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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 decribed 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 {$\delta = -60\pm2$ppm for $[(18C6)_2Cs]^+$ and $\delta = +27\pm3$ppm 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 {λ_{max}/nm: Na - 670±10; K - 840±20; Rb - 890±20; Cs - 990±20}. Although $^{23}Na^-$ and $^{89}Rb^-$ gave singlet n.m.r. peaks at high field {δ = -61.8±0.1 ppm, $\Delta\nu_{1/2}$ = 10 Hz for Na^-; δ = -191±2ppm, $\Delta\nu_{1/2}$ = 1000 H_z 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 δ ~ 8ppm for NaF or NaCl to δ = -52ppm for NaBPh4}, 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

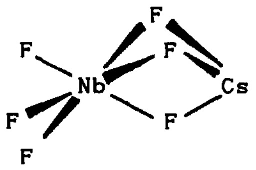
Presumably for the reasons outlined in the 1985 review[1] interest in the elements has declined such that the number of papers abstracted no longer warrants the retention of a separate section. Those which have been abstracted will be considered, as appropriate, in other subsections of the review; the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



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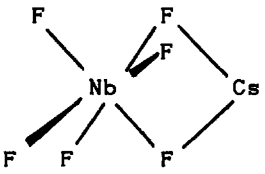

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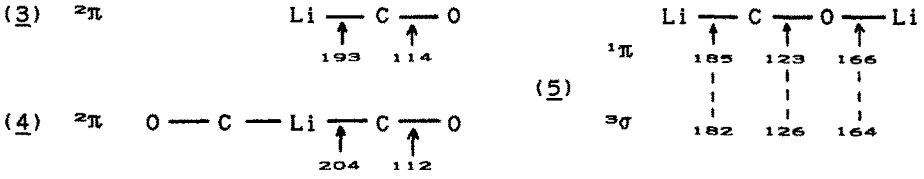
has been correlated with the separation between terminal and bridging ν(C...O) in matrix isolated $CsClO_4$;[11] the given sequence of decreasing frequency separation is assumed to correlate with increasing host-guest interaction

$Ne > Ar > O_2 \sim F_2 > Kr > Xe > N_2 > CO$

The complexes formed during the codeposition of alkali metal atoms and NH_3,[12] CO,[13] CO_2[14] and SO_2[15] in low temperature matrices have been studied by vibrational (i.r. and Raman) spectroscopic techniques. The 1:1 complexes formed between M(Li-K,Cs) and 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 Li-NH_3 complex.

The products of the codeposition of Li and CO[13] include (i) four mononuclear species $Li(CO)_n$ (n = 1-4) which are closely related to transition metal carbonyls, (ii) species with several Li atoms and one or two 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* basis sets, of the electronic structures and equilibrium geometries of the simpler lithium carbonyl species formed in these experiments suggest that Li(CO)(3) and $Li(CO)_2$(4) exist in the $^2\pi$ state and that $Li_2(CO)$(5) adopts two inequivalent geometries with $^1\pi$ and $^3\sigma$ states.[16]



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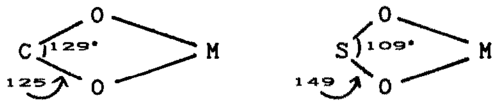
1:1 M:CO_2[14] and M:SO_2[15] and 1:2 M:CO_2[15] (M = Na,K,Cs) species are formed on codeposition of alkali metals with CO_2 and SO_2. Whereas M(CO_2) and M(SO_2) have planar ring symmetry (6) $M_2(CO_2)$ adopts both a W-shape structure with C_{2v} symmetry (7) and a C_s symmetry structure of uncertain geometry.



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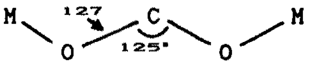

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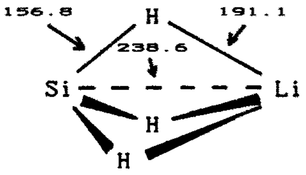
1.3.2 Theoretical Treatment of Small Moieties

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 MBO_2 (M = Na,K),[21] $NaCH_2CN$[26] and NaCHO.[27]

Ab initio calculations of the interaction of Li^+ with NH_3 indicate that the ion-molecule interaction is mainly electrostatic in character.[17] Monte Carlo simulations of $Li(H_2O)_n{}^+:NO_2{}^-$ clusters ($1 \leqslant n \leqslant 28$) suggest that the affinity to form an ion pair decreases as more H_2O molecules are added;[18] for the larger clusters, solvent separated ion pairs are more stable than intimate ion pairs by $87kJ.mol^{-1}$. Owing to the more favourable electrostatic interactions in the ion pair $SiH_3{}^-Li^+$, the inverted C_{3v} geometry (<u>8</u>) of $LiSiH_3$ is calculated, using a 6-31G* basis set, to be more stable than the classical C_{3v} isomer (<u>9</u>) by $10.0kJ.mol^{-1}$;[19] the energy barrier separating (<u>8</u>) and (<u>9</u>) ($56.5kJ.mol^{-1}$) involves movement of Li^+ from one side of the $SiH_3{}^-$ moiety to the other. Calculations based on SCEP and CISD methods suggest that the ground states of $LiMgH_3$ and $LiAlH_4$ have bidentate (C_{2v}) geometries.[20] Although these conclusions contrast, in part, with earlier data for $LiBH_3$ and $LiBH_4$ which show



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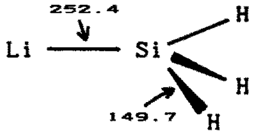

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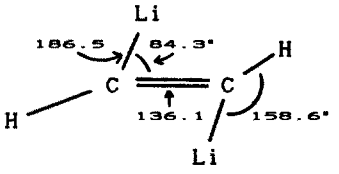
ground state configurations with bidentate (C_{2v}) and tridentate (C_{3v}) geometries, respectively, the energy differences between the bidentate and tridentate geometries for both $LiBH_4$ and $LiAlH_4$ are extremely small (within 8.5-25.1kJ.mol^{-1}).[20] The experimentally observed increase in the dissociation energies of the M-BO_2 (M = Li,Na,K) bonds from 478 and 480kJ.mol^{-1} for M = Na and K, respectively, to 560kJ.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-BO_2.[21] In a separate study, the ionic character of the M-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



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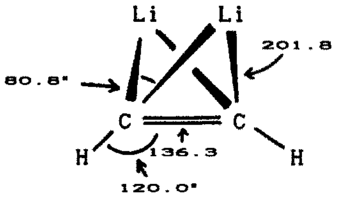

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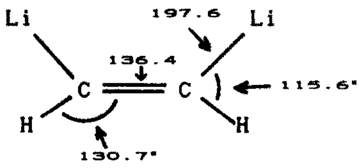

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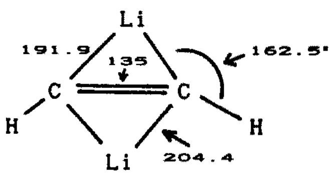

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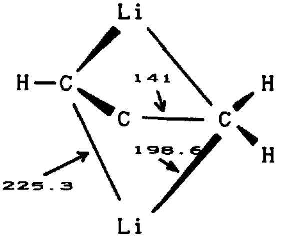
indicate that the trans-isomer (10) is more stable than either of the two cis-isomers (11,12) in agreement with recent experimental findings[31] but contrary to the earlier theoretical conclusions.[32] Furthermore, although (10) and (11) were found to be minima, (12) was found to be a transition state 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 25.4kJ.mol^{-1} above the latter which possesses a 2-lithioallyllithium structure (16) in which both lithiums lie on the C_s plane with one lithium bridging the terminal carbons and the other adjacent to the central carbon.[23]



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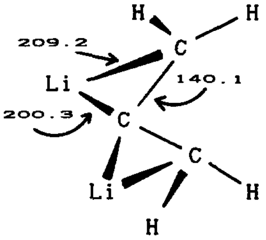

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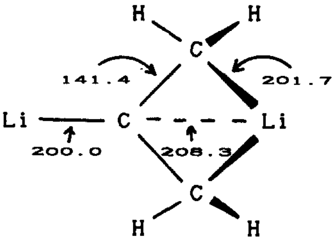

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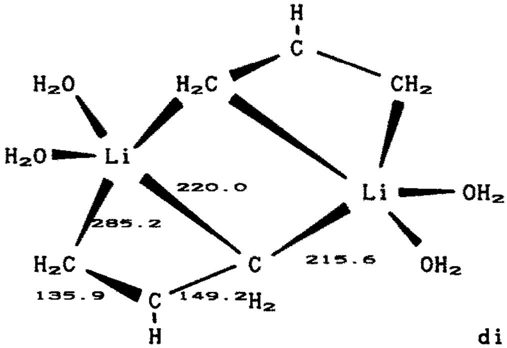
∠CCC/°	121.0	116.6	119.9
∠LiCLi/°	144.8	113.2	133.3

distances/pm

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 ^{13}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 Li^+ are 60.2 and 25.1 $kJ.mol^{-1}$, respectively. It is suggested that the effect should be general for alkyl radical addition to alkene-metal complexes.[25]



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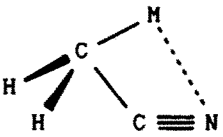
(17)

Extended ab initio examination[26] of the Li, Na derivatives of the CH_2CN^-, CH_2NC^- 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 effects of the lithium compounds were probed by MNDO calculations.[26] The most stable unsolvated dimers of both $LiCH_2CN$ and $LiCH_2NC$ have 8-membered ring structures (22). Solvation, however, favours the formation of the alternative



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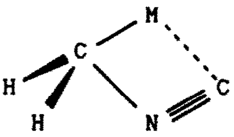


(19)

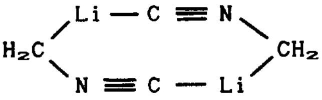
$M-N=C=CH_2$

(20)

$M-\overset{-}{C}=\overset{+}{N}=CH_2$

(21)

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



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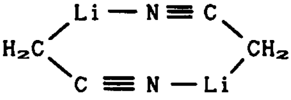

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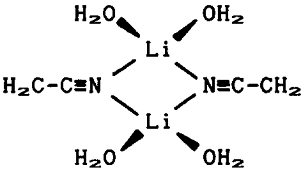
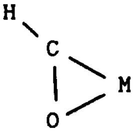


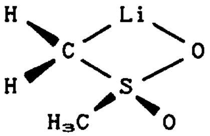
(23)

Ground state metal bridged geometries (24) are also predicted for the formyl complexes MCHO (M = Li,Na) from ab initio calculations.[27] Such η^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(H...C)/pm	110.4	-
r(C...O)/pm	124.3	123.9
r(C...M)/pm	190.2	224.3
r(M...O)/pm	178.2	216.5
∠OCM/°	65.1°	70.3°

(24)



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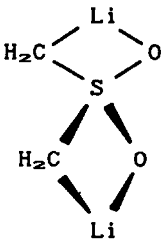
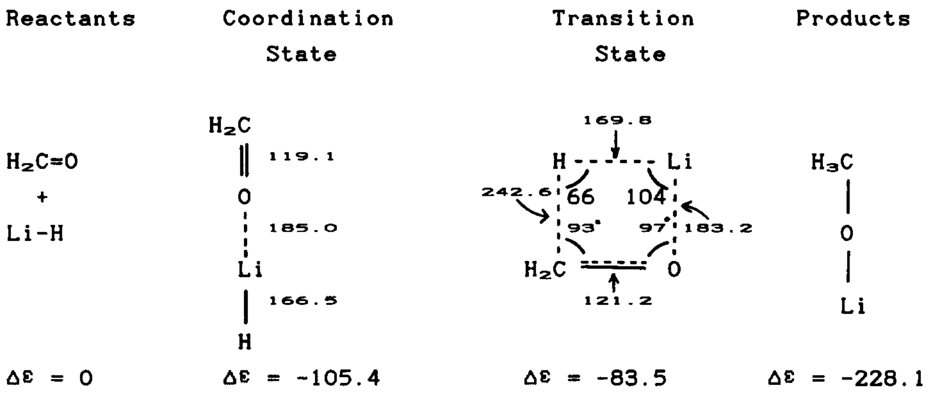


(26)

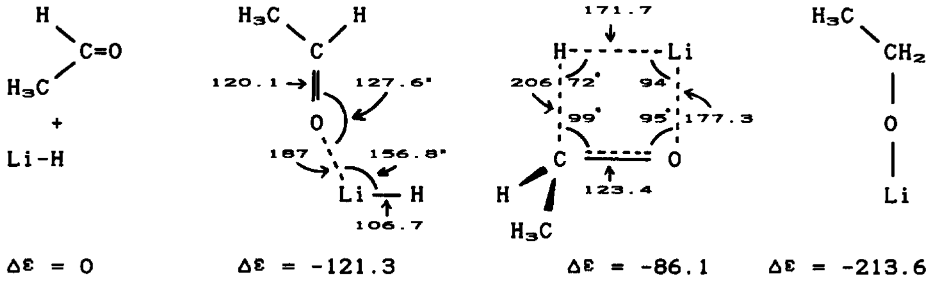
character in the formyl group and predominantly ionic M-C interactions.[27]

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 ($Li^+...^-CH_2SO_2CH_3$ and $Li^+...^-CH_2SO_2CH_2^-...Li^+$).[28]

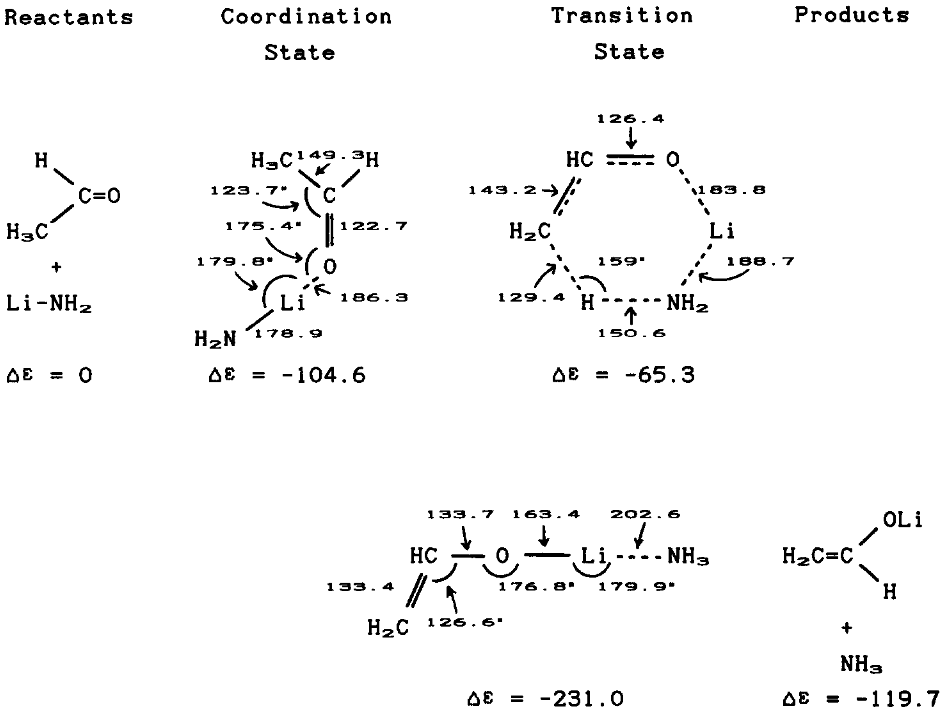
Theoretical analyses of the reaction of LiH with methanol and ethanol (3-21G* basis set)[29] and of $LiNH_2$ with ethanol (3-21+G basis set)[30] predict the mechanisms given in schemes 1 - 3.



Scheme 1



Scheme 2



Scheme 3

(Distances/pm; Energies/kJ.mol^{-1} 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_3LiSi_4 or $K_7Li(Si_4)_2$, 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 μ_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 μ_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

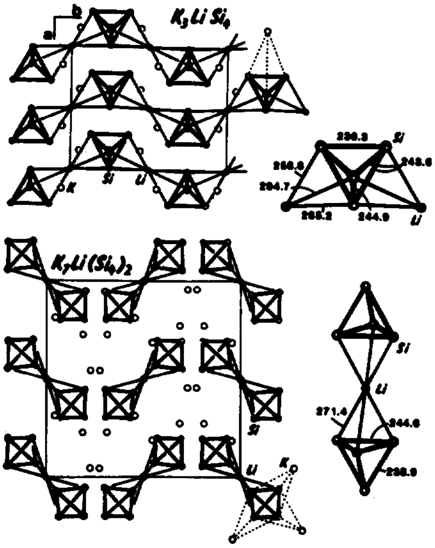


Figure 1. Crystal structures of K_3LiSi_4 and $K_7Li(Si_4)_2$ showing the polymeric $[Li(Si_4)]^{3-}$ chain and the dumb-bell shaped $[Li(Si_4)_2]^{7-}$ unit. In both structures, the μ_3-coordinated potassiums are shown using hatched lines (reproduced by permission from Angew. Chem., Int. Ed. Engl., 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 Si_4^{4-} anion (symmetry $\bar{4}3m$-T_d) were observed at 482, 285 and 356cm^{-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 $NaTe_3$.[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 = 2193pm) contains three crystallographically independent 6-coordinate sodiums each of which lies on a 3-fold symmetry axis (Na(1)...Te = 307.0,331.4pm; Na(2)...Te = 316.1,324.0pm; Na(3)...Te = 316.9,319.4pm).[36]

^{197}Au-Mossbauer spectra of MAu (M = Li-Cs) intermetallics and of $[C222M]^+Au^-$ (M = K-Cs)[37] are consistent with a cubic environment for the Au atom in all three complexes, $[C222M]^+Au^-$ (M = K-Cs), but only two intermetallics, RbAu and CsAu. For the other two intermetallics, NaAu and 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

NaO^tBu or KO^tBu with BuLi in hexane/tmeda solutions gave highly reactive NaH and KH in suspension. Whereas the latter instantaneously metalated $^tBuCOCH_3$ at 253K, the former was less vigorous, completion of enolate formation requiring 20 minutes at 273-293K.[38]

The use of Li_3N as a reducing agent has been demonstrated.[39] Stoichiometric reactions of Cp_2TiCl_2 or $CpTiCl_3$ with Li_3N (in various molar ratios) in thf result in reduction to $(Cp_2TiCl_2)_2$, $(CpTiCl_2)_n$ and $(CpTiCl)_4$. Further reduction produces hexanuclear nitrido titanium clusters Cp_8Ti_6N and $Cp_8Ti_6N_3$ characterised from mass spectrometric evidence. $Cp_2Ti(CO)_2$ is formed by the reaction between Cp_2TiCl_2 and Li_3N in thf in the presence of 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}P-n.m.r. techniques. Baudler[41-44] has also reported the preparation of MP_5 (M = Li,Na),[41] M_3P_{19} (M = Li-K),[42] and Na_2P_{16}.[43,44] Lithium pentaphosphacyclopentadienide (LiP_5) was obtained by reaction of $LiPH_2$ with white phosphorus (1:5 molar ratio) in dry thf;[41] sodium pentaphosphacyclopentadienide (NaP_5) was formed, together with sodium tetraphosphacyclopentadienide (NaP_4CH) and sodium triphosphacyclobutadienide (NaP_3CH_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 mesommerism. The nonadecaphosphides, M_3P_{19} (M = Li-K) were prepared by nucleophilic cleavage of white phosphorus with $LiPH_2$ sodium or potassium, as appropriate.[42] Li_3P_{19} also results from the reaction of Li_3P_7 with white phosphorus or iodine or 1,2-dibromoethane as well as from the degradation of Li_2P_{16} with $LiPH_2$.[42] Reaction of white phosphorus with sodium (molar ratio 3:1) in boiling thf or monoglyme in the presence of 18C6 gives sodium hexadecaphosphide Na_2P_{16} as a solvated adduct $Na_2P_{16}.(18C6)_3.2thf$.[43] In liquid ammonia, as well as Na_2P_{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 (Li_3P_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 = 759.6pm).[45]

The interalkali metal sulphide, KNaS, has been crystallised by annealing a mixture of Na_2S and K_2S (sealed corundum tube under argon; 6 days heating at 873K);[46] it is isostructural with $PbCl_2$ (orthorhombic; space group Pnma; a = 770.3, b = 460.4, c = 829.3pm).

The degradation of sodium sulphide in the solid phase (as $Na_2S,5H_2O$)[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 $Na_2S.5H_2O$;[47] a topotactic process was put forward to account for the structural transformation mechanisms. U.v. irradiation (λ = 248nm) of Na_2S in aqueous solution leads to hydrogen and Na_2S_2 ($\Phi(H_2)$ = 0.34 at λ = 254nm);[48] light adsorption occurs via HS^-, which is produced by hydrolysis of Na_2S, affording the solvated electron and the $HS^\cdot$ radical. In the presence of formate anions, hydrogen evolution becomes catalytic with respect to HS^- ($\Phi(H_2)$ = 0.12 at λ = 254nm).[48] Aqueous sodium polysulphide (Na_2S_x; $2 \leqslant x \leqslant 4.6$) undergoes autoxidation by either air or pure oxygen according to the equation:[49]

$$8Na_2S_{2+x} + 12O_2 \rightarrow 8Na_2S_2O_3 + xS_8$$

Iodometric determination, vibrational spectroscopy and ion-pair chromatography showed that neither SO_4^{2-}, SO_3^{2-} nor polythionates are formed and that the sulphur consists of S_8 ($\geqslant$99%).[49]

Single crystals of RbO_3 have been synthesised by repeated ozonisation of RbO_2 at 298K followed by extraction using liquid ammonia.[50] The packing of the ions within the structure (monoclinic; space group $P2_1/c$; a = 645.2, b = 602.2, c = 876.3pm; β = 122.34°) strongly resembles the CsCl-type structure, with nine Rb...O interatomic distances varying from 293.2 to 319.1pm and a tenth more remote 342.1pm contact.[50]

A linear relationship has been noted between the dissociation energy of the alkali metal halides (MX; M = Na-Cs, X = Cl-I) and the magnetic shielding constants of the alkali metal (^{23}Na, ^{39}K, ^{87}Rb, ^{123}Cs) and halogen (^{35}Cl, ^{79}Br, ^{127}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}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-$AlCl_3$ 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 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 Cl^- ion. As the ions are separated an unstable octahedron is generated. At further separations the 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 LiX (X = Cl,Br) and 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, tmurea or propylene carbonate. No aggregates involving LiI were noted in any of these solvents.[54] Tetrameric aggregates of stoichiometry $Li_4Br_3(NCS)$ were seen in diethylether;[54] the corresponding chloride aggregates were not accessible owing to the insolubility of LiCl in ethers. In some ethers (di-n-butylether, s-butylethylether and i-propyl-n-propylether), however, mixed tetramers of stoichiometry $Li_4I_n(NCS)_{4-n}$ are formed between LiI and LiSCN.[54]

^{7}Li-n.m.r. and potiometric studies of lithium salts (LiX; X = Cl, Br, ClO_4^-, AsF_6^-, NO_3^-) dissolved in the n-butylpyridinium chloride-$AlCl_3$ ambient temperature molten salt indicate the presence of $LiCl_2^-$ monomers and $Li_2Cl_4^{2-}$ dimers in a fast two site exchange mechanism.[55]

As part of a search for fast solid Li^+ ion conductors, Rabenau et al.[56] have reinvestigated the phase diagram of the LiI-CH_3OH system and the crystal structure of the highest conducting phase, LiI.4CH_3OH. Unlike earlier phase diagrams, which showed the formation of LiI.CH_3OH 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 $LiI.4CH_3OH$ melts congruently 322K, $LiI.CH_3OH$ and $2LiI.3CH_3OH$ undergo peritectic decomposition reactions at 253K and 249K, respectively (Figure 2(a)). In the structure of $LiI.4CH_3OH$ (Figure 2(b)), the Li^+ ions are surrounded tetrahedrally by oxygen atoms with formation of $[Li(CH_3OH)_4]^+$ units (Li...O = 191.9pm);[56] the arrangement of the $[Li(CH_3OH)_4]^+$ and 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)).

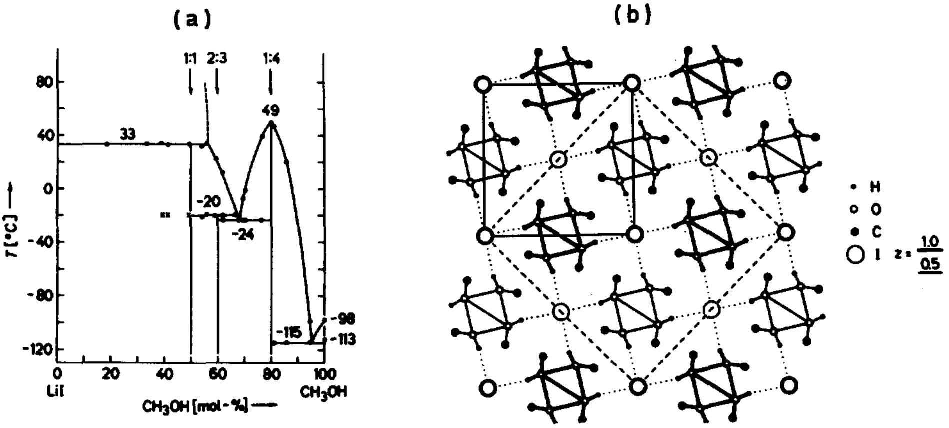


Figure 2. (a) Phase relationships in the $LiI-CH_3OH$ system and (b) projection of the crystal structure of $[Li(CH_3OH)_4]^+I^-$ viewed along (001). {The Li^+ ions in the centres of the tetrahedra are omitted. The centres of the tetrahedra are located on the z = 0.75(thick) and z = 0.25(thin) layers; the 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).

The complex adduct, $2NaI.3CH_3CN.3H_2O$, crystallises with hexagonal symmetry.[57] Each Na^+ ion is located on a 3-fold symmetry axis and is octahedrally coordinated to three water (Na...O = 241.6pm) and three acetonitrile molecules (Na...N = 252.3pm). The sodium centered octahedra share opposite faces with two adjacent octahedra to form continuous $[Na(H_2O)_3(CH_3CN)_3]^\infty$ chains; the shared faces contain either three nitrogens or three oxygens alternately along the chain.[57]

The structure of RbI_3 (orthorhombic; space group Pnma; a = 1090.8, b = 665.5, c = 971.1pm) is isotypic with that of CsI_3.[58] The I_3^- ions are asymmetric and slightly bent (I...I = 283.3, 305.1pm; ∠III = 178.11°); the Rb^+ ions are surrounded by seven iodine atoms in an irregular geometry (Rb...I = 363.4-415.8pm).[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, $CsLi(NH_2)_2$ and $CsLi_2(NH_2)_3$, were obtained by reaction of the metals with ammonia in high pressure autoclaves.[59] The structure of the hexagonal modification of $CsLi(NH_2)_2$, including the hydrogens, was established from single crystal xrd data.[59] The Li atoms occupy distorted nitrogen tetrahedra (Li...N = 211pm) which are connected by trans-located edges along (001) to generate an infinite $[Li(NH_2)_2^-]$ chain (Li...Li = 280.3pm); the Cs atoms combine the chains with ten amide anions surrounding each Cs atom (Cs...N = 342.3, 353.7, 390.4pm).[59] For the hydroxides, the influence of the asymmetric charge distribution of the anion decreases with increasing temperature.[60,61] In the low temperature TlI-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 KF,2.5HF and KF,3HF have revealed the structural formulae $K_2[H_2F_3][H_3F_4]$ and $K[H_3F_4]$.[63] Full details of the structures of the $[H_nF_{n+1}]$- anions are given.

Table 1. Crystallographic parameters for various polymorphs of $CsLi(NH_2)_2$,[59] $CsLi_2(NH_2)_3$,[59] RbOH,[60] RbOD,[60] CsOH[61] and CsOD.[61]

Compound	Temp. Range	Symmetry	Space Group	Z	a/pm	b/pm	c/pm	β/°
$CsLi(NH_2)_2$		monoclinic	$C2/c$	-	656.4	1166.5	577.0	117.4
		hexagonal	$P6_222$	-	633.4	-	840.9	-
$CsLi_2(NH_2)_3$		orthorhombic	Cmcm	-	875.1	1118.4	545.0	-
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	-	-	-
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	-	-	-
CsOH	200-498	orthorhombic	Cmcm	4	435.0	1199.2	451.6	-
	498-m.p	cubic	Fm3m	4	642.7	-	-	-
CsOD	23-230	orthorhombic-I	$P2_12_12_1$	4	431.9	1153.8	446.9	-
	230-460	orthorhombic-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 KF,2.5HF with an additional fluorine above a square face of one of the two independent polyhedra and cube-like in KF,3HF with K...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
$-\Delta H_f^\circ(MHF_2(s))/kJ.mol^{-1}$	942.3	920.3	927.7	922.6	923.8
$U_L(MHF_2(s))/kJ.mol^{-1}$	939	841	753	724	693
$-\Delta H_f^\circ(MF(s))/kJ.mol^{-1}$	616.0	573.6	567.3	557.7	553.5
$U_L(MF(s))/kJ.mol^{-1}$	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 Li_2ZnGe 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 Rb_3As_7 in a sealed niobium tube, rubidium was added in excess; the reaction product, clearly not Rb_3As_7, was dissolved in a solution of C222 in ethylenediamine from which red crystals of $[C222Rb]_2[Rb(NbAs_8)]$ (27) crystallised.[68] In (27), only two of the three Rb atoms are enclosed in the C222 molecules. The third forms a one dimensional $[Rb(NbAs_8)]^{2-}$ chain with the complex anion $[NbAs_8]^{3-}$. Evidently the Rb...As interactions in the chains are able to compete not only with those between Rb^+ and ethylenediamine but also with those between Rb^+ and C222. This surprising observation has been probed using INDO calculational methods to study the electronic structure of $[VAs_8]^{3-}$ and $[K(VAs_8)]^{2-}$. 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
α-Li_2ZnGe	Na_3As	hexagonal	-	432.6	828.6	64
β-Li_2ZnGe	Li_3Bi	cubic	-	614.0	-	64
LiLnGe (Ln=Pr,Tb,Dy,Yb)*	Fe_2P	hexagonal	P62m	731.6	437.3	65
LiYbBi	LiYSn	hexagonal	-	959.5	763.5	65
NaMnX (X=P,As,Sb,Bi)*	-	tetragonal	P4/nmm	408.7	687.6	66
MMnX (M=Li,K)*	-	tetragonal	P4/ncc	426.7	617.8	66
$NaCu_4X_2$ (X=As,Sb)*	$CaCu_4P_2$	rhombohedral	$R\bar{3}m$	410.0	2389.3	67
KCu_4X_2 (X=As,Sb)*	$CaCu_4P_2$	rhombohedral	$R\bar{3}m$	412.0	2595.6	67

* 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 ($Na_3Li_5Mn_5O_9$,[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
$Na_3Li_5Mn_5O_9$	$Na_2O:Li_2O:MnO$	1:2:2	973	14	Ni	69
KLi_6IrO_6	$Li_2O:K_4IrO_4$	3:1	1023	30	Ag	72
$Rb_2Li_{14}Tb_3O_{14}$	$Rb_2O:Li_8TbO_6$	2:1	973	27	Au	73
KNa_2AuO_2	$K_2O_2:Na_2O_2:NaAu$	1:1:2	703	6	Ag	74
$Rb_7NaZn_2O_6$	$Rb_2O:Na_2O:ZnO$	1.2:1.2:1	1223	36	Pt	70
$Cs_2K_2Cd_3O_5$	$Cs_2O:K_2O:CdO$	1:1:1	823	17	Ag	71
Li_6CoO_4	$Na_2O:Li_2O:CoO$	1.3:1.3:2	853	22	Co	80
β-$LiRhO_2$	$Na_2O:Li_2O:Rh_2O_3$	1.45:2.91:1	1223	18	Pd	81
Li_8IrO_6	$Li_2O:IrO_2$	5:1	1098	30	Ag	75
Li_8IrO_6	$Li_2O:Na_2IrO_3$	5:1	1098	40	Ag	75
Li_2PdO_2	$Na_2O:Li_2O_2:Tb_4O_7$	1:3:1	1373	7	Pd	82
Li_8PtO_6	$Li_2O:Na_3LiPt_2O_6$	10:1	1098	100	Au	75
Li_8CeO_6	$Li_2O_2:KCeO_2$	4.5:1	923	63	Ag	75
$Li_6Tb_2O_7$	$Li_2O_2:Tb_4O_7$	6.8:1	1023	13	Au	73
$Li_6Tb_2O_7$	$Rb_2Li_{14}Tb_3O_{14}$	-	1123	25	Au	73
Na_4CrO_4	$Na_2O:Cr_2O_3$	4:1	1273	30	Ni	76
Na_3AuO_2	$Na_2O_2:NaAu$	1:1	703	6	Ag	77
$NaPrO_2$	$K_2O:Na_2O:PrO_{1.83}$	1.1:1.2:1	1273	2	Ni	78
$NaTbO_2$	Na_2TbO_3	-	1273	10	Ni	78
K_4ZnO_3	$K_2O:ZnO$	2.1:1	873	30	Pt	70
K_4ZnO_3	$K_2O:K_2ZnO_2$	1:1	823	14	Ag	70
$Cs_{14}Cd_9O_{16}$	$Cs_2O:CdO$	~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 (Li_8IrO_6,[75] $Li_6Tb_2O_7$,[73] Na_4CrO_4,[76] Na_3AuO_2,[77] $NaTbO_2$,[78] K_4ZnO_3,[70] $Cs_{14}Cd_9O_{16}$[79]), several were obtained from reaction systems containing two alkali metal oxides (Li_6CoO_4,[80] β-$LiRhO_2$,[81] Li_8IrO_6,[75] Li_2PdO_2,[82] Li_8PtO_6,[75] Li_8CeO_6,[75] $NaPrO_2$[78]). In general, similar preparative routes to those described above were used. Others, worthy of comment, involved thermal decomposition of higher ternary oxides ($NaTbO_2$[78]) or mixed alkali metal oxides ($Li_6Tb_2O_7$[73]), and oxidation of metals (Li_2PdO_2[82]), intermetallic compounds (Na_3AuO_2[77]), binary oxides ($Li_6Tb_2O_7$[73]) or ternary oxides (Li_8CeO_8[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 $LiFeO_2$ prepared from α-$NaFeO_2$ 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 $K_2Fe_4O_7$ has been observed in a study of the kinetics of the reaction of α-Fe_2O_3 and K_2CO_3;[84] it is thought to be produced by interaction of α-Fe_2O_3 with the initally formed $KFeO_2$. Xrd, dta and electrical conductivity studies of the Li_2O-RuO_2 system[85] have revealed the formation of Li_8RuO_6, Li_2RuO_3 and bronzes of variable composition $Li_{2x}RuO_{2+x}$ ($0.05<x<0.15$). All three compositions are stable to 1773K. Li_8RuO_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 Li_8RuO_6-I, heating it to 1273K for 20 to 30 hours yields Li_8RuO_6-II. Similar studies of the K_2O-RuO_2 system[86] indicate the formation of K_4RuO_4 and K_2RuO_3, both of which decompose in peritectic reactions at 1238 and 1323K, respectively. Russian authors[87] have also reported the KVO_3-V_2O_5 phase diagram which is a complex section of the K_2O-V_2O_5-VO_2 system. Four compounds are formed, all of which undergo peritectic decomposition reactions, KV_5O_{13-x} (828K)), $K_2V_8O_{21}$ (803K), KV_3O_8 (773K) and $K_3V_5O_{14}$ (691K), together with the vanadium bronze $K_xV_2O_5$.[87]

Spectroscopic methods have been used to probe the structural chemistry of Li_2TiO_3,[88] Li_2ZrO_3[89] and Li_2HfO_3.[89] The ^{7}Li-n.m.r. spectra of Li_2TiO_3 ($300\leqslant T/K\leqslant 520$)[88] indicate that Li_2TiO_3 contains two 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	β/°	Ref
$Na_3Li_5Mn_5O_9$	Trigonal	$R\bar{3}m$	335.6	-	2612.0	-	69
$KLiIrO_6$	Trigonal	$R\bar{3}m$	819.6	-	710.0	-	72
$Rb_2Li_{14}Tb_3O_{14}$	Orthorhombic	Immm	1283.1	790.9	736.9	-	73
KNa_2AuO_2	Orthorhombic	Pnnm	1025.6	547.2	400.0	-	74
$Rb_7NaZn_2O_6$	Triclinic	$P\bar{1}$	1128.3	974.5	711.8	-	70
			(114.1°	88.5°	106.4°)		
$Cs_2K_2Cd_3O_5$	Triclinic	$P\bar{1}$	983.2	918.0	653.5	-	71
			(108.3°	113.7°	99.9°)		
$LiFeO_2$	Hexagonal	-	295.6	-	1457	-	83
Li_8RuO_6-I	Tetragonal	-	537.2	-	1488	-	85
Li_8RuO_6-II	Tetragonal	-	617.2	-	1162	-	85
Li_2RuO_3	Monoclinic	-	507.8	875.5	984.5	99.9	85
Li_6CoO_4	Tetragonal	$P4_2/nmc$	653.6	-	465.4	-	80
β-$LiRhO_2$	Cubic	$F4_132$	841.3	-	-	-	81
Li_8IrO_6	Trigonal	$R\bar{3}$	541.5	-	1505.3	-	75
Li_2PdO_2	Orthorhombic	Immm	375.3	298.2	931.6	-	82
Li_8PtO_6	Trigonal	$R\bar{3}$	541.5	-	1501.4	-	75
Li_8CeO_6	Trigonal	$R\bar{3}$	564.3	-	1620.7	-	75
$Li_6Tb_2O_7$	Monoclinic	$P2_1/a$	1056.3	613.5	546.6	109.7	73
Na_4CrO_4	Triclinic	$P\bar{1}$	859.7	569.8	640.0	-	76
			(124.0°	98.4°	98.9°)		
Na_3AuO_2	Tetragonal	$P4_2/mnm$	970.5	-	457.8	-	77
$NaPrO_2$	Tetragonal	$I4_1/amd$	476.2	-	1096.1	-	78
$NaTbO_2$	Tetragonal	$I4_1/amd$	463.1	-	1037.4	-	78
$K_2Fe_4O_7$	Cubic	-	1681	-	-	-	84
K_4RuO_4	Tetragonal	-	1158	-	767.0	-	86
K_2RuO_3	Orthorhombic	-	1029	705.4	566.8	-	86
K_4ZnO_3	Triclinic	$P\bar{1}$	1103.3	881.3	698.2	-	70
			(109.7°	89.6°	102.4°)		
$Cs_{14}Cd_9O_{16}$	Monoclinic	C2/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 Li_2ZrO_3 and Li_2HfO_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 metallothermic reductions of lanthanide(III) halides with alkali metals.[93]

Reactants	Reactant ratio	T/K	Time/d	Products
$NdCl_3$, Li	1:1	1123	7	$NdCl_2$, LiCl
$DyCl_3$, Li	2:2	973	7	$LiDy_2Cl_5$, LiCl
$SmCl_3$, Na	1:1	1173	3	$SmCl_2$, NaCl
$NdCl_3$, K	2:2	1123	5	KNd_2Cl_5, KCl
$TmCl_3$, Cs	1:1	873	7	$CsTmCl_3$
$YbBr_3$, Rb	1:1	1023	7	$RbYbBr_3$
$YbCl_3$, Li	1:1	1173	3	Yb_4OCl_6, $YbCl_2$, LiCl
$SmCl_3$, Sm_2O_3, Li	10:1:12	1173	4	Sm_4OCl_6, LiCl
$EuBr_3$, Eu_2O_3, Li	6:1:8	1123	7	Eu_4OBr_6, LiBr, Li_2O
$NdCl_3$, Na	1:1	1123	7	NdOCl
$PrBr_3$, Li	1:1	1123	10	Pr_2Br_5, LiBr
$GdCl_3$, Li	1:1	973	6	$LiGdCl_4$, Gd
$GdCl_3$, Na	1:1	973	3	Na_3GdCl_6, Gd
$ErCl_3$, Na	1:1	973	9	Na_3ErCl_6, Er
$GdCl_3$, K	1:1	973	10	KGd_2Cl_7, K_2GdCl_5, Gd
$LuCl_3$, Li	1:1	1223	30	Li_3LuCl_6, Lu
$CsLu_2Cl_7$, Li	1:1	773	19	$Cs_2LiLuCl_6$, Lu
KGd_2Cl_7, Li	1:1	773	20	$Li_2GdClH_x{}^*$, K_2GdCl_5
$LuCl_3$, Cs	2:1	973	7	$LuClH_x{}^*$, $Cs_3Lu_2Cl_9$, $Cs_2Lu_7Cl_{18}C^*$

* 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 Na_2S, Fe and S at 970K for 2 days in a corundum vessel gave Na_5FeS_4 (orthorhombic; space group Pbca; a = 1194.7, b = 709.1, c = 2154pm).[91] Similarly, reaction of Na_2Te_2, Cu and Te in a 1:6:2 molar ratio at 973K for 2 days in a corundum vessel, yielded $NaCu_3Te_2$ (rhombohedral; space group R3m; a = 427.6, c = 2378pm).[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 MX_3 (X = Cl,Br) or $A_xM_yX_z$ (e.g. KGd_2Cl_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 $KCl-IrCl_3$,[94] $RbCl-CeCl_3$[95] and $CsCl-FeCl_3$[96] systems using a variety of dta, tga, xrd and spectroscopic methods. Only one compound K_3IrCl_6 was found in the $KCl-IrCl_3$ system;[94] the previously observed $K_4Ir_2Cl_{10}$ could not be detected. K_3IrCl_6 is polymorphic, changing phase at 693K, before decomposing at temperatures above 1123K to give K_2IrCl_6.[94] Three compounds were discovered in the $RbCl-CeCl_3$ system;[95] $RbCeCl_6$ which melts congruently at 1019K, Rb_2CeCl_5 and $RbCe_2Cl_7$ which decompose in peritectic reactions at 881 and 889K, respectively. Dta, tga, xrd and spectroscopic data for the thermal decomposition of $CsFeCl_4$, Cs_2FeCl_5,H_2O and Cs_3FeCl_6,H_2O have been used to revise the $CsCl-FeCl_3$ phase diagram.[96] Two ternary chlorides exist: $CsFeCl_4$ which melts congruently at 656K and $Cs_3Fe_2Cl_9$ which decomposes in a peritectic reaction at 543K; anhydrous Cs_2FeCl_5 does not exist and anhydrous Cs_3FeCl_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 $MCl-PdCl_2$ (M = Li-Cs) systems. Two compounds occur in the $MCl-PdCl_2$ (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_7LnI_{10}	Na-Gd	Na-Er						
M_4LnI_7	Li-Sm	Rb-Sm						
M_3LnI_6	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	
$M_7Ln_3I_{16}$	Na-Nd	Na-Dy						
M_2LnI_5	K-La	K-Pr	K-Nd					
$M_3Ln_2I_9$	Li-Sm	Rb-Ce	Cs-Pr	Cs-Sm	Cs-Ho	Cs-Tm		
		Rb-Sm	Cs-Nd	Cs-Gd	Cs-Er			
$MLnI_4$	K-Sm	K-Ho	Rb-Ho					
MLn_2I_7	Rb-Ce	Rb-Dy						
MLn_4I_{13}	Cs-Nd							
MLn_9I_{28}	Cs-La	Cs-Pr						
Lanthanum(II)								
M_3YbI_5	Li-Yb							
$MYbI_3$	Na-Yb	Rb-Yb	K-Yb	Cs-Yb				
MYb_2I_5	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_3 and MI-YbI_2 systems are summarised in Table 7. Gromov et al.[95] have reported the phase diagram of the RbI-CeI_3 system; it contains three compounds, of which two melt congruently, Rb_3CeI_6 (879K) and $RbCe_2I_7$ (771K), and one decomposes in a peritectic reaction, $Rb_3Ce_2I_9$ (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_2MI_6 (M = Zr,Hf),[102] Na_3CrCl_6,[103] $Rb_3V_2Br_9$,[111] $Cs_3V_2Cl_9$[111]) or of a ternary halide/binary halide mixture ($NaMn_3F_{10}$[104]). Using

Table 8. Crystallographic parameters for diverse ternary halides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	β/°	Ref
Li_2ZrI_6	cubic	Im3m*	1358				102
Li_2HfI_6	cubic	Im3m*	1357				102
$LiMnF_4$	monoclinic	$P2_1/c$	541.4	462.9	569.4	113.2	107
Na_3CrCl_6	trigonal	$P\bar{3}1c$	682.0		1203.4		103
Na_2MnF_5	monoclinic	$P2_1/c$	771.9	523.6	1086.2	109.0	109
$NaMn_3F_{10}$	orthorhombic	Fdd2	1318.1	1561.8	730.9		104
$KCrF_4$	orthorhombic	Pnma	1576	743	1838		105
$KCrF_4$	orthorhombic	Pnma	1573.2	743.2	1833.1		106
K_4CdCl_6	trigonal	$R\bar{3}c$	1210.5		1490.9		110
$Rb_3V_2Br_9$	hexagonal	$P6_3/mmc$	736.1		1853		111
Rb_4CdCl_6	trigonal	$R\bar{3}c$	1243.9		1557.0		110
$Cs_3V_2Cl_9$	hexagonal	$P6_3/mmc$	724.0		1795		111
Cs_2CuF_4	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 $KCrF_4$; whereas Dewan et al.[105] heated a mixture of KHF_2,CrF_3 and $PbCl_2$ to 1203K followed by slow cooling (6K h^{-1}) to 623K. Hoppe et al.[106] annealed a mixture of KF,CuF_2 and 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 ($LiMnF_4$[107]) or of a mixed alkali metal halide (Cs_2CuF_4[108]), and crystallisation from aqueous solution (Na_2MnF_5,[109] M_4CdCl_6 (M = K,Rb)[110]). The synthetic route to Cs_3IrI_6, which has been the subject of a vibrational analysis, is also worthy of note;[112] it was prepared by repeated iodination of Cs_3IrBr_6 with NaI at 433K with intermediate regrinding and repressing. Vibrational spectroscopic analyses have also been completed[113] for $M_3Mo_2X_9$ (M = K, X = Cl; M = Rb, X = Cl; M = Cs, X = Cl,Br,I). The temperature dependences of ^{81}Br n.q.r. frequencies and quadrupolar relaxation times of Cs_2ZnBr_4 have been measured.[114] Single crystal luminescence and absorption spectra as well as luminescence decay times of $CsMg_{1-x}Ni_xX_3$ (X = Cl,Br) have been determined ($10 \leqslant T/K \leqslant 273$);[115] the presence of excitation energy transfer was established in $CsNiCl_3$ and $CsNiBr_3$.

Five mixed alkali metal halides with cubic (Fm3m) structures have been reported. Cubic Rb_2LiFeF_6 (a = 824.4pm)[112] and Cs_2NaFeF_6 (a = 873.9pm)[116] are metastable high pressure phases obtained by heating the normal pressure variants, previously prepared from the binary fluorides, to 523K at 30 x 10^8 Nm^{-2} for 2h. in a platinum vessel. Cubic $Cs_2LiLuCl_6$ (a = 1040.9pm)[117] and Cs_2KScCl_6 (a = 1087.3pm)[117] were prepared by reaction of $CsLu_2Cl_7$ with lithium and of $Cs_3Sc_2Cl_9$ with potassium in arc welded tantalum vessels at 773K; the former product is metastable at room temperature. Single crystals of cubic Cs_2KCuF_6 (a = 889.4pm)[118] were obtained by annealing powders, manufactured by heating a CsCl:KCl: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 $Cs_3Cr_2Br_3Cl_6$ has been investigated using single crystal xrd and spectroscopic (optical, vibrational) methods.[119,120] Its structure is based on closest packing of $Cs(Cl,Br)_3$ layers with chromium atoms ordered in octahedral sites to form isolated pairs of face-shared octahedra (i.e. binuclear $Cr_2Cl_6Br_3^{3-}$ 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 = 739.1pm, β = 125.3°) 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:

$$2xMBH_4 \;+\; 2A \;\rightarrow\; 2M_x^+[A^{x-}] \;+\; xB_2H_6 \;+\; H_2$$

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 $M_{0.30}MoO_3$ (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 = 750.8pm from time-of-flight single crystal neutron X-ray diffraction data. The mixed alkali metal tungsten bronzes, $M_yK_xWO_3$ (M = Li,Na) have been prepared[125] from binary oxide mixtures in closed vessels ($773 \leqslant T/K \leqslant 1123$) 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 ($Li_xMo_6X_8$; X = S,Se; x = 1,3, 3.8 and 4) have been identified[126] as a result of the electrochemical intercalation of lithium into the Mo_6X_8 (X = S,Se) host lattices by cathodic reduction in the galvanic cell:

$Li/LiClO4$,propylene carbonate/Mo_6X_8 (X = S,Se).

Table 9. Intercalated products synthesised using MBH_4 (M = Li-K) reagents.[122]

Compound $M_x[A^{x-}]$	Solvent	$[A]:[BH_4^-]$ ratio	Time	T/K	Color
$Li_{0.76}MoO_3$	ether	1.0:80	12h	298	dark blue
$Na_{0.55}MoO_3$	i-PrOH	1:1	5h	338	blue
$Na_{0.82}(H_2O)_{1.23}MoO_3$	wet EtOH	1:11	6h	333	blue
$K_{0.41}MoO_3$	i-PrOH	1:1	12h	338	blue
$Li_{0.88}V_2O_5$	ether	1:1	4h	298	dark green
$Li_{0.47}V_2O_5$	ether	1:1	3h	298	dark green
$Li(H_2O)_3FeOCl$	wet ether	1:13	2h	298	black
$Na_{0.6}(MeOH)_{0.3}FeOCl$	MeOH	1:1	2h	298	black
$K_{0.26}FeOCl$	MeOH	1:0.9	2h	298	black
$Li_{0.08}TaS_2$	pyridine	1:1.9	6h	338	metallic gray
$Li_{0.21}TaS_2$	pyridine	1:5	10h	338	metallic gray
$Li_{0.17}(H_2O)_{0.4}TaS_2$	wet MeOH	1:3.5	12h	298	metallic gray
$Na_{0.40}TaS_2$	pyridine	1:1.4	22h	338	metallic gray
$Na_{0.4}(H_2O)_4TaS_2$	wet pyridine	1:1.4	22h	338	metallic gray
Li_xTiS_2	EtOH	1:1	22h	338	metallic gray

The results are closely similar for the two systems. ^{7}Li-n.m.r. data indicate that partial charge transfer occurs in $Li_3Mo_6S_8$ with formation of triangular $(Li_3)^{2+}$ clusters suggesting the formulation, $Li_3{}^{2+}[Mo_6S_8]^{2-}$;[126] the Li^+ ions appear to be "normal" in the other intercalates. A similar rhombohedral phase, $Li_{3.5}Mo_6Te_8$, has been produced by reaction of Mo_6Te_8 with n-butyllithium in evacuated Schlenk tubes at 298K for 5 days.[127] Crystallographic parameters for the $Li_xMo_6X_8$ intercalates[126,127] are collected in Table 10.

Table 10. Rhombohedral lattice parameters of lithium intercalates, $Li_xMo_6X_8$ (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
α/°	92.55	94.29	94.23	94.52	92.23	94.43	94.40	92.52

The intercalates A_zMXH_x and their host lattices 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 MX_3, MH_2 (or 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 $AM_2P_3O_{12}$ (A = Li,Na; M = Ti,Zr) and $NbTiP_3O_{12}$ could only be achieved for those phases containing chemically reducible species;[129] singly and doubly lithiated phases were prepared from $ATi_2P_3O_{12}$ (A = Li,Na) and $NbTiP_3O_{12}$ but $AZr_2P_3O_{12}$ (A = Li,Na) were unreactive (Ti(IV) and Nb(V) can be reduced but Zr(IV) is inert).

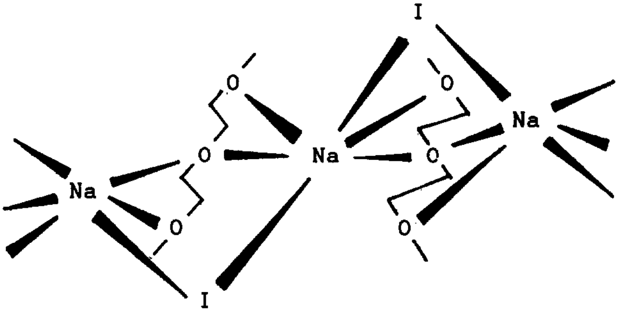
1.4 COMPOUNDS OF THE ALKALI METALS CONTAINING ORGANIC MOLECULES OR COMPLEX IONS

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 860cm^{-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 (Na...I = 316.4pm) and two of the oxygens of the diglyme molecules (Na...O = 242.7,271.4pm) in a distorted octahedral arrangement. The retention of the Na...I bonds is surprising snce complexation with chelating ligands such as diglyme normally results in "solvent separated" ion pair formation.[131]



(28)

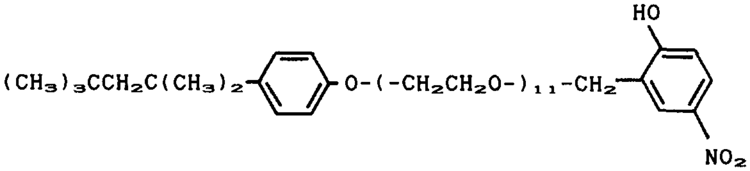
Enhanced binding and transport of alkali metal cations through an organic model membrane (0.1M $^nBu_4NClO_4$ in CH_2Cl_2) via a novel electrochemical switching mechanism has been demonstrated.[132] Whereas the neutral anthraquinone podand (29) has very limited ability to transport Li$^+$ across the membrane, the corresponding radical anion $(29)^{\dot{-}}$, obtained by electrochemical reduction, exhibits much higher Li$^+$ transport rates.[132]

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

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

$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$

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



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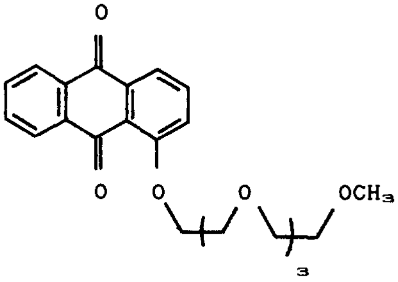

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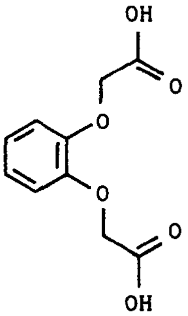

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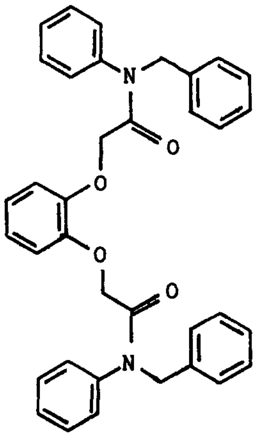

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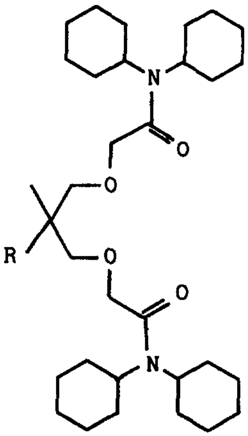
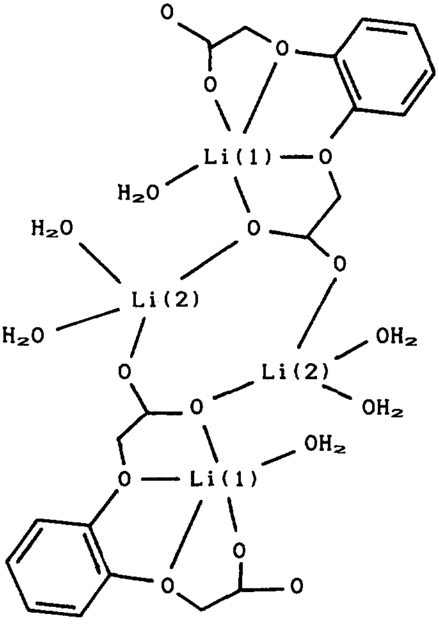


R = Me, ^{n}Bu

(33)

calcium[135] salts of benzene-1,2-dioxydiacetic acid (31). The lithium salt, $[(31)_2Li_4],6H_2O$ (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, $[(31)_2Ca_2],4H_2O$ (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).



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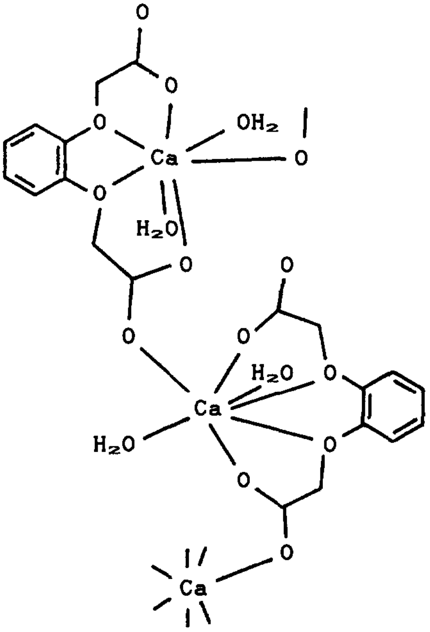


(35)

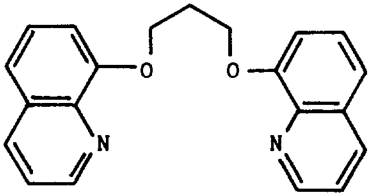
A series of ionophores, based on (32) have been prepared by substitution of the aromatic ring carrying the ether oxygens.[136] None of the substituents, despite their widely varying electronegativities ($-CH_3$, $-OCH_3$, -CHO, -CN, $-NO_2$, -Br) have a discernible effect on the selectivity of the ionophores for M^+ (M = Li-Cs) and M^{2+} (M = Mg-Ba) which vary in the sequences:

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

$$Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}.$$

The ionophores (33) exhibit remarkable selectivity for Li^+ in the presence of Na^+ in highly lipophilic liquid membranes.[137] The crystal structure of $[(33)Li]^+NCS^-$ (methyl version) shows the Li atom to be coordinated by the four oxygens of a chelating ligand (Li...O = 195.0,197.9,208.5,222.9pm) and the nitrogen of the anion (Li...N = 203.2pm) 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 $[(31)_2Li_4],6H_2O$ and $[(33)Li]^+NCS^-$, $[(36)Li]^+ClO_4^-$ has been been structurally analysed.[138] Again a five-coordinate Li atom occurs, its square pyramidal geometry comprising the four heteroatoms of the ionophore (Li...O = 217; Li...N = 121pm) and an oxygen of the anion (Li...O = 200pm).



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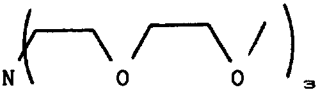


(37)

Complexation of M+ (M = Li-Cs) by (37) has been examined by fast atom bombardment mass spectroscopy.[139] It binds Li^+ most strongly followed by K^+ and Na^+; it binds Rb^+ and 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+ and K+ 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 spectrscopic[142-144] and single crystal xrd methods.[144-148] The conformational changes which occur in 12C4[142] and 18C6[143] on complexation with M^+ (M = Li-K) have been studied by Russian authors using i.r. and Raman spectroscopy. When free, both ligands adopt conformations with C_1 symmetry; when complexed, 12C4 forms conformations with C_4 or D_4 symmetry and 18C6 adopts forms conformations with D_{3d}, C_{3v} or C_1 symmetry. Fourier transform infrared spectroscopic studies[144] of the solution ($CHCl_3$) and solid state structure of the KNO_3 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, γ-cyclodextrin.12C4.LiSCN.H_2O (3:3:1:23) and γ-cyclodextrin.12C4.KCl.H_2O (3:3:1:27) have been determined by xrd analyses.[145] Three γ-cyclodextrin molecules each of which includes a 12C4 mnolecule 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, $[(12C4)_2M]^+$ (M = Li,K) (Fig. 3(b,c)) which is included in the hydrophobic channel formed by the two γ-cyclodextrin molecules, while the third is free of cation.[145]

Single crystal xrd structural analysis[146] of $[18C6Sr]^{2+}[(BuO)_2PO_2]_2^-.H_2O$ 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 $[18C6Li]^+[18C6Li(thf)]^+[FePc]^{2-}$ (Pc = phthalocyanine) has been reported in a letter;[147] no details of the structure of the cations are provided.

The crystal structure of $[DB18C6K]^+NCS^-$ 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

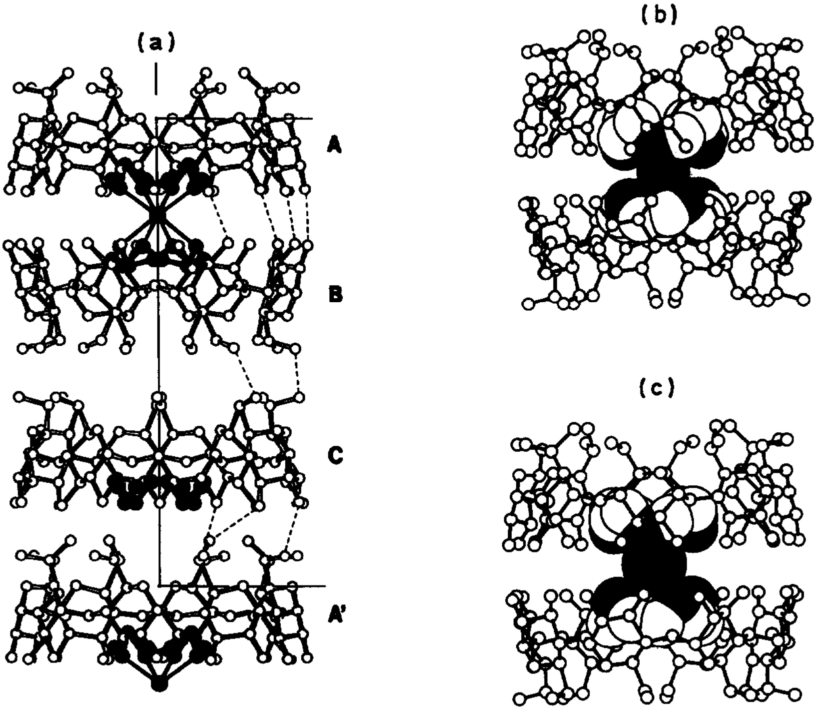


Figure 3. The channel-type structure (a) of γ-cyclodextrin.-12C4.LiSCN (3:3:1) inclusion complex (Li^+ and 12C4 molecules are shown by full circles; SCN^- anions are omitted for clarity, and the structures of γ-cyclodextrin.12C4.Li^+ (b) and γ-cyclodextrin.-12C4.K^+ (c) (2:2:1) complexes (M^+ and 12C4 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).

oxygens of the ether ring (K(1)...O = 262-283; K(2)...O = 266-283pm). The hexagonal pyramidal coordination geometries of the K atoms are completed by the nitrogens of the anion (K(1)...N = 280; K(2)...N = 269pm).[148] The thermal stabilities of $[DB18C6K]^+X^-$ (X = NCS,Br,I,NO_3) and of some of their adducts with C_2H_5OH and $CHCl_3$ have been determined by dsc methods. Whereas $[DB18C6K]^+NCS^-$ melts congruently, $[DB18C6K]^+X^-$ (X = I,NO_3) when melting undergo partial dissociation into their components. Of the adducts, $[DB18C6K]^{+}I^{-}.C_2H_5OH$ loses the ethanol without dissociation, but $[DB18C6K]^{+}Br^{-}.3CHCl_3$ 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 M^{+} and 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 M^{+} (M = Na,K) with B15C5 or DB30C10 in CH_3CN-H_2O mixtures:[149]

$$[DB30C10K]^{+} > [B15C5K]^{+} > [B15C5Na]^{+}$$

does not differ with solvent concentration, and that the stability sequence of the 1:1 complexes of M^{2+} (M = Ca-Ba) with DB30C10 in CH_3OH, dmf and dmso:[150]

$$[DB30C10Sr]^{2+} > [DB30C10Ba]^{2+} > [DB30C10Ca]^{2+}$$

is independent of solvent.

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

Popov et al. have applied ^{133}Cs n.m.r. spectroscopic methods to investigate the complexation of 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 M^{+} (M = Li-Cs) and 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 = 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 = Ca-Ba) in H_2O-CH_2Cl_2 systems in the presence of diverse crown ether (15C5, B15C5, 18C6, DCH24C8, DB30C10) and cryptand (C221, C222) complexing agents,[156] for M^+ (M = Na-Cs) in H_2O-$CHCl_3$ systems in the presence of 18C6[157] and for M^+ (M = Li-Cs) and M^{2+} (M = Ca-Ba) in H_2O-$CHCl_3$ 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 K^+ in the presence of Na^+; separation of Li^+ from Na^+ (using (38) or (39)), of K^+ from Rb^+ (using (38)) and of Sr^{2+} from Ca^{2+} and Ba^{2+} (using (39)) can also be effected.[158]

The mechanism of M^+ (M = 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 K^+ (as picrate) from water into $CHCl_3$ containing 18C6, DCH18C6 or DB18C6, and its rate of transfer across a $H_2O/CHCl_3$ 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 Na^+ across a $H_2O/C_6H_5NO_2$ 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 M^+ (M = Li-Cs) and M^{2+} (M = Mg-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 $Li^+ < Na^+ \sim Cs^+ < Rb^+ < K^+$

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

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

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

Alkali metal cation (Li-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 M^+ at the interface mirrors that of B18C6 in solution.[164]

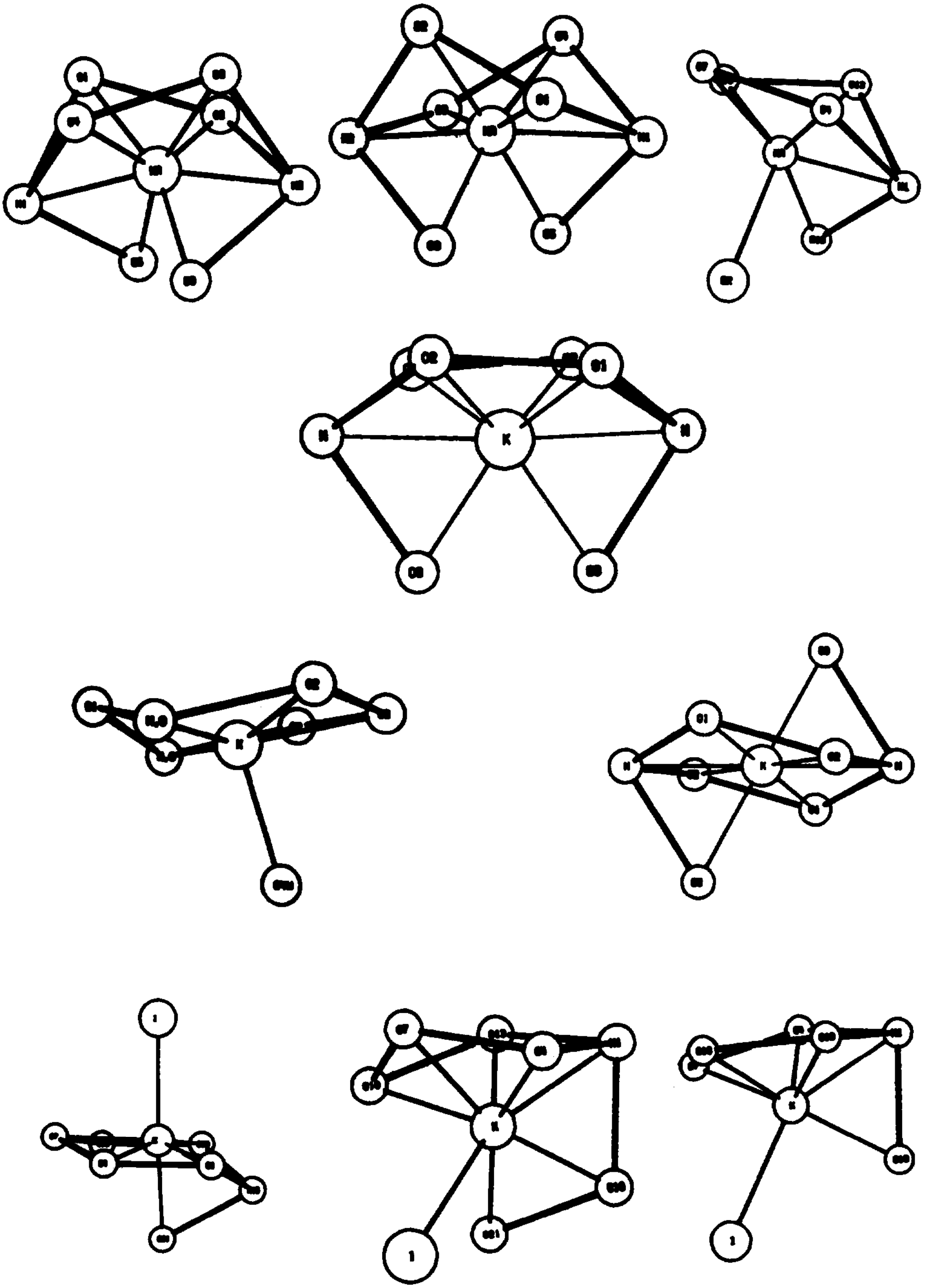
The distribution of M^+ (M = Li-Cs) as picrates between water and polyester-based polyurethane foam in the presence of DCH18C6 can be considered as an ion pair extraction of $[DCH18C6M]^+X^-$ by an organic solvent;[165] as for more conventional systems, the sequence of extraction constants is governed 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 charactersied 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 chorands 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 Na^+ and 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 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 Li^+, Na^+ or K^+, but the changes are most marked for Na^+. The radical anion sidearm complexes are thought to be relatively rigid species since the strongest side-arm interaction is observed for Na^+ which is closest in size to the cavity formed by cooperating macrocycle and side-arm.[168]

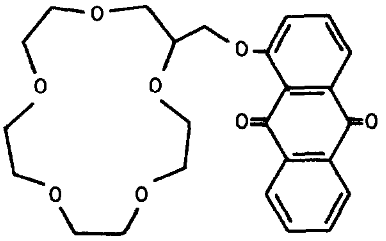
Using cyclic voltammetric methods, Gokel et al.[169] have also observed enhanced cation binding for the C-pivot lariat ether (<u>40</u>) when electrochemically reduced according to Scheme 5. For Li^+, the reduction induced binding enhancements are $K_2/K_1 = 2.4 \times 10^3$ (for one electron transfer)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



Scheme 4

observed.[169]

$$\begin{array}{ccc} (\underline{40}) + M^+ & \overset{K_1}{\rightleftharpoons} & [(\underline{40})M]^+ \\ \downarrow\uparrow e & & \downarrow\uparrow e \\ (\underline{40})^{\cdot -} + M^+ & \overset{K_2}{\rightleftharpoons} & [(\underline{40})M]^{\cdot} \\ \downarrow\uparrow e & & \downarrow\uparrow e \\ (\underline{40})^{2-} + M^+ & \overset{K_3}{\rightleftharpoons} & [(\underline{40})M]^- \end{array}$$



(40)

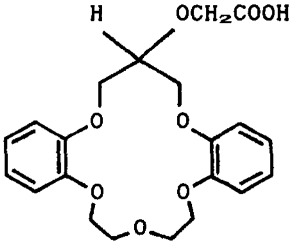
Scheme 5

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

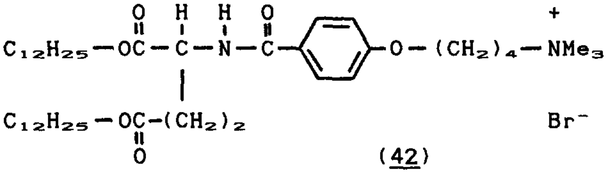
Those of the deprotonated ligand exhibited completely reversed behaviour:

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

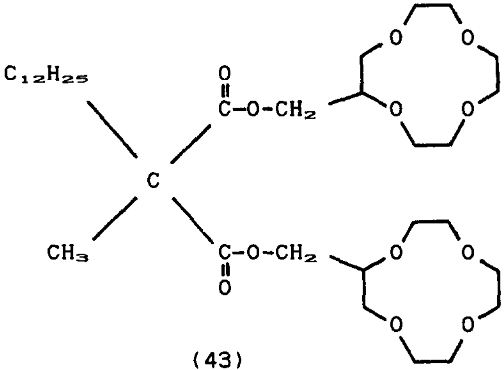


(41)

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



(42)



(43)

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

Addition of Na$^+$ or K$^+$, but not Li$^+$, to a methanol solution of the N-pivot lariat ethers (44) results in the enhancement of the fluorescence quantum yield (Φ_F) of (44) by factors of $\leqslant$47.[172] It is suggested that this perturbation of the fluorescence may lead to quantitative remote signalling of the presence of M$^+$ (M = Na,K) in biological environments.

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

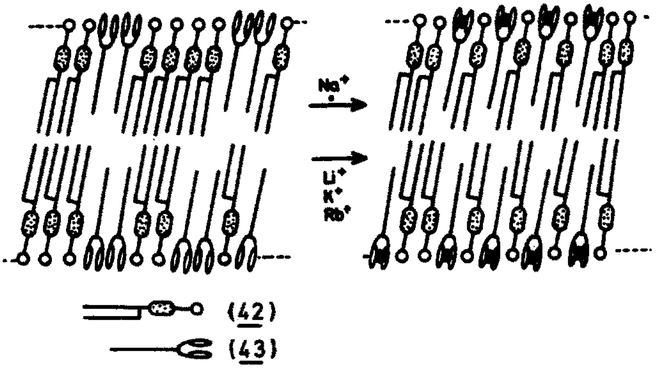
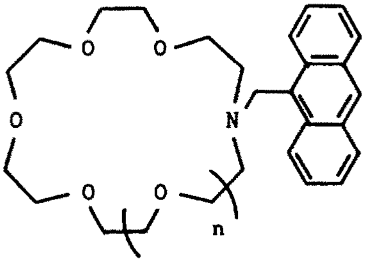
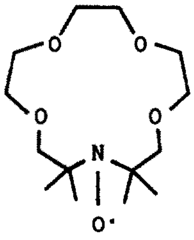


Figure 4. Schematic illustration of the suppression of c.d. intensity in an amphiphile-crown ether bilayer (reproduced by permission from J. Chem. Soc., Chem. Commun., (1987)617).

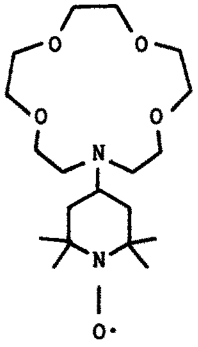


(n = 0,1)

(44)

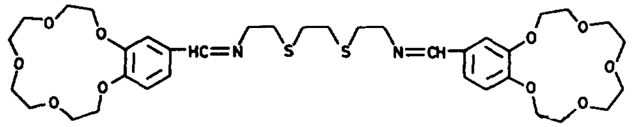


(45)



(46)

Beer[174] has shown that the complexation of alkali metal cations (Na^+,K^+) by the novel Schiff base bis(crown ether) ligand (47) is modified by the presence of transition metals (Ag^+,Cu^{2+}). In the absence of transition metals, the two B15C5 units of (47) act independently to complex two Na^+ ions giving (48) and cooperatively to complex one K^+ ion giving (49). In the presence of Ag^+, which prefers tetrahedral coordination by the N_2S_2 chromophore, the 1:1 intramolecular sandwich complex type is no longer available for K^+; instead a 2:1 complex (50) similar to



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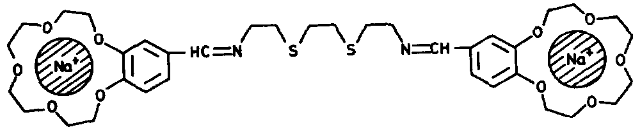

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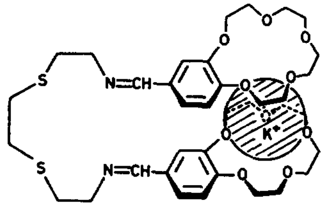

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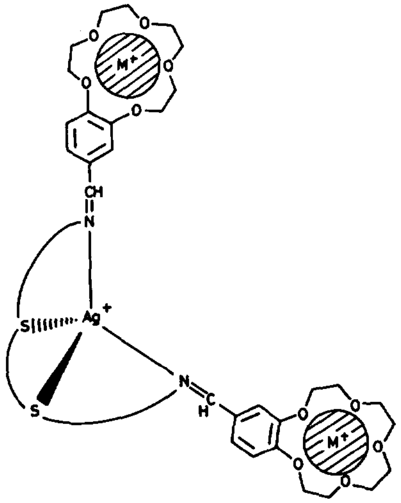
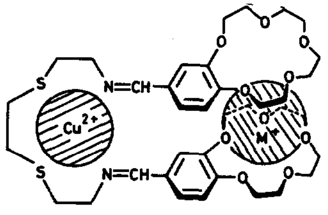


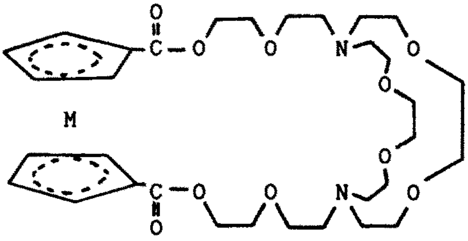
(50)



(51)

that formed by Na^+ (50) is formed. In the presence of Cu^{2+}, however, which prefers square planar coordination by the N_2S_2 chromophore, the formation of the 1:1 intramolecular sandwich complex type can occur giving (51); with 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 K^+ to the exclusion of Li^+, Na^+ and Cs^+.



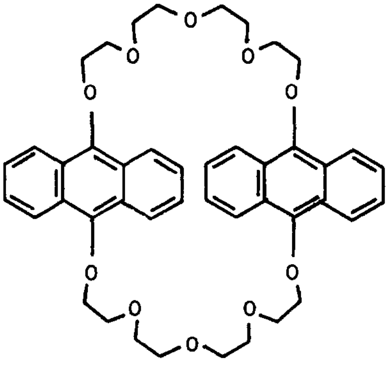
(52: M = Fe, Ru)

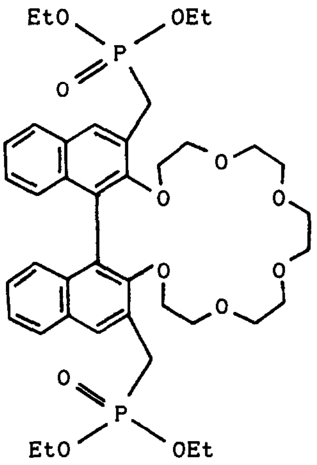
Alkali metal cations (Na^+,K^+) bound to 18C6 with a pendant thiazolium ion have been found to increase the rate of the oxidative decarboxylation of pyruvic acid in ethanol by binding the substrate and acting as the catalytic centre.[176]

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 $[(53)Na_2]^{2+}(ClO_4^-)_2$[177] and $[(54)K]^+SCN^-.CHCl_3$.[178] In the centrosymmetric structure of $[(53)Na_2]^{2+}(ClO_4^-)_2$,[177] each Na atom is located in a pentagonal bipyramidal coordination sphere comprising (equatorially) five adjacent oxygens of the polyether ring (Na...O = 245.5-255.9pm) and (axially) two oxygens of separate anions (Na...O = 243.6,246.5pm); 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 struture of $[(\underline{54})K]^+SCN^-.CHCl_3$[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.


(53)



(54)

The novel cylindrical crown ether, tridecalino-18C6[180] exhibits higher complexing selectivity for K^+ over Na^+, as well as a higher intrinsic complexing ability for K^+ than either DCH18C6 or didecalino-18C6. The stability of the complex of K^+ 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^+ (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_3OH by calorimetric titration methods, increase in the sequence:[181]

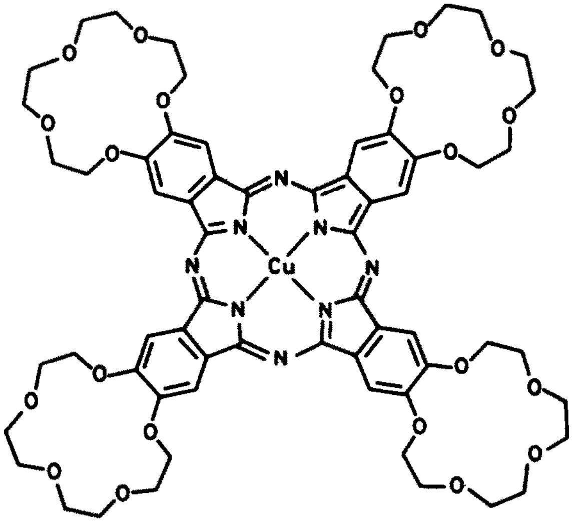
(55) $\log K_{ML}$ Na^+ (1.14) < Cs^+ (1.81) < K^+ (1.97)

(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)

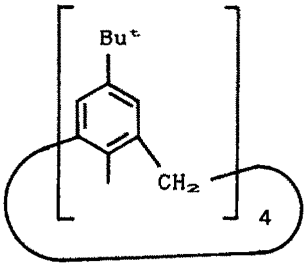
Dutch[182] and Japanese[183] chemists have independently synthesised the polytopic ligand system (59) by refluxing 4,5-dibromo-B15C5, obtained by bromination of B15C5 (Fe-Br_2; solvent CH_2Cl_2) with CuCN in dmf for 20h. The Dutch group[182] report that (59) has a high affinity for M^+ (M = Na-Cs) but a relatively low affinity for Li^+. They also note[182] that K^+ ions induce dimerisation forming a complex of 4:2 stoichiometry, but that Li^+ ions form a monomeric complex of 4:1 stoichiometry; presumably the K^+ ions bind two 15C5 residues, whereas Li^+ 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^+-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 $[(\underline{60})Na.C_6H_5CH_3]^+[C_6H_5COO(AlMe_2)_2OAlMe_3]^-$,[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 $[(\underline{61})K.CH_3OH]^+SCN^-$,[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]



($\underline{60}$) R = OMe
($\underline{61}$) R = OCH_2CONEt_2

1.4.5 Natural Product Ionophores

Pangborn et al. have reinvestigated the molecular structure of the Na$^+$ complex of the monocarboxylic acid polycyclic polyether antibiotic A204A (acetone adduct),[186] and have determined, for the first time, that of the K$^+$ 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$^+$ and have obtained preliminary results (only alluded to in this paper) on the corresponding K$^+$ 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 $C21C_5$, 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]

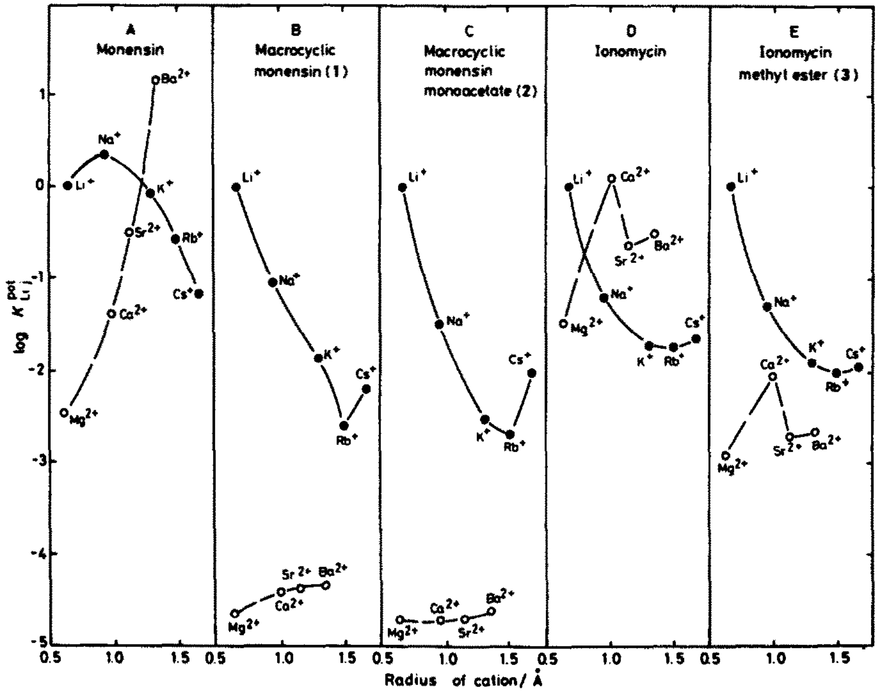


Figure 5. Selectivity factors ($\log K^{pot}_{Li}$;j:interfering ion) for monensin, ionomycin and their derivatives (reproduced by permission from J Chem. Soc., Chem. Commun.,(1987) 932).

The ionophore also exists in the inclusive form in the molecular structure of [C21C$_5$Li]$^+$NCS$^-$ in which there are three Li...O (200.1,214.2,236.0pm) and two Li...N interactions (211.1,227.5pm) in a highly irregular geometry. The NCS$^-$ anion does not coordinate the Li atom.

Lincoln et al.[193-195] have undertken a comparative study of the complexation of Na^+ by $C21C_5$ and C211. The stability constants[193] of $[C21C_5Na]^+$, determined in dmf, pyridine, methanol, acetone, acetonitrile and propylene carbonate in the presence of 0.05M $(C_2H_5)_4NClO_4$ are substantially lower than those observed for $[C211Na]^+$. The relative instability of $[C21C_5Na]^+$ is mirrored in the rate constants[194] for the formation and decomplexation of $[C21C_5Na]^+$ and $[C211Na]^+$ 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 $C21C_5$ (5) compared with C211 (6).[193,194] This conclusion is supported by the results of an xrd study[195] of the crystal and molecular structures of $[C21C_5Na]^+SCN^-$ and $[C211Na]^+SCN^-$ which shows that all the heteroatoms in the ligands, which adopt the exclusive form, coordinate the Na atom: in the $[C21C_5Na]^+$ cation, the Na atom is surrounded by the three oxygens (Na...O = 229.7-235.6pm) and two nitrogens (Na...N = 257.6,275.9pm) of the cryptand and by the nitrogen of the anion (Na...N = 235.8pm); in the $[C211Na]^+$ cation, it is encapsulated by the four oxygens (Na...O = 228.9-266.2pm) and two nitrogens (Na...N = 247.8,249.2pm) of the cryptand and by the nitrogen of the anion (Na...N = 240.9pm).[195]

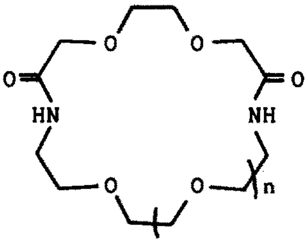
Reaction of C222, when dissolved in ethylenediamine, with $K_{1.6}As_{1.6}Te$ and with mixtures of K_2S_5 and sulphur yields crystals of $[C222K]^+{}_3[As_{11}Te]^{3-}$.en[196] and of $[C222K]^+{}_2S_6{}^{2-}$ and $[C222K]^+{}_2S_7{}^{2-}$.en.[197] Whereas the three $[C222K]^+$ cations in the former complex are crystallographically distinct,[196] those in the latter two complexes are symmetry related;[197] all five cations are unremarkable. Reaction of $[C222K]^+[{}^tBuS]^-$ in C_6H_5Cl with iron(II) phthalocyanine gave, after addition of pentane, crystals of $[C222K]^+[FePc]$ (Pc = phthalocyanine);[198] although structural analysis was undertaken no details are reported for the cation.

The stability constants of $[C222Cs]^+$ have been determined in the four binary solvent systems, acetone/dmso, acetonitrile/dmso, propylene carbonate/dmso and propylene carbonate/dmf using ^{133}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

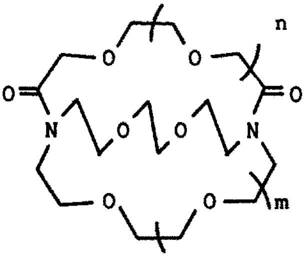
In the binary mixtures, the stability constants varied monatonically with composition.[199]

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.



n = 0,1

(62)



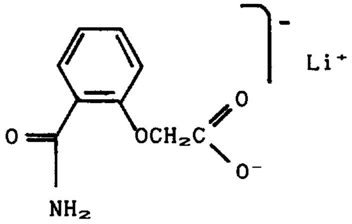
n = 0,1

(63)

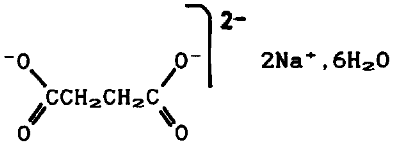
1.4.7 Salts of Carboxylic, Thiocarboxylic and Dithiocarbamic Acids

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.

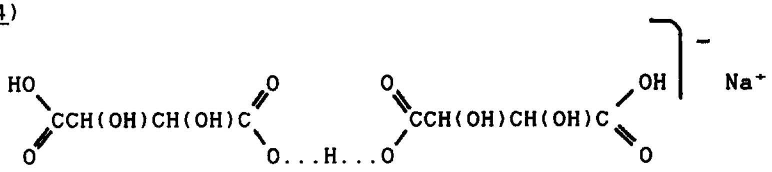
Single crystal xrd structural analyses have been successfully completed for lithium 2-carbamoylphenoxyacetate (64),[201] disodium succinate, hexahydrate (65),[202] monosodium di-meso-tartrate (66),[203] potassium dihydroxyacetate (67)[204] and monopotassium cyclobutanedicarboxylate (68).[205] The Li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



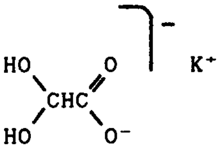
(64)



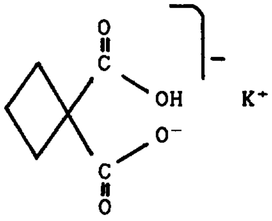
(65)



(66)



(67)

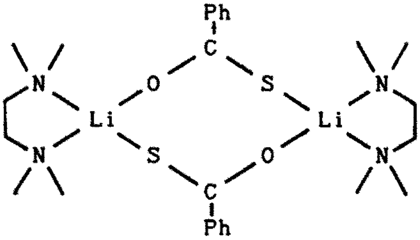


(68)

(64)[201] is 4-fold coordinate; its distorted tetrahedral geometry comprises one oxygen from the 2-carbamoyl moiety (Li...O = 195.0pm) and three carboxyl oxygens from different anions (Li...O = 191.3-198.5pm). 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 (Na...O = 238.0pm) and five water molecules (Na...O = 234.6-256.3pm); the distorted cubic coordination polyhedron of the Na atom in (66) is based on four hydroxyl (Na...O = 253.0,257.0pm) and four carboxyl oxygens (Na...O = 246.8,260.7pm). The structure of (67)[204] contains two crystallographically independent K atoms; the distorted octahedral coordination sphere of K(1) comprises two hydroxyl (K...O = 274,275pm) and four carboxyl oxygens (K...O = 272-283pm) and the distorted sqaure 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, $[PhCOS]^-Li^+$,tmeda (69)[206] and $[SOCNHNHCOS]^{2-}2K^+,2H_2O$ (70) and of one dithiocarboxylate, $[S_2CPhCS_2]^{2-}2K^+,2H_2O$ (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)

$(HCOSLi)_2$, 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_2O_2 yielded the formate peroxohydrates, HCO_2Na,H_2O_2 and $HCO_2M,1.5H_2O_2$ (M = K-Cs);[209] they are unstable at ambient temperature (293K) slowly losing active oxygen.

Alkali metal N,N'-diphenyl-N-formimidoyldithiocarbamate solvates, $[S_2C\text{-}N(Ph)\text{-}CH{=}N(Ph)]^-M^+,xL$ (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 = 318.1,344.8pm) and a monodentate dithiocarboxylate moiety (K...S = 334.1pm), a nitrogen of a separate anion (K...N = 293.0pm) and an oxygen of the solvent molecule (K...O = 271.6pm) 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, $[S_2C\text{-}N{=}C(CH_3)\text{-}NH_2]^-M^+$ (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: $[Li(thf)_{4.5}]^+[Co\{N(SiMe_3)_2\}\text{-}(OC^tBu_3)_2]^-$,[214] $[Li(tmeda)_2]^+[Mo(CO)_3\{\eta^5\text{-}C_5(CH_3)_5\}]^-$,[215]

$[Li(tmeda)_2]^+[Lu(^tBu)_4]^-$ [216] and $[Na(tmeda)_2]^+[Ni(C_2H_4)_2H]^-$. [217] Blue crystals of the Li-Co complex were prepared by reaction of $[Co\{N(SiMe_3)_2\}_2]$ with $^tBu_3COH$ in n-hexane followed by addition of $LiN(SiMe_3)_2$ in thf.[214] The Li-Mo complex was synthesised as a moisture sensitive yellow crystalline solid by reaction of ^nBuLi with $[Mo(CO)_3H\{\eta^5\text{-}C_5(CH_3)_5\}]$ in toluene containing tmeda.[215] A crystalline sample of the Li-Lu complex was obtained by interaction of ^tBuLi with $LuCl_3$ in diethylether containing tmeda.[215] Of the four cations, $[Li(thf)_{4.5}]^+$ [214] is unique since, in the presence of thf, Li^+ usually crystallises as the tetrahedral $[Li(thf)_4]^+$. In $[Li(thf)_{4.5}]^+$, four normal thf molecules coordinate to Li^+ (Li...O = 190-209pm) with a fifth more remote thf molecule (Li...O = 256pm) 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 31pm towards the other, more tightly bound, axial thf molecule.[214]

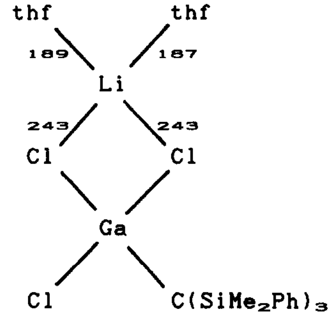
A significant number of molecular heterobimetallic complexes containing Li have been synthesised; they include Li-Ga,[218] Li-In,[218] Li-Ti,[219] Li-V,[220] Li-Cr,[221] Li-Mo,[222] Li-W,[223-225] Li-Co,[214] Li-Ni,[217] and Li-Lu[226] complexes. In the majority of cases, [214,217-221,223-226] characterisation 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 MCl_3 (M = Ga,In) with $Li\{C(SiMe_3)_3\}$ at 273K 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.

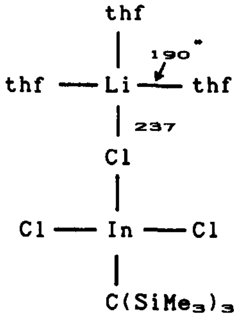
The Li-Ti complex (76) was prepared in poor yield by reaction of the lithiated triaminosilane $PhSi\{NLi(SiMe_3)\}_3$ with $(\eta^5\text{-}C_5H_5)TiCl_3$ in Et_2O at 243K.[219] It contains an unusual heteronuclear bicyclo [311]-heptane entity which contains titanium and silicon bridgeheads and includes a novel Cl-Li-N bridge;[219] the roughly trigonal planar Li coordination is completed by an ether molecule.

Treatment of µ-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 η^6-coordination of the benzene molecule to both Li and V atoms; the Li atom is coordinated in a distorted pseudo-

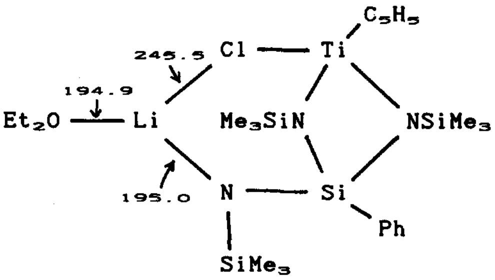
Figure 6. Schematic representations of the molecular structures of heterobimetallic complexes containing lithium.



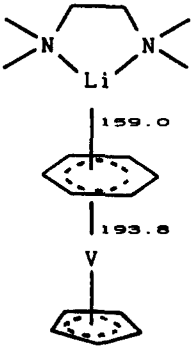
(74); [218] tetrahedral Li;
88-129°



(75);[218] tetrahedral Li;
102-120°
*average value

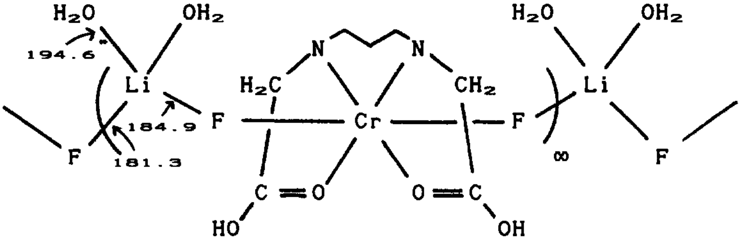


(76):[219] trigonal
planar Li

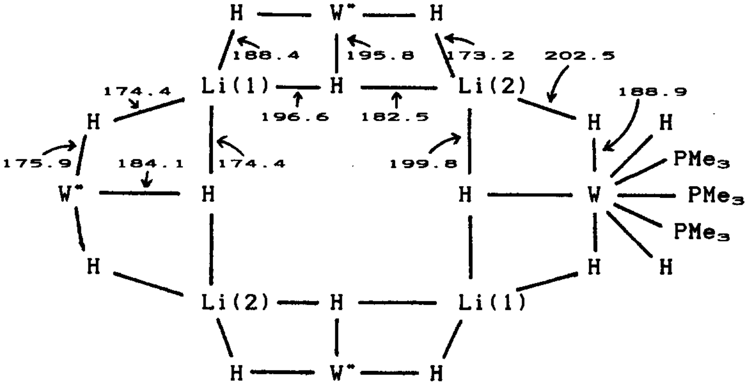


(77);[220] trigonal
planar Li

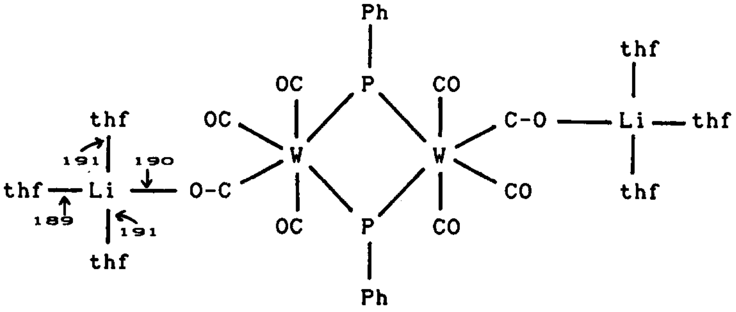
Figure 6 continued.



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

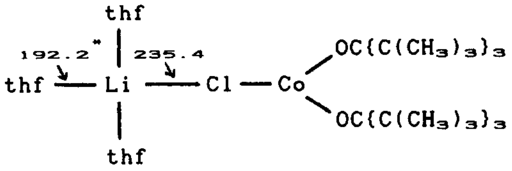


(79);[223;224] severely distorted tetrahedral Li
* The complete W coordination sphere is omitted for clarity.

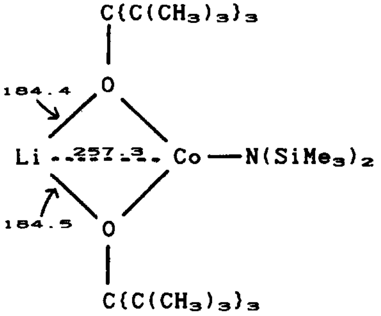


(80);[225] tetrahedral Li; 105-115°

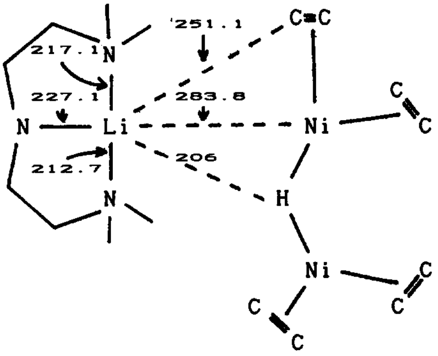
Figure 6 continued.



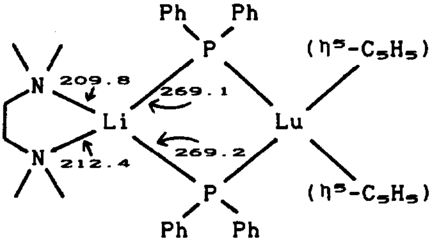
(81);[214] tetrahedral Li;
105-113°
*average value



(82);[214] (Li...H = 207pm)
(OLiO = 95.6°)



(83)[217]



(84);[226] distorted tetrahedral Li; PLiP = 91.2°
NLiN = 87.8°

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]-∞ 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 Na^+, K^+ nor 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 $[(Me_3P)_3H_3W(\mu\text{-}H)_2AlH(\mu\text{-}H)]_2$ 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 $W(\mu_2\text{-}H)Li$ bridges and then by one $W(\mu_3\text{-}H)Li_2$ bridge;[223,224] the Li atoms are thus 4-coordinate with a severely distorted tetrahedral geometry.

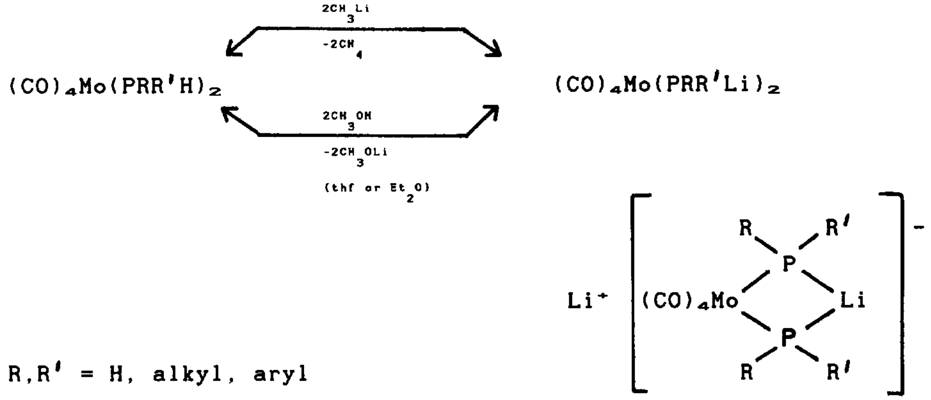
The Li-W complex (80), which is based on a planar 4-membered W_2P_2 ring and in which the Li atom possesses an almost regular tetrahedral oxygen environment composed of an equatorial CO and three thf molecules, was synthesised by reduction of $W_2(CO)_8(\mu\text{-}PPh_2)_2$ using two equivalents of $LiBEt_3H$ in thf.[225]

Addition of a solution of $LiOC^tBu_3$, formed by mixing of solutions of ^nBuLi (in n-hexane) and $^tBu_3COH$ (in thf) to a slurry of $CoCl_2$ in Et_2O 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 $[Co\{N(SiMe_3)_2\}_2]$ in thf firstly with $^tBu_3COH$ and secondly with a solution of $LiN(SiMe_3)_2$ 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 $CoN(SiMe_3)_2$ moiety, the two alkoxide groups;[214] there is, however, in the structure of (82) a close Li...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 $[Li(pmdeta)]^+$ cation and one Ni atom, one ethene molecule and the hydride anion in the $[\{(\eta^2\text{-}C_2H_4)_2Ni\}_2(\mu\text{-}H)]^-$ anion giving the Li atom a pseudo-octahedral coordination geometry.

A puckered 4-membered LuP_2Li ring is the core of the structure of (84) which was obtained by reaction of the corresponding di-μ-methyl complexes with $HPPh_2$ via stepwise substitution of the methyl ligands;[226] the approximately tetrahedral geometry of the Li atom is completed by the tmeda ligand.

Low temperature ^{7}Li and ^{31}P n.m.r. studies[222] of $(CO)_4Mo(PRR'Li)_2$, prepared as per scheme 6, may be assigned on an ionic type (solvated) of structure $Li^+[cis\text{-}Mo(CO)_4(\mu\text{-}PRR')_2\text{-}Li]^-$ in which the core of the anion comprises a four-membered MoP_2Li ring system (85).



R,R' = H, alkyl, aryl

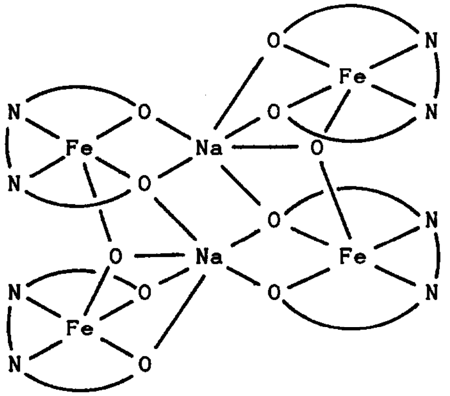
(85)

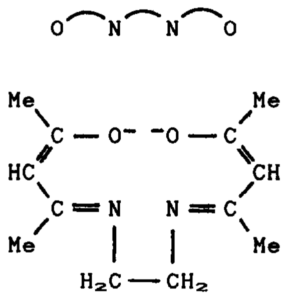
Scheme 6.

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 $\{[Fe(acacen)]_2O\}$ with sodium metal in thf yields the centrosymmetric Na-Fe complex $\{[Fe(acacen)]_2ONa\}_2$ (86) in which the ten oxygen atoms from the two {$[Fe(acacen)]_2O$} 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 M(tmtaa) {M = Fe,Co,Ni; tmtaa = dibenzotetramethyltetra-aza[14]annulene dianion}

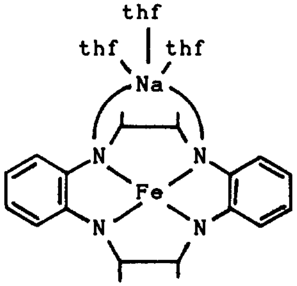
Figure 7. Schematic representations of the molecular structures of heterobimetallic complexes containing sodium.



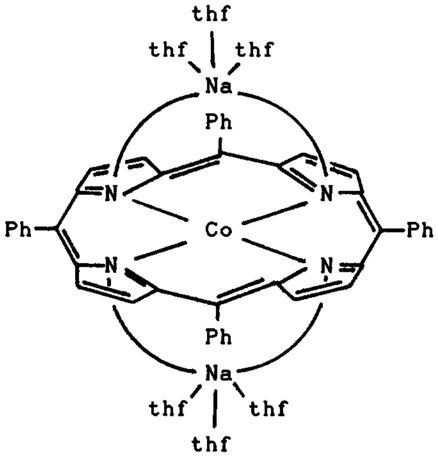


acacen

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

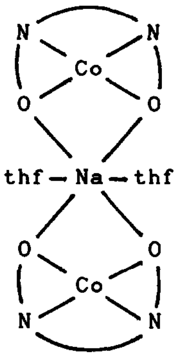


(<u>87</u>);[228]
Na...O = 233.4-239.1pm
Na...N = 277.5,280.1pm



(<u>88</u>);[229]
Na...O = 231.2-234.1pm
Na...N = 275.7,276.6pm

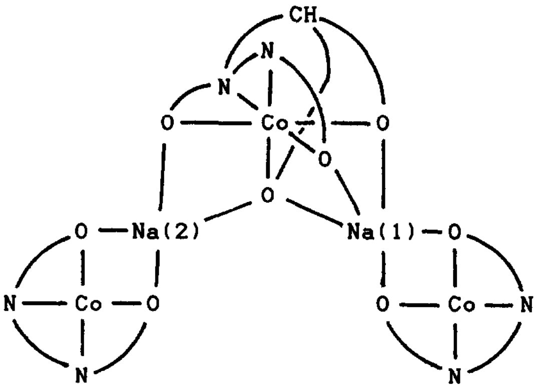
Figure 7 continued



(90); [230]

Na...O(salen) = 239.3-256.3pm

Na...O(thf) = 248.6,252.9pm



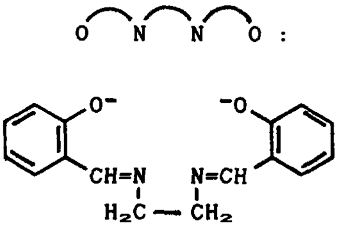
(91); [231]

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

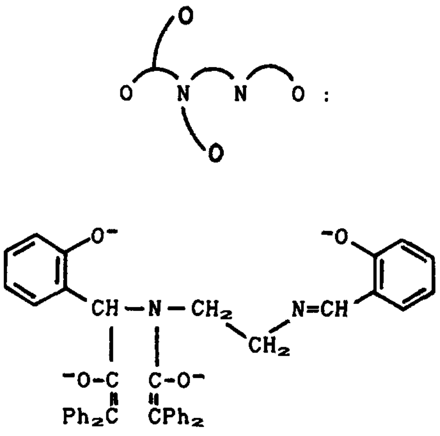
Na(1)...O(salendpk) = 228,230, 269pm

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

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

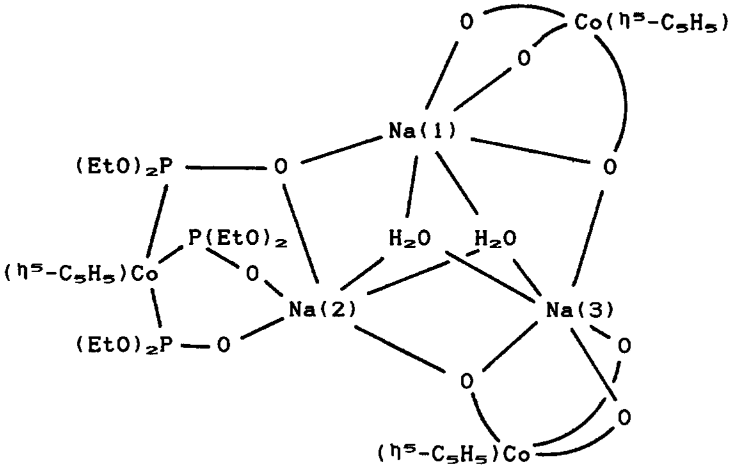


salen



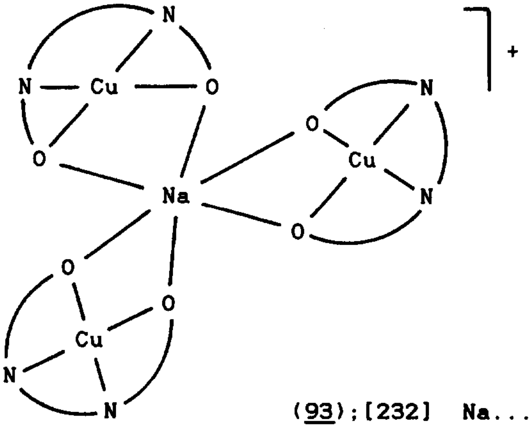
salendpk

Figure 7 continued



Only one of the anionic oxygen tripod ligands, $[(\eta^5\text{-}C_5H_5)Co\{OP(OEt)_2\}_3]^-$, is shown in full.

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



acacen

(<u>93</u>);[232] Na...O = 236-255pm

gives the complexes $[M(tmtaa)Na(thf)_3]$.[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 $[Na(thf)_3]^+{}_2[Co(tpp)]^{2-}$ (tpp = 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]

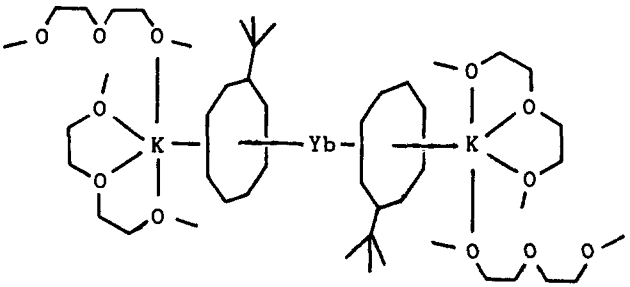
Reaction of the bifunctional complex $[Co(salen)Na(thf)_n$ (89) with the parent complex $[Co(salen)]$ gives the Na-Co complex (90)[230] in which two identical $[Co(salen)]$ units act as bidentate equatorial ligands for the Na atom which completes its coordination sphere with two thf molecules located 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 $[(\eta^5\text{-}C_5H_5)Co\{OP(OEt)_2\}_3]^-$ 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 [Cu(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 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 (Yb...C(average) = 277pm). The K atoms cap the other sides of the rings (K...C(average) = 308pm) and are also coordinated by the three oxygens of a chelating diglyme molecule (K(1)...O = 275.1-305.6pm; K(2)...O = 276.2-302.0pm) and a single oxygen of the other diglyme molecule (K(1)...O = 286.5pm; K(2)...O = 285.7pm).[234]



(94)

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 multinuclear 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, $LiNa_3[O{=}P(NMe_2)_3]_3$-$[N{=}C(NMe_2)_2]_4$ (95) has been reported by Wade et al.[237] Produced by sequentially adding $HN{=}C(NMe_2)_2$ (2 equiv.) and $O{=}P(NMe_2)_3$ (excess) to a mixture of ^{n}BuLi (1 equiv.) and ^{n}BuNa (1 equiv.) in hexane, (95) has a $LiNa_3N_4$ cubane-type structure (Figure 8) with each of the $O{=}P(NMe_2)_3$ ligands terminally attached through its oxygen to a Na atom. Although the Li atom does not have a terminal moiety, each of the adjacent guanidino groups has a methyl group which leans perceptibly towards the Li atom suggesting three Li...H interactions.[237]

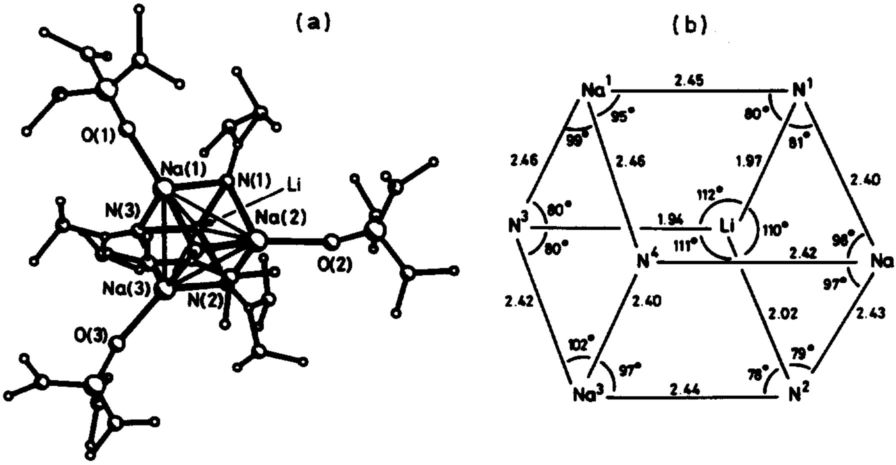


Figure 8. The molecular structure of $LiNa_3[O{=}P(NMe_2)_3]_3$-$[N{=}C(NMe_2)_2]_4$ (a) with selected interatomic distances (in Å) and angles (in °) (b) (reproduced by permission from J. Chem. Soc., Chem. Commun., (1986)1740).

1.4.9.1 Hexamers and Higher Oligomers

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

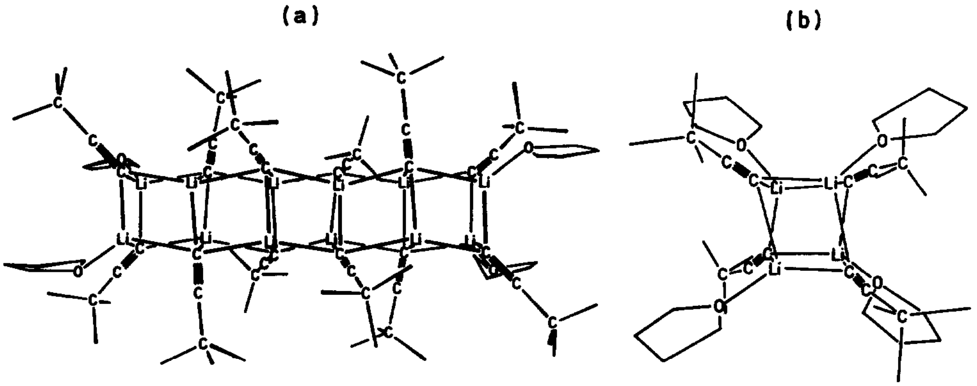
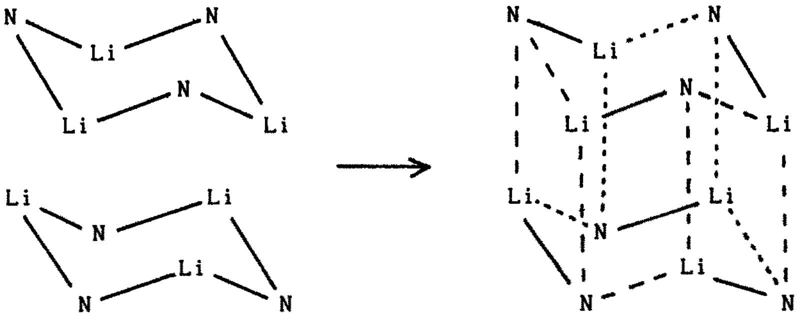


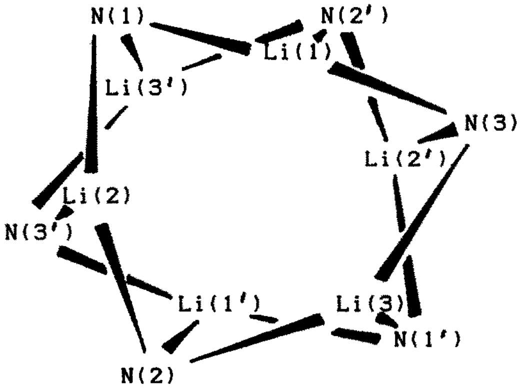
Figure 9. Crystal structure of (a) $[(^{t}BuC\equiv CLi)_{12}(thf)_{4}$ and (b) $[(^{t}BuC\equiv CLi)_{4}(thf)_{4}]$. The centres of both the dodecamer and the tetramer lie on 2-fold axes perpendicular to the plane of projection (reproduced by permission from Angew. Chem., Int. Ed. Engl., 26(1987)587).

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 $[(^{t}BuC\equiv C)_{2}Li_{2}]$ is stacked into aggregates $[(^{t}BuC\equiv C)_{2}Li_{2})]_{n}$ (n = 1,2,3...).[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 $(RR'C{=}NLi)_{6}$ (R' = Ph, R = ^{t}Bu or $Me_{2}N$; R' = R = $Me_{2}N$ or ^{t}Bu). All four compounds have remarkably similar solid state structures based on slightly folded chair-shaped Li_{6} cores, the six smaller (isosceles) 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 $(RR'C{=}NLi)_{3}$ brought together in a staggered conformation (scheme 7). The projection of the $Li_{6}N_{6}$ core of $[Me_{2}N(Ph)C{=}NLi]_{6}$ perpendicular to its pseudo-three fold axis (98) clearly shows the stacking principle.



Scheme 7



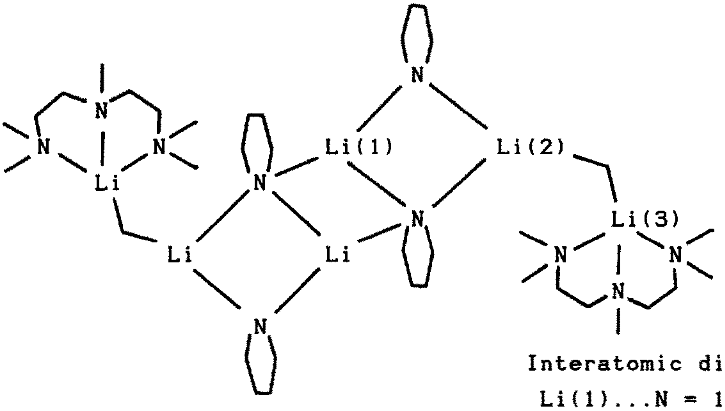
(98)

Interatomic distances/pm

Li...N = 196.1-208.1
N...N = 317.2-318.7
Li...Li = 247.2-248.7

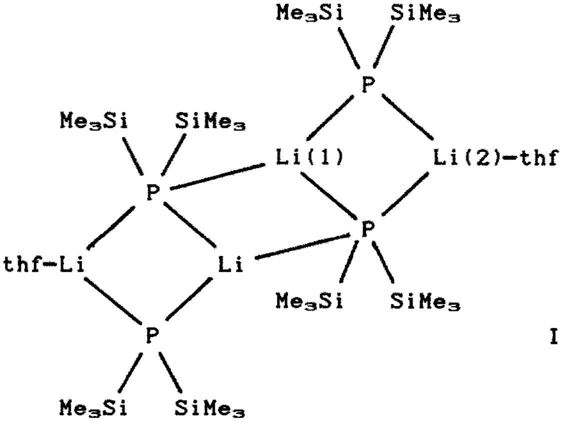
Similar folded chair Li_6 cores are found in the hexameric structures of $[Me_3SiCH_2Li]_6$ (99)[242] and $[^tBuC(=CH_2)OLi]_6$ (100);[243] as for the hexameric iminolithium clusters neither structure has an exocyclic ligand, the electronic structure of the Li atom of (100) being satisfied by an interaction with the π system of the CH_2=C< fragment of the enolate anion. The hexameric structures of $[PhSi(N(^tBu)Li)_3]_2$ (101)[244] and $[H_2C(CH_2)_3NLi]_6(pmdeta)_2$ (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 Li_6 trigonal antiprism centered on the $\bar{1}$ symmetry sites of the $P\bar{1}$ space group; six Li_3 faces are bridged by nitrogens, the other two by silicons, the overall symmetry approaching $\bar{3}m$ (D_{3d})). That of (102)[245] is a laddered structure consisting of two attached

Li_2N_2 rings (alternatively four Li-N rungs) with two terminal LiN units complexed by pmdeta so preventing further association. Cryoscopic and ^{7}Li n.m.r. spectroscopic studies of arene solutions of (102) imply that the ladder framework can be extended suggesting that similar compounds $[RR'NLi,x\ donor]_n$ 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

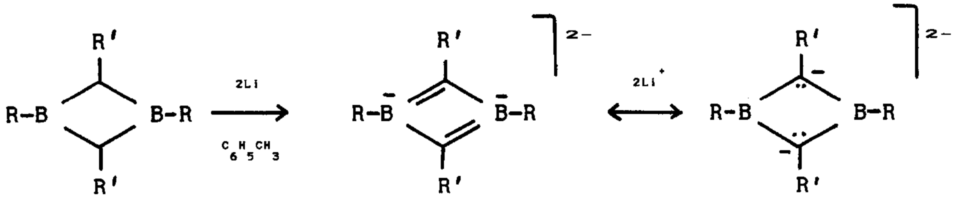
1.4.9.2 Tetramers

The tetrameric decomposition product $[\{(Me_3Si)_2PLi\}_4(thf)_2]$ (103), of the dimer $[\{(Me_3Si)_2PLi\}_2(thf)_4]$ 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 Li_2P_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 $[(^tBuC{\equiv}CLi)_4(thf)_4]$ (97),[238] $[Me_2NCH_2CH_2CH_2Li]_4$ (104),[248] and $[(Me_3Si)CH\{S(O)(NSiMe_3)Ph\}Li]_4$ (105).[249] That of (97)[238] is shown in Figure 9b, it is based on a Li_4C_4 core (Li...C = 217-229pm; Li...Li = 259-278pm) with thf molecules completing the tetrahedral coordination geometry of the Li atom (Li...O = 192,199pm). A similar Li_4C_4 core (Li...C = 224.0-227.6pm) occurs in the structure of (104);[248] in this case, however, the fourth coordination position of the Li atom is occupied by a pendant NMe_2 group (Li...N = 206.2, 206.7pm). A cubane type Li_4O_4 skelteton (Li...O = 193.4-240.8pm) lies at the centre of the structure of (105);[249] each Li atom attains penta-coordination through the carbon (Li...C = 243.0pm) and nitrogen (Li...N = 211.3pm) 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 alternatingly annelated to the central Li_4O_4 cube.[249]

A somewhat irregular Li_4N_4 core occurs in the structure of the tetramer, $[Me_2Si\{(^tBu)NLi\}_2]_2$ (106);[244] the distortion arises because of the restricted geometry of the dianion. In reality, the molecular structure of (106) is based on a Li_4 bisphenoid, the two pairs of Li_3 faces being linked by the two N-Si-N bridges (Li...N = 200.3,203.6pm), 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 Li_4 layer (Figure 10).[250]



(108) (107)

Scheme 8; R = $-C(CH_3)_3$; R' = $-Si(CH_3)_3$

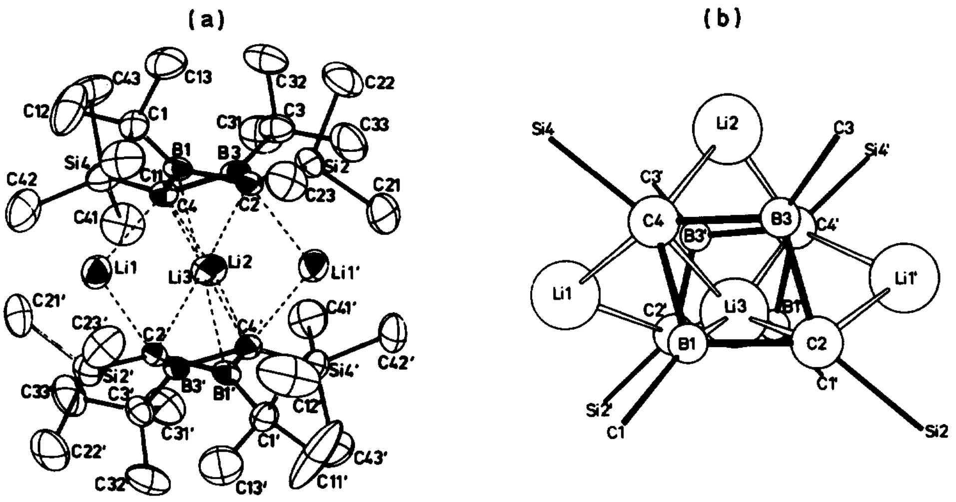


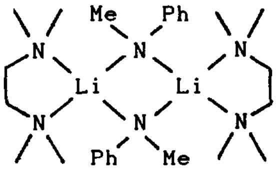
Figure 10. Projections of the dimeric structure of the dilithium salt of a diboratacyclobutadiene (a) in the direction of the pseudo-C_2 axis and (b) in the direction of the "sandwich axis". Interatomic distances (averaged over both halves of the dimer) Li(1)...Li(3) = 233, Li(2)...Li(3) = 247, Li(1)...Li(2) = 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 $[\{(Me_3Si)_2CH\}_2Li]_3$ (109),[251] prepared by reaction of lithium with $\{(Me_3Si)_2CH\}_2AsCl$ in Et_2O at 298K. The Li_3As_3 ring has a boat conformation with an average Li...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 ^nBuLi. Single crystal xrd structural analysis has shown that the majority are based on Li_2X_2 (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, Et_2O 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 Li_2X_2 rings are those of $[\{H_2C{=}C(^tBu)N(Ph)Li\}_2(Et_2O)_2]$ (113),[266] $[\{Me_2N.N.C(CH_2)_4C.CH(OMe)OLi\}_2(thf)_2]$ (114)[256] and $[\{Ph_2PCH_2C(^tBu)_2OLi\}_2\{(^tBu)_2C{=}O\}]$ (115).[263] The Li atom in the centrosymmetric dimeric structure of (113)[266] is coordinated to the two nitrogens of the Li_2N_2 ring (Li...N = 200.0,207.6pm) and to two benzene carbons (Li...C = 243.7,266.2pm) and to the ether oxygen (Li...O = 193.7pm). The two Li atoms in



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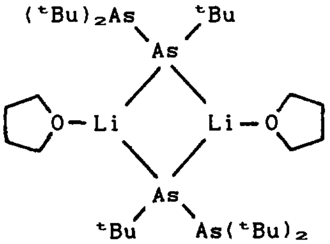

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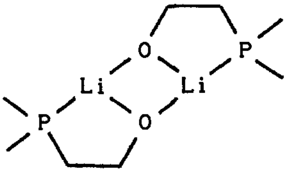


(112)

Table 11. Structural details for diverse dimeric lithium complexes based on Li_2X_2 rings.

Molecule	Li_2X_2 ring	r(Li..X) pm.	Li C.N	Exocyclic ligand(Y)	r(Li..Y) pm.	Ref
Solvated Lithium Derivatives:						
$[\{PhN(CH)_3CLi\}_2(tmeda)_2]$	Li_2C_2	219.1,218.4	4	tmeda	219.9,230.4	252
$[\{(Me_3Si)_2NLi\}_2(thf)_2]$	Li_2N_2	202.5,202.5	3	thf	188.2	253
$[\{Me_2Si.NH.SiMe_2.NH.SiMe_2.NLi\}_2(thf)_2]$*	Li_2N_2	203.5(av)	3	thf	192.6(av)	254
$[\{Me_2Si.N(SiMe_3).SiMe_2.NH.SiMe_2.NLi\}_2(thf)_2]$	Li_2N_2	201.7,206.1	3	thf	191.2	255
$[\{Ph_2NLi\}_2\{(^iPr)_2NH\}_2]$	Li_2N_2	201.2,207.8	3	$(^iPr)_2NH$	212.4	256
$[\{Ph(Me)NLi\}_2(tmeda)_2]$	Li_2N_2	208.2,208.2	4	tmeda	229.6,229.6	257
$[(PhCH{:}C{:}NLi)_2(tmeda)_2]$	Li_2N_2	204(av)	4	tmeda	205(av)	258
$[\{(2,4,6\text{-}Me_3C_6H_2)_2PLi\}_2(Et_2O)_2]$*	Li_2P_2	249.8(av)	3	Et_2O	190.8(av)	259
$[\{Ph_2PLi\}_2(tmeda)_2]$*	Li_2P_2	261(av)	4	tmeda	213.8(av)	274
$[\{(Me_3Si)_2PLi\}_2(thf)_4]$	Li_2P_2	262,262	4	thf	192,203	247
$[\{(^tBu)_2As(^tBu)AsLi\}_2(thf)_2]$	Li_2As_2	258,258	3	thf	189	260
$[\{Ph_2AsLi\}_2(Et_2O)_4]$	Li_2As_2	270.8,275.7	4	Et_2O	197.4,199.7	261
$[\{(SiMe_3)_3C.SiMe_2.OLi\}_2(thf)_2]$	Li_2O_2	181(av)	3	thf	206(av)	262
$[\{Ph(Me)C{:}S(Ph)OLi\}_2(tmeda)_2]$	Li_2O_2	192(av)	4	tmeda	213(av)	264

Table 11 continued:

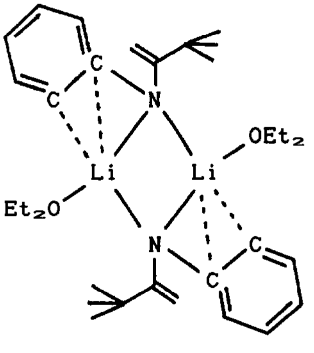
Intramolecularly coordinated Lithium Derivatives:

$[Me_2PCH_2C(^tBu)_2OLi]_2$						
	Li_2O_2	181,176	3	$-PMe_2$	250	263
$[Ph_2PCH_2C(^tBu)_2OLi]_2$						
	Li_2O_2	178.7,179.7	3	$-PPh_2$	265.1	263
$[(Ph_2P(O)CH_2CH_2)_3NLi]_2^{2+}$						
	Li_2O_2	196,208	4	$-P(O)Ph_2$	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 Li_2O_2 ring (Li...O = 191.9pm) and the two nitrogens of the hydrazone residue (Li...N = 202.3pm); Li(2) is encapsulated by the two oxygens of the Li_2O_2 ring (Li...O = 192.7pm) and two thf molecules (Li...O = 192.9pm). The coordination polyhedra of the Li atoms are both flattened tetrahedra. A similar arangement pertains in the structure of (115);[263] Li(1) is coordinated by the two oxygens of the Li_2O_2 ring (Li...O = 180,187pm) and the two phosphorus atoms of the derivitised alkoxide anion (Li...P =



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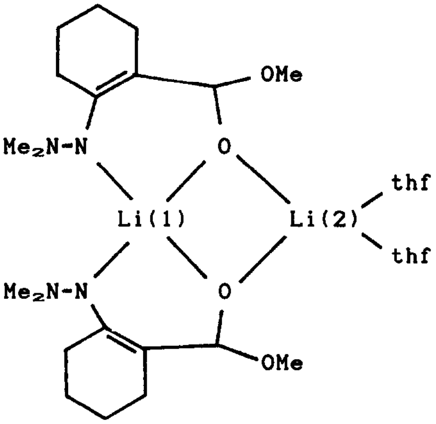

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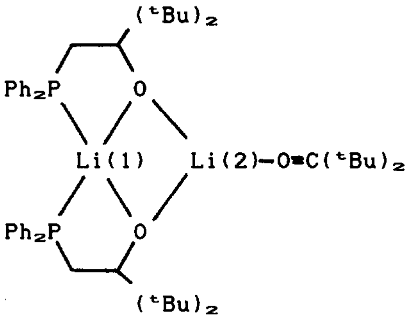
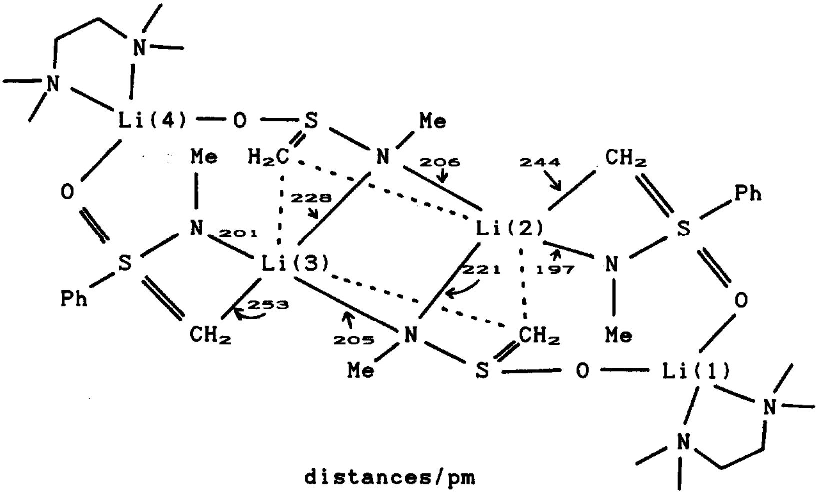


(<u>115</u>)

259,263pm) in a distorted tetrahedral array; Li(2) is surrounded by the two oxygens of the Li_2O_2 ring (Li...O = 180,183pm) and by the oxygen of the solvating ketone (Li...O = 197pm) in a trigonal planar geometry.

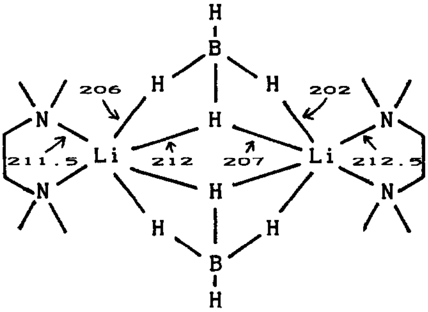
The structure of the pseudo-tetrameric complex (<u>116</u>) is also based on a Li_2X_2 ring.[267] The two Li atoms in the Li_2N_2 core are coordinated by the nitrogen atoms of the bridging sulphoximide anions and the nitrogen and carbon atoms of the other two anions; they also have a relatively remote contact with the methylene group of the bridging anion (Li(2)...C = 324,337; Li(3)...C = 303,334pm). The other two Li atoms are encapsulated by two oxygen atoms of separate anions (Li...O(average) = 190pm) and the two nitrogen atoms of the tmeda ligand (Li...N(average) = 210pm).[267]



distances/pm

(<u>116</u>)

Unusual bridges occur in the dimeric structures of [LiBH$_4$.tmeda]$_2$ (117),[268] [{EtOLi}$_2$(PhCH$_2$NO$_2$)$_2$]$_n$ (118),[269] [(Me$_3$Si)$_2$NSi(Me)(F)O(CMe$_3$)$_2$N(Li).Si(CHMe$_2$)$_2$F]$_2$ (119),[270] [{CH$_2$=CH.CH.S(Ph)O$_2$Li}$_2$(diglyme)$_2$] (120)[271] and [(MeO.SiMe$_2$)$_3$CLi]$_2$ (121).[272] The centrosymmetric dimer (117)[268] contains both doubly and triply bridging hydrogen atoms; each μ_2,η^3-BH$_4$ group bonds to two Li atoms through one μ_2-H atom apiece and through one μ_3-H atom. The Li coordination sphere is completed by the nitrogens of the tmeda molecule.



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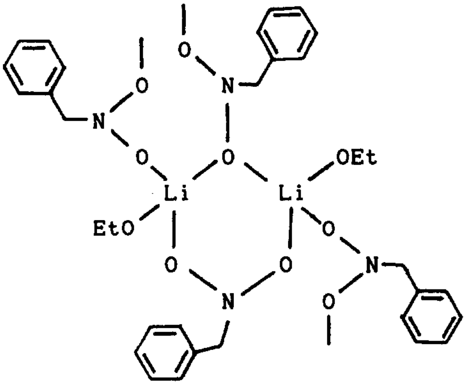

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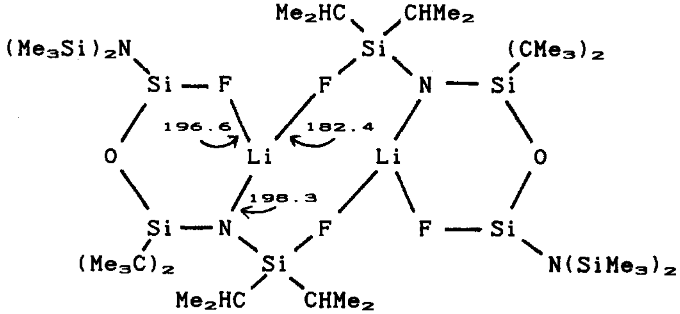

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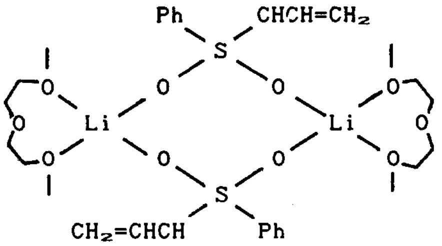

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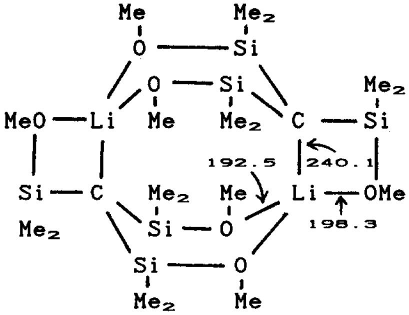

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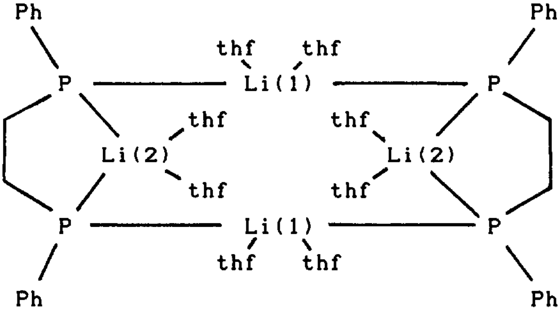


(122)

distances/pm

M.O. calculations at the 6-31G level[268] on $[LiBH_4]_2$ and its adducts with η^2- and η^3-BH_4 geometries show how their stabilities reflect the number of Li...H contacts, whilst illustrating the inadequacies of LiHB and Li_2HB 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 (Li...O = 191.9-197.9pm). The bridges in the centrosymmetric structure of (119)[270] comprise the $-N^-$-$Si(CHMe_2)_2F$ moieties of the $[(Me_3Si)_2NSi(F)OSiN$-$Si(CHMe_2)_2F]^-$ 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 $(MeOSiMe_2)_3CLi$ 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 (PLi(1)P = 86.9°), and, intermolecularly (PLi(2)P = 113.5°), respectively; the Li(1) atoms lie out of the plane defined by the remaining P_4Li_2 system giving the 8-membered ring the appearance of an elongated chair.[273]

1.4.9.5 Monomers and Polymers

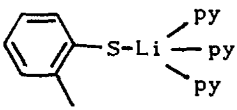
Single crystal xrd data have been collected and analysed for 19 monomeric (or polymeric) lithium derivatives. The majority are stabilised by coordination of the Li atom by both the anions and solvate molecules such as thf, Et_2O, tmeda, pmdeta and diacetamide; for the remainder, stability is generated 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, [{Ph(naphthyl)NLi}.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 (Li...C = 312,315pm), 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 $[Li(thf)_n]^+$ and anions $[R_2P]^-$ held together by Li...P interactions.

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

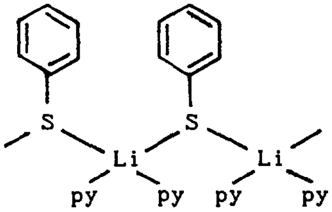
Compound	Li	R_2X^- anion		Solvate	Molecule	Ref
	C.N.	X	r(Li..X)/pm	X	r(Li..X)/pm	
[{Ph(naphthyl)NLi}.pmdeta	4	N	200	N	218,221,222	257
[{Ph(naphthyl)NLi}.tmeda	3	N	197	N	212,213	257
[{Ph_2PLi}.pmdeta]	4	P	256.7	N	209.1,212.6,215.0	274
[{2,4,6-$Me_3C_6H_2$(H)PLi}.$(thf)_3$]	4	P	253.3	O	194.9-198.2	259
[{Ph_2PLi}.$(thf)_2$]∞	4	P	262.9,263.4	O	193.7,198.8	275
[{$(C_6H_{11})_2$PLi}.thf]∞	3	P	245.5,254.3	O	193.6	275
[{Ph_2PLi}.Et_2O]∞*						
(1)	3	P	248.6,249.6	O	192.5	275
(2)	3	P	248.3,249.2	O	196.6	275
[{Ph_2AsLi}.$(thf)_3$]	4	As	266.0	O	193.1-196.8	261

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

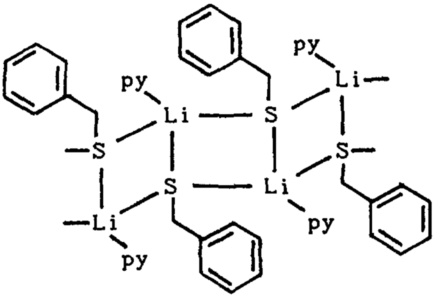
Minor changes in the anion often induce remarkable structural variation. An xrd study[276] of a series of crystalline lithium aryl thiolates, prepared by addition of hexane solutions of ^{n}BuLi to chilled (253K) toluene solutions of thiol and pyridine, has shown that the 2-MeC$_6$H$_4$S$^-$ derivative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



(<u>123</u>)



(<u>124</u>)

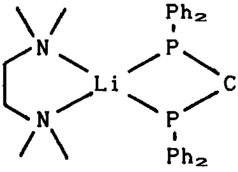


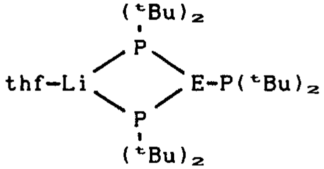
(<u>125</u>)

	r(Li...S)/pm	r(Li...N)/pm
(<u>123</u>)	241.2	208.1,208.1,208.3
(<u>124</u>)	245.9,251.3	206.3,208.5
(<u>125</u>)	245.4-250.8	204.5,206.8

Four membered LiP$_2$C, LiP$_2$Sn and LiP$_2$Pb rings have been found as the core of the molecular structures of [(Ph$_2$P)$_2$CHLi.tmeda] (<u>126</u>),[277] [{(^{t}Bu)$_2$P}$_3$SnLi.thf] (<u>127</u>)[278] and

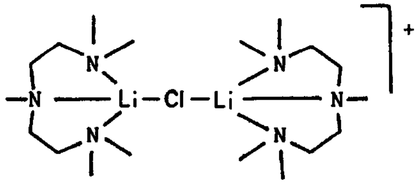
$[\{(^{t}Bu)_2P\}_3PbLi.thf]$ (<u>128</u>).[278] The LiP_2C rings in (<u>126</u>),[277] synthesised by lithiation of bis(diphenylphosphino)methane with MeLi in Et_2O containing tmeda, exhibit mean Li...P and Li...C

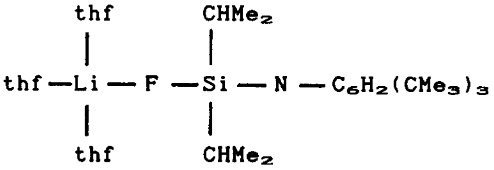

(<u>126</u>)


E = Sn (<u>127</u>)
E = Pb (<u>128</u>)

distances of 258.2 and 172.2pm, respectively; the tetrahedral geometry of the Li atom is completed by the bidentate tmeda molecule (Li...N = 203.3,207.2pm). The "ate" complexes, (<u>127</u>) and (<u>128</u>),[278] obtained by treatment of $[(^{t}Bu)_2PLi]$ with $SnCl_2/PbCl_2$ in thf solution, are isostructural. The LiP_2Sn/-LiP_2Pb rings have mean Li...P and Sn/Pb...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; $[\{(pmdeta)Li\}_2Cl]^+[Li\{C(SiMe_3)_3\}_2]^-$ (<u>129</u>)[279] and $[\{2,4,6\text{-}(Me_3C)_3C_6H_2N.Si(^{i}Pr)_2FLi\}(thf)_3]$ (<u>130</u>).[280] The former ionic complex, prepared by addition of pmdeta to toluene containing both LiCl and $[Li(thf)_4]^+[Li\{C(SiMe_3)_3\}_2]^-$, contains a centrosymmetric linear chlorine centred cation (<u>131</u>)[279] in which the Li atom is encapsulated by the chlorine (Li...Cl = 217pm) and the three nitrogens of the tridentate pmdeta ligand in a distorted tetrahedral array. The latter molecular complex (<u>130</u>),[280] obtained by reaction of the parent aminofluorosilane with MeLi in


(<u>131</u>)

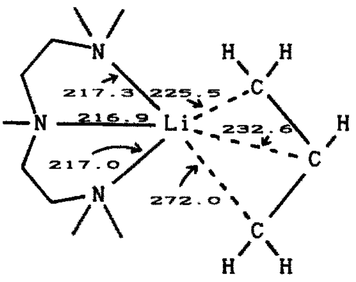


$$\begin{array}{ccccccccc} & \text{thf} & & & \text{CHMe}_2 & & \\ & | & & & | & & \\ \text{thf}- & \text{Li} & -\text{F}- & & \text{Si} & -\text{N}- & \text{C}_6\text{H}_2(\text{CMe}_3)_3 \\ & | & & & | & & \\ & \text{thf} & & & \text{CHMe}_2 & & \end{array}$$

(<u>130</u>)

thf, contains an approximately tetrahedral Li coordination sphere comprising the fluorine of the anion (Li...F = 182.2pm) 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 Li...C contacts of 214.1, 209.3 and 214.1pm. Similar η^3-bonding occurs in the structure of (134);[283] it represents a beautiful example of $C^-Li^+N^-Li^+C^-$ charge communication and confirms the predictions of theoretical calculations undertaken for the simplified model (137).[283]



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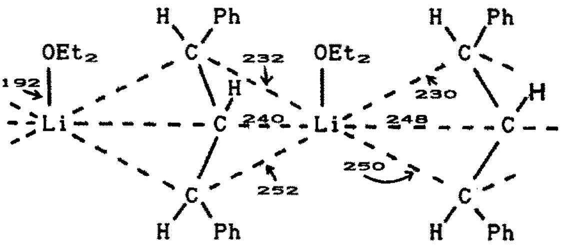
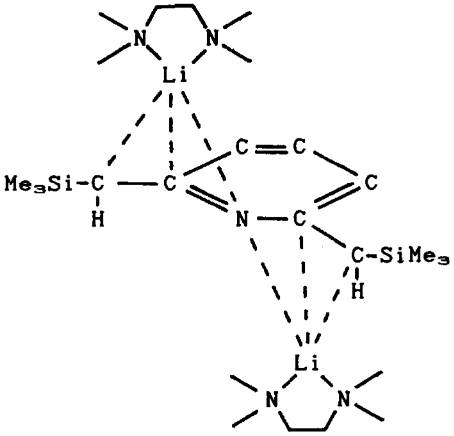
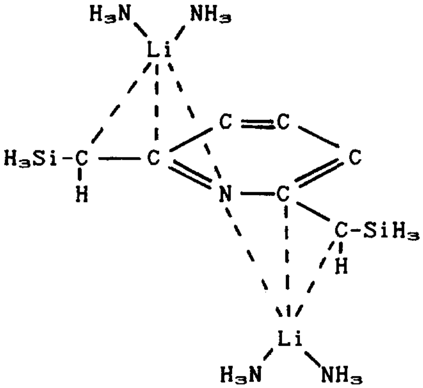


(133)

A triple decker sandwich structure with crystallographic 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 (Li...C = 226.3-236.8pm; Li...B = 247,255.3pm). The coordination of the Li atoms is completed by the nitrogens of the bidentate tmeda molecule (216.2, 216.4pm).[284]

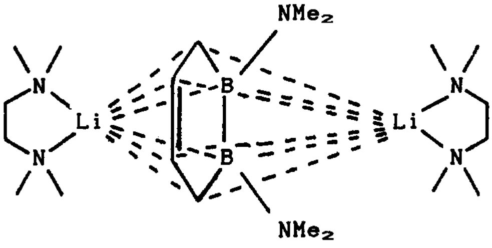


(134)

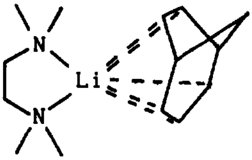


(137)

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 (Li...C = 219.4,244.0,251.5pm) but also the olefinic part of the carbanion (Li...C = 239.9,242.9pm) is engaged in metal-ligand bonding. The 7-fold Li atom coordination geometry is achieved by tmeda solvation.



(135)



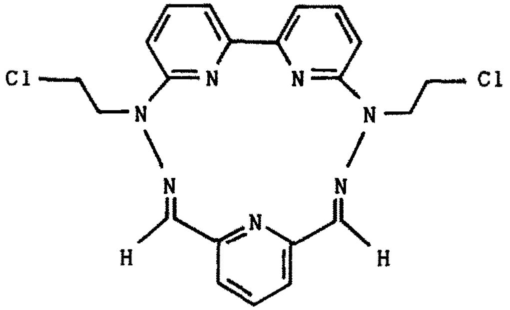
(136)

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

The monomeric cations in $[N(CH_2CH_2OH)_3Li]^+[2,4\text{-}(NO_2)_2C_6H_3O]^-$ [287] and $[N(CH_2CH_2P(O)Ph_2)_3Li]^+_2[\{N(CH_2CH_2P(O)Ph_2)_3Li\}_2]^{2+}$-

$(BPh_4)_4$ (138)[265] contain Li atoms partially or wholly encapsulated by tripodands. In $[N(CH_2CH_2OH)_3Li]^+$[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 $[N(CH_2CH_2P(O)Ph_2)_3Li]^+$,[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 phthalocyanaine $Li_2{}^+pc^{2-}$ at 0.15v vs saturated calomel electrode in CH_3CN gives a lithium complex of the phthalocycanine radical,[289] the structure of which (Figure 11) contains a unit cell with four nearly planar Li^+pc^- molecules of S_4 symmetry, stacked metal-over-metal but staggered by 38.7°; its effective magnetic moment decreased from $1.3\mu_B$ at 298K to $1.0\mu_B$ at 150K, but upon further cooling it increased to approach the free spin value.[289]

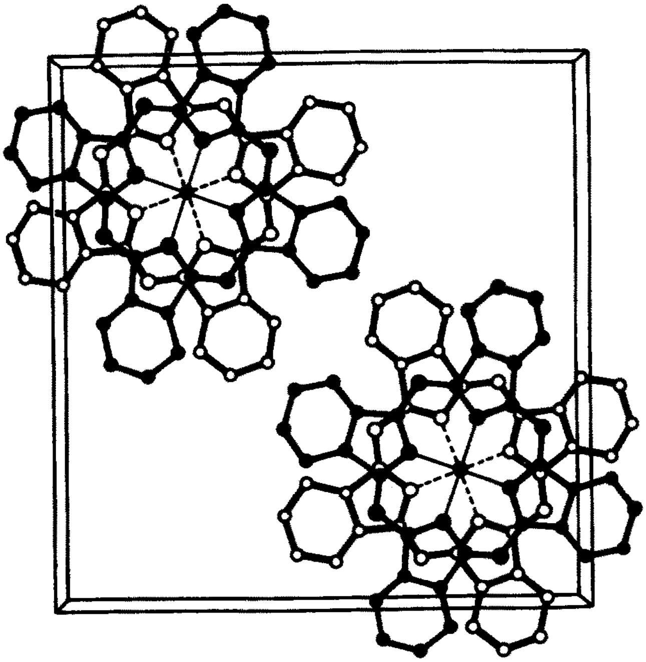


Figure 11. View down the c axis of the unit cell of the lithium complex of the phthalocyanine radical: Dimensions Li...Li = 324.5, Li...N = 194.2pm (reproduced by permission from J. Chem. Soc., Chem. Commun., (1986)962).

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}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 $[Ph(^tBu)C=NLi]_6$, $[(Me_2N)_2C=NLi]_6$ and $[(PhCH_2)_2C=NLi]_6$, dimeric $[PhN(H)Li.hmpa]_2$ and monomeric $[(^nBu)C_5H_5NLi.(py)_2]$}, others engage in concentration-dependent equilibria also involving monomeric species {tetrameric $[Ph_2C=NLi.py]_4$, trimeric $[(PhCH_2)_2NLi]_3$, and dimeric $[(^tBu)_2C=NLi.hmpa]_2$ and $[(C_6H_{11})_2NLi.hmpa]_2$} and one complex {dimeric $[(PhCH_2)_2NLi.OEt_2]_2$} loses donor on dissolution before rearranging to a trimer and a monomer.[239] Reed, Snaith et al.[290] have also concluded from ^1H and ^7Li 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 Li_2C_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 ^1H and ^{13}C n.m.r. spectra for both ^nBuLi in thf-d_8 and 1-lithionaphthalene in C_6D_6 have been obtained by Schleyer et al[292] from 2-D n.m.r. experiments. ^6Li-^1H HOESY exhibits cross peaks for $H(C_1)$ and $H(C_2)$ in the ^nBuLi tetramer indicating some of the Li-H distances to be unusually short (<350pm); it also reveals a short distance between Li and $H(C_2)$ for 1-lithionaphthalene.tmeda. For a 1:1 molar mixture of the two reagents, however, ^6Li-^1H HOESY reveals a short contact between Li and $H(C_8)$. These observations are supported by the results of MNDO calculations for the solvated 1-lithionaphthalene dimer, $[C_{10}H_7Li.en]_2$ (140) and for the mixed "dimer" $[C_{10}H_7Li, CH_3Li, (en)_2]$ (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 ^7Li n.m.r. study of 1:1 molar mixtures of two structurally related phenylsilyllithiums (Ph_3SiLi, $Ph_2MeSiLi$ or $PhMe_2SiLi$) in thf and 2-Methf supports a bimolecular exchange mechanism between monomeric structures as being responsible for the collapse of the ^7Li 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}Li and ^{11}B n.m.r. spectroscopic, cryscopic and conductometric measurements indicate that $LiBF_4$.4hmpa exists in solution as tight lithium and tetrafluoroborate components held together by Li...F interactions.[294]

Evidence for the presence of ion triplets $M^+A^-M^+$ ($M^+ = Li^+$ or 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 (A^-) with a neutral electrophile (RX) under conditions where cation association is important. For total accuracy these treatments must allow for the formation of the ion triplets $M^+A^-M^+$.[295]

The enthalpies of intramolecular etheration of tetrameric organolithium compounds of the type $[MeO(CH_2)_nCH(R)Li]_4$ (R = H,Me; n = 2,3) have been determined in benzene by comparison of the enthalpies of formation of the unsubstituted organolithium tetramer $[CH_3(CH_2)_nCH(R)Li]_4$ and its 3-methoxy- analogue $[MeO(CH_2)_nCH(R)Li]_4$;[296] whereas for n = 2, the enthalpy difference is $-30kJ.mol^{-1}$, for n = 3, it is $-41kJ.mol^{-1}$.

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}Si n.m.r. chemical shift of 30.9ppm. Normal metallating agents (^{n}BuLi, ^{t}BuLi, PhLi) usually give substituted rather than deprotonated products.[297]

Lithiation of the aminosilanes $Me_{4-x}Si\{NH(^nBu)\}_x$ ($1 \leqslant x \leqslant 4$) using ^{n}BuLi yields $Me_{4-x}Si\{NH(^nBu)\}_y\{NLi(^nBu)\}_{x-y}$ (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}H and ^{7}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 Na^+ (and 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 Na^+ (and 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 (Na...O = 231.5/305.4; 255.8/294.3pm), two monodentate anions (Na...O = 227.8,242.0pm) and the water molecule (Na...O = 241.1pm) 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 (Na(1)...O = 237.1-247.1; Na(2)...O = 233.9-246.0pm) and two water molecules (Na(1)...O = 237.2,249.9; Na(2)...O = 236.5,242.3pm) 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 (Na(1)...O = 242.4,248.1; Na(2)...O = 245.8,247.5pm) and four water molecules (Na(1)...O = 238.8-239.5; Na(2)...O = 240.1-248.4pm).

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, $[CH_3.CO.NSO_2.C_6H_4NH_2]^-Na^+$,-$H_2O$,[303] the Na atom is surrounded by three oxygens (Na...O = 227.3-244.0pm) and one nitrogen (Na...N = 261.3pm) from anions and a water molecule (Na...O = 229.6pm) in a 5-fold array. In the latter salt, $[Cl.NSO_2.C_6H_4CH_3]^-Na^+$,[304] the Na atom is roughly octahedrally coordinated by an oxygen (Na...O = 236.5pm) and a chlorine (Na...Cl = 315.3pm) from neighbouring anions and by four water molecules (Na...O = 235.4-248.7pm).

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 (Na...O = 235.3-264.8pm) 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 (Na...O = 233.0-247.6pm).

Treatment of a butanol solution of $NaBPh_4$ with a CH_2Cl_2 solution of $N(CH_2CH_2P(O)Ph_2)_3$, previously prepared by oxidation of $N(CH_2CH_2PPh_2)_3$ with H_2O_2, gave crystals of $[(Ph_2P(O)CH_2CH_2)_3NNa.H_2O.BuOH]^+BPh_4^-$ (<u>142</u>).[265] In the structure of (<u>142</u>), the tripodand does not encapsulate the Na atom; instead the latter is surrounded in a tetrahedral fashion by two oxygens of the tripodand (Na...O = 217.7,223.7pm) and by the oxygens of the water (Na...O = 230.2pm) and the butanol molecules (Na...O = 229.3pm).[265]

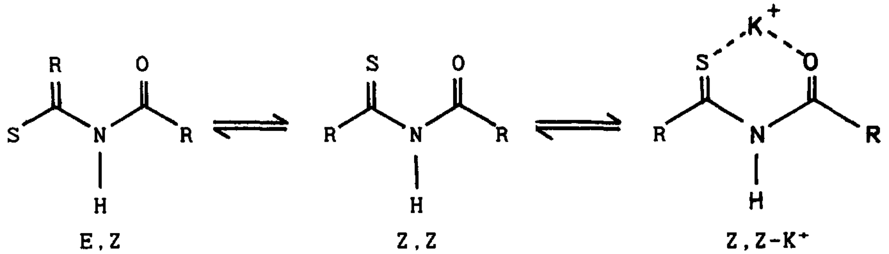
1.4.11 Potassium, Rubidium and Caesium Derivatives

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 ^nBuK by metal-metal exchange between ^nBuLi 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 ^nBuNa, ^nBuK is monomeric under these conditions.[307]

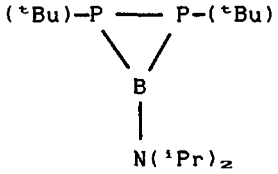
Complexation of K^+ by n-acyl thioamides has been studied using n.m.r. techniques.[308] Addition of KSCN to solutions of (<u>143</u>) or (<u>144</u>) results in rearrangement of the E,Z-n-acyl thioamide to the Z,Z-form followed by complexation of the cation (scheme 9).

Low temperature (<195K) reaction of (<u>145</u>)[309] and (<u>146</u>)[310] with potassium or potassium naphthalenide in thf results in P-P bond cleavage and formation of (<u>148</u>) and (<u>149</u>) 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)



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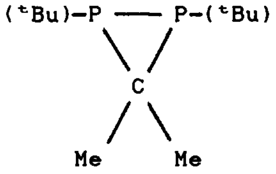

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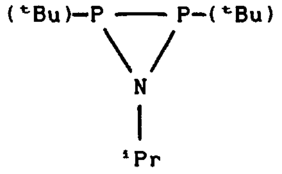

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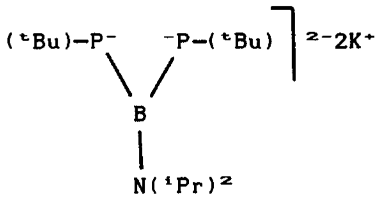

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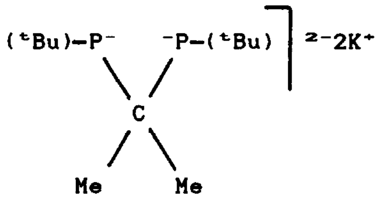

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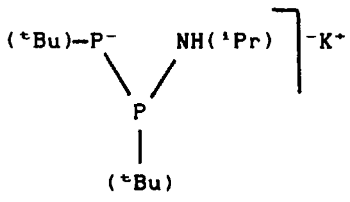
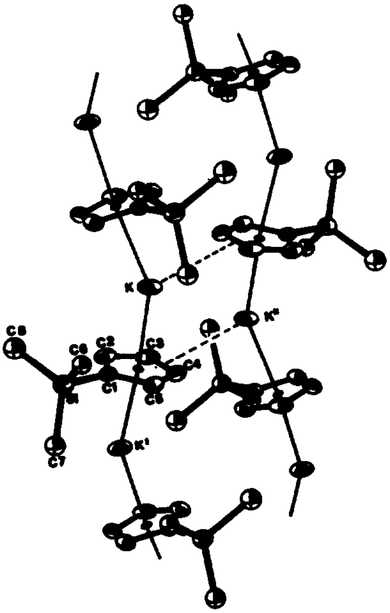


(150)

interconverts into the asymmetric compound [^{t}BuP$^-$-P(^{t}Bu)-BHN(^{i}Pr)$_2$]$^-$K$^+$,[309] whereas (<u>149</u>) decomposes into the monophosphides KHP(^{t}Bu) and KP(^{t}Bu)(^{i}Pr);[310] (<u>150</u>) is stable to 298K.[310] All reagents and products were characterised by ^{31}P n.m.r. spectroscopy.

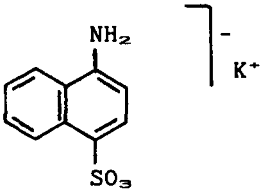
The synthesis and structural characterisation of [(Me$_3$Si)C$_5$H$_4$K] (<u>151</u>) has been reported by Jutzi, Pohl et al;[311] it is the first example of a base-free alkali metal cyclopentadienide to be crystallised and analysed using single crystal xrd methods. Prepared by treatment of trimethylsilylcyclopentadiene with potassium metal or potassium hydride in toluene,[311] it has the structure depicted in Figure 12. It comprises a "supersandwich complex" which is made up of a repeating sequence of K atoms and (on both sides) η^5-C$_5$H$_5$ rings. The average K...C contact (K...C



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

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

The K atoms in the crystal structures of the potassium salts of 4-amino-1-napthalenesulphonic 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)...O = 274.7-285.6; K(2)...O = 275.6-290.0pm) 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...O = 274.4-285.1pm) the other two by solvent molecules (K...O = 271.9,275.9pm).



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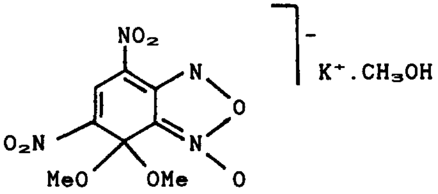

(153)

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...O = 320.7pm) as nearest neighbours with six somewhat more remote bromines (Cs...Br = 394.6pm) completing its distorted 12-fold coordination. Cs(2) is surrounded by a puckered hexagonal bipyramid of six oxygens (Cs...O = 324.4pm) and two bromines (Cs...Br = 365.1pm).

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