222 and of diverse  $M^+$  and  $M^{2+}$  cations by the dilactam derivatives of C21, C22, C211, C221 and C222[200] is covered in this subsection; although structural data predominate, some thermodynamic data are included.

The molecular structures of  $[C22BLi]^+AlCl_4^-$ , isolated from the n-butylpyridinium chloride-aluminium trichloride molten salt, is inclusive with six  $Li...O$  interactions ( $220.7-252.5pm$ ) in a near octahedral geometry; [191] the two  $Li...N$  contacts ( $277.7, 294.5pm$ ) are long, indicating weak or zero interaction. The  $AlCl_4^-$  anion does not enter into the Li atom coordination polyhedron.[191]

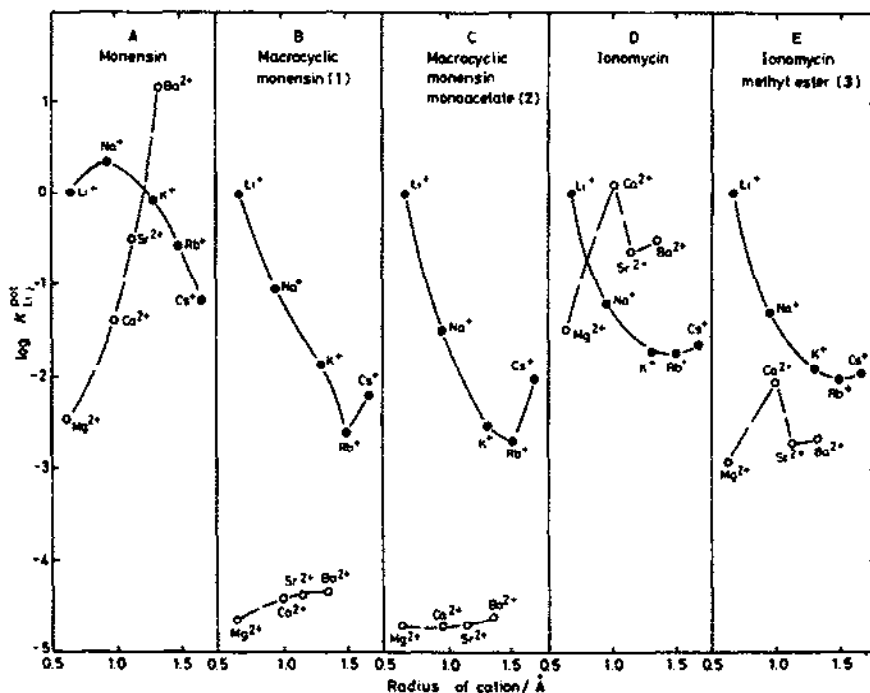


Figure 5. Selectivity factors ( $\log K_{Li:j}$ :interfering ion) for monensin, ionomycin and their derivatives (reproduced by permission from J Chem. Soc., Chem. Commun., (1987) 932).

The ionophore also exists in the inclusive form in the molecular structure of  $[C_{21}C_5Li]^+NCS^-$  in which there are three  $Li \cdots O$  (200.1, 214.2, 236.0 pm) and two  $Li \cdots N$  interactions (211.1, 227.5 pm) in a highly irregular geometry. The  $NCS^-$  anion does not coordinate the Li atom.

Lincoln et al. [193-195] have undertaken a comparative study of

the complexation of  $\text{Na}^+$  by  $\text{C21C}_5$  and  $\text{C211}$ . The stability constants[193] of  $[\text{C21C}_5\text{Na}]^+$ , determined in dmf, pyridine, methanol, acetone, acetonitrile and propylene carbonate in the presence of  $0.05\text{M } (\text{C}_2\text{H}_5)_4\text{NClO}_4$  are substantially lower than those observed for  $[\text{C211Na}]^+$ . The relative instability of  $[\text{C21C}_5\text{Na}]^+$  is mirrored in the rate constants[194] for the formation and decomplexation of  $[\text{C21C}_5\text{Na}]^+$  and  $[\text{C211Na}]^+$  in these solutions which indicate that the former complex is much more labile to decomplexation than the latter. The difference in stability is attributed to the reduced number of potential coordinating sites in  $\text{C21C}_5$  (5) compared with  $\text{C211}$  (6).[193,194] This conclusion is supported by the results of an xrd study[195] of the crystal and molecular structures of  $[\text{C21C}_5\text{Na}]^+\text{SCN}^-$  and  $[\text{C211Na}]^+\text{SCN}^-$  which shows that all the heteroatoms in the ligands, which adopt the exclusive form, coordinate the Na atom: in the  $[\text{C21C}_5\text{Na}]^+$  cation, the Na atom is surrounded by the three oxygens ( $\text{Na}\dots\text{O} = 229.7\text{--}235.6\text{pm}$ ) and two nitrogens ( $\text{Na}\dots\text{N} = 257.6, 275.9\text{pm}$ ) of the cryptand and by the nitrogen of the anion ( $\text{Na}\dots\text{N} = 235.8\text{pm}$ ); in the  $[\text{C211Na}]^+$  cation, it is encapsulated by the four oxygens ( $\text{Na}\dots\text{O} = 228.9\text{--}266.2\text{pm}$ ) and two nitrogens ( $\text{Na}\dots\text{N} = 247.8, 249.2\text{pm}$ ) of the cryptand and by the nitrogen of the anion ( $\text{Na}\dots\text{N} = 240.9\text{pm}$ ).[195]

Reaction of  $\text{C222}$ , when dissolved in ethylenediamine, with  $\text{K}_{1.6}\text{As}_{1.6}\text{Te}$  and with mixtures of  $\text{K}_2\text{S}_5$  and sulphur yields crystals of  $[\text{C222K}]^+_{.5}[\text{As}_{1.6}\text{Te}]^{3-}$ .en[196] and of  $[\text{C222K}]^+_{.2}\text{S}_6^{2-}$  and  $[\text{C222K}]^+_{.2}\text{S}_7^{2-}$ .en.[197] Whereas the three  $[\text{C222K}]^+$  cations in the former complex are crystallographically distinct,[196] those in the latter two complexes are symmetry related:[197] all five cations are unremarkable. Reaction of  $[\text{C222K}]^+[\text{tBuS}]^-$  in  $\text{C}_6\text{H}_5\text{Cl}$  with iron(II) phthalocyanine gave, after addition of pentane, crystals of  $[\text{C222K}]^+[\text{FePc}]$  ( $\text{Pc} = \text{phthalocyanine}$ );[198] although structural analysis was undertaken no details are reported for the cation.

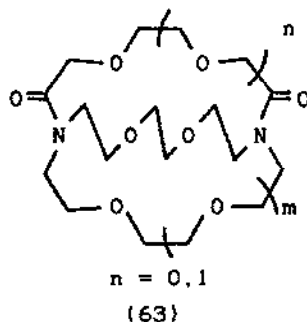
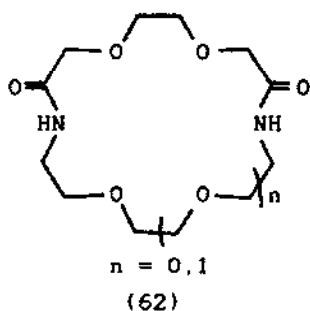
The stability constants of  $[\text{C222Cs}]^+$  have been determined in the four binary solvent systems, acetone/dmsO, acetonitrile/dmsO, propylene carbonate/dmsO and propylene carbonate/dmf using  $^{133}\text{Cs}$  n.m.r. techniques.[199] In the neat solvents, the stability constants increased in the inverse order of their solvating abilities as given by Gutmann donor number:



dmso < dmf < acetone < propylene carbonate < acetonitrile

In the binary mixtures, the stability constants varied monotonically with composition.[199]

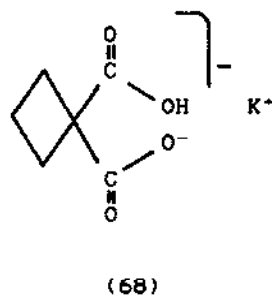
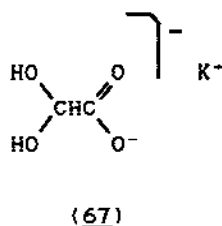
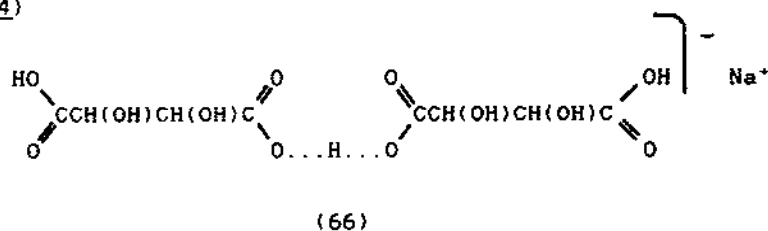
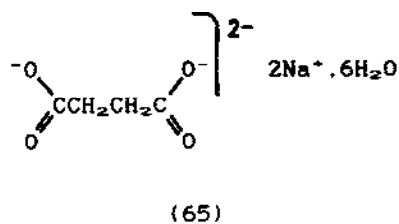
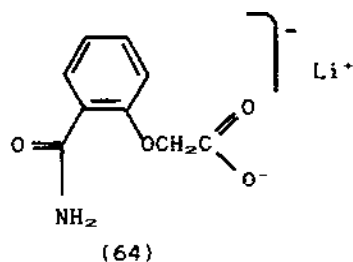
The ability of the dilactam derivatives of C21, C22, C211, C221 and C222 (62,63) to complex alkali and alkaline earth metal cations has been compared with that of the unsubstituted ionophores in methanol and acetonitrile using calorimetric and potentiometric methods;[200] the stability constants of the complexes of the dilactam ligands are lower by a factor of ca.  $10^6$  probably owing to a marked reduction in the values of the reaction enthalpies.



#### 1.4.7 Salts of Carboxylic, Thiocarboxylic and Dithiocarbamic Acids

The reduction in the number of abstracted papers describing the chemistry of alkali and alkaline earth metal salts of carboxylic and thiocarboxylic acids, first commented on in the 1985 review, has been maintained for this review; one interesting development in this field, however, is the description of the crystal and molecular structures of lithium and potassium salts of monothiocarboxylic acids. In view of Gattow's continuing interest in the chemistry of dithiocarbamic acid derivatives, again first noted in the 1985 review, their inclusion in this subsection has been continued.

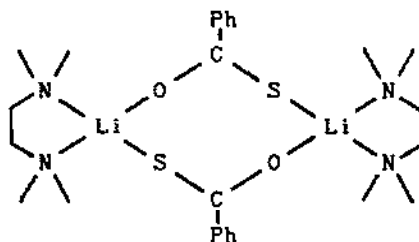
Single crystal xrd structural analyses have been successfully completed for lithium 2-carbamoylphenoxyacetate (64).[201] disodium succinate, hexahydrate (65).[202] monosodium di-meso-tartrate (66).[203] potassium dihydroxyacetate (67)[204] and monopotassium cyclobutanedicarboxylate (68).[205] The Li atom in



(64)[201] is 4-fold coordinate; its distorted tetrahedral geometry comprises one oxygen from the 2-carbamoyl moiety ( $\text{Li}\dots\text{O} = 195.0\text{pm}$ ) and three carboxyl oxygens from different anions ( $\text{Li}\dots\text{O} = 191.3\text{--}198.5\text{pm}$ ). The symmetry related Na atoms in (65)[202] and the centrosymmetrically located Na atom in (66)[203] are 6- and 8-fold coordinate, respectively. The distorted octahedral geometry of the Na atom in (65) is generated by one oxygen from an anion ( $\text{Na}\dots\text{O} = 238.0\text{pm}$ ) and five water molecules ( $\text{Na}\dots\text{O} = 234.6\text{--}256.3\text{pm}$ ); the distorted cubic coordination polyhedron of the Na atom in (66) is based on four hydroxyl ( $\text{Na}\dots\text{O} = 253.0, 257.0\text{pm}$ ) and four carboxyl oxygens ( $\text{Na}\dots\text{O} = 246.8, 260.7\text{pm}$ ). The structure of (67)[204] contains two crystallographically independent K atoms; the distorted octahedral coordination sphere of K(1) comprises two hydroxyl ( $\text{K}\dots\text{O} = 274, 275\text{pm}$ ) and four carboxyl oxygens ( $\text{K}\dots\text{O} = 272\text{--}283\text{pm}$ ) and the distorted square antiprismatic geometry of K(2) is generated by four hydroxyl

(K...O = 274-302pm) and four carboxyl oxygens (K...O = 278-289pm). In (68), [205] the K atom is surrounded by seven oxygens (K...O = 260.2-301.0pm) from four different anions in a highly distorted geometry.

The crystal and molecular structures of two monothiocarboxylates, [PhCOS]<sup>-</sup>Li<sup>+</sup>, tmeda (69) [206] and [SOCNHNHCOS]<sup>2-</sup>2K<sup>+</sup>·2H<sub>2</sub>O (70) and of one dithiocarboxylate, [S<sub>2</sub>CPhCS<sub>2</sub>]<sup>2-</sup>2K<sup>+</sup>·2H<sub>2</sub>O (71) [208] have also been elucidated. The structure of (69) [206] is that of a centrosymmetric dimer with an 8-membered ring composed of coplanar C, O and S atoms and tetrahedrally coordinated Li atoms (Li...O = 188.1, Li...S = 247.8, Li...N (quoted as typical of Li-tmeda complexes)) above and below this plane; ab initio optimisation calculations on



(69)

(HCOSLi)<sub>2</sub>, which is all planar, imply that displacement of the Li atoms in the complex occurs in order to reduce excessively large ring angles at oxygen and, most crucially, at Li in order to accommodate the tmeda molecule. [206] The two K atoms in (70) [207] lie on a 2-fold axis; they are, however, crystallographically independent. Each is surrounded by four oxygens (K(1)...O = 272.9, 273.8; K(2)...O = 272.7, 278.5pm) and two sulphurs of different anions (K(1)...S = 319.9; K(2)...S = 350.8pm) in a distorted 6-fold coordination geometry. The two K atoms in (71) [208] are symmetry related; they are coordinated by five sulphurs (K...S = 322.4-353.1pm) from different anions and two water molecules (K...O = 274.8, 276.8pm) in a distorted 7-fold arrangement.

Reaction of alkali metal formates with H<sub>2</sub>O<sub>2</sub> yielded the formate peroxohydrates, HCO<sub>2</sub>Na·H<sub>2</sub>O<sub>2</sub> and HCO<sub>2</sub>M·1.5H<sub>2</sub>O<sub>2</sub> (M = K-Cs); [209] they are unstable at ambient temperature (293K) slowly losing

active oxygen.

Alkali metal N,N'-diphenyl-N-formimidoyldithiocarbamate solvates,  $[S_2C-N(Ph)-CH=N(Ph)]^-M^+, xL$  ( $M = Na-Cs$ ;  $L =$  solvent) have been produced by Gattow et al. [210] by reaction of N,N'-diphenylformamidine ( $H-N(Ph)-CH=N(Ph)$ ) with  $CS_2$  in different solvents containing the appropriate alkali metal hydroxide. They have been characterised by u.v.-visible, i.r., n.m.r. and mass spectroscopic techniques and their thermal behaviour has been elucidated from dta and tga data. [211] Single crystal xrd studies of the dioxane adduct of the potassium salt [212] have shown that the K atom is coordinated by three sulphurs of a bidentate dithiocarboxylate moiety ( $K...S = 318.1, 344.8 pm$ ) and a monodentate dithiocarboxylate moiety ( $K...S = 334.1 pm$ ), a nitrogen of a separate anion ( $K...N = 293.0 pm$ ) and an oxygen of the solvent molecule ( $K...O = 271.6 pm$ ) in the form of a distorted trigonal bipyramid. This is the smallest coordination number of all the related potassium dithiocarbamates structurally studied thus far. [212]

Gattow et al. [213] have also prepared and characterised, using u.v.-visible, i.r., n.m.r. and mass spectroscopic techniques, the N-acetimidoyl dithiocarbamates,  $[S_2C-N=C(CH_3)-NH_2]^-M^+$  ( $M = Rb, Cs$ ).

#### 1.4.8 Heterobimetallic Complexes containing Alkali Metals

Sustained growth of interest in the chemistry of heterobimetallic complexes containing alkali metals can be perceived during the period of this and recent reviews. As for the earlier reviews, lithium containing complexes [214-226] predominate in this particular review, despite a sharp rise in interest in sodium containing complexes. [225, 227-234] For the heavier alkali metals only one paper has been abstracted; it describes the structural chemistry of a K-Yb complex. [235]

These complexes fall into one of two distinct types; those in which the two metals form discrete cationic and anionic centres and those in which the two metals are joined by bridging ligands in a single molecular complex. In this review, emphasis is placed on the latter type since the former type normally contain common cationic species such as  $[Li(tmeda)_2]^+$  or  $[18C6K]^+$  which have unremarkable chemistries. Only four examples of the former type of complex are included:  $[Li(thf)_{4.5}]^+[Co(N(SiMe_3)_2)-(OC^tBu)_2]^-$ . [214]  $[Li(tmeda)_2]^+[Mo(CO)_3(\eta^5-C_5(CH_3)_5)]^-$ . [215]

$[\text{Li}(\text{tmeda})_2]^+[\text{Lu}(\text{tBu})_4]^-$  [216] and  $[\text{Na}(\text{tmeda})_2]^+[\text{Ni}(\text{C}_2\text{H}_4)_2\text{H}]^-$ . [217] Blue crystals of the Li-Co complex were prepared by reaction of  $[\text{Co}(\text{N}(\text{SiMe}_3)_2)_2]$  with  $\text{tBu}_3\text{COH}$  in *n*-hexane followed by addition of  $\text{LiN}(\text{SiMe}_3)_2$  in thf. [214] The Li-Mo complex was synthesised as a moisture sensitive yellow crystalline solid by reaction of  $\text{tBuLi}$  with  $[\text{Mo}(\text{CO})_3\text{H}(\eta^5\text{-C}_5\text{(CH}_3)_5)]$  in toluene containing tmeda. [215] A crystalline sample of the Li-Lu complex was obtained by interaction of  $\text{tBuLi}$  with  $\text{LuCl}_3$  in diethylether containing tmeda. [215] Of the four cations,  $[\text{Li}(\text{thf})_4.5]^+$  [214] is unique since, in the presence of thf,  $\text{Li}^+$  usually crystallises as the tetrahedral  $[\text{Li}(\text{thf})_4]^+$ . In  $[\text{Li}(\text{thf})_4.5]^+$ , four normal thf molecules coordinate to  $\text{Li}^+$  ( $\text{Li}\cdots\text{O} = 190\text{-}209\text{pm}$ ) with a fifth more remote thf molecule ( $\text{Li}\cdots\text{O} = 256\text{pm}$ ) statistically disordered about a centre of symmetry. The near trigonal bipyramidal geometry at the Li atom indicates that the "fifth" thf molecule is stereochemically active and occupies an axial position; the Li atom is pulled out of the trigonal plane by  $31\text{pm}$  towards the other, more tightly bound, axial thf molecule. [214]

A significant number of molecular heterobimetallic complexes containing Li have been synthesised; they include Li-Ga, [218] Li-In, [218] Li-Ti, [219] Li-V, [220] Li-Cr, [221] Li-Mo, [222] Li-W, [223-225] Li-Co, [214] Li-Ni, [217] and Li-Lu [226] complexes. In the majority of cases, [214, 217-221, 223-226] characterisation has included single crystal xrd structural analysis; schematic representations of all the molecular structures, including pertinent interatomic distances and angles, are collected in Figure 6.

The Li-Ga (74) and Li-In (75) complexes [218] were obtained by treatment of  $\text{MCl}_3$  ( $\text{M} = \text{Ga}, \text{In}$ ) with  $\text{Li}\{\text{C}(\text{SiMe}_3)_3\}$  at  $273\text{K}$  in thf. The former has two bridging Cl atoms between Li and Ga, but the latter has only one bridging Cl atom between Li and In; [218] the distorted tetrahedral coordination geometries of the two lithium atoms are completed by two and three thf molecules, respectively.

The Li-Ti complex (76) was prepared in poor yield by reaction of the lithiated triaminosilane  $\text{PhSi}(\text{NLi}(\text{SiMe}_3))_3$  with  $(\eta^5\text{-C}_5\text{H}_5)\text{TiCl}_3$  in  $\text{Et}_2\text{O}$  at  $243\text{K}$ . [219] It contains an unusual heteronuclear bicyclo [311]-heptane entity which contains titanium and silicon bridgeheads and includes a novel Cl-Li-N bridge; [219] the roughly trigonal planar Li coordination is completed by an

ether molecule.

Treatment of  $\mu$ -benzene(dicyclopentadienyl)divanadium with lithium cyclopentadienide in thf containing tmeda at 333K gave the Li-V complex (77).[220] A novel feature of the structure of (77) is the  $\eta^6$ -coordination of the benzene molecule to both Li and V atoms; the Li atom is coordinated in a distorted pseudo-

**Figure 6.** Schematic representations of the molecular structures of heterobimetallic complexes containing lithium.

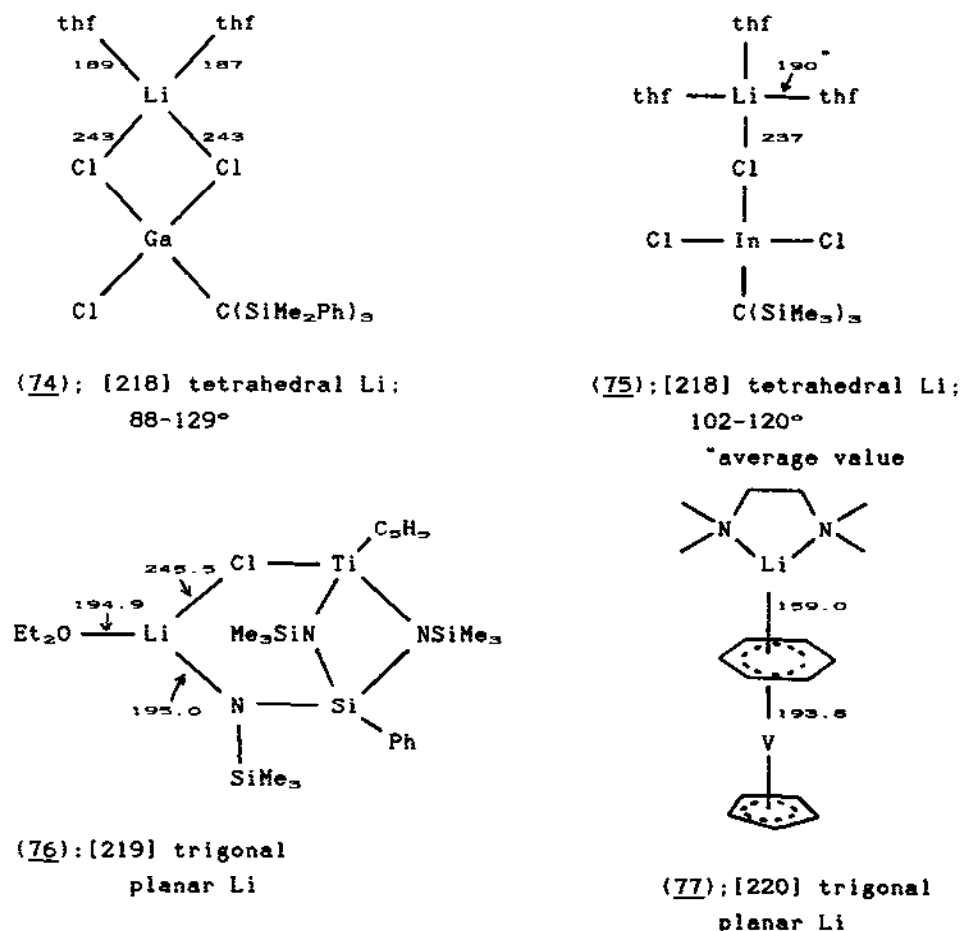
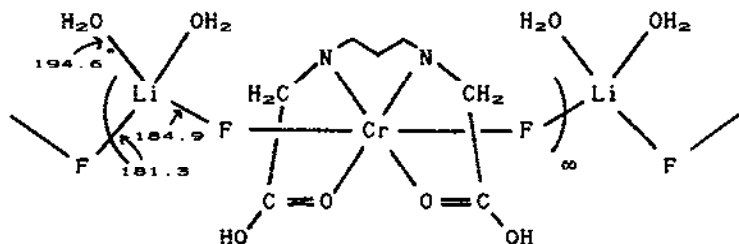
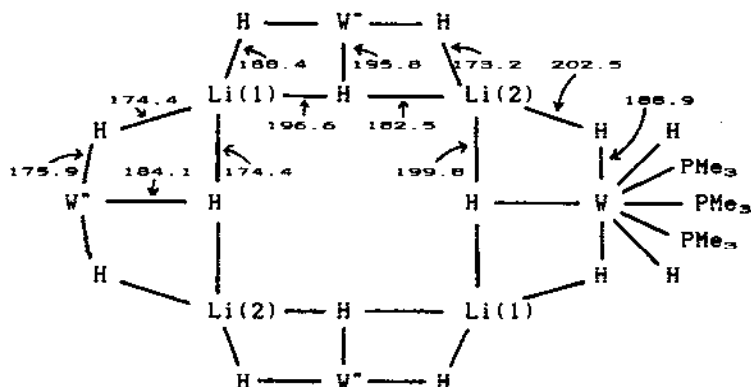


Figure 6 continued.



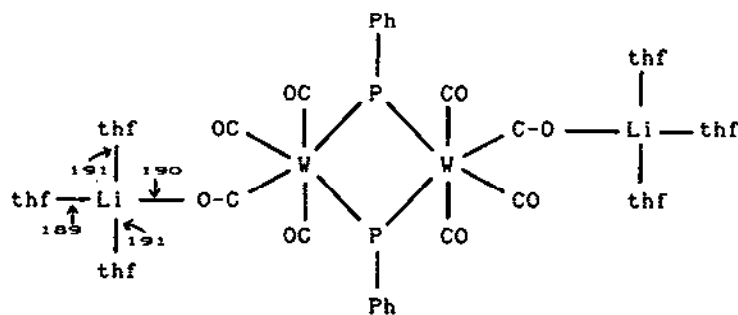
(78); [221] tetrahedral Li; 104.8-115.6°

average value



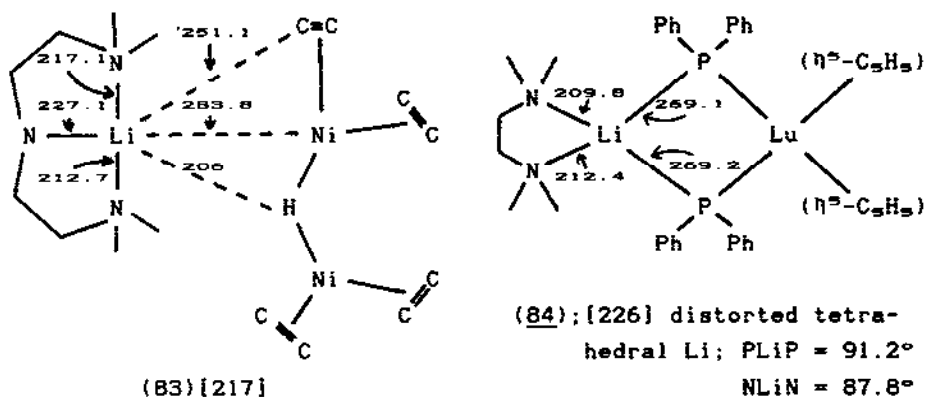
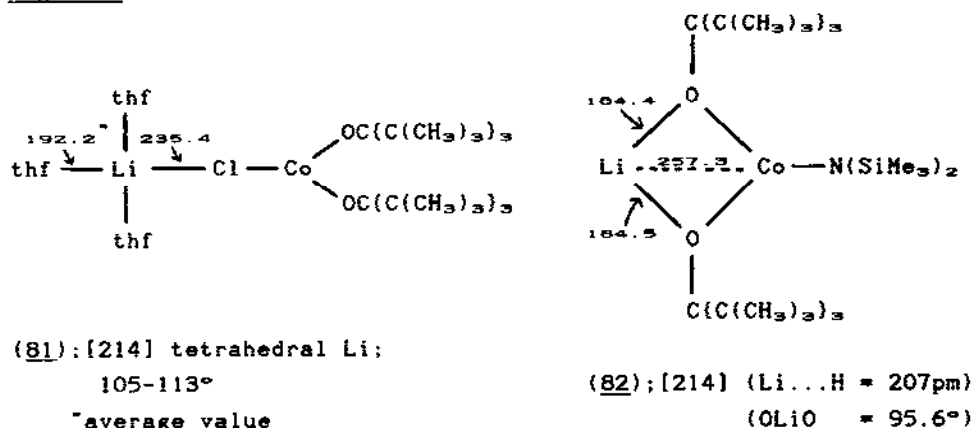
(79); [223;224] severely distorted tetrahedral Li

\* The complete W coordination sphere is omitted for clarity.



(80); [225] tetrahedral Li; 105-115°

Figure 6 continued.



trigonal planar fashion, while the V atom is sandwiched between the parallel  $C_6H_6$  and  $C_5H_5^-$  rings.

The Li-Cr complex (78) was obtained on elution, using LiCl, of the products of the reaction of crystalline  $trans-[CrF_2(py)_4](NO_3)$  with an aqueous solution of 1,3-propanediamine-N,N'-diacetic acid hydrochloride adjusted to pH 8 by  $K_2CO_3$ , when separated on a QAE-Sephadex column.[221] Each Li atom in (78) is coordinated in a distorted tetrahedral geometry to two fluorines from different Cr-containing complex moieties and to two water molecules forming  $-[Li-F-Cr-F]_\infty$  chains along the a direction;[221] the  $Li^+$  ion



seems to be of optimum size for the stabilisation of a strongly interacting 3-D network since neither  $\text{Na}^+$ ,  $\text{K}^+$  nor  $\text{Ba}^{2+}$  yielded crystalline products.

Wilkinson et al. [223,224] have reported the preparation of the Li-W complex (79) by reaction of the aluminopolyhydride complex  $[(\text{Me}_3\text{P})_3\text{H}_3\text{W}(\mu\text{-H})_2\text{AlH}(\mu\text{-H})]_2$  with lithium alkyls. This is the same product as that reported by Green et al. several months earlier [235] and discussed in the 1985 review; [1] better quality xrd data ( $R = 0.0315$  [223,224] as opposed to 0.0359 [235]), however, permitted location of the hydrogen atoms. The structure of (79) is that of a centrosymmetric tetramer in which the W atoms are connected to two neighbouring Li atoms by normal  $\text{W}(\mu_2\text{-H})\text{Li}$  bridges and then by one  $\text{W}(\mu_3\text{-H})\text{Li}_2$  bridge; [223,224] the Li atoms are thus 4-coordinate with a severely distorted tetrahedral geometry.

The Li-W complex (80), which is based on a planar 4-membered  $\text{W}_2\text{P}_2$  ring and in which the Li atom possesses an almost regular tetrahedral oxygen environment composed of an equatorial CO and three thf molecules, was synthesised by reduction of  $\text{W}_2(\text{CO})_8(\mu\text{-PPh}_2)_2$  using two equivalents of  $\text{LiEt}_3\text{H}$  in thf. [225]

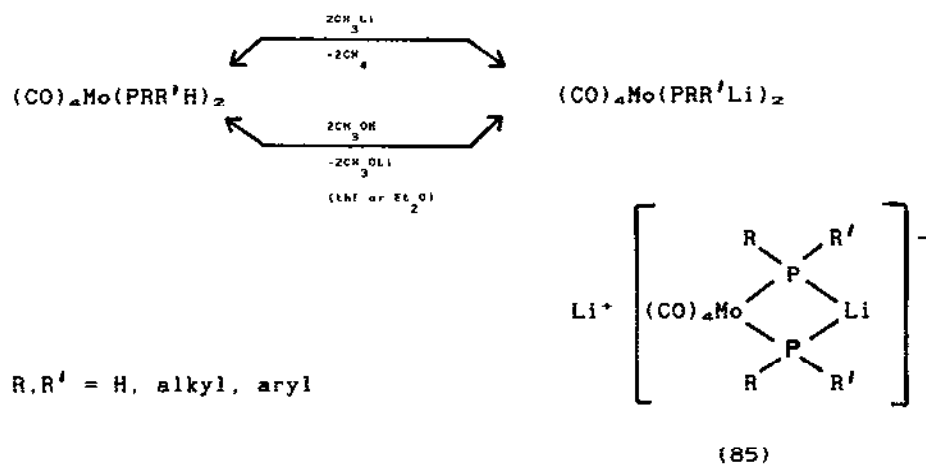
Addition of a solution of  $\text{LiOC}^t\text{Bu}_3$ , formed by mixing of solutions of  $^t\text{BuLi}$  (in n-hexane) and  $^t\text{Bu}_3\text{COH}$  (in thf) to a slurry of  $\text{CoCl}_2$  in  $\text{Et}_2\text{O}$  resulted in the formation of the Li-Co complex (81). [214] The other Li-Co complex (82) was prepared by treatment of a solution of  $[\text{Co}(\text{N}(\text{SiMe}_3)_2)_2]$  in thf firstly with  $^t\text{Bu}_3\text{COH}$  and secondly with a solution of  $\text{LiN}(\text{SiMe}_3)_2$  in thf. [214] Whereas, in (81) the Li atom is surrounded in an approximately tetrahedral fashion by the bridging chlorine atom and three thf molecules, in (82) the Li atom is apparently 2-coordinate bridging, together with the  $\text{CoN}(\text{SiMe}_3)_2$  moiety, the two alkoxide groups; [214] there is, however, in the structure of (82) a close  $\text{Li}\cdots\text{H}$  interaction with a methyl group of one of the alkoxide anions.

Reaction between tris(ethene)nickel(0) and lithium trialkylborohydrides yielded the Li-Ni complex (83). [217] Its structure exhibits an ion pair contact between the  $[\text{Li}(\text{pmdeta})]^+$  cation and one Ni atom, one ethene molecule and the hydride anion in the  $[(\eta^2\text{-C}_2\text{H}_4)_2\text{Ni}]_2(\mu\text{-H})^-$  anion giving the Li atom a pseudo-octahedral coordination geometry.

A puckered 4-membered  $\text{LuP}_2\text{Li}$  ring is the core of the structure

of (84) which was obtained by reaction of the corresponding di- $\mu$ -methyl complexes with  $\text{HPPH}_2$  via stepwise substitution of the methyl ligands; [225] the approximately tetrahedral geometry of the Li atom is completed by the tmeda ligand.

Low temperature  $^7\text{Li}$  and  $^{31}\text{P}$  n.m.r. studies [222] of  $(\text{CO})_4\text{Mo}(\text{PRR}'\text{Li})_2$ , prepared as per scheme 6, may be assigned on an ionic type (solvated) of structure  $\text{Li}^+[\text{cis-Mo}(\text{CO})_4(\mu\text{-PRR}')_2\text{-Li}]^-$  in which the core of the anion comprises a four-membered  $\text{MoP}_2\text{Li}$  ring system (85).



$\text{R}, \text{R}' = \text{H}, \text{alkyl}, \text{aryl}$

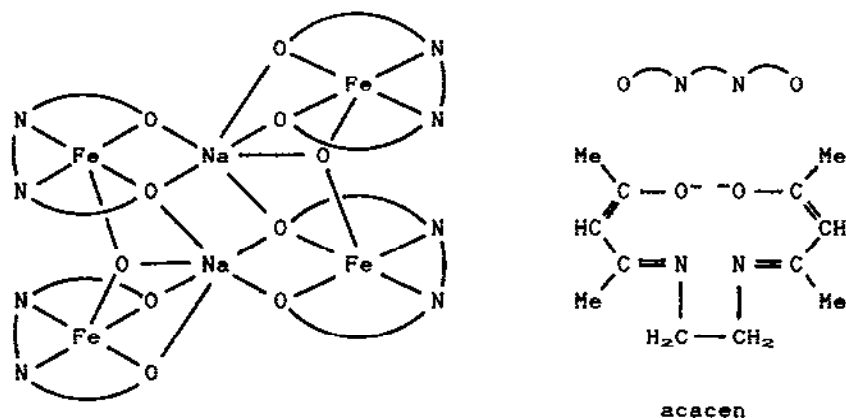
Scheme 6.

The sharp rise in the number of papers describing the synthesis and characterisation, mainly by structural methods, of heterobimetallic complexes containing sodium, can be attributed principally to collaboration between Floriani's group in New York (USA) and Chiesi-Villa and Guastini in Parma (Italy); between them they have reported on Na-Fe, [227, 228] Na-Co, [229-231] and Na-Cu [232] complexes. The only other pertinent paper is that published by Klaui, Boese et al. [233] on a Na-Co complex. In all cases, characterisation has included single crystal xrd structural analysis; schematic representations of the molecular structures, including pertinent interatomic distances, are collected in Figure 7.

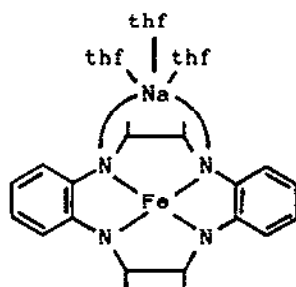
Single electron reduction of  $([\text{Fe}(\text{acacen})]_2\text{O})$  with sodium metal in thf yields the centrosymmetric Na-Fe complex  $([\text{Fe}(\text{acacen})]_2\text{ONa})_2$  (86) in which the ten oxygen atoms from the

two  $\{[\text{Fe}(\text{acacen})]_2\text{O}\}$  units provide 6-fold coordination polyhedra for the two symmetry related Na atoms.[227] Although the complex crystallises with three thf molecules, none are involved in the Na atom coordination sphere. Similar reduction of  $\text{M}(\text{tmtaa})$  ( $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ ;  $\text{tmtaa} = \text{dibenzotetramethyltetra-aza[14]annulene dianion}$ )

**Figure 7.** Schematic representations of the molecular structures of heterobimetallic complexes containing sodium.



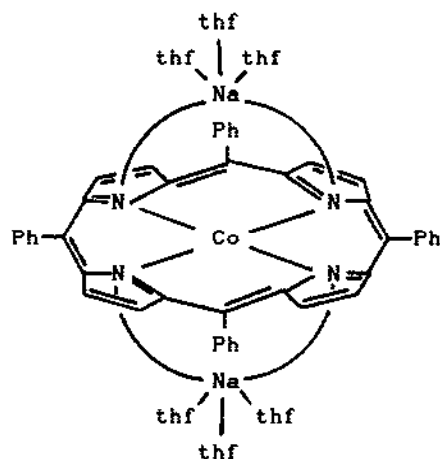
(86); [227] octahedral Na : Na...O = 230.8-257.7pm



(87); [228]

Na...O = 233.4-239.1pm

Na...N = 277.5, 280.1pm

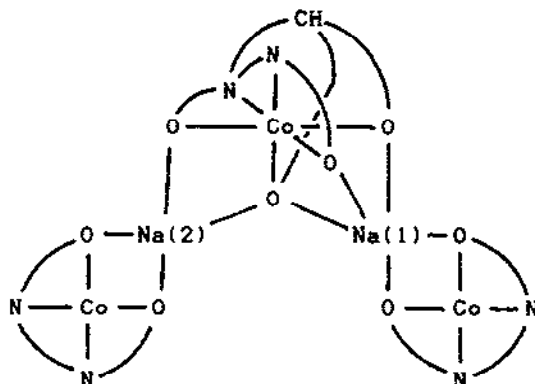
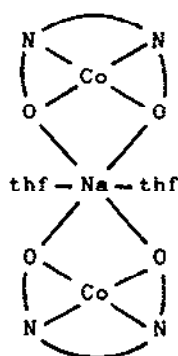


(88); [229]

Na...O = 231.2-234.1pm

Na...N = 275.7, 276.6pm

Figure 7 continued



(90): [230]

Na...O(salen)  $\approx$  239.3-256.3pmNa...O(thf)  $\approx$  248.6, 252.9pm

(91): [231]

Na(1)...O(salen) = 227, 240pm

Na(1)...O(salendpk) = 228, 230, 269pm

Na(2)...O(salen) = 223, 234pm

Na(2)...O(salendpk) = 229, 231pm

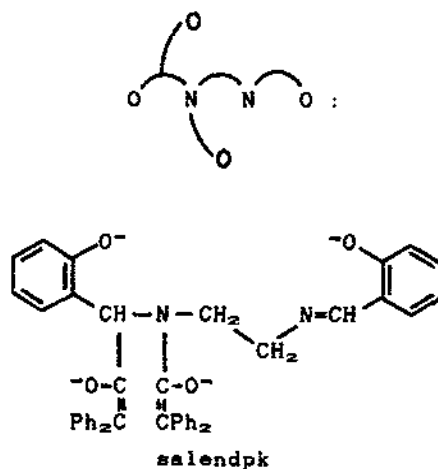
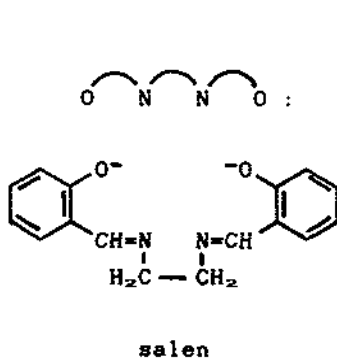
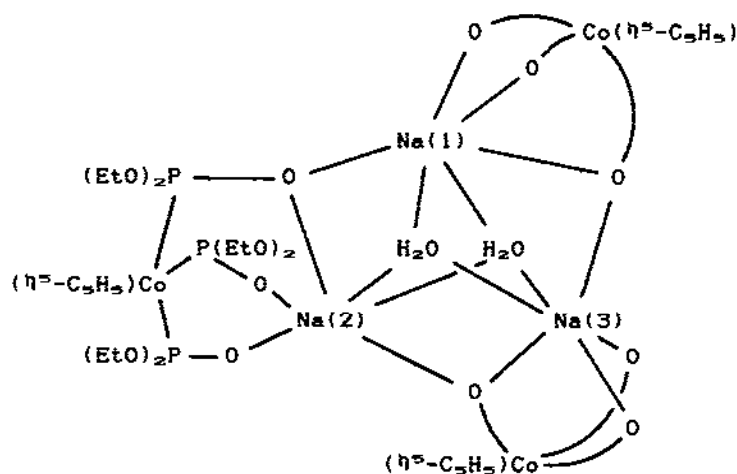
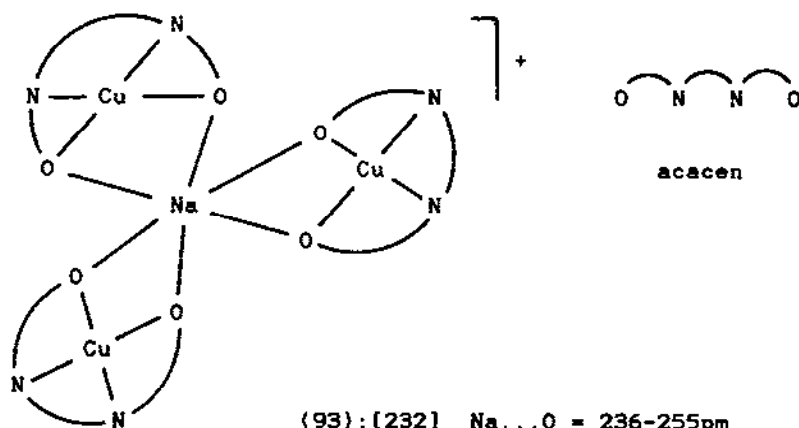


Figure 7 continued



Only one of the anionic oxygen tripod ligands,  
 $[(\eta^5\text{-C}_5\text{H}_5)\text{Co}\{\text{OP}(\text{OEt})_2\}_3]^-$ , is shown in full.

(92); [233] Na...O(bridging) = 234pm )  
 Na...O(axial) = 228pm ) (mean values)  
 Na...O(equatorial) = 236pm )  
 Na...Na = 327.7, 329.0, 343.1pm



(93); [232] Na...O = 236-255pm

gives the complexes  $[H(tmtaa)Na(thf)_3]$ . [228] Structural analysis of the Na-Fe complex (87) shows both metal atoms to be associated with the macrocyclic ligand; [228] the Fe atom is located in the  $N_4$  square planar coordination plane whilst the Na atom is coordinated by two of the nitrogen atoms of the macrocyclic ligand and three thf molecules. The rather long Na...N distances (277.5, 280.1pm), however, are indicative of a contact ion pair interaction between the  $[Na(thf)_3]^+$  cations and the  $[Fe(tmtaa)]^-$  anion. [228] A similar interaction must occur between the  $[Na(thf)_3]^+$  and  $[Co(tpp)]^-$  ions in the Na...Co complex  $[Na(thf)_3]_2[Co(tpp)]^{2-}$  (tp = tetraphenylporphyrin dianion) (88) [229] in which the two crystallographically related  $[Na(thf)_3]^+$  cations are located at somewhat extended distances from the nitrogen atoms of the porphyrin ligand (275.7, 276.6pm), which also provide square planar coordination for the Co atom. The latter complex, which is isomorphous with the recently reported [236] Na-Fe complex,  $[Na(thf)_3]_2[Fe(tpp)]^{2-}$ , was also prepared by single electron reduction, in the case of  $[Co(tpp)]$ , using sodium metal in thf. [229]

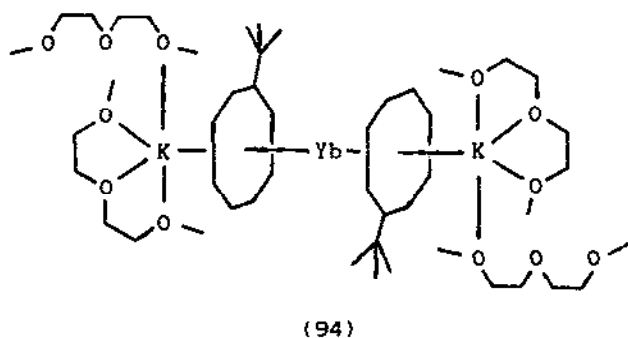
Reaction of the bifunctional complex  $[Co(salen)Na(thf)_n]$  (89) with the parent complex  $[Co(salen)]$  gives the Na-Co complex (90) [230] in which two identical  $[Co(salen)]$  units act as bidentate equatorial ligands for the Na atom which completes its coordination sphere with two thf molecules located trans to each other. Treatment of (89) with diphenylketene in a 1:1 molar ratio affords a second more complicated Na-Co complex (91) [231] in which two Na atoms bridge two intact  $[Co(salen)]$  moieties to a third cobalt(II) unit where the metal is surrounded by a hexadentate (salendpk) ligand resulting from the addition of two diphenylketene molecules across one of the two imino ( $>C=N-$ ) functionalities of the salen ligand.

A fourth Na-Co complex (92) has been crystallised from acetone. [233] It forms a trimeric aggregate in which a triangle of Na atoms is asymmetrically bicapped by two water molecules. Each Na atom is also coordinated to the three oxygen donor atoms of the  $[(\eta^3-C_3H_5)Co(OP(OEt)_2)_3]^-$  anionic tripod ligands; of these one bridges two Na atoms, while the others are located in axial and equatorial positions of the  $Na_3$  triangle. [233]

Demetallation of  $[Cu(acacen)]$  by PhSNa produced the ion separated dithiocuprate(I)  $[(Cu(acacen)_3Na)]^-[Cu(SPh)_2]^-$ . [232]

In the structure of the cation (93), three  $[\text{Cu}(\text{acacen})]$  moieties chelate the Na atom giving the latter a pseudo-octahedral coordination geometry. This is thought to be the first example of a coordination cage for  $\text{Na}^+$  provided by three metal complex units.[232]

The molecular structure of the tetrakis (diglyme) adduct of dipotassium bis(*t*-butyl[8]annulene)ytterbate(III) (94) is complex.[234] The Yb atom is sandwiched between the two parallel

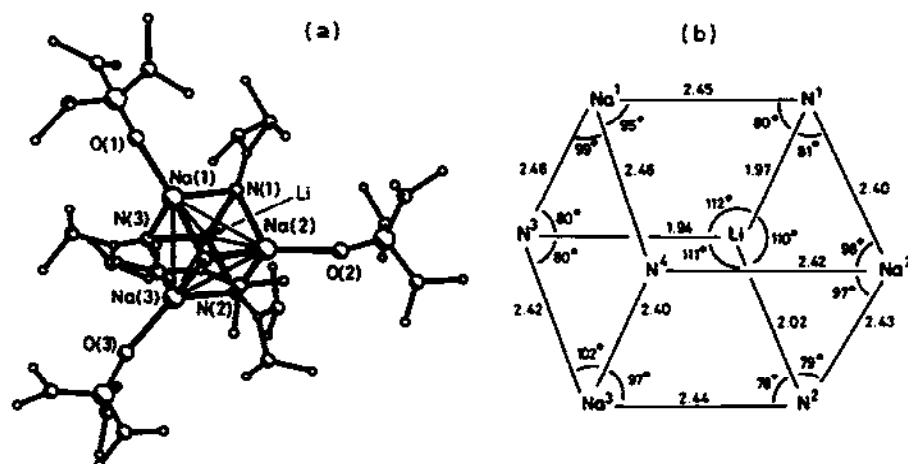


[8] annulene rings ( $\text{Yb} \dots \text{C}(\text{average}) = 277\text{pm}$ ). The K atoms cap the other sides of the rings ( $\text{K} \dots \text{C}(\text{average}) = 308\text{pm}$ ) and are also coordinated by the three oxygens of a chelating diglyme molecule ( $\text{K}(1) \dots \text{O} = 275.1\text{--}305.6\text{pm}$ ;  $\text{K}(2) \dots \text{O} = 276.2\text{--}302.0\text{pm}$ ) and a single oxygen of the other diglyme molecule ( $\text{K}(1) \dots \text{O} = 286.5\text{pm}$ ;  $\text{K}(2) \dots \text{O} = 285.7\text{pm}$ ). [234]

#### 1.4.9 Lithium Derivatives

A veritable explosion in interest in lithium chemistry has occurred during the period of this review, with more than sixty abstracted papers, necessitating further division of this subsection. A high proportion of these papers describe the synthesis and structural characterisation either in the solid state (from single crystal xrd data) or in solution (from multi-nuclear n.m.r. spectroscopic data) of novel lithiated derivatives. Structural chemistry predominates because the tendency for lithium to use its four valence shell atomic orbitals as fully as possible results in a rich diversity of molecular types varying from dodecameric, hexameric and tetrameric aggregates through trimeric and dimeric ring systems to monomeric moieties; the subsection has

been divided accordingly. The first example of a mixed alkali metal organonitrogen molecular cluster,  $\text{LiNa}_3[\text{O}=\text{P}(\text{NMe}_2)_3]_3^- [\text{N}=\text{C}(\text{NMe}_2)_2]_4$  (**95**) has been reported by Wade et al.[237] Produced by sequentially adding  $\text{HN}=\text{C}(\text{NMe}_2)_2$  (2 equiv.) and  $\text{O}=\text{P}(\text{NMe}_2)_3$  (excess) to a mixture of  $^n\text{BuLi}$  (1 equiv.) and  $^n\text{BuNa}$  (1 equiv.) in hexane, (**95**) has a  $\text{LiNa}_3\text{N}_4$  cubane-type structure (Figure 8) with each of the  $\text{O}=\text{P}(\text{NMe}_2)_3$  ligands terminally attached through its oxygen to a Na atom. Although the Li atom does not



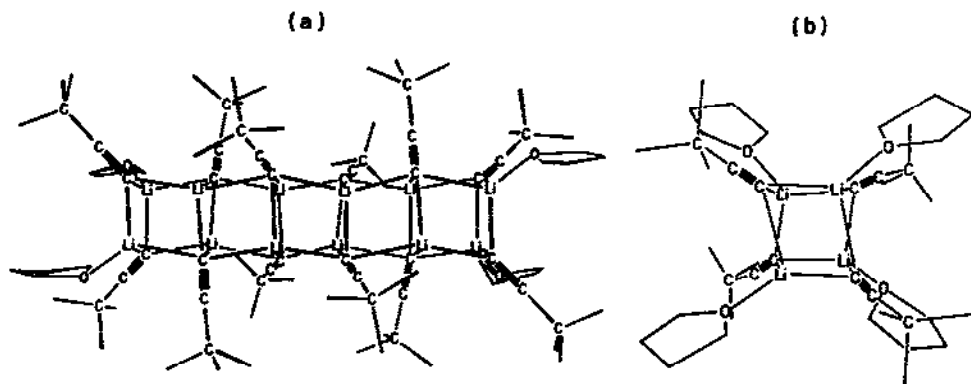
**Figure 8.** The molecular structure of  $\text{LiNa}_3[\text{O}=\text{P}(\text{NMe}_2)_3]_3^- [\text{N}=\text{C}(\text{NMe}_2)_2]_4$  (a) with selected interatomic distances (in Å) and angles (in °) (b) (reproduced by permission from J. Chem. Soc., Chem. Commun., (1986)1740).

have a terminal moiety, each of the adjacent guanidino groups has a methyl group which leans perceptibly towards the Li atom suggesting three  $\text{Li}\cdots\text{H}$  interactions.[237]

#### 1.4.9.1 Hexamers and Higher Oligomers

The largest structurally characterised organolithium aggregate described so far is the dodecamer  $[(^n\text{BuC}\equiv\text{CLi})_{12}(\text{thf})_4]$  (**96**) reported by Weiss, Schleyer et al.[238] to form from the tetramer  $[(^n\text{BuC}\equiv\text{CLi})_4(\text{thf})_4]$  (**97**) by thf cleavage. Since the structure of the dodecamer (**96**) (Figure 9a) can be envisaged to

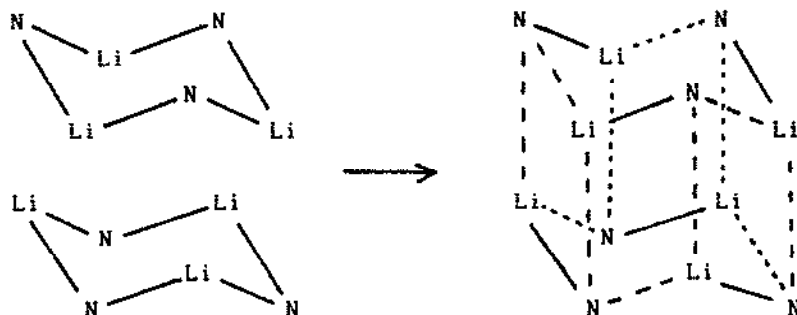




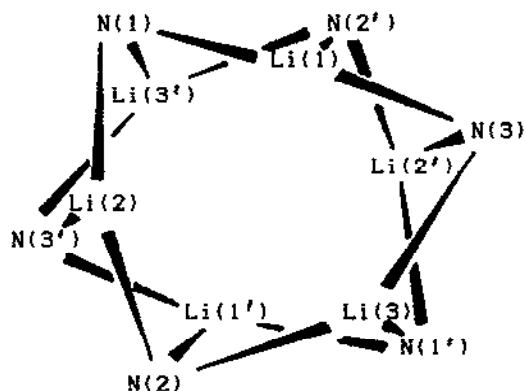
**Figure 9.** Crystal structure of (a)  $[({}^t\text{BuC}\equiv\text{CLi})_{12}(\text{thf})_4]$  and (b)  $[({}^t\text{BuC}\equiv\text{CLi})_4(\text{thf})_4]$ . The centres of both the dodecamer and the tetramer lie on 2-fold axes perpendicular to the plane of projection (reproduced by permission from *Angew. Chem., Int. Ed. Engl.*, 26(1987)587).

result from linear coupling of three cubane-like units of the tetramer (97) (Figure 9b), the aggregation being terminated by thf donors at each end, it is suggested that these aggregates represent a novel structural principle according to which the dimeric ring  $[({}^t\text{BuC}\equiv\text{C})_2\text{Li}_2]$  is stacked into aggregates  $[({}^t\text{BuC}\equiv\text{C})_2\text{Li}_2]_n$  ( $n = 1, 2, 3, \dots$ ). [238]

A similar ring-stacking principle has been proposed by Snaith, Wade et al. [239-241] to account for the structures of the hexameric iminolithium clusters  $(\text{RR}'\text{C}=\text{NLi})_6$  ( $\text{R}' = \text{Ph}$ ,  $\text{R} = {}^t\text{Bu}$  or  $\text{Me}_2\text{N}$ ;  $\text{R}' = \text{R} = \text{Me}_2\text{N}$  or  ${}^t\text{Bu}$ ). All four compounds have remarkably similar solid state structures based on slightly folded chair-shaped  $\text{Li}_6$  cores, the six smaller (isosceles)  $\text{Li}_3$  triangular faces of which are bridged by three electron imino ligands through electron deficient bonds. The hexameric structures are thought to be formed by stacking of two slightly puckered trimeric rings  $(\text{RR}'\text{C}=\text{NLi})_3$  brought together in a staggered conformation (scheme 7). The projection of the  $\text{Li}_6$  core of  $[\text{Me}_2\text{N}(\text{Ph})\text{C}=\text{NLi}]_6$  perpendicular to its pseudo-three fold axis (98) clearly shows the stacking principle.



Scheme 7



Interatomic distances/pm

Li...N = 196.1-208.1

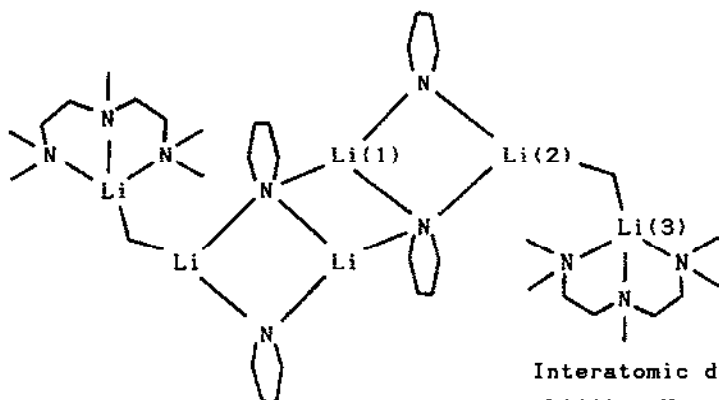
N...N = 317.2-318.7

Li...Li = 247.2-248.7

(98)

Similar folded chair  $\text{Li}_6$  cores are found in the hexameric structures of  $[\text{Me}_3\text{SiCH}_2\text{Li}]_6$  (99)[242] and  $[\text{t-BuC(=CH}_2\text{)OLi}]_6$  (100);[243] as for the hexameric iminolithium clusters neither structure has an exocyclic ligand, the electronic structure of the Li atom of (100) being satisfied by an interaction with the  $\pi$  system of the  $\text{CH}_2=\text{C}<$  fragment of the enolate anion. The hexameric structures of  $[\text{PhSi}\{\text{N}(\text{t-Bu})\text{Li}\}_3]_2$  (101)[244] and  $[\text{H}_2\text{C}(\text{CH}_2)_3\text{NLi}]_6(\text{pmdeta})_2$  (102),[245] however, do not fall into this pattern. The molecular structure of (101)[244] is dictated by the restricted geometry of the trianion. It is based on an  $\text{Li}_6$  trigonal antiprism centered on the  $\bar{1}$  symmetry sites of the  $\text{P}\bar{1}$  space group; six  $\text{Li}_3$  faces are bridged by nitrogens, the other two by silicons, the overall symmetry approaching  $\bar{3}m$  ( $\text{D}_{3d}$ ). That of (102)[245] is a ladder structure consisting of two attached

$\text{Li}_2\text{N}_2$  rings (alternatively four Li-N rungs) with two terminal LiN units complexed by pmdeta so preventing further association. Cryoscopic and  $^7\text{Li}$  n.m.r. spectroscopic studies of arene solutions of (102) imply that the ladder framework can be extended suggesting that similar compounds  $[\text{RR}'\text{NLi}, x \text{ donor}]_n$  but of various ladder lengths should be preparable. [245]



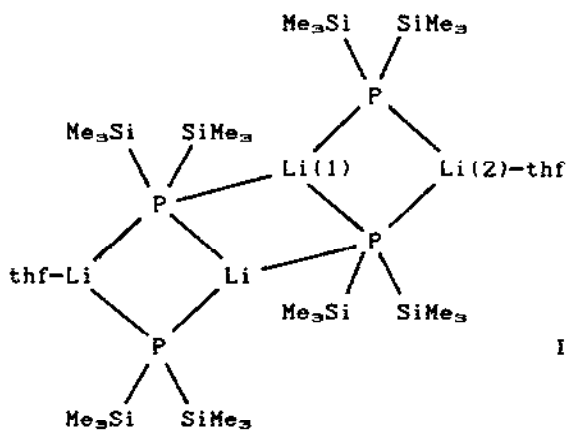
(102)

Interatomic distances/pm.

Li(1)...N = 193-204

Li(2)...N = 201-212

Li(3)...N = 197-221



(103)

Interatomic distances/pm

Li(1)...P = 244-264

Li(2)...P = 248, 255

Li(2)...O = 189

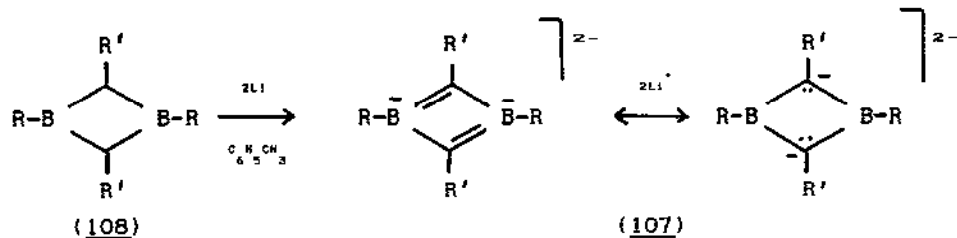
#### 1.4.9.2 Tetramers

The tetrameric decomposition product  $[(\text{Me}_3\text{Si})_2\text{PLi}]_4(\text{thf})_2$  (103), of the dimer  $[(\text{Me}_3\text{Si})_2\text{PLi}]_2(\text{thf})_4$  first prepared by Fritz and Holderich, [246] has been shown by Lappert et al. [247] to adopt a ladder framework similar to that of (102). It comprises two attached  $\text{Li}_2\text{P}_2$  rings (alternatively four Li-P rungs), with thf molecules complexing the terminal Li atoms thus preventing extension of the latter structure. Hence, the two terminal Li atoms are coordinated by two anions and one thf molecule, while the two internal Li atoms are surrounded by three anions.

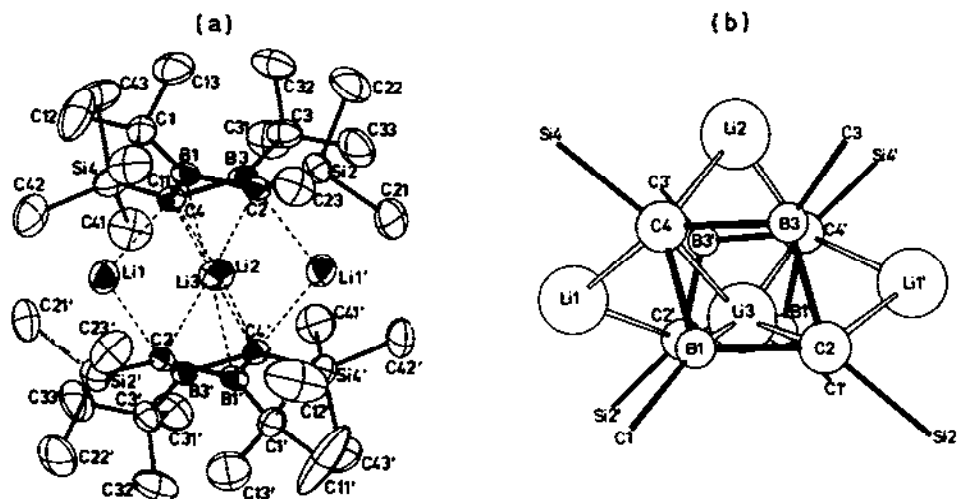
Cubane type tetrameric structures have been found in the solid state structures of  $[(^t\text{BuC}\equiv\text{CLi})_4(\text{thf})_4]$  (97), [238]  $[\text{Me}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Li}]_4$  (104), [248] and  $[(\text{Me}_3\text{Si})\text{CH}(\text{S}(\text{O})(\text{NSiMe}_3)\text{Ph})\text{Li}]_4$  (105), [249]. That of (97) [238] is shown in Figure 9b, it is based on a  $\text{Li}_4\text{C}_4$  core ( $\text{Li}\dots\text{C} = 217\text{--}229\text{pm}$ ;  $\text{Li}\dots\text{Li} = 259\text{--}278\text{pm}$ ) with thf molecules completing the tetrahedral coordination geometry of the Li atom ( $\text{Li}\dots\text{O} = 192, 199\text{pm}$ ). A similar  $\text{Li}_4\text{C}_4$  core ( $\text{Li}\dots\text{C} = 224.0\text{--}227.6\text{pm}$ ) occurs in the structure of (104); [248] in this case, however, the fourth coordination position of the Li atom is occupied by a pendant  $\text{NMe}_2$  group ( $\text{Li}\dots\text{N} = 206.2, 206.7\text{pm}$ ). A cubane type  $\text{Li}_4\text{O}_4$  skelteton ( $\text{Li}\dots\text{O} = 193.4\text{--}240.8\text{pm}$ ) lies at the centre of the structure of (105); [249] each Li atom attains penta-coordination through the carbon ( $\text{Li}\dots\text{C} = 243.0\text{pm}$ ) and nitrogen ( $\text{Li}\dots\text{N} = 211.3\text{pm}$ ) atoms of separate sulphonimidoyl anions. The carbon and nitrogen atoms of the four anions are anchimerically coordinated to the Li atoms, thereby forming a chain of eight 4-membered O-S-C-Li and O-S-N-Li rings alternately annelated to the central  $\text{Li}_4\text{O}_4$  cube. [249]

A somewhat irregular  $\text{Li}_4\text{N}_4$  core occurs in the structure of the tetramer,  $[\text{Me}_2\text{Si}((^t\text{Bu})\text{NLi})_2]_2$  (106); [244] the distortion arises because of the restricted geometry of the dianion. In reality, the molecular structure of (106) is based on a  $\text{Li}_4$  bisphenoid, the two pairs of  $\text{Li}_3$  faces being linked by the two N-Si-N bridges ( $\text{Li}\dots\text{N} = 200.3, 203.6\text{pm}$ ), giving approximate  $\bar{4}2m(D_{2d})$  symmetry to the molecule.

The dilithium salt of the 1,3-diboratacyclobutadiene (107), prepared by reduction of the 1,3-dihydro-1,3-diborete (108) with lithium powder in toluene (scheme 8), crystallises as a novel dimeric sandwich compound with a  $\text{Li}_4$  layer (Figure 10). [250]



**Scheme 8;** R = -C(CH<sub>3</sub>)<sub>3</sub>; R' = -Si(CH<sub>3</sub>)<sub>3</sub>



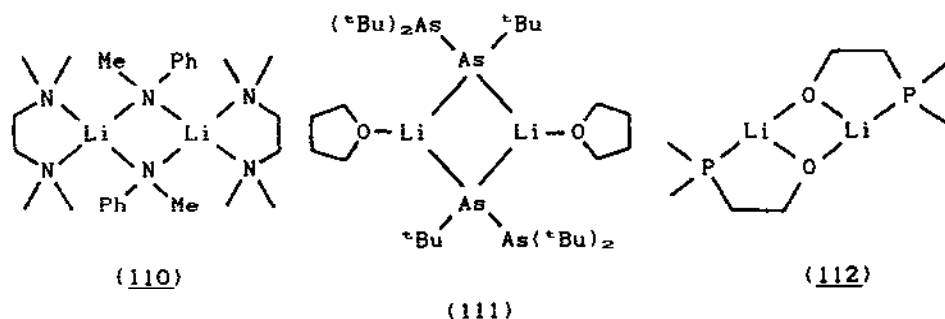
**Figure 10.** Projections of the dimeric structure of the dilithium salt of a diboratacyclobutadiene (a) in the direction of the pseudo-C<sub>2</sub> axis and (b) in the direction of the "sandwich axis". Interatomic distances (averaged over both halves of the dimer) Li(1)...Li(3) = 233, Li(2)...Li(3) = 247, Li(1)...Li(2) = 313, Li(1)...C(2) = 227.6, Li(1)...C(4) = 234.6, Li(2)...C(4) = 225.4, Li(3)...C(2) = 209.9, Li(3)...C(4) = 219.6, Li(3)...B(1) = 223.7, Li(3)...B(3) = 245.5pm (reproduced by permission from *Angew. Chem., Int. Ed. Engl.*, 25(1986)1111).

1.4.9.3 Trimers

The only lithium derivative with a trimeric geometry to be structurally characterised within the period of this review is  $[(\text{Me}_3\text{Si})_2\text{CH})_2\text{Li}]_3$  (109), [251] prepared by reaction of lithium with  $(\text{Me}_3\text{Si})_2\text{CH})_2\text{AsCl}$  in  $\text{Et}_2\text{O}$  at 298K. The  $\text{Li}_3\text{As}_3$  ring has a boat conformation with an average  $\text{Li}\dots\text{As}$  interatomic distance of 260(4)pm.

1.4.9.4 Dimers

The synthesis of a large number of dimeric lithium-containing complexes has been described; the favoured preparative method was direct lithiation using a metallating agent such as  $^t\text{BuLi}$ . Single crystal xrd structural analysis has shown that the majority are based on  $\text{Li}_2\text{X}_2$  ( $\text{X}$  = carbon, [252] nitrogen, [253-258] phosphorus, [247, 259, 274] arsenic [260, 261] and oxygen [262-265]) rings, the Li atom coordination geometry being extended to either distorted trigonal planar or distorted tetrahedral by inclusion of either solvent molecules typically thf,  $\text{Et}_2\text{O}$  or tmeda (e.g. (110), (111)) or intramolecularly bonded functional groups (e.g., (112)). Those complexes with structures exemplified by



(110, 111, 112) are listed in Table 11 together with pertinent structural details. Three slightly more complicated structures based on  $\text{Li}_2\text{X}_2$  rings are those of  $[(\text{H}_2\text{C}=\text{C}(^t\text{Bu})\text{N}(\text{Ph})\text{Li})_2(\text{Et}_2\text{O})_2]$  (113), [266]  $[(\text{Me}_2\text{N}\cdot\text{N}\cdot\text{C}(\text{CH}_2)_4\text{C}\cdot\text{CH}(\text{OMe})\text{OLi})_2(\text{thf})_2]$  (114) [256] and  $[(\text{Ph}_2\text{PCH}_2\text{C}(^t\text{Bu})_2\text{OLi})_2(^t\text{Bu})_2\text{C}=\text{O}]$  (115), [263]. The Li atom in the centrosymmetric dimeric structure of (113) [266] is coordinated to the two nitrogens of the  $\text{Li}_2\text{N}_2$  ring ( $\text{Li}\dots\text{N}$  = 200.0, 207.6pm) and to two benzene carbons ( $\text{Li}\dots\text{C}$  = 243.7, 266.2pm) and to the ether oxygen ( $\text{Li}\dots\text{O}$  = 193.7pm). The two Li atoms in

**Table 11.** Structural details for diverse dimeric lithium complexes based on  $\text{Li}_2\text{X}_2$  rings.

Molecule	$\text{Li}_2\text{X}_2$ ring	$r(\text{Li} \cdots \text{X})$ pm.	Li C.N	Exocyclic ligand(Y)	$r(\text{Li} \cdots \text{Y})$ pm.	Ref
Solvated Lithium Derivatives:						
$[(\text{PhN}(\text{CH}_3)\text{CLi})_2(\text{tmeda})_2]$	$\text{Li}_2\text{C}_2$	219.1, 218.4	4	tmeda	219.9, 230.4	252
$[(\text{Me}_3\text{Si})_2\text{NLi}]_2(\text{thf})_2]$	$\text{Li}_2\text{N}_2$	202.5, 202.5	3	thf	188.2	253
$[(\text{Me}_2\text{Si} \cdot \text{NH} \cdot \text{SiMe}_2 \cdot \text{NH} \cdot \text{SiMe}_2 \cdot \text{NLi})_2(\text{thf})_2]^+$	$\text{Li}_2\text{N}_2$	203.5(av)	3	thf	192.6(av)	254
$[(\text{Me}_2\text{Si} \cdot \text{N}(\text{SiMe}_3) \cdot \text{SiMe}_2 \cdot \text{NH} \cdot \text{SiMe}_2 \cdot \text{NLi})_2(\text{thf})_2]$	$\text{Li}_2\text{N}_2$	201.7, 206.1	3	thf	191.2	255
$[(\text{Ph}_2\text{NLi})_2((^i\text{Pr})_2\text{NH})_2]$	$\text{Li}_2\text{N}_2$	201.2, 207.8	3	$(^i\text{Pr})_2\text{NH}$	212.4	256
$[(\text{Ph}(\text{Me})\text{NLi})_2(\text{tmeda})_2]$	$\text{Li}_2\text{N}_2$	208.2, 208.2	4	tmeda	229.6, 229.6	257
$[(\text{PhCH}:\text{C}:\text{NLi})_2(\text{tmeda})_2]$	$\text{Li}_2\text{N}_2$	204(av)	4	tmeda	205(av)	258
$[(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2\text{PLi}]_2(\text{Et}_2\text{O})_2]^+$	$\text{Li}_2\text{P}_2$	249.8(av)	3	$\text{Et}_2\text{O}$	190.8(av)	259
$[(\text{Ph}_2\text{PLi})_2(\text{tmeda})_2]^+$	$\text{Li}_2\text{P}_2$	261(av)	4	tmeda	213.8(av)	274
$[(\text{Me}_3\text{Si})_2\text{PLi}]_2(\text{thf})_4]$	$\text{Li}_2\text{P}_2$	262, 262	4	thf	192, 203	247
$[(^t\text{Bu})_2\text{As}(^t\text{Bu})\text{AsLi}]_2(\text{thf})_2]$	$\text{Li}_2\text{As}_2$	258, 258	3	thf	189	260
$[(\text{Ph}_2\text{AsLi})_2(\text{Et}_2\text{O})_4]$	$\text{Li}_2\text{As}_2$	270.8, 275.7	4	$\text{Et}_2\text{O}$	197.4, 199.7	261
$[(\text{SiMe}_3)_3\text{C} \cdot \text{SiMe}_2 \cdot \text{OLi}]_2(\text{thf})_2]$	$\text{Li}_2\text{O}_2$	181(av)	3	thf	206(av)	262
$[(\text{Ph}(\text{Me})\text{C}:\text{S}(\text{Ph})\text{OLi})_2(\text{tmeda})_2]$	$\text{Li}_2\text{O}_2$	192(av)	4	tmeda	213(av)	264

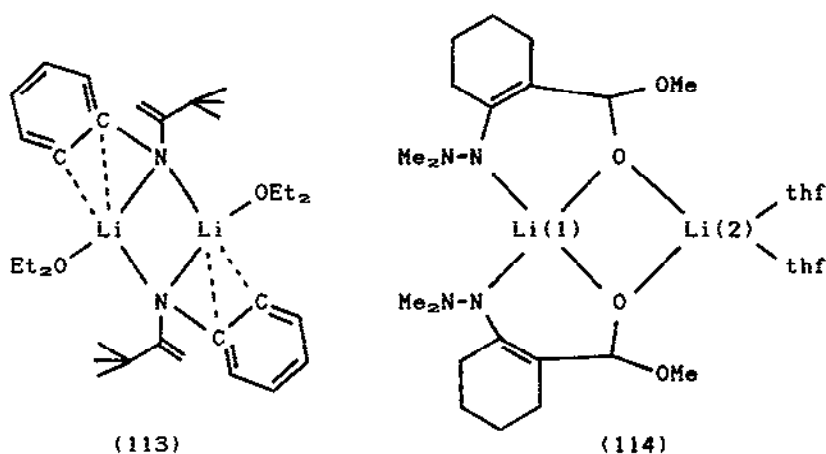
Table 11 continued:

Intramolecularly coordinated Lithium Derivatives:

$[\text{Me}_2\text{PCH}_2\text{C}(\text{tBu})_2\text{OLi}]_2$						
$\text{Li}_2\text{O}_2$	181,176	3	$-\text{PMe}_2$	250		263
$[\text{Ph}_2\text{PCH}_2\text{C}(\text{tBu})_2\text{OLi}]_2$						
$\text{Li}_2\text{O}_2$	178.7,179.7	3	$-\text{PPh}_2$	265.1		263
$[(\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2)_3\text{NLi}]_2^{2+}$						
$\text{Li}_2\text{O}_2$	196,208	4	$-\text{P}(\text{O})\text{Ph}_2$	189,192		265

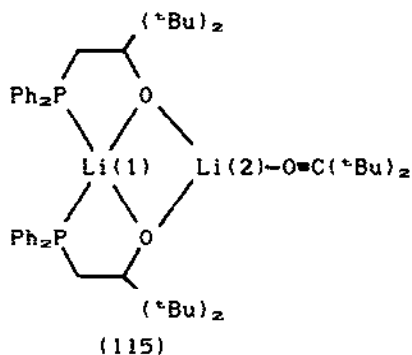
\* Two crystallographically independent dimers are present in the structure; average data are quoted.

the structure of (114) although located on a 2-fold symmetry axis, are chemically distinct; [256] Li(1) is coordinated by the two oxygens of the  $\text{Li}_2\text{O}_2$  ring ( $\text{Li}\dots\text{O} = 191.9\text{pm}$ ) and the two nitrogens of the hydrazone residue ( $\text{Li}\dots\text{N} = 202.3\text{pm}$ ); Li(2) is encapsulated by the two oxygens of the  $\text{Li}_2\text{O}_2$  ring ( $\text{Li}\dots\text{O} = 192.7\text{pm}$ ) and two thf molecules ( $\text{Li}\dots\text{O} = 192.9\text{pm}$ ). The coordination polyhedra of the Li atoms are both flattened tetrahedra. A similar arrangement



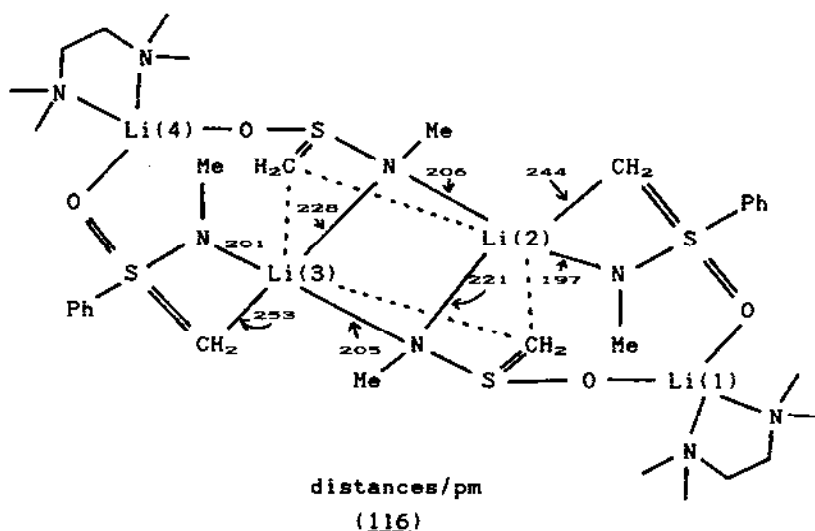
pertains in the structure of (115); [263] Li(1) is coordinated by the two oxygens of the  $\text{Li}_2\text{O}_2$  ring ( $\text{Li}\dots\text{O} = 180,187\text{pm}$ ) and the two phosphorus atoms of the derivitised alkoxide anion ( $\text{Li}\dots\text{P} =$



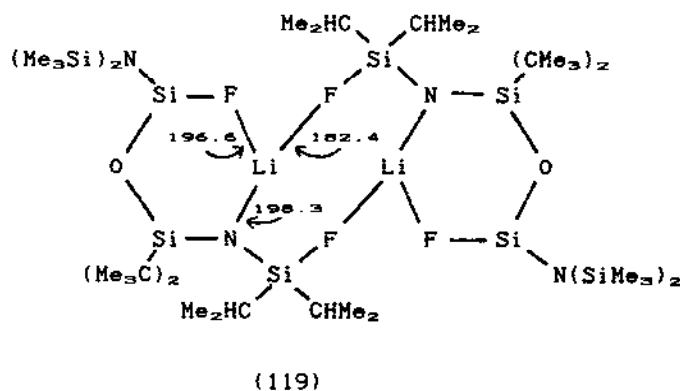
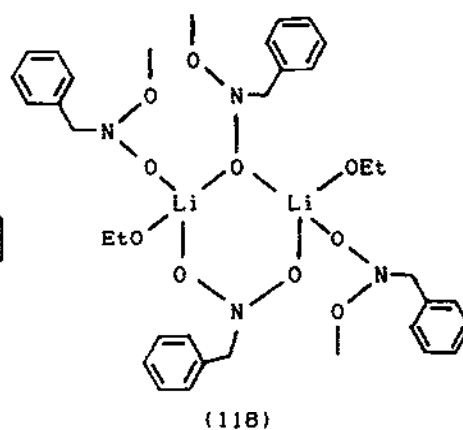
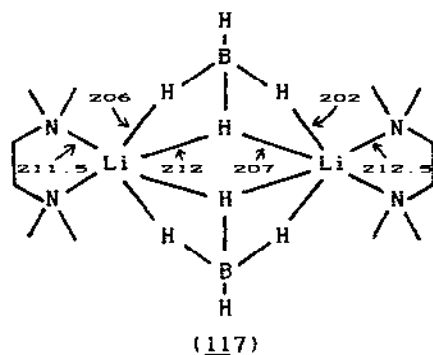


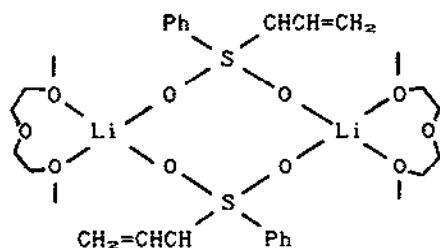
259,263pm) in a distorted tetrahedral array; Li(2) is surrounded by the two oxygens of the  $\text{Li}_2\text{O}_2$  ring ( $\text{Li}\cdots\text{O} = 180,183\text{pm}$ ) and by the oxygen of the solvating ketone ( $\text{Li}\cdots\text{O} = 197\text{pm}$ ) in a trigonal planar geometry.

The structure of the pseudo-tetrameric complex (116) is also based on a  $\text{Li}_2\text{X}_2$  ring.[267] The two Li atoms in the  $\text{Li}_2\text{N}_2$  core are coordinated by the nitrogen atoms of the bridging sulfoximide anions and the nitrogen and carbon atoms of the other two anions; they also have a relatively remote contact with the methylene group of the bridging anion ( $\text{Li}(2)\cdots\text{C} = 324,337$ ;  $\text{Li}(3)\cdots\text{C} = 303,334\text{pm}$ ). The other two Li atoms are encapsulated by two oxygen atoms of separate anions ( $\text{Li}\cdots\text{O}(\text{average}) = 190\text{pm}$ ) and the two nitrogen atoms of the tmeda ligand ( $\text{Li}\cdots\text{N}(\text{average}) = 210\text{pm}$ ). [267]

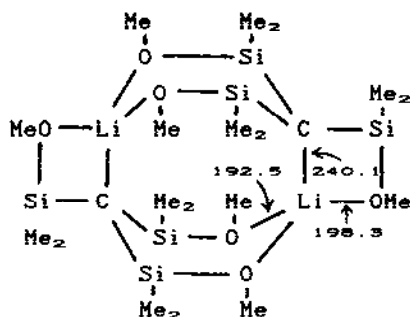


Unusual bridges occur in the dimeric structures of  $[\text{LiBH}_4 \cdot \text{tmeda}]_2$  (117), [268]  $[(\text{EtOLi})_2(\text{PhCH}_2\text{NO}_2)_2]_n$  (118), [269]  $[(\text{Me}_3\text{Si})_2\text{NSi}(\text{Me})(\text{F})\text{O}(\text{CMe}_3)_2\text{N}(\text{Li}) \cdot \text{Si}(\text{CHMe}_2)_2\text{F}]_2$  (119), [270]  $[(\text{CH}_2=\text{CH} \cdot \text{CH} \cdot \text{S}(\text{Ph})\text{O}_2\text{Li})_2(\text{diglyme})_2]$  (120) [271] and  $[(\text{MeO} \cdot \text{SiMe}_2)_3\text{CLi}]_2$  (121), [272]. The centrosymmetric dimer (117) [268] contains both doubly and triply bridging hydrogen atoms; each  $\mu_2, \eta^3\text{-BH}_4$  group bonds to two Li atoms through one  $\mu_2\text{-H}$  atom apiece and through one  $\mu_3\text{-H}$  atom. The Li coordination sphere is completed by the nitrogens of the tmeda molecule.

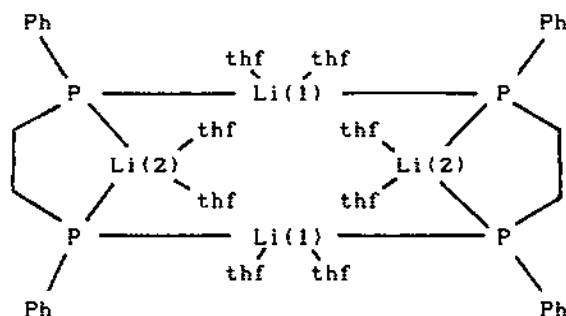




(120)



(121)



(122)

distances/pm

M.O. calculations at the 6-31G level[268] on  $[\text{LiBH}_4]_2$  and its adducts with  $\eta^2$ - and  $\eta^3$ - $\text{BH}_4$  geometries show how their stabilities reflect the number of  $\text{Li}\cdots\text{H}$  contacts, whilst illustrating the inadequacies of  $\text{LiHB}$  and  $\text{Li}_2\text{HB}$  3- and 4-centre bond structures for such compounds.

The Li atoms in (118)[269] are bridged by two nitronate anions, one using its O-N-O moiety, the other a single oxygen to give a Li-O-N-O-Li-O 6-membered ring. The distorted tetrahedral geometries of the Li atoms are completed by the free oxygen of the second nitronate anion giving a ribbon-like framework of annelated 6-membered rings, and the ethanol molecule ( $\text{Li}\cdots\text{O} = 191.9\text{--}197.9\text{pm}$ ). The bridges in the centrosymmetric structure of (119)[270] comprise the  $-\text{N}^--\text{Si}(\text{CHMe}_2)_2\text{F}$  moieties of the  $[(\text{Me}_2\text{Si})_2\text{NSi}(\text{F})\text{OSiN-Si}(\text{CHMe}_2)_2\text{F}]^-$  anions. The trigonal planar coordination polyhedron of the Li atom is completed by the other

fluorine atom. Hence, 3 rings exist in the structure, two Li-F-Si-O-Si-N 6-membered rings and a single Li-F-Si-N-Li-F-Si-N 8-membered ring. A similar 8-membered ring occurs in the centrosymmetric structure of (120);[271] in this case, a Li-O-S-O-Li-O-S-O ring is formed by sulphonyl bridging of the Li atoms, the 5-fold distorted trigonal bipyramidal geometries of which are completed by the three oxygens of the diglyme molecules.

The structure of (121)[272] is essentially that of a cage dimer. Each of the component  $(\text{MeOSiMe}_2)_3\text{CLi}$  molecules in the dimer, which has  $C_{2h}$  point group symmetry, has one of its own -OMe groups coordinated to its own Li atom, giving a planar 4-membered ring, and its two remaining -OMe groups coordinated to the other Li atom giving two 6-membered rings in boat conformations. There is considerable distortion from tetrahedral in the Li atom coordination cage.[272]

Reaction of alkane-1,n-diylbis(diphenylphosphine) with lithium in thf with low power sonication gives the diphosphide resulting from cleavage of a P-acyl bond at each end of the chain.[273] The structure of the ethane derivative (122) is very unusual:[273] it exists as a centrosymmetric dimer in which the P and Li atoms alternate in an 8-membered ring with no systematic or significant variation in the Li...P interatomic distance (257.3pm average). There are two types of Li atom which bridge intramolecularly ( $\text{PLi}(1)\text{P} = 86.9^\circ$ ), and, intermolecularly ( $\text{PLi}(2)\text{P} = 113.5^\circ$ ), respectively; the Li(1) atoms lie out of the plane defined by the remaining  $\text{P}_4\text{Li}_2$  system giving the 8-membered ring the appearance of an elongated chair.[273]

#### 1.4.9.5 Monomers and Polymers

Single crystal xrd data have been collected and analysed for 19 monomeric (or polymeric) lithium derivatives. The majority are stabilised by coordination of the Li atom by both the anions and solvate molecules such as thf,  $\text{Et}_2\text{O}$ , tmeda, pmdeta and diacetamide; for the remainder, stability is generated by encapsulation of the Li atom by a polydentate ligand. Several lithium diorgano-amides,[257] phosphides[274,275 and arsenides[261] and a single monoorganophosphide[259] fall into the former category; pertinent structural features are collected in Table 12. The diorganoamide,  $[(\text{Ph}(\text{naphthyl})\text{NLi}).\text{tmeda}]$ , forms "loose dimers";[257] each formally 3-coordinate Li atom interacts

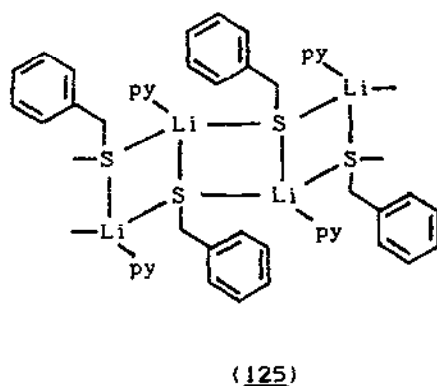
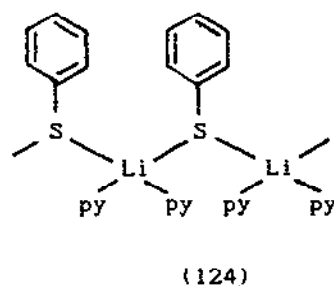
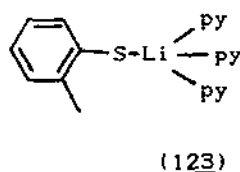
intermolecularly with one ortho and one meta CH unit of the neighbouring phenyl group. Although weakly bound ( $\text{Li}\cdots\text{C} = 312,315\text{pm}$ ), such association is emphasised by the displacement of the pairs of molecules towards each other.[257] Three of the diorganophosphides are polymeric;[275] they consist of chains of alternating cations  $[\text{Li}(\text{thf})_n]^+$  and anions  $[\text{R}_2\text{P}]^-$  held together by  $\text{Li}\cdots\text{P}$  interactions.

**Table 12.** Structural details for diverse monomeric lithium organoamides, organophosphides and organoarsenides.

Compound	Li	R <sub>2</sub> X <sup>-</sup> anion	Solvate	Molecule	Ref	
	C.N.	X	r(Li...X)/pm	X	r(Li...X)/pm	
[Ph(naphthyl)NLi].pmdeta						
	4	N	200	N	218,221,222	257
[Ph(naphthyl)NLi].tmeda						
	3	N	197	N	212,213	257
[(Ph <sub>2</sub> PLi).pmdeta]						
	4	P	256.7	N	209.1,212.6,215.0	274
[(2,4,6-Me <sub>3</sub> C <sub>6</sub> H <sub>2</sub> (H)PLi).(thf) <sub>3</sub> ]						
	4	P	253.3	O	194.9-198.2	259
[(Ph <sub>2</sub> PLi).(thf) <sub>2</sub> ] <sup>∞</sup>						
	4	P	262.9,263.4	O	193.7,198.8	275
[[(C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> PLi).thf] <sup>∞</sup>						
	3	P	245.5,254.3	O	193.6	275
[(Ph <sub>2</sub> PLi).Et <sub>2</sub> O] <sup>∞</sup>						
(1)	3	P	248.6,249.6	O	192.5	275
(2)	3	P	248.3,249.2	O	196.6	275
[(Ph <sub>2</sub> AsLi).(thf) <sub>3</sub> ]						
	4	As	266.0	O	193.1-196.8	261

\* Two crystallographically independent formula units exist in the asymmetric unit.

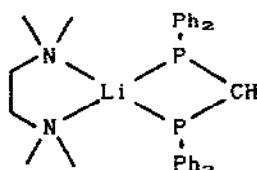
Minor changes in the anion often induce remarkable structural variation. An xrd study[276] of a series of crystalline lithium aryl thiolates, prepared by addition of hexane solutions of  $n\text{BuLi}$  to chilled (253K) toluene solutions of thiol and pyridine, has shown that the  $2\text{-MeC}_6\text{H}_4\text{S}^-$  derivative is a monomer  $[(2\text{-MeC}_6\text{H}_4\text{SLi})\cdot(\text{py})_3]$  (123), the  $\text{C}_6\text{H}_5\text{S}^-$  derivative is a polymer with an infinite  $-(\text{Li-S})-$  chain  $[\text{PhSLi}(\text{py})_2]_\infty$  (124) while the  $\text{C}_6\text{H}_5\text{CH}_2\text{S}^-$  derivative forms an infinite folded ladder polymer with Li-S rungs,  $[(\text{PhCH}_2\text{SLi})\cdot\text{py}]_\infty$  (125); in all three structures the Li atom is tetrahedrally coordinated while the coordination around the sulphur varies from 2 to 4. [276]



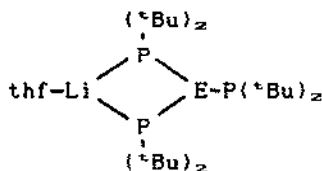
	$r(\text{Li}\dots\text{S})/\text{pm}$	$r(\text{Li}\dots\text{N})/\text{pm}$
(123)	241.2	208.1, 208.1, 208.3
(124)	245.9, 251.3	206.3, 208.5
(125)	245.4-250.8	204.5, 206.8

Four membered  $\text{LiP}_2\text{C}$ ,  $\text{LiP}_2\text{Sn}$  and  $\text{LiP}_2\text{Pb}$  rings have been found as the core of the molecular structures of  $[(\text{Ph}_2\text{P})_2\text{CHLi}\cdot\text{tmeda}]$  (126), [277]  $[((n\text{-Bu})_2\text{P})_3\text{SnLi}\cdot\text{thf}]$  (127) [278] and

$[(^t\text{Bu})_2\text{P})_3\text{PbLi}\cdot\text{thf}]$  (128), [278] The  $\text{LiP}_2\text{C}$  rings in (126), [277] synthesised by lithiation of bis(diphenylphosphino)methane with  $\text{MeLi}$  in  $\text{Et}_2\text{O}$  containing tmeda, exhibit mean  $\text{Li}\dots\text{P}$  and  $\text{Li}\dots\text{C}$

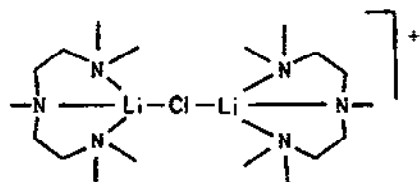


(126)

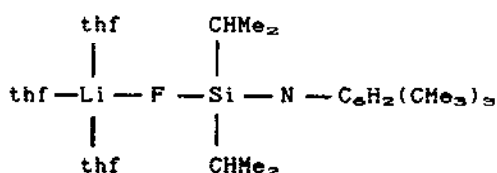
E = Sn (127)E = Pb (128)

distances of 258.2 and 172.2pm, respectively; the tetrahedral geometry of the Li atom is completed by the bidentate tmeda molecule ( $\text{Li}\dots\text{N} = 203.3, 207.2\text{pm}$ ). The "ate" complexes, (127) and (128), [278] obtained by treatment of  $[(^t\text{Bu})_2\text{PLi}]$  with  $\text{SnCl}_2/\text{PbCl}_2$  in thf solution, are isostructural. The  $\text{LiP}_2\text{Sn}/\text{LiP}_2\text{Pb}$  rings have mean  $\text{Li}\dots\text{P}$  and  $\text{Sn/Pb}\dots\text{P}$  distances of 248.5/-251.5 and 268.7/278.6pm, respectively; the trigonal planar coordination sphere of the Li atom is completed by the thf molecule.

Two monomeric complexes containing halogen coordinated Li atoms have been structurally characterised;  $[\{(\text{pmdeta})\text{Li}\}_2\text{Cl}]^+[\text{Li}(\text{C}(\text{SiMe}_3)_3)_2]^-$  (129), [279] and  $[(2,4,6-(\text{Me}_3\text{C})_3\text{C}_6\text{H}_2\text{N}\cdot\text{Si}(\text{tPr})_2\text{FLi})(\text{thf})_3]$  (130), [280]. The former ionic complex, prepared by addition of pmdeata to toluene containing both  $\text{LiCl}$  and  $[\text{Li}(\text{thf})_4]^+[\text{Li}(\text{C}(\text{SiMe}_3)_3)_2]^-$ , contains a centrosymmetric linear chlorine centred cation (131) [279] in which the Li atom is encapsulated by the chlorine ( $\text{Li}\dots\text{Cl} = 217\text{pm}$ ) and the three nitrogens of the tridentate pmdeata ligand in a distorted tetrahedral array. The latter molecular complex (130), [280] obtained by reaction of the parent aminofluorosilane with  $\text{MeLi}$  in



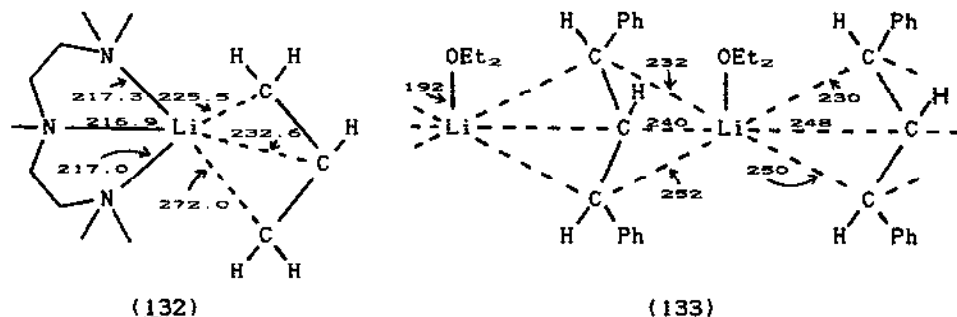
(131)



(130)

thf, contains an approximately tetrahedral Li coordination sphere comprising the fluorine of the anion ( $\text{Li}\cdots\text{F} = 182.2\text{pm}$ ) and three thf molecules.

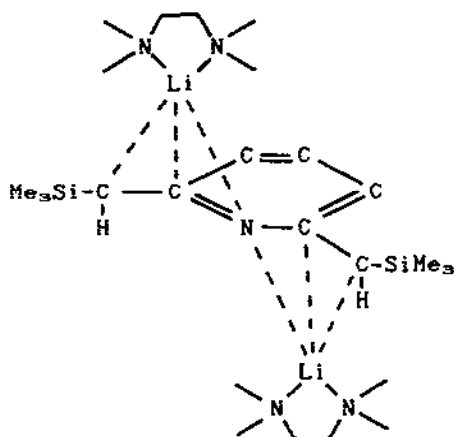
Five organolithium compounds pertinent to this section have been synthesised and structurally characterised: allyllithium, pmdeta adduct (132), [281] 1,3-diphenylallyllithium, ether adduct (133), [282] 2,6-bis(trimethylsilylmethyl)pyridinedilithium, bis(tmeda) adduct (134), [283] 1,2-diboratabenzenelithium, bis(tmeda) adduct (135) [284] and bicyclo[3.2.1]octa-2,6-dienyl lithium, tmeda adduct (136), [285] Although the allyl group in the monomeric structure of (132) [281] is asymmetrically bonded to the Li atom, that in the polymeric structure of (133) [282] lies almost symmetrically above the Li atom. Theoretical ab initio



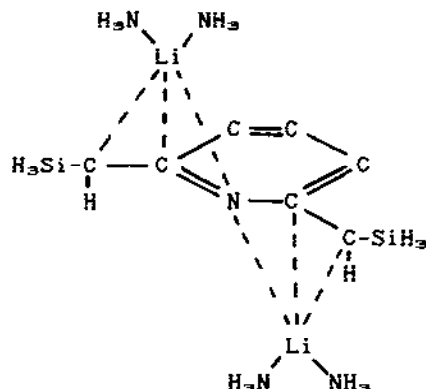
calculations [281] for unsolvated allyllithium using a 3-21G basis set predict a symmetrical disposition of the allyl group above the Li atom with  $\text{Li}\cdots\text{C}$  contacts of 214.1, 209.3 and 214.1 pm. Similar  $\text{h}^3$ -bonding occurs in the structure of (134); [283] it represents a beautiful example of  $\text{C-Li}^+\text{N}^-\text{Li}^+\text{C}^-$  charge communication and confirms the predictions of theoretical calculations undertaken for the simplified model (137), [283]

A triple decker sandwich structure with crystallographic  $\text{C}_2$  symmetry is adopted by (135), [284] The Li atoms lie above and below the diboratabenzene ring slightly shifted from the borons in the direction of the carbons ( $\text{Li}\cdots\text{C} = 226.3\text{-}236.8\text{pm}$ ;  $\text{Li}\cdots\text{B} = 247.2\text{-}255.3\text{pm}$ ). The coordination of the Li atoms is completed by the nitrogens of the bidentate tmeda molecule (216.2, 216.4 pm), [284]



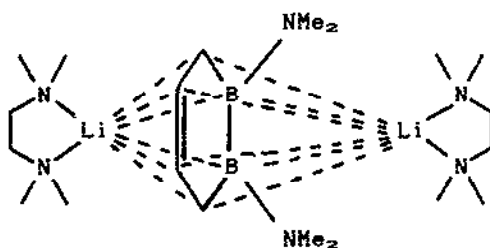


(134)



(137)

In the molecular structure of (136), [285] the Li atom occupies an almost central position below the 7-membered ring, such that not only the allylic ( $\text{Li} \cdots \text{C} = 219.4, 244.0, 251.5 \text{ pm}$ ) but also the olefinic part of the carbanion ( $\text{Li} \cdots \text{C} = 239.9, 242.9 \text{ pm}$ ) is engaged in metal-ligand bonding. The 7-fold Li atom coordination geometry is achieved by tmeda solvation.



(135)



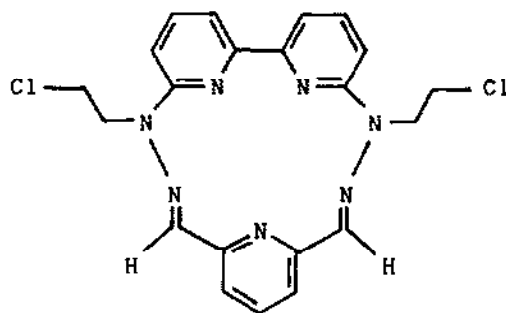
(136)

The last of the solvated complexes to be considered is bis(diacetamide)(nitrate)lithium in which the Li atom is surrounded by five oxygens, provided by two bidentate diacetamide molecules ( $\text{Li} \cdots \text{O} = 198.7-206.8 \text{ pm}$ ) and a monodentate nitrate anion ( $\text{Li} \cdots \text{O} = 200.1 \text{ pm}$ ), in a slightly distorted trigonal bipyramidal geometry. [286]

The monomeric cations in  $[\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3\text{Li}]^+ [2,4-(\text{NO}_2)_2\text{C}_6\text{H}_3\text{O}]^-$  [287] and  $[\text{N}(\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3\text{Li}]^+ [(\text{N}(\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3\text{Li})_2]^{2-}$

(BPh<sub>4</sub>)<sub>4</sub> (138)[265] contain Li atoms partially or wholly encapsulated by tripodands. In [N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub>Li]<sup>+</sup>[287] the Li atom is coordinated by the tetradentate tripodand (Li...O = 198.3-201.8; Li...N = 220.6pm) and the water molecule (Li...O = 192.4pm) in a trigonal bipyramidal arrangement. In [N(CH<sub>2</sub>CH<sub>2</sub>P(O)Ph<sub>2</sub>)<sub>3</sub>Li]<sup>+</sup>, [265] however, the Li atom is trigonally coordinated by the three oxygens of the tripodand (Li...O = 181-188pm) with the pivotal nitrogen at a slightly more remote position (Li...N = 257pm). [The structure of the second cation in (138) was considered in the subsection 1.4.9.4.]

The preparation and structural characterisation of a lithium complex of a pentadentate macrocycle incorporating only pyridine and imine donors (139) has been described by Lewis et al. [288] The structure contains two crystallographically independent molecules. Each Li atom is in a very unusual pentagonal-based pyramidal environment, in which the equatorial sites are occupied by five of the macrocycle's seven heteroatoms (Li(1)...N = 214.8-227.1pm; Li(2)...N = 214.2-228.3pm) and the axial site is occupied by a solvent methanol molecule (Li(1)...O = 204.1; Li(2)...O = 201.7pm).



(139)

A Japanese group has shown that controlled potential electrolysis of the dilithium salt of phthalocyanine  $\text{Li}_2^+\text{pc}^{2-}$  at 0.15v vs saturated calomel electrode in CH<sub>3</sub>CN gives a lithium complex of the phthalocyanine radical, [289] the structure of which (Figure 11) contains a unit cell with four nearly planar  $\text{Li}^+\text{pc}^-$  molecules of S<sub>4</sub> symmetry, stacked metal-over-metal but staggered by 38.7°; its effective magnetic moment decreased from 1.3μ<sub>B</sub> at 298K to 1.0μ<sub>B</sub> at 150K, but upon further cooling it

increased to approach the free spin value.[289]

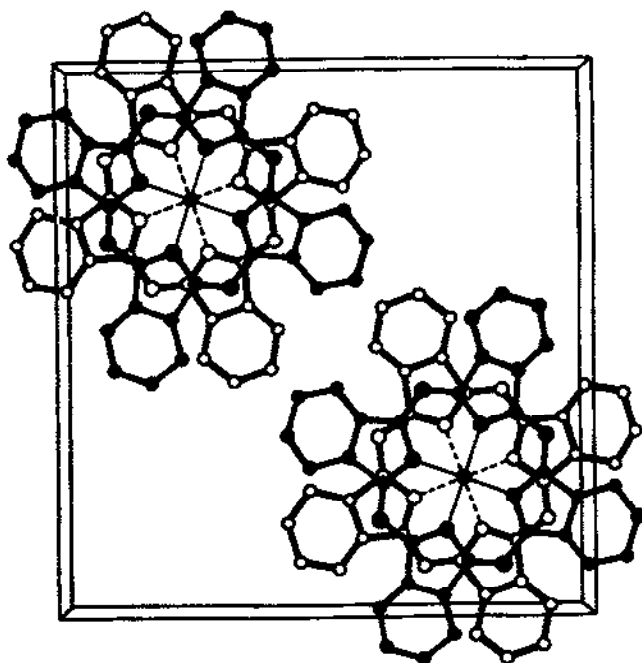


Figure 11. View down the *c* axis of the unit cell of the lithium complex of the phthalocyanine radical: Dimensions  $\text{Li} \dots \text{Li} = 324.5$ ,  $\text{Li} \dots \text{N} = 194.2\text{pm}$  (reproduced by permission from J. Chem. Soc., Chem. Commun., (1986)962).

#### 1.4.9.6 Solution Chemistry

The nature of the species present in solutions of lithium derivatives has been probed using high field n.m.r. techniques by a number of investigators.[239,290-294] From the results of  $^7\text{Li}$  n.m.r. spectroscopic and cryoscopic studies of a representative selection of amido- and imido-lithium derivatives in benzene and toluene, Reed, Snaith et al[239] have concluded that more diverse

behaviour is often observed in solution than in the solid state. Thus while some of the components essentially retain their solid association states (hexameric  $[\text{Ph}(\text{}^t\text{Bu})\text{C}=\text{NLi}]_6$ ,  $[(\text{Me}_2\text{N})_2\text{C}=\text{NLi}]_6$  and  $[(\text{PhCH}_2)_2\text{C}=\text{NLi}]_6$ , dimeric  $[\text{PhN}(\text{H})\text{Li.hmpa}]_2$  and monomeric  $[(\text{}^t\text{Bu})\text{C}_5\text{H}_5\text{NLi}(\text{py})_2]$ ), others engage in concentration-dependent equilibria also involving monomeric species (tetrameric  $[\text{Ph}_2\text{C}=\text{NLi.py}]_4$ , trimeric  $[(\text{PhCH}_2)_2\text{NLi}]_3$ , and dimeric  $[(\text{}^t\text{Bu})_2\text{C}=\text{NLi.hmpa}]_2$  and  $[(\text{C}_6\text{H}_{11})_2\text{NLi.hmpa}]_2$  and one complex (dimeric  $[(\text{PhCH}_2)_2\text{NLi.OEt}_2]_2$ ) loses donor on dissolution before rearranging to a trimer and a monomer.[239] Reed, Snaith et al.[290] have also concluded from  $^1\text{H}$  and  $^7\text{Li}$  n.m.r. data for the mono- and dilithiated products of N'-benzyl-N,N-dimethylethylene diamine in arene solutions that whereas the former is trimeric the latter is tetrameric with a totally rigid structure brought about by intra- and inter-molecular N...Li interactions.

Low temperature n.m.r. data for 3-lithio-1,5-dimethoxypentane are consistent with a dimeric structure in which the Li atoms are identical and form part of a  $\text{Li}_2\text{C}_2$  core:[291] the tetrahedral coordination geometry of the Li atom is assumed to be completed by intramolecular coordination of the pendant alkoxy groups.

Complete structural assignments of the  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r. spectra for both  $^t\text{BuLi}$  in  $\text{thf-d}_6$  and 1-lithionaphthalene in  $\text{C}_6\text{D}_6$  have been obtained by Schleyer et al.[292] from 2-D n.m.r. experiments.  $^6\text{Li}$ - $^1\text{H}$  HOESY exhibits cross peaks for  $\text{H}(\text{C}_1)$  and  $\text{H}(\text{C}_2)$  in the  $^t\text{BuLi}$  tetramer indicating some of the Li-H distances to be unusually short ( $<350\text{pm}$ ); it also reveals a short distance between Li and  $\text{H}(\text{C}_2)$  for 1-lithionaphthalene.tmeda. For a 1:1 molar mixture of the two reagents, however,  $^6\text{Li}$ - $^1\text{H}$  HOESY reveals a short contact between Li and  $\text{H}(\text{C}_8)$ . These observations are supported by the results of MNDO calculations for the solvated 1-lithionaphthalene dimer,  $[\text{C}_{10}\text{H}_7\text{Li.en}]_2$  (140) and for the mixed "dimer"  $[\text{C}_{10}\text{H}_7\text{Li}, \text{CH}_3\text{Li}(\text{en})_2]$  (141) which indicate that the 2-position of (140) exhibits the shortest Li...H distance, but that the 8-position of (141) should be activated.[292]

A variable temperature  $^7\text{Li}$  n.m.r. study of 1:1 molar mixtures of two structurally related phenylsilyllithiums ( $\text{Ph}_3\text{SiLi}$ ,  $\text{Ph}_2\text{MeSiLi}$  or  $\text{PhMe}_2\text{SiLi}$ ) in  $\text{thf}$  and 2-Methf supports a bimolecular exchange mechanism between monomeric structures as being responsible for the collapse of the  $^7\text{Li}$  signals of the two

species.[293] The experimental data also provide support for a mainly ionic Li...Si interaction, although some orbital involvement is indicated.[293]

$^7\text{Li}$  and  $^{11}\text{B}$  n.m.r. spectroscopic, cryoscopic and conductometric measurements indicate that  $\text{LiBF}_4 \cdot 4\text{hmpa}$  exists in solution as tight lithium and tetrafluoroborate components held together by Li...F interactions.[294]

Evidence for the presence of ion triplets  $\text{M}^+\text{A}^-\text{M}^+$  ( $\text{M}^+ = \text{Li}^+$  or  $\text{Na}^+$ ), as well as free ions and ion pairs in dmf solutions of lithium and sodium aryloxides has been reported.[295] This observation is of particular significance to quantitative treatments of the rate of reaction of an anionic reactant ( $\text{A}^-$ ) with a neutral electrophile ( $\text{RX}$ ) under conditions where cation association is important. For total accuracy these treatments must allow for the formation of the ion triplets  $\text{M}^+\text{A}^-\text{M}^+$ . [295]

The enthalpies of intramolecular etheration of tetrameric organolithium compounds of the type  $[\text{MeO}(\text{CH}_2)_n\text{CH}(\text{R})\text{Li}]_4$  ( $\text{R} = \text{H}, \text{Me}$ ;  $n = 2, 3$ ) have been determined in benzene by comparison of the enthalpies of formation of the unsubstituted organolithium tetramer  $[\text{CH}_2(\text{CH}_2)_n\text{CH}(\text{R})\text{Li}]_4$  and its 3-methoxy- analogue  $[\text{MeO}(\text{CH}_2)_n\text{CH}(\text{R})\text{Li}]_4$ ; [296] whereas for  $n = 2$ , the enthalpy difference is  $-30\text{kJ}\cdot\text{mol}^{-1}$ , for  $n = 3$ , it is  $-41\text{kJ}\cdot\text{mol}^{-1}$ .

Reaction of bromotrichlorosilane with 2,4,6-tri(*t*-butyl)-phenyllithium or mesityllithium at 195K in thf affords trichlorosilyllithium; [297] it was detected as trichlorosilane which is obtained by protonation and characterised by a  $^{29}\text{Si}$  n.m.r. chemical shift of 30.9ppm. Normal metallating agents ( $^n\text{BuLi}$ ,  $^t\text{BuLi}$ ,  $\text{PhLi}$ ) usually give substituted rather than deprotonated products. [297]

Lithiation of the aminosilanes  $\text{Me}_{4-x}\text{Si}(\text{NH}(^n\text{Bu}))_x$  ( $1 \leq x \leq 4$ ) using  $^n\text{BuLi}$  yields  $\text{Me}_{4-x}\text{Si}(\text{NH}(^n\text{Bu}))_y(\text{NLi}(^n\text{Bu}))_{x-y}$  ( $x = 1, y = 0$ ;  $x = 2, y = 1-2$ ;  $x = 3, y = 1-3$ ;  $x = 4, y = 1-4$ ); [298] the products were characterised by i.r. and  $^1\text{H}$  and  $^7\text{Li}$  n.m.r. spectroscopic techniques.

The addition of lithium to acyclic alkynes in ether results in the relatively slow (293K; 48h) formation of insoluble trans-dilithioalkenes; [299] cyclic alkynes react much more rapidly (238K; 2h) to give cis-dilithiocycloalkenes.

#### 1.4.10 Sodium Derivatives

Only eight papers[265,300-306] on sodium chemistry remain to be discussed after consideration of the specialised topics covered earlier in the review; of these, all[265,300-305] bar one[306] report the results of single crystal xrd analyses. In the exception,[306] the results of an investigation of the thermodynamics of the binding of  $\text{Na}^+$  (and  $\text{Ca}^{2+}$ ) to bile salts (in particular, glycocholate and taurocholate) using n.m.r. methods, are reported; the derived dissociation constants suggest that the sulphonate bearing taurocholate has a lower affinity for  $\text{Na}^+$  (and  $\text{Ca}^{2+}$ ) than the carboxylate bearing glycocholate.

Coiro et al. have described the crystal and molecular structures of the hemi-[300] and mono-hydrates[301] of sodium dodecyl sulphate. The Na atom in the hemihydrate[300] is coordinated by seven oxygens provided by two bidentate anions ( $\text{Na}\dots\text{O} = 231.5/305.4; 255.8/294.3\text{pm}$ ), two monodentate anions ( $\text{Na}\dots\text{O} = 227.8, 242.0\text{pm}$ ) and the water molecule ( $\text{Na}\dots\text{O} = 241.1\text{pm}$ ) in an irregular geometry. The monohydrate[301] contains two crystallographically independent, but structurally similar, Na atoms; each is coordinated by six oxygens provided by four monodentate anions ( $\text{Na}(1)\dots\text{O} = 237.1-247.1; \text{Na}(2)\dots\text{O} = 233.9-246.0\text{pm}$ ) and two water molecules ( $\text{Na}(1)\dots\text{O} = 237.2, 249.9; \text{Na}(2)\dots\text{O} = 236.5, 242.3\text{pm}$ ) in a distorted octahedral arrangement.

Groth has reported the 123K structure of 3-hydroxy-2-propenal sesquihydrate.[302] Again the asymmetric unit contains two crystallographically independent, but structurally similar, Na atoms; they are located in approximately octahedral coordination spheres generated by two oxygens from separate anions ( $\text{Na}(1)\dots\text{O} = 242.4, 248.1; \text{Na}(2)\dots\text{O} = 245.8, 247.5\text{pm}$ ) and four water molecules ( $\text{Na}(1)\dots\text{O} = 238.8-239.5; \text{Na}(2)\dots\text{O} = 240.1-248.4\text{pm}$ ).

The Na atom coordination polyhedra in the sodium salts of N-(4-aminobenzenesulphonyl)acetamide monohydrate[303] and N-chloro-4-methylbenzenesulphonamide trihydrate[304] differ considerably. In the former salt,  $[\text{CH}_3\text{CO.NSO}_2\text{C}_6\text{H}_4\text{NH}_2]^- \text{Na}^+ \cdot \text{H}_2\text{O}$ , [303] the Na atom is surrounded by three oxygens ( $\text{Na}\dots\text{O} = 227.3-244.0\text{pm}$ ) and one nitrogen ( $\text{Na}\dots\text{N} = 261.3\text{pm}$ ) from anions and a water molecule ( $\text{Na}\dots\text{O} = 229.6\text{pm}$ ) in a 5-fold array. In the latter salt,  $[\text{Cl.NSO}_2\text{C}_6\text{H}_4\text{CH}_3]^- \text{Na}^+ \cdot 3\text{H}_2\text{O}$ , [304] the Na atom is roughly octahedrally coordinated by an oxygen ( $\text{Na}\dots\text{O} = 236.5\text{pm}$ ) and a

chlorine ( $\text{Na}\dots\text{Cl} = 315.3\text{pm}$ ) from neighbouring anions and by four water molecules ( $\text{Na}\dots\text{O} = 235.4\text{--}248.7\text{pm}$ ).

Two crystallographically independent Na atoms occur in the structure of the disodium salt of D-fructose-6-phosphate heptahydrate.[305] Whereas Na(1) is ligated by two sugar hydroxyl oxygens and four water molecules ( $\text{Na}\dots\text{O} = 235.3\text{--}264.8\text{pm}$ ) in a distorted octahedral arrangement, Na(2) is coordinated in the form of a somewhat distorted tetragonal pyramid by a single sugar hydroxyl oxygen and four water molecules ( $\text{Na}\dots\text{O} = 233.0\text{--}247.6\text{pm}$ ).

Treatment of a butanol solution of  $\text{NaBPh}_4$  with a  $\text{CH}_2\text{Cl}_2$  solution of  $\text{N}(\text{CH}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)_3$ , previously prepared by oxidation of  $\text{N}(\text{CH}_2\text{CH}_2\text{PPh}_2)_3$  with  $\text{H}_2\text{O}_2$ , gave crystals of  $[(\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2)_3\text{NNa}\cdot\text{H}_2\text{O}\cdot\text{BuOH}]^+\text{BPh}_4^-$  (142).[265] In the structure of (142), the tripodand does not encapsulate the Na atom; instead the latter is surrounded in a tetrahedral fashion by two oxygens of the tripodand ( $\text{Na}\dots\text{O} = 217.7, 223.7\text{pm}$ ) and by the oxygens of the water ( $\text{Na}\dots\text{O} = 230.2\text{pm}$ ) and the butanol molecules ( $\text{Na}\dots\text{O} = 229.3\text{pm}$ ).[265]

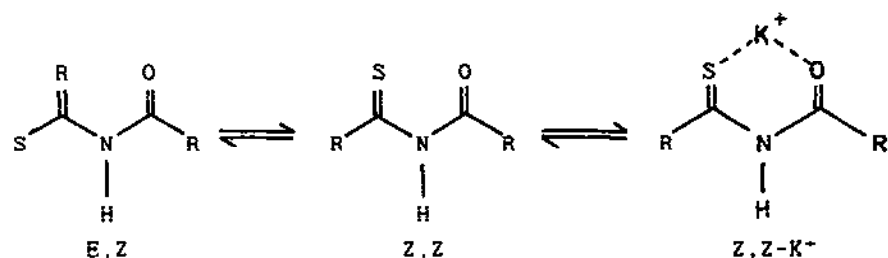
#### 1.4.11 Potassium, Rubidium and Caesium Derivatives

As for earlier reviews, very few papers pertinent to this subsection were found during the literature search; a total of seven were abstracted for potassium,[307-313] none for rubidium and one for caesium.[314] Clearly, the vast majority of the data reported for these elements is adequately covered by the various specialised topics of current interest and significance.

Schleyer et al[307] have prepared solid  $^n\text{BuK}$  by metal-metal exchange between  $^n\text{BuLi}$  and potassium t-amylate. It can be solubilised in hexane by addition of tmeda; the resultant solution is an effective metallation reagent. Low temperature n.m.r. studies in thf suggest that, like  $^n\text{BuNa}$ ,  $^n\text{BuK}$  is monomeric under these conditions.[307]

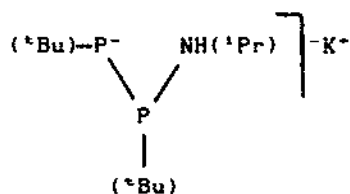
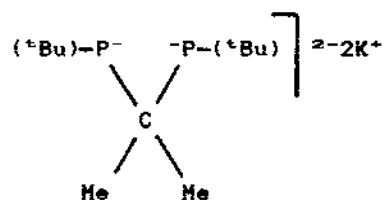
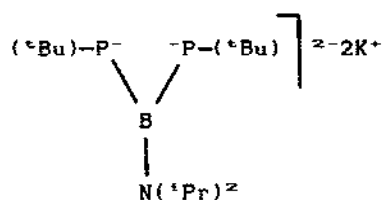
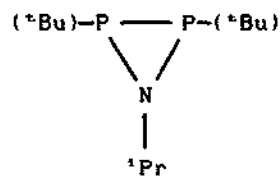
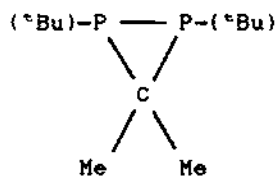
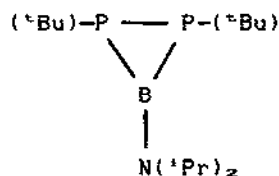
Complexation of  $\text{K}^+$  by n-acyl thioamides has been studied using n.m.r. techniques.[308] Addition of  $\text{KSCN}$  to solutions of (143) or (144) results in rearrangement of the E,Z-n-acyl thioamide to the Z,Z-form followed by complexation of the cation (scheme 9).

Low temperature ( $<195\text{K}$ ) reaction of (145)[309] and (146)[310] with potassium or potassium naphthalenide in thf results in P-P bond cleavage and formation of (148) and (149) respectively.



Scheme 9: (143) R = Me; (144) R = Et

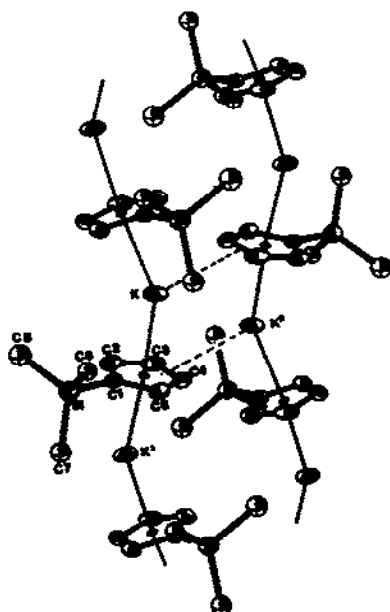
In the case of (147) [310] under analogous conditions the P-N bond fractures to give (150). At higher temperatures (>195K) (148)





interconverts into the asymmetric compound  $[\text{tBuP}^--\text{P}(\text{tBu})-\text{BHN}(\text{iPr})_2]^- \text{K}^+$ , [309] whereas (149) decomposes into the mono-phosphides  $\text{KHP}(\text{tBu})$  and  $\text{KP}(\text{tBu})(\text{iPr})$ ; [310] (150) is stable to 298K. [310] All reagents and products were characterised by  $^{31}\text{P}$  n.m.r. spectroscopy.

The synthesis and structural characterisation of  $[(\text{Me}_3\text{Si})\text{C}_5\text{H}_4\text{K}]$  (151) has been reported by Jutzi, Pohl et al; [311] it is the first example of a base-free alkali metal cyclopentadienide to be crystallised and analysed using single crystal xrd methods. Prepared by treatment of trimethylsilylcyclopentadiene with potassium metal or potassium hydride in toluene, [311] it has the structure depicted in Figure 12. It comprises a "supersandwich

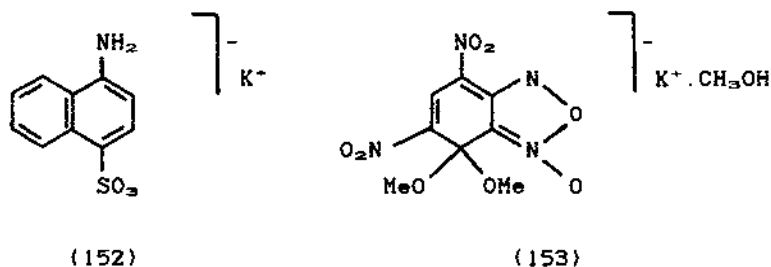


**Figure 12.** Crystal and molecular structure of potassium trimethylsilylcyclopentadienide (reproduced by permission from *Angew. Chem., Int. Ed. Engl.*, 26(1987)583).

complex" which is made up of a repeating sequence of K atoms and (on both sides)  $\text{h}^5\text{-C}_5\text{H}_5$  rings. The average K...C contact (K...C

= 298.8-307.9;  $K' \dots C = 300.1-307.4\text{pm}$ ) corresponds to a distance between the K atom and ring centre of  $\sim 278\text{pm}$ . An additional weak  $K-(\eta^2-C_5H_5)$  bonding relationship occurs between neighbouring strands ( $K \dots C = 366.6, 367.8\text{pm}$ ); it results in their zig-zag shape. The interatomic distances found for (151) are exceptionally large, indicating an electrostatic interaction between anionic  $\pi$ -systems and potassium cations.[311]

The K atoms in the crystal structures of the potassium salts of 4-amino-1-naphthalenesulphonic acid (152)[312] and of 1,4-dihydro-4,4-dimethoxy-5,7-dinitrobenzofurazan-3-oxide methanol (1/1) adduct (153)[313] are 7-coordinate. The two crystallographically independent K atoms in each asymmetric unit of (152)[312] are surrounded by seven oxygens from four separate anions ( $K(1) \dots O = 274.7-285.6$ ;  $K(2) \dots O = 275.6-290.0\text{pm}$ ) in



pentagonal bipyramidal arrangements. The K atom in (153)[313] is located in a cage of seven oxygens, five of which are provided by three anions ( $K \dots O = 274.4-285.1\text{pm}$ ) the other two by solvent molecules ( $K \dots O = 271.9, 275.9\text{pm}$ ).

In the crystal structure of caesium tris(N-bromosuccinimide)-bromate(1-),  $Cs[Br(CO.CH_2CH_2.CO.N.Br)_3]$ [314] which contains two crystallographically independent formula units per asymmetric unit, the central bromine atoms are on the  $\bar{3}$  axes of the trigonal cell with the Cs atoms at the centres. Cs(1) is enclosed in a cage formed by two complexes: it has six oxygens ( $Cs \dots O = 320.7\text{pm}$ ) as nearest neighbours with six somewhat more remote bromines ( $Cs \dots Br = 394.6\text{pm}$ ) completing its distorted 12-fold coordination. Cs(2) is surrounded by a puckered hexagonal bipyramid of six oxygens ( $Cs \dots O = 324.4\text{pm}$ ) and two bromines ( $Cs \dots Br = 365.1\text{pm}$ ).

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