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Chapter 1

ELEMENTS OF GROUP 1

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1.1 INTRODUCTION

As for the 1984 review,[1] the pattern chosen for Chapters 1 and 2 is such that papers describing aspects of the chemistry of these two groups of metals, have been categorised into sections which reflect subjects of topical interest and importance. One such subject - organometallic chemistry - has, however, been omitted since it is reviewed in detail elsewhere. For certain subjects, notably complexes of crowns, cryptates and related compounds, the chemistry of the two groups of metals is so similar that it is convenient to consider it once only in the relevant section of this Chapter.

Firm evidence for the potasside anion (K^-) has been obtained by Dye et al[2] using ^{39}K n.m.r. techniques; this completes the synthesis and identification of all the alkalide anions from Na^- to Cs^-. The spectra show that K^- is a genuine anion with two electrons in the 4s orbital that shield the electrons in the 3p orbitals from appreciable interaction with the surroundings.[2] Dye et al[3] have also achieved unequivocal differentiation between, and identification of Rb^- and complexed Rb^+ in alkalides and electrides using XANES and EXAFS techniques. Whereas the X-ray absorption spectra of $[18C6Rb]^+Br^-,2H_2O$ shows a large "white line" (absorption threshold resonance) and distinctive EXAFS characteristic of Rb^+, those of $[(18C6)_2Cs]^+Rb^-$ do not show a "white line" and there is no discernible EXAFS presumably owing to the very large size of the Rb^- anion (estimated radius 340pm). The formation of the sodide anion (Na^-) in N,N-diethylacetamide, N,N-dipropylacetamide, N,N-dimethylpropanamide and tetramethylurea has been confirmed by Edwards et al[4] using ^{23}Na-n.m.r. techniques. Similar evidence for genuine alkalide anions was not obtained for any of the heavier metals (K,Rb,Cs) in these solvents. The e.s.r. spectra of these latter solutions at 298K show a singlet resonance arising from a time average of the signals from the solvated electron (e_s^-) and the ion pair species ($M^+.e_s^-$); those of the corresponding vitreous solids at 77K, however, exhibit signals due to the corresponding trapped electron (e_s^-) and the electron-cation encounter species ($M_s^+.e_s^-$).[4]

1.2 THE ELEMENTS

A significant decrease in interest in the solution chemistry of the lighter alkali metals can be perceived. It undoubtedly results from two causes; firstly, the current antagonism initiated by the Three Mile Island accident and exacerbated more recently by the Chernobyl accident towards energy production from nuclear fission devices including the liquid sodium-cooled fast breeder reactor, and secondly, the decision to shift emphasis from liquid lithium to solid lithium compounds as tritium breeder materials for future nuclear fusion devices. Consequently it has been decided to consider the solution chemistry of the alkali metals on a biannual basis. Metallic solutions containing the alkali metals, however, continue to be of academic interest owing to the presence of chemical short range order and will still be considered annually as will intermetallic compounds.

1.2.1 General Properties

In situ (i.r., SIMS, XPS, XRD and SEM) methods have been developed[5] and used[6,7] to study surface layers formed on lithium immersed in polypropylene carbonate containing $LiClO_4$. In the absence of water,[6] electrodeposited lithium showed a highly porous micromorphology with surface layers containing primarily a partially chlorinated hydrocarbon polymer and Li_2CO_3. Increasing concentrations of water[7] result in the formation of protective surface layers consisting primarily of Li_2O.

1.2.2 Metallic Solutions

Van der Lugt et al[8] have extended their investigations of chemical short range order in metallic solutions by measuring electrical resistivity data for liquid Li-Pb, K-Pb, Na-In and K-In solutions. The results are compared with literature data for liquid Na-Pb and Li-In solutions. The resistivities (ρ) of the lead alloys (Figure 1(a)) exhibit a single sharp maximum at $\sim Li_{80}Pb_{20}$, a maximum at $\sim Na_{80}Pb_{20}$ with a shoulder at $\sim Na_{50}Pb_{50}$ and a single sharp maximum at $\sim K_{50}Pb_{50}$; the corresponding temperature dependence ($d\rho/dT$) data (Figure 1(b)) exhibit minima at $\sim Li_{80}Pb_{20}$, $\sim Na_{80}Pb_{20}$ and $\sim K_{50}Pb_{50}$.[8] These maxima and minima are consistent with chemical short range order and occur at compositions which correspond to those of the intermetallic compounds $Li_{22}Pb_5$, $Na_{15}Pb_4$, NaPb and KPb. Hence assuming a correlation between solid state and solution structures the change in behaviour is attributed to a transition from simple ionic behaviour in Li-Pb solutions to polyanion formation in K-Pb solutions; in idealised terms, crystalline $Li_{22}Pb_5$ contains individual ions whereas, KPb comprises K^+ cations and Pb_4^{4-} anions.[8]

The resistivities (ρ) of the indium alloys (Figure 1(c)) exhibit

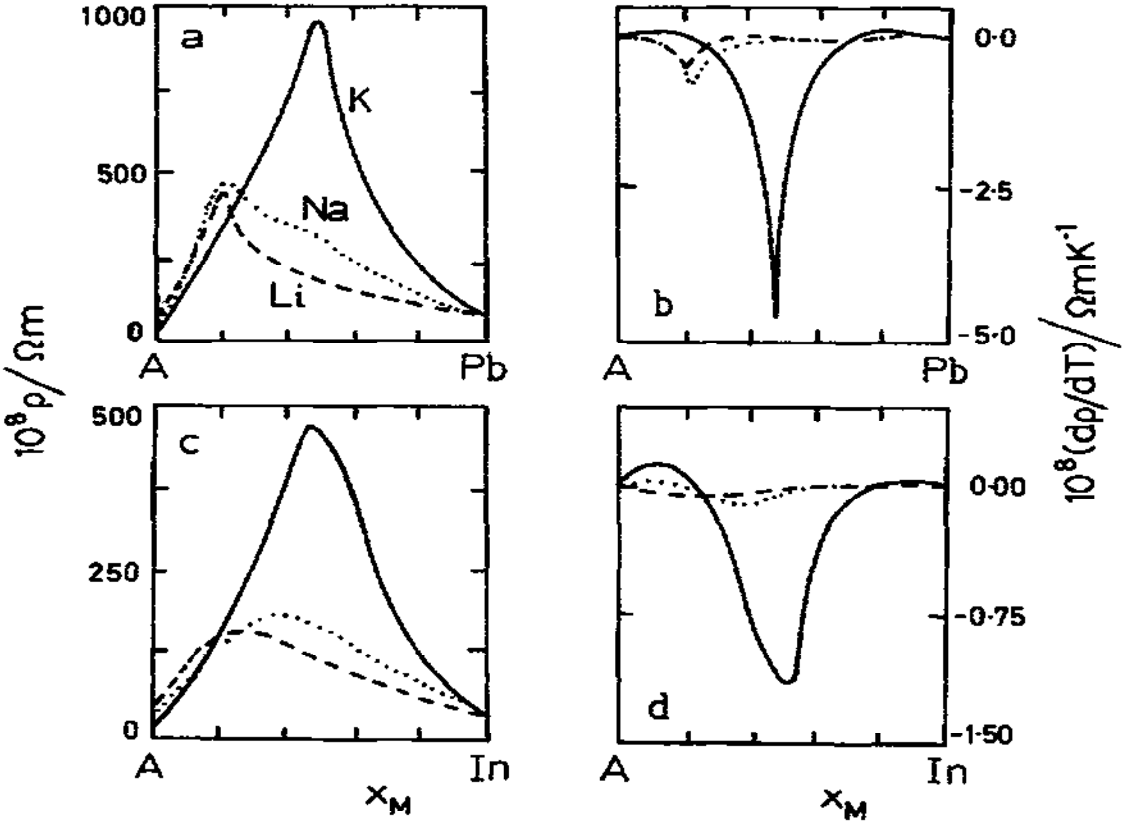


Figure 1. Resistivity (a,c) and temperature dependent resistivity (b,d) data for liquid alkali metal-lead (a,b) and liquid alkali metal-indium (c,d) solutions.

less pronounced minima which shift from ~$Li_{75}In_{25}$ through ~$Na_{67}In_{33}$ to ~$K_{50}In_{50}$; the corresponding temperature dependence (dρ/dT) data (Figure 1(d)) exhibit broad minima at similar compositions.[8] Although these data cannot be readily correlated with solid state structures, the magnitude of the effects clearly indicate that a transition occurs from a metallic Li-In system to an ionic K-In system.[8]

Several theoretical analyses of metallic solutions which exhibit chemical short range order have been described.[9-12] Morgan et al[9,10] suggest that the electrical resistivities of liquid Cs-Au solutions, the classical example of chemical short range order, may be understood using their recently developed theory based on a generalised kinetic equation for electrons in disordered solids;[9] their calculations of the resistivity of liquid K-KCl and K-KBr solutions show remarkable agreement with the experimentally observed rapid increase in resistivity as the composition of the salt is approached.[10] The other more traditionally based calculations confirm that the resistivities of these systems cannot be interpreted within the framework of the nearly free electron approximation and that electronic rearrangements must be considered.[11]

Theoretical calculations have been completed[13] which permit quite accurate reproduction of the experimentally observed ideal behaviour of the concentration dependence of the entropy of formation of liquid Na-Cs solutions.

1.2.3 Intermetallic Compounds

Analysis of the bonding in the intermetallic B32-type compounds LiM (M = Al-In; Zn; Cd) using relativistic augmented plane wave methods[14] shows it to be a superposition of covalent and metallic components with a small ionic contribution; the extent of the charge transfer (from Li to M), which is less than one electron per formula unit, can be correlated to the difference in electronegativities of the two atoms.[14]

A novel high pressure NaGe phase with NaPb-type structure (tetragonal; $I4_1/acd$; a = 984.0, c = 1609.6pm) has been prepared from the low pressure NaGe phase (monoclinic; $P2_1/c$, a = 1233, b = 670, c = 1142pm; β = 119.9°) at 4GPa and 775K.[15]

Potassium-tin ($[KSn_9]^{3-}$)(1)[16] and potassium-gold-tellurium ($[KAu_9Te_7]^{4-}$(2), $[K_2Au_4Te_4(dmf)_2(CH_3OH)_2]^{2-}$(3) and $[K_2Au_4Te_4(en)_4]^{2-}$(4))[17] polyanions have been synthesised by extraction from K-Hg-Sn and K-Au-Te ternary systems. Reaction of KHgSn with C222 in en followed by precipitation with ethylamine yielded $[C222K]_3^+[KSn_9]^{3-}$.[16] The structure of the anion (1) comprises

$$......K(1)-(Sn_9)-K(2)-Sn_9)-K(1)......$$

infinite chains running diagonally through the cell with both K atoms at centres of symmetry. The K atoms bridge opposite edges of the waist of the monocapped square antiprismatic Sn_9 cluster (r(Sn...Sn) = 293.1–330.3pm); they each have four relatively close and two more remote tin neighbours (r(K(1)...Sn) = 355.2, 376.2, 422.0pm; r(K(2)...Sn) = 370.0, 374.3, 411.4pm) in a distorted trigonal prismatic coordination geometry.[16]

Treatment of "K_3AuTe_2" with methanol in the presence of Ph_4PBr afforded an orange crystalline precipitate which when dissolved in dmf yielded red crystals of both $[Ph_4P]_4[KAu_9Te_7]$ and $[Ph_4P]_2[K_2Au_4Te_4(dmf)_2(CH_3OH)_2]$ on addition of more Ph_4PBr in methanol.[17] Red crystals of $[Ph_4P]_2[K_2Au_4Te_4(en)_4]$ were prepared in high yield by dissolving KAuTe in en followed by addition of Ph_4PBr in en.[17] The structures of the $[K_2Au_4Te_4(dmf)_2(CH_3OH)_2]^{2-}$ ($\underline{3}$) and $[K_2Au_4Te_4(en)_4]^{2-}$ ($\underline{4}$) anions are analogous.[17] Both consist of planar Au_4Te_4 rings to which two K atoms are coordinated on opposite faces; in ($\underline{3}$) there are four approximately equal K–Au contacts (343.2, 346.3, 350.1, 351.3pm) whereas in ($\underline{4}$) there are two short and two long K–Au contacts (348.3, 351.2, 387.3, 387.4pm). Two solvent molecules, dmf in ($\underline{3}$), bidentate en in ($\underline{4}$) bridge K atoms of separate $[K_2Au_4Te_4]$ moieties giving an infinite chain structure. The seventh coordination site of the K atom is occupied either by CH_3OH in ($\underline{3}$) or by monodentate en in ($\underline{4}$).[17]

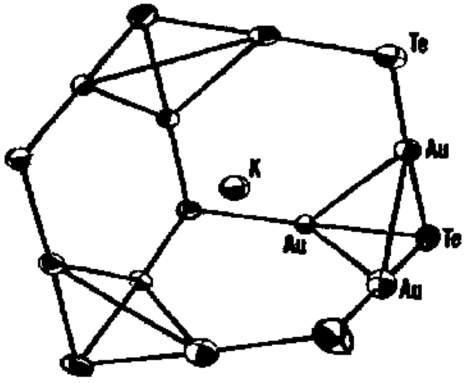


Figure 2. Molecular structure of the $[KAu_9Te_7]^{4-}$ anion (reproduced by permission from Angew. Chem., Int. Ed. Engl., 24(1985)432).

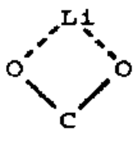
The structure of the $[KAu_9Te_7]^{4-}$ anion ((2); Figure 2) is of particular interest as it comprises a K atom embedded in a Au_9Te_7 cluster which can be described as a derivative of an $[M_{12}X_8]^{4-}$ cube with one corner and three edges missing.[17] As for (1) and (4), the K-Au contacts in (2) are shorter than the K-Te contacts, presumably owing to the greater electronegativity of Au (2.4) compared to Te (2.1); they are, however, somewhat longer on average (364pm) than those in (3; 349pm) and in (4; 359pm) presumably owing to the fairly rigid geometry of the Au_9Te_7 cluster.[17]

1.3 SIMPLE COMPOUNDS OF THE ALKALI METALS

Continuing interest in the isolation and characterisation of ion pairs in low temperature matrices and in the theoretical treatment of small molecules, especially those containing lithium, has ensured the retention of subsections to cater for these topics; subsections devoted to the chemistry of binary and ternary derivatives are also included although the continually decreasing number of papers on these topics indicates a general decline in interest.

1.3.1 Ion Pairs

The products of the codeposition of Li atoms with CO_2[18] and with C_2H_2[19] in low temperature matrices have been studied using i.r. spectroscopic techniques. In Kr matrices,[18] Li and CO_2 interact to form two isomers of $LiCO_2$ which are shown to adopt C_{2v} (5) and C_s (6) structures, two isomers of $Li(CO_2)_2$ which are thought to have D_{2h} (7,8) structures (proof of this suggestion requires isotopic studies using $C^{16}O^{18}O$) and lithium oxalate, $Li_2C_2O_4$. In the $LiCO_2$ isomers the CO_2 groups adopt bent structures which, by analogy with the structure of the CO_2^- anion in the gas phase, indicate that these complexes are stabilised by strong electron transfer from Li atom to CO_2 molecule. These results, with the



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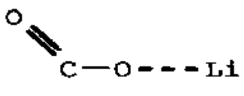

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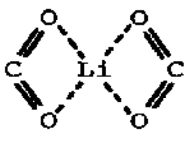

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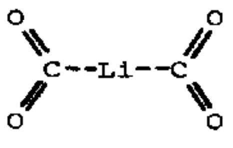

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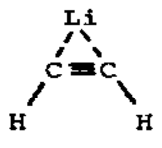


(9)

exception that no Li_2CO_2 species was observed, are consistent with those of an independent study in Ar matrices,[20] reported in the 1983 review.[21]

In Ar matrices,[19] Li and C_2H_2 interact to form a planar species (9) in which the Li atom bridges the π-system of the ethyne molecule resulting in cis C-H groups with estimated CCH angles of 140(10)°. Considerable weakening of the C-C bond occurs; it is attributed to sharing of electron density between the π-system of the C_2H_2 molecule and the Li atom rather than electron transfer from the Li atom into a π* orbital of C_2H_2.[19]

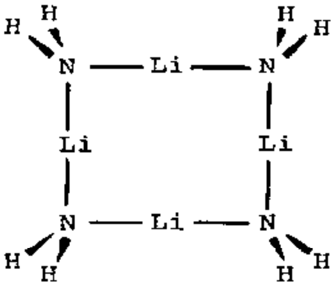
1.3.2 Theoretical Treatment of Small Moieties

The subjects of the papers abstracted for this subsection conveniently fall under one of three headings: low molecular weight inorganic species;[22-33] organometallic compounds;[34-41] and reaction intermediates.[42-48] The subsection is divided accordingly. With the exception of investigations of the Na_2 diatomic molecule,[22] and of the reaction of Na (or K) with CH_3Cl[43] the species under investigation are exclusively derivatives of lithium.[23-48]

Theoretical Hartree-Fock calculations on Li_2[23] and Na_2[22] have been completed. Whereas symmetry adapted cluster (SAC) and symmetry adapted cluster-configuration interaction (SAC-CI) calculations based on the cluster expansion of the wave function using well established basis sets were undertaken for the former, a new family of high quality Gaussian-type function basis sets capable of producing near Hartree-Fock atomic and molecular wave functions were used for the latter.

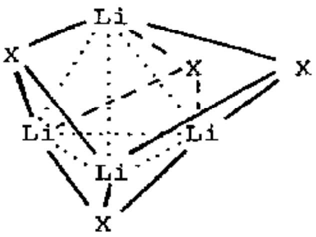
The influence of electron correlation, in the form of the self consistent electron pair (SCEP) method, on calculations of the stabilities and structures of the alternative mono-, bi- and tridentate configurations of the $LiBeH_3$ and $LiBH_4$ molecules has been assessed using 6-31G** basis sets in the SCF approximation.[24] The relative energies of the three geometries are changed by 8-13 kJ mol^{-1} and their decomposition energies by 12-21 kJ mol^{-1}. As in the absence of electron correlation the bidentate configuration is the most stable for $LiBeH_3$ and the tridentate one for $LiBH_4$.[24]

Optimised geometry and electronic structure calculations of tetrameric,[25] dimeric[26] and monomeric[26] $LiNH_2$ have been completed. The data for the tetramer, obtained using large 3-21G basis sets,[25] are compared with similar results for tetrameric LiF and LiOH. Although a square planar (D_{4h}) structure (<u>10</u>) with lithium bridges is favoured for the $(LiNH_2)_4$ tetramer, tetrahedral (T_d) cluster structures (<u>11</u>) are found for the $(LiF)_4$ and $(LiOH)_4$ tetramers.[25] The data for the monomer and dimer, obtained in an independent study using 6-31G and 6-31G** basis sets,[26] are compared with similar results for monomeric and dimeric Li_2NH and Li_3N. The monomers are planar reflecting the ionic nature of the Li...N bond; the Li...N bond distance approximates to 174pm. The dimers are more stable with lithium bridges than hydrogen bridges; the bridging and terminal Li...N bond distances lie in the ranges 192-194pm and 175-177pm, respectively.[26] Two sets of donor-acceptor complexes of lithiated ammonias, $O.NH_{3-x}Li_x$ and $H_3B.NH_{3-x}Li_x$ (x = 0-3) have also been examined.[26] In the former species, the lithium atoms occupy bridging positions between oxygen and nitrogen; the Li...O bond distances (169.1-173.5) increase and the Li...N bond distances (187.9-180.7) decrease with increasing lithiation. In the latter species the Li-N bonds are bent towards the B-N bond. For the di- and tri-lithiated derivatives, long range Li....H interactions result in more stable eclipsed rather than staggered conformations; for the monolithiated



(<u>10</u>)

r(Li...Li) = 300.3pm
r(Li...N) = 190.6pm
∠NLiN = 166°
∠LiNLi = 104°



(<u>11</u>)

For $(LiF)_4$:
r(Li...Li) = 241.7pm
r(Li...X) = 179.3pm

For $(LiOH)_4$:
r(Li...Li) = 237.2pm
r(Li...X) = 185.4pm

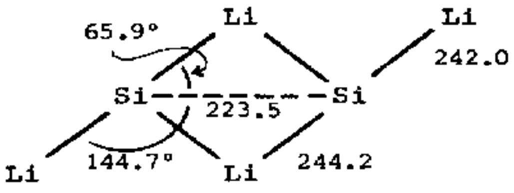
derivative, the more conventional staggered conformation is the more stable. As for the lithiated ammonia oxides, the Li...N bond distance (189.0-198.3) decreases with increasing lithiation.[26]

Two independent ab initio theoretical calculations of the potential energy surface of the LiBO system have been undertaken by Nemukhin et al[27] and by Zyubina et al[28] in attempts to resolve an apparent ambiguity in the results of an earlier study by Nemukhin et al.[29] Depending on the computational method, different ground state isomers were formed. Whereas the SCF method gave a more stable linear LiOB molecule, the CASSCF method indicated the linear LiBO molecule to be the more stable. Nemukhin et al,[27] using improved SCF and CASSCF methods, both of which incorporated a proper treatment of electron correlation showed that the energy of the LiBO isomer is invariably lower than that of the LiOB isomer. Zyubina et al,[28] using similar methods determined the energy of the cyclic isomer as well as those of the linear isomers both with and without allowance for electron correlation. In the absence of electron correlation they found the LiOB molecule to be the ground state isomer; when it was included, however, the relative energies of the isomers were reversed and the LiBO molecule became the ground state isomer. In both cases the cyclic isomer was the least stable.

Zyubina[30] has also considered the potential energy surface of the LiO_2 system. Only two minima, corresponding to the linear LiOO molecule and to the cyclic isomer were observed; the latter was found to be the ground state configuration by ~25kJ mol^{-1}. The linear OLiO molecule was shown to be unstable.

Ab initio MO calculations using a 6-31G* basis set have been completed for Li_2Si and Li_4Si_2.[31] The monomer has a triplet ground state with a linear geometry (r(Li...Si) = 242.9pm), and a bent singlet excited state (r(Li...Si) = 253.3pm, ∠LiSiLi = 92°). For the dimer, there is a minimum on the potential energy surface corresponding to a conventional disilene or silylsilylene. Instead a distorted planar structure (12) of C_{2h} symmetry with two bridging lithium atoms has been located as the global minimum for singlet Li_4Si_2.

To gain insight into the bonding between the sublattices of lithium and of graphite in intercalation compounds, MO calculations have been performed on the bonding in complexes of lithium with polynuclear aromatic hydrocarbons.[32] Two energy



distances/pm

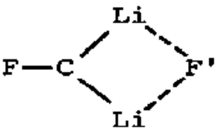
(12)

wells indicating possible sites for the lithium atoms were discerned. The more stable was located 180-190pm along the C_6 axis above each of the aromatic rings; the less stable was found in a site on the edge of the molecule. The calculated partial charge on the Li atoms falls within the range from +0.20 to +0.35.[32]

A theoretical model of bonding in the series of hyperlithiated carbon species CLi_n^q ($n = 4,5,6$; $q = 0,\pm1,\pm2$), based on "natural population analysis" suggests a significantly higher degree of ionic character than that based on "Mulliken population analysis".[33] In all seven species considered, the carbon atom appears to achieve nearly a complete octet which is stabilised by back-transfer into the enveloping cage of empty lithium orbitals. In general terms, special stability appears to occur for the complexes XLi_n^q with $Z + n - q = 12$ where Z is the atomic number of the central atom, X.

Lithiated methanes[34,35] and perfluoromethanes[36] have been subjected to spectroscopic[34,35] and theoretical[36] analysis. XPS[34] and solid phase ^{13}C n.m.r[35] studies of CH_3Li, which has a tetrameric structure and CH_2Li_2, for which structural data are not available, imply that both species are of high symmetry and contain only one carbon environment. Thus the XPS data[34] contain peaks at low binding energy for only one type of carbon and lithium environment while the ^1H- and ^6Li-decoupled ^{13}C n.m.r. spectra[35] consist of sharp singlets. An excellent correlation between calculated carbon charge (based on Fenske-Hall MO calculations) and C 1s chemical shift is observed, the degree of ionic character increasing as the number of Li atoms increases. This increase in charge density at the carbon atom results in a downfield ^{13}C n.m.r. shift in CH_2Li_2 relative to CH_3Li. Ab initio MO calculations[36] of the potential surface of CF_2Li_2 at the 4-31G level suggest a planar Li bridged structure having $CFLi_2^+F^-$ character; geometry optimisation was undertaken at both the 4-31G and 6-31+G levels (13).

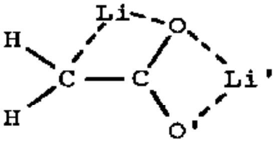
Ab initio MO calculations[37] at the 3-21G level and semi-empirical MNDO calculations indicate that monomeric dilithiated acetic acid favours the 1,3—1,3' doubly bridged structure (14) generally found in metallated Y conjugated dianion systems. In the minimum energy 3-21G structure (14) one lithium atom is roughly in the carboxylate plane while the second is involved in π-enolate anion bridging.[37]



(13)

	4-31G	6-31+G
r(C...F)	136.4	138.3
r(C...F')	281.5	280.7
r(C...Li)	211.8	212.1
θ(LiCLi)	73.8°	75.5°

distances/pm



(14)

	3-21G
r(C...Li)	216.9
r(O...Li)	175.3
r(O...Li')	181.0
r(O'...Li')	179.3

distances/pm

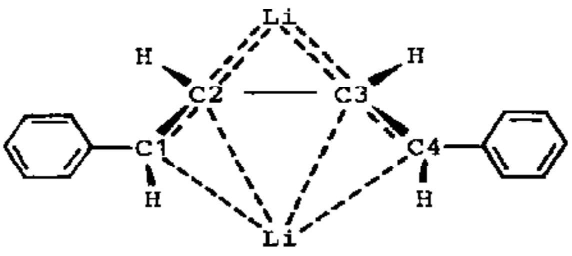
A single dilithiated cycloalkane (1,1-dilithio-2,2,3,3-tetramethylcyclopropane[38]) and two dilithiated alkenes (dilithium tetraphenylallenide[39] and 1,4-dilithio-1,4-diphenyl-cis-2-butene)[40] have been synthesised and characterised; for one of the alkene derivatives (1,4-dilithio-1,4-diphenyl-cis-2-butene) MNDO calculations[40,41] have been undertaken to interpret the results of a single crystal X-ray diffraction study of the bis(tmeda) adduct.[40]

Lagow et al[38] have prepared pure 1,1-dilithio-2,2,3,3-tetramethylcyclopropane in ~40% yield by pyrolysis of 1-lithiotetramethylcyclopropane for 8-10 hours under an inert atmosphere at 470K. The product was characterised by hydrolysis with D_2O,

^{1}H-n.m.r. spectroscopy and flash vaporisation mass spectroscopy; the latter was consistent with the presence of monomers and dimers in the gas phase.[38]

Dilithium tetraphenylallenide, obtained by reaction of tetraphenylallene with Li in thf at 195K, was analysed using multinuclear (^{1}H- and ^{7}Li-) n.m.r. methods.[39] It exists as a monomer with a symmetric C_2 structure in which there is strong interaction between the central carbon atom and equivalent Li atoms.

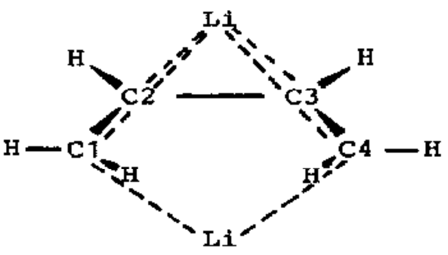
Schleyer et al,[40] using both single crystal X-ray diffraction analysis (of the bis(tmeda) adduct) and MNDO calculations, have shown that 1,4-dilithio-1,4-diphenyl-cis-2-butene (<u>15</u>) prefers a doubly Li-bridged cis structure (C_2 rather than C_{2v}) in contrast to the trans geometry expected for the isolated 1,4-diphenylbutadiene dianion. The structure of the bis(tmeda) complex contains a disordered cis-butene moiety; half of the molecules are as shown, the other half are symmetry related by a C_2 rotation about the C1-C4 vector giving a pseudo six-membered ring. The Li atoms occupy twisted doubly bridging positions being coordinated to three carbons of the anion and two nitrogens of the tmeda



(<u>15</u>)

MNDO
r(Li...C1) = 215
r(Li...C2) = 214
r(Li...C3) = 225
r(Li...C4) = 242

distances/pm



(<u>16</u>)

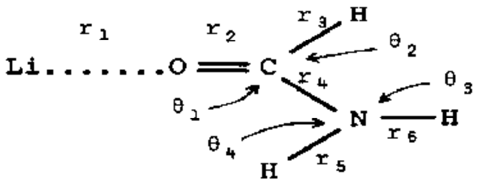
3-21G
r(Li...Li) = 339.1
r(Li...C) = 224.5

distances/pm

molecule. The MNDO data (15) are in full accord with this geometry giving three short and one longer Li...C contact. A MNDO search by Schleyer et al[41] of the many structural possibilities for the parent molecule 1,4-dilithio-2-butene revealed three favourable local minima. Subsequent ab initio MO calculations at the 3-21G level indicated that the doubly bridged structure with an entirely planar C_4H_6 moiety (16) is the most stable. Although the alternative cis-isomer, with non-planar protons on the terminal carbons was competitive in energy (only 28 kJ mol^{-1} less stable), the trans-isomer was significantly less stable (100 kJ mol^{-1}).[41]

Both semi-empirical MNDO and ab initio SCF MO calculational methods have been used to study some relatively simple reactions; transition structures considered include those formed by Li^+ with $HCONH_2$,[42] by M(M = Li,Na,K) with CH_3Cl,[43] by LiH with C_2H_2,[44] C_2H_4[44] or H_2CO,[45] by CH_3Li with C_2H_2,[44] C_2H_4,[44] H_2CO[45] or LiRNOR',[46,47] and by LiRNR' with H_2CO.[48]

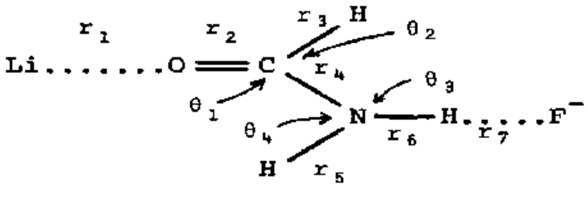
The equilibrium geometries of the complexes formed between Li^+ and H_2CO both in the absence and presence of F^- have been optimised using the 4-31G basis set:[42]



(17)

	(17)	(18)		(17)	(18)
r_1	169.4	161.6	θ_1	124.3	126.2
r_2	124.5	129.2	θ_2	116.0	115.4
r_3	107.5		θ_3	122.1	117.4
r_4	131.5	127.8	θ_4	120.8	118.5
r_5	99.7	100.1			
r_6	99.4	138.6			
r_7	-	98.3			

distances (r_n)/pm
angles (θ_n)/°

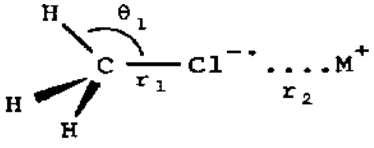


(18)

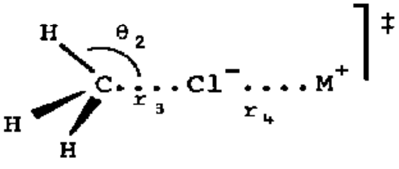
The bonding in these systems is discussed in the light of localised orbitals.[42]

Model calculations[43] of the reduction of CH_3Cl by M(M = Li,Na,K) using the 6-31+G* basis set invariably led to the C_{3v} ion pair (19). This was found to dissociate via the C_{3v} transition state (20) to give weak Me·ClM complexes (21) which also have C_{3v} symmetry. The barrier to dissociation increases from 11.8kJ mol^{-1} for (19)-Li to a maximum of 14.3kJ mol^{-1} for (19)-Na and then decreases to 6.3 kJ mol^{-1} for (19)-K.[43]

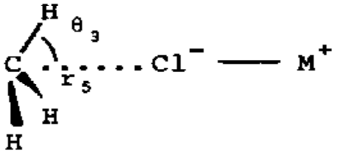
Using 3-21G and/or 6-31G* basis sets Schleyer et al[44,45] have completed calculations on the transition structures formed on addition of LiH and CH_3Li to C_2H_2, C_2H_4 and H_2CO; the reactions of LiH and CH_3Li dimers with H_2CO have also been considered. The two reactants behave in an analogous manner; representative reaction schemes are given below for the interaction of CH_3Li with C_2H_4 (Scheme 1),[44] of CH_3Li with H_2CO (Scheme 2)[44] and of $(CH_3Li)_2$ with H_2CO (Scheme 3).[45]



(19)



(20)

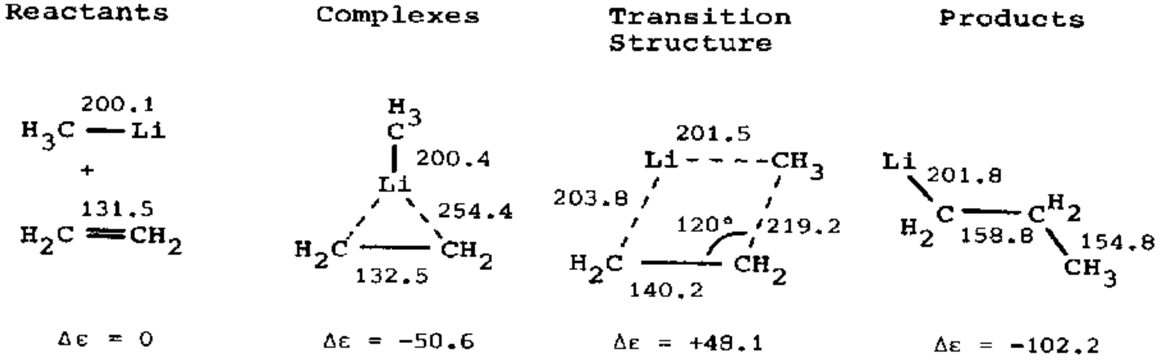


(21)

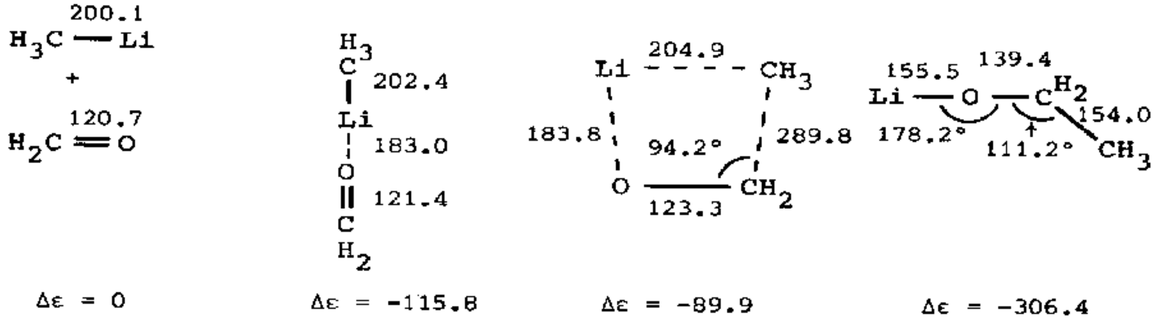
M	r_1	r_2	θ_1	r_3	r_4	θ_2	r_5	θ_3
Li	181.2	249.3	107.7	199.9	240.5	104.5	~430	~80
Na	180.5	270.7	108.0	200.6	263.6	104.7	~430	~80
K	180.2	316.5	108.3	194.2	316.2	106.2	~430	~80

distances (r_n)/pm; angles (θ_n)/°

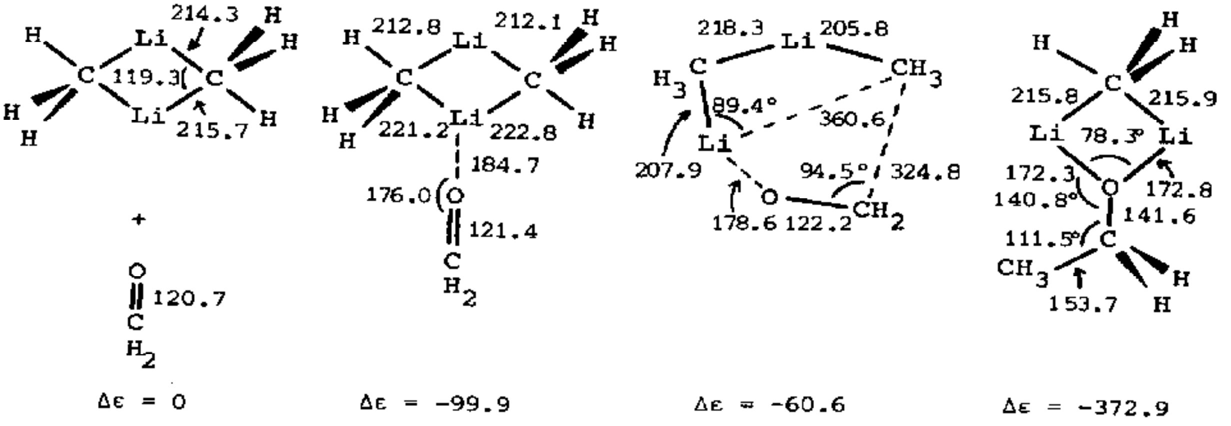
Following the publication by Boche and Wagner,[49] reported in the 1984 review,[50] of the results of an MNDO MO investigation of the amination of R"Li by LiRNOR', two further independent theoretical studies[46,47] of this reaction have been described. McKee,[46] on the basis of MNDO and ab initio 3-21G and 3-21+G level calculations suggests scheme 4 for the amination of CH_3Li by $LiCH_3NOCH_3$. Although this mechanism incorporates as the reactant complex the N,C-dilithium bridged moiety (22) proposed as intermediate by Boche and Wagner, it is extended to include a transition state (23) which is best described as a trigonal



Scheme 1.



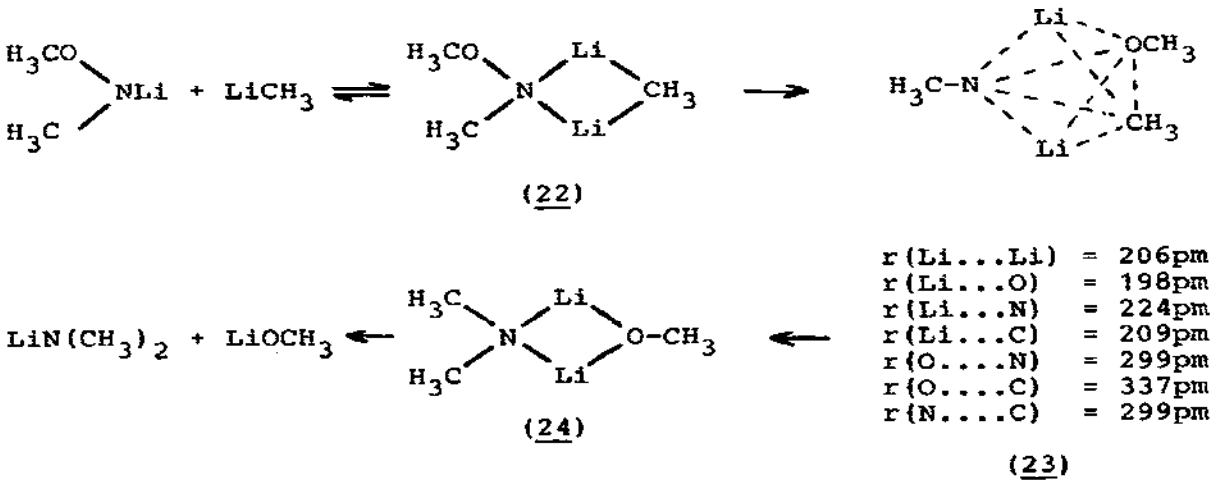
Scheme 2.



Scheme 3.

(Distances/pm; Energies/kJ mol^{-1} are quoted relative to that of the reactants).

bipyramid with two axial Li cations and equatorial alkoxyl, methyl and alkyl nitrene substituents, and a more stable N,O-dilithium bridged complex (<u>24</u>) from which the ultimate products are formed. Armstrong et al,[47] having optimised, at the 6-31G level, the



(<u>22</u>)

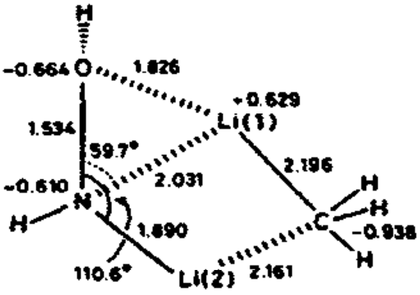
(<u>24</u>)

r(Li...Li) = 206pm
r(Li...O) = 198pm
r(Li...N) = 224pm
r(Li...C) = 209pm
r(O....N) = 299pm
r(O....C) = 337pm
r(N....C) = 299pm

(<u>23</u>)

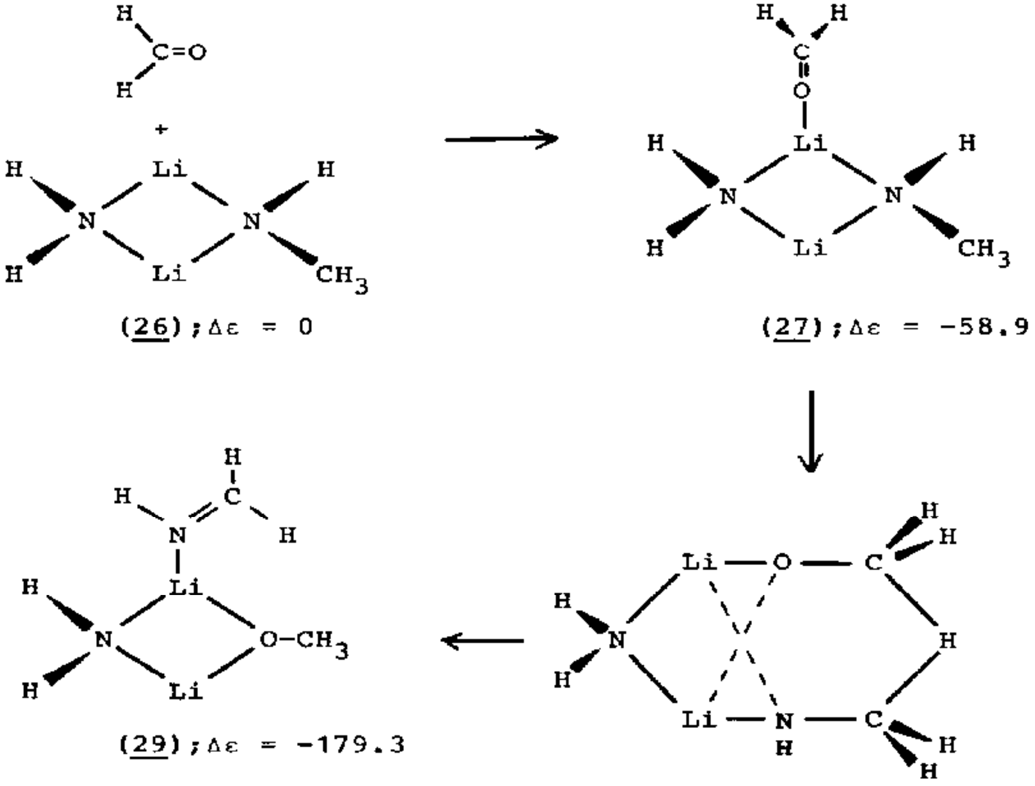
<u>Scheme 4</u>.

geometry of the intermediate proposed by Boche and Wagner (<u>22</u>) and those of several other possible models, concluded that (<u>22</u>) does not lie at a minimum, the global minimum being represented by the more complex intermediate (<u>25</u>).



(<u>25</u>)

McKee has also completed an MNDO and ab initio (3-21+G basis level) theoretical study of the reduction of H_2CO by $LiNHCH_3$.[48] His proposed mechanism (Scheme 5) involves the formation of a reactant complex (<u>27</u>) composed of a dimer model ($LiNH_2.LiNHCH_3$) (<u>26</u>) coordinated to H_2CO through one Li atom. A hydrogen β to nitrogen is transferred to the carbon of H_2CO in the transition state complex (28) forming methoxide which is stabilised in the product complex (29) by lithium complexation.[48]



(26); Δε = 0

(27); Δε = −58.9

(28); Δε = +69.0

(29); Δε = −179.3

Scheme 5.

(Energies/kJ mol^{-1} are quoted relative to that of the reactants)

1.3.3 Binary Compounds

Owing to the limited number and fragmented nature of the papers abstracted for this section, the data are not considered in separate subsections but as a single group. In a significant development first noted in the 1984 review,[51] Sabrowsky et al[52-55] have described the synthesis of both interalkali metal oxides (KLiO and RbNaO) and sulphides (NaLiS and KLiS). Prepared by reaction of equimolar mixtures of the appropriate binary oxides in inert crucibles (Ag or Al_2O_3) for several days at elevated temperatures, they have been characterised by XRD methods; pertinent crystallographic data are collated with preparative details in Table 1.

Table 1. Crystallographic parameters and preparative details for interalkali metal oxides and sulphides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	Crucible	t/days	T/K	Ref
KLiO	ortho.	Cmca	861.8	640.3	641.7	Ag	7	773	52
RbNaO	tetrag.	P4/nmn	406.8	–	649.4	Al_2O_3	7	750	53
NaLiS	tetrag.	P4/nmn	402.6	–	649.5	Al_2O_3	7	870	54
KLiS	tetrag.	P4/nmn	431.8	–	696.2	Ag	6	975	55

The fluorescence spectra of ^{85}RbD(^{85}RbH) have been measured[56] by irradiating a mixture of ^{85}Rb, $^{85}Rb_2$ and $D_2(H_2)$ with laser light at 514.5 or 488.0nm (476.2, 476.5 or 488.0nm). Analysis of the data has given molecular constants for both ^{85}RbD and ^{85}RbH.

The synthesis and characterisation, using ^{31}P-n.m.r. spectroscopic methods, of the novel lithium phosphide solvates $Li_2H_2P_{14}$.6thf[57] and Li_2P_{16}.8thf,[58] has been reported by Baudler et al. The former was obtained either by reaction of Bu^{n}Li, Li_3P_7 or LiH_4P_5 with P_2H_4 in thf or by disproportionation of LiH_4P_7 in thf;[57] the latter was prepared by disproportionation of Li_2HP_7 in thf.[58] Further extensive details of the chemistry of the species are given in Chapter 5.

The crystal structures of RbO_3 and CsO_3 have been determined at 248K;[59] they are based on the CsCl bcc structure type. The shortest contacts between the anion and cation are, in the case of KO_3 exclusively and in the case of RbO_3 predominantly, to the terminal oxygen atoms of the anion confirming mesomers of the type: $O{=}\overset{+}{O}{-}O^-$. For KO_3 the anion has C_{2v} symmetry [θ O(2)O(1)O(2) = 113.4°; r(O(2)...O(1)) = 135.7pm] and there are eight K...O(2) contacts at 285.3pm; for RbO_3, the anion has C_s symmetry [θ O(2)O(1)O(3) = 114.6°; r(O(2)...O(1)) = 134.7, r(O(3)...O(1)) = 133.4pm] and there are three Rb...O(2) contacts at 292.2-308.5pm, four Rb...O(3) contacts at 296.7-307.0 and a single Rb...O(1) contact at 305.8pm.[59] Unit cell parameters are collected in Table 2.

Thermal treatment (843K) of 1:4 molar mixtures of CsN_3 and Te in sealed quartz tubes leads to $CsTe_4$, which has been characterised by XRD methods;[60] pertinent crystallographic data are included in Table 2.

Table 2. Crystallographic parameters for MO_3 (M = K,Rb) and $CsTe_4$

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	β/°	Ref.
KO_3	tetragonal	I4/mcm	864.8	-	716.4	-	59
RbO_3	monoclinic	$P2_1/c$	644.1	603.0	874.6	122.3	59
$CsTe_4$	monoclinic	$P2_1/c$	785.7	728.6	1415.5	93.8	60

Two empirical expressions for the estimation of the bond dissociation energies, D_{AB}, of diatomic alkali or alkaline earth metal halide molecules:

$$D_{AB} = \overline{D_{AB}} + 31.973e^{0.363\Delta x} \quad \ldots(1)$$

$$D_{AB} = \overline{D_{AB}}\,(1 - 0.2075\Delta x.r_e) + 52.29\Delta x \quad \ldots(2)$$

where $\overline{D_{AB}} = (D_{AA}.D_{BB})^{0.5}$, $\Delta x = (x_A - x_B)$ [the difference in Pauling electronegativities] and r_e is the internuclear distance, have been derived by Indian authors.[61,62] The bond energies estimated for the alkali metal halides using the two equations have average deviations from experimental data of 4.5 and 5.3%, respectively.[61] The corresponding deviations for the alkaline earth metal halides are 9.9 and 7.5%, respectively.[62] A simplified formula relating bond orders, q, to spectroscopic constants (ω_e, r_e and B_e) has also been suggested; the estimated

$$q = 1.5783 \times 10^{-3}\,(\omega_e{}^2 r_e/B_e)^{0.5} \quad \ldots(3)$$

bond orders are in reasonably good agreement with literature values.[61,62]

The salts MPH_2 (M = Li-Cs) have been synthesised by reaction of PH_3 with the corresponding solutions of the metals or the metal amides in liquid NH_3;[63] they were characterised by XRD, i.r. spectroscopic and thermochemical methods. $LiPH_2$ is unstable at

298K, evolving PH_3 and an, as yet, unidentified yellow solid. $NaPH_2$ is stable at temperatures below 393K. Temperature dependent XRD studies of KPH_2 ($110 < T/K < 422$), $RbPH_2$ ($110 < T/K < 372$) and $CsPH_2$ ($110 < T/K < 423$) revealed both monoclinic and cubic crystalline modifications for KPH_2 (T_{trans} = 373K) and $RbPH_2$ (T_{trans} = 347K) and a single cubic modification for $CsPH_2$. DSC studies indicate the existence of a further lower temperature modification for both KPH_2 and $RbPH_2$.[63]

Single crystals of NaOH have been obtained by recrystallisation of NaOH powder from liquid NH_3 (p = 6 kbar; $473 < T/K < 523$; $t <$ 6 days).[64] Under comparable conditions, the protolysis of KNH_2 and $RbNH_2$ with $K(H_2O)OH$ ($T <$ 423K) and $Rb(H_2O)OH$ ($T <$ 365K) leads to single crystals of KOH and RbOH, respectively.[64] The heavy atom arrangement of NaOH is confirmed as that of the TlI-structure type; the positions of the H atoms were found to lie on the extension of the Na...O bond vectors. The heavy atom arrangement of KOH and RbOH, which are isotypic, is that of a deformed NaCl-structure type; the libration of the OH^- anions prevented the location of the H atoms at 298K.[64]

Accurate lattice energies of the alkali metal bifluorides have been derived[65] as a result of the direct determination of the hydrogen bond energy (163(4) kJ mol^{-1}) of the bifluoride anion:

$$F^-(g) + HF(g) \rightarrow HF_2^-(g) \qquad \ldots(4)$$

by ion cyclotron resonance methods. Using these data the so-called thermochemical radius (164pm) of the HF_2^- anion can be calculated and hence lattice energies may be predicted for the alkaline earth metal bifluorides.[65] Alkali and alkaline earth metal bifluoride lattice energies are collected in Table 3.

Table 3. Alkali and alkaline earth metal bifluoride lattice energies at 298.15K.[65]

M	Li	Na	K	Rb	Cs
$U[MHF_2]$/kJ mol^{-1}	903	807	725	692	640
M	–	Mg	Ca	Sr	Ba
$U[M(HF_2)_2]$/kJ mol^{-1}	–	2743	2452	2312	2158

1.3.4 Ternary Phosphides

In this and subsequent subsections devoted to ternary derivatives, the only compounds considered are those containing both an alkali metal and a transition metal; ternary compounds containing main group metals are omitted to avoid unnecessary duplication with other Chapters of this review.

The only paper abstracted for this subsection is that submitted by Eisenmann and Somer[66] in which they report the synthesis and characterisation of K_2CuP, NaZnP and K_4CdP_2; unit cell parameters for these materials are included in Table 4.

Table 4. Crystallographic parameters for a number of ternary phosphides.[66]

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	β/°
K_2CuP	orthorhombic	Cmcm	983.9	739.7	579.5	-
NaZnP	tetragonal	P4/nmm	406.6	-	689.3	-
K_4CdP_2	monoclinic	C2/m	984.0	568.1	957.5	110.0

1.3.5 Ternary Oxides and Chalcogenides

A minor resurgence of interest in ternary oxides can be perceived. It is twofold in origin. Firstly the synthesis and characterisation of diverse novel oxides containing two alkali metals has been the subject of an intensive research programme developed by Hoppe et al and secondly, the intercalation of alkali metals, especially Li, into transition metal oxides has been investigated by several independent groups.

Following their earlier communications on oxides containing pairs of alkali metals, first discussed in the 1984 review,[67] Hoppe et al[68-72] have published data on six more novel compounds of this type during 1985. A seventh example has been reported by Forster et al.[73] Synthesised by heating mixtures of the binary oxides in the appropriate molar quantities in sealed inert containers for several days at elevated temperatures, they were structurally characterised using XRD methods. The products are listed in Table 5 together with pertinent unit cell parameters.

Hoppe et al[74-80] have also continued to dominate the preparation and characterisation of regular ternary oxides, providing fifteen of the twentytwo novel examples reported in 1985; a complete listing is given in Table 5 together with pertinent unit cell parameters. With the exception of $MOsO_4$ (M = Na-Cs), which were obtained by reduction of OsO_4 using MI,[84] and $Na_2Mn_3O_7$ which was crystallised hydrothermally under high oxygen pressures (p = 2 kbar),[82] the ternary oxides were prepared by classical solid state methods starting from the appropriate binary oxides. Although M_2O (M = Li-Cs) was generally used as the alkali metal source, for the lanthanide (Li_8LnO_6; Ln = Pr,Tb)[79] and uranium (αLi_6UO_6,[80] α- and β-Na_4UO_5,[85] α- and β-Na_2UO_4[85] and $Na_2U_2O_7$[85]) derivatives, M_2O_2 (M = Li,Na) was used.

A phase transformation has been observed at 973K in the structure of $KFeO_2$.[86] Owing to superstructural ordering analogous to that in $KAlO_2$, the cubic unit cell parameter is modified by a factor of 2:

$$KFeO_2(298K;\ a_0 = 1590.0pm) \xrightleftharpoons{973K} KFeO_2(1013K;\ a_0 = 807.3pm) \quad ...(5)$$

High resolution electron microscopy has been used to probe the structural chemistry of perovskite[87] and of potassium ferrite.[88] For $CaTiO_3$[87] pseudosymmetric twinning yields domains related to each other by either a 180° or 90° rotation about the normal to (101); no evidence was found for the previously reported third type of twin involving a 180° rotation about the normal to (121).[87] For K_2O, 4FeO, $15Fe_2O_3$,[88] the material is much more sensitive to the electron beam than is the isostructural β'''-alumina and readily suffers from structural degradations; the nature and mechanisms of these structural changes are discussed.[88]

Thermodynamic data for the formation of a limited number of ternary oxides have been reported.[83,85,89] The free energies of formation of $MCrO_2$ (M = Li-K):

$$\Delta G_f^\circ(LiCrO_2,c,750<T/K<1200)/kJ.mol^{-1} = -926.84 + 0.17397T/K \quad ...(6)$$

$$\Delta G_f^\circ(NaCrO_2,c,750<T/K<1200)/kJ.mol^{-1} = -869.68 + 0.18575T/K \quad ...(7)$$

$$\Delta G_f^\circ(KCrO_2,c,750<T/K<1200)/kJ.mol^{-1} = -803.84 + 0.15253T/K \quad ...(8)$$

Table 5. Crystallographic parameters for diverse oxides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	3/°	Ref
$KNaTiO_3$	monoclinic	$C2/c$	579.6	1096.1	547.4	97.36	68
$RbNaMo_3O_{10}$	orthorhombic	Pnma	758.9	757.9	1548.9	-	73
$Na_6Li_2W_2O_{10}$	triclinic	$P\bar{1}$	784.7	602.5	563.8	-	69
			(106.8°)	(114.6°)	(91.1°)		
$KLiMnO_2$	monoclinic	$C2/m$	1108.5	338.9	835.7	120.67	70
$Na_2Li_3FeO_4$	orthorhombic	Pnnm	832.2	796.0	656.3	-	71
$K_2Li_3FeO_4$	monoclinic	$P2_1/c$	557.7	880.6	1101.8	111.51	71
$KLiZnO_2$	monoclinic	$C2/m$	1083.2	334.4	823.7	120.11	72
$K_5V_3O_{10}$	tetragonal	$P4_12_12$	817.6	–	1873.1	-	81
$Na_2Mn_3O_7$	triclinic	$P\bar{1}$	663.6	685.4	754.8	-	82
			(105.8°)	(106.9°)	(111.6°)		
$K_2Mn_2O_3$	monoclinic	$P2_1/c$	599.2	645.4	637.4	113.9	74
$Rb_6Fe_2O_6$	monoclinic	$C2/m$	715.0	1175.9	691.4	95.0	83
$MOsO_4$*	tetragonal	$I4_1/a$	567.5	-	1271.3	-	84
M_5OsO_6*	monoclinic	$C2/m$	507.2	875.2	502.2	110.1°	75
K_4IrO_4	monoclinic	$C2/m$	917.3	632.8	612.6	105.5°	76
K_3CuO_2	tetragonal	$P4_12_12$	859.4	-	1331.9	-	77
MCuO*	tetragonal	$I\bar{4}m2$	851.4	-	380.9	-	78
MAgO*	tetragonal	$I\bar{4}m2$	952.0	-	459.9	-	78
Li_8LnO_6*	rhombohedral	$R\bar{3}$	560.9	-	1598.2	-	79
α-Li_6UO_6	rhombohedral	$R\bar{3}$	838.1	-	738.3	-	80
α-Na_4UO_5	cubic	-	476.4	-	-	-	85
β-Na_4UO_5	tetragonal	-	755.6	-	463.9	-	85
α-Na_2UO_4	orthorhombic	-	976.7	573.1	349.8	-	85
β-Na_2UO_4	orthorhombic	-	597.9	581.3	1172.6	-	85
$Na_2U_2O_7$	monoclinic	-	1279.4	782.8	688.8	111.4	85

*Several isostructural compounds were studied; $MOsO_4$ (M = Na-Cs), M_5OsO_6 (M = Li,Na), MCuO (M = Li-Rb), MAgO (M = Na,Rb,Cs), Li_8LnO_6 (Ln = Pr,Tb). The crystallographic data refer to the element listed first, with the exception of $MOsO_4$ for which they refer to $KOsO_4$.

have been determined by a group of Indian authors[89] using e.m.f. data from cells of the type:

$$\mathrm{Pt,LiCrO_2,Li_2CrO_4,Cr_2O_3}\,|\,\mathrm{ZrO_2(Y_2O_3)}\,|\,\mathrm{O_2}\ (p_{\mathrm{O_2}} = 0.21\ \mathrm{atm.})\mathrm{Pt} \qquad ...(9)$$

together with literature data for Li_2CrO_4 and Cr_2O_3. At 750K, the free energies of formation decrease from $LiCrO_2$ (-796 kJ.mol^{-1}) through $NaCrO_2$ (-731kJ.mol^{-1}) to $KCrO_2$ (-689kJ.mol^{-1}).[89] The free energy of formation of $Rb_6Fe_2O_6$:

$$\Delta G_f^\circ(\mathrm{Rb_6Fe_2O_6},c,673<T/K<773K)/\mathrm{kJ.mol^{-1}} = -2157.713 + 0.5985T/K \qquad ...(10)$$

has been derived by Gadd and Borgstedt[83] from equilibrium oxygen potential measurements in liquid rubidium using an electrochemical oxygen meter. The enthalpies of formation of several sodium uranates(VI), $\Delta H_f^\circ(\beta\text{-Na}_4\text{UO}_5,c,298K) = -2457.3(2.8)$kJ.mol^{-1}, $\Delta H_f^\circ(\alpha\text{-Na}_2\text{UO}_4,c,298K) = -1901.3(2.3)$kJ.mol^{-1}, $\Delta H_f^\circ(\beta\text{-Na}_2\text{UO}_4,c,298K) = -1889.0(2.3)$kJ.mol^{-1}, $\Delta H_f^\circ(\text{Na}_2\text{U}_2\text{O}_7,c,298K) = -3203.8(2.8)$kJ.mol^{-1}, have been determined by Tso et al[85] from measured enthalpies of solution in 1.00 mol.dm^{-3} HCl.

Technological demand for species containing mobile alkali metal cations has resulted in a resurgence of interest in alkali metal intercalation compounds. Substrates considered include both traditional (V_2O_5[90,91] MoO_3,[90] WO_3,[90,92] U_3O_8,[90] TiS_2,[93] NbS_2,[94] $NbSe_2$[94]) and novel ($VOPO_4.2H_2O$,[95] $LiFeSnO_4$,[96] YClO[97]) layered compounds.

Lithium intercalation compounds and bronzes, Li_xMO_n, have been prepared[90] by treatment of the oxides V_2O_5, MoO_3, WO_3 and U_3O_8 with ethoxyethane solutions of $LiAlH_4$ and $LiBH_4$(~0.2 mol.dm^{-3}):

$$x\mathrm{LiAlH_4(soln)} + \mathrm{MO}_n\mathrm{(s)} \rightarrow \mathrm{Li}_x\mathrm{MO}_n\mathrm{(s)} + \mathrm{AlH_3(soln)} + 0.5\mathrm{X_2(g)};$$

$$\mathrm{MO}_n = \mathrm{V_2O_5,MoO_3,WO_3,U_3O_8}. \qquad ...(11)$$

$$x\mathrm{LiBH_4(soln)} + \mathrm{MO}_n\mathrm{(s)} \rightarrow \mathrm{Li}_x\mathrm{MO}_n\mathrm{(s)} + \mathrm{BH_3(soln)} + 0.5\mathrm{X_2(g)};$$

$$\mathrm{MO}_n = \mathrm{V_2O_5,MoO_3,WO_3}. \qquad ...(12)$$

Unfortunately, when using $LiAlH_4$, some aluminium formed by the decomposition of aluminium hydride:

$$2AlH_3(soln) \rightarrow 2Al(s) + 3H_2(g) \qquad ...(13)$$

was always found in the product, although reaction (13) was very slow for all substrates but MoO_3. Since boron hydride is stable under similar conditions, $LiBH_4$ appears to be a potentially more useful reagent for the preparation of pure lithium intercalation compounds than $LiAlH_4$.

E.m.f. data have been used[91] to determine thermodynamic parameters for the formation of the vanadium bronze β-$Na_{0.22}V_2O_5$ from α-$Na_{0.02}V_2O_5$:

$$\alpha\text{-}Na_{0.02}V_2O_5 + 0.2Na \rightarrow \beta\text{-}Na_{0.22}V_2O_5;\ \Delta H^\circ_{298} = -1630.4(4.1)\,kJ.mol^{-1}$$

$$\Delta S^\circ_{298} = 141(5)\,JK^{-1}mol^{-1} \qquad ...(14)$$

The formation of the tungsten bronze K_xWO_3 $(0.43 < x < 0.57)$ by reaction of potassium vapour with WO_3 crystals has been followed[92] using transmission electron microscopy. It is concluded that K atoms bonded to the crystal surface diffuse through the substrate converting the WO_3 to the bronze in a surface reaction. The reaction, which is kinetically aided by the ease of penetration of K atoms along (100) planes, is more complex than the simple moving boundary model indicated by optical microscopy.[92]

The effects of sodium intercalation in TiS_2 on the electronic structure of a TiS_2 slab have been probed[93] using the tight binding model.

The lithium intercalation compounds, Li_xNbS_2 $(0 < x < 0.5)$ and Li_xNbSe_2 $(0 < x < 1)$, have been prepared[94] by high temperature reaction of Li_2S, Nb and S or Li_2Se, Nb and Se. Although the structure of Li_xNbSe_2 was found to be that of 2H-$NbSe_2$ (Figure 3 (a)) for the entire series, the structure of Li_xNbS_2 varies with composition. For $x < 0.01$ and $x > 0.10$ the majority phase was 2H-$NbSe_2$ (Figure 3(a)). For $0.01 < x < 0.1$ the 3R-MoS_2 polytype (Figure 3(b)) was prevalent. Evidence for lithium ordering both within and between the layers was obtained and crystal parameters were proposed for the second stage sample, $Li_{0.2}NbSe_2$ (Figure 3(c)).

The layered oxide hydrate $VOPO_4.2H_2O$ readily undergoes redox intercalation reactions with alkali and alkaline earth metal cations in the presence of a reducing agent (the appropriate metal iodide) to form the series $M_xVOPO_4.2H_2O$ (M = Li-Cs, Mg; $0 < x < 1$).[95] The reactions are thought to proceed via intercalation of the reducing agent and reduction of electronically isolated vanadium(V) sites. Only the smallest cations (Li^+, Mg^{2+}) form intercalation compounds in which all of the vanadium(V) is reduced to vanadium(IV).[95]

The high and low temperature polymorphs of $LiFeSnO_4$ (with γ-SnO_2 ramsdellite-type structures) undergo reversible topotactic lithium intercation reactions with n-butyllithium or by electrochemical means to form the series $Li_{1+x}FeSnO_4$ (high-temp. polymorph - $0 < x < 1$; low temp. polymorph - $0 < x < 0.8$).[96] Mössbauer data confirm that intercalation has no effect on tin(IV) but leads to reduction of iron(III) to iron(II). The intercalated Li^+ is thought to be located in the tunnels of the ramsdellite lattice.[96]

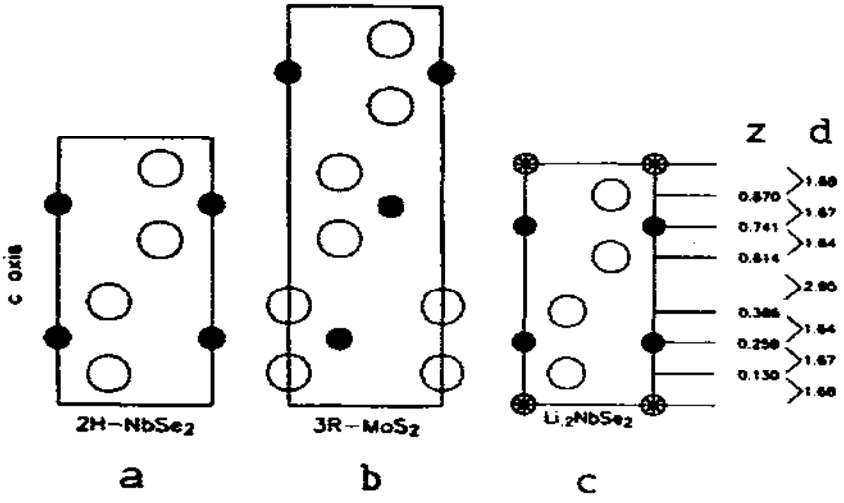


Figure 3 (110) projections of the 2H-$NbSe_2$ (a), 3R-MoS_2 (b) and $Li_{0.2}NbSe_2$ (c) structures showing, in the latter case, crystallographic positions (z) and the distances/Å between the atomic planes (d); ●-Nb; ○-S or Se; ⊛ - possible Li sites which are partially occupied (reproduced by permission from Inorg. Chem., 24(1985) 1656).

The series M_xYClO (M = Li–Cs; 0 < x < 1) have been prepared by reaction of MCl with yttrium and YCl_3–Y_2O_3 or YOCl at ~1223K.[97] They adopt three types of structures: 2H-M_xYClO for Na–Cs (Figure 4(a)), 3R-M_xYClO for Li–Cs (Figure 4(b)) and 1T-M_xYClO for Cs (cf. Figure 4(c)). The coordination geometry of the alkali metal is trigonal antiprismatic in 3R-M_xYClO and trigonal prismatic in 2H-M_xYClO and 1T-M_xYClO. Moist air reversibly hydrates 3R-K_xYClO, 3R-Rb_xYClO and 2H-Rb_xYClO with coherent conversion of the former to a structure analogous to that of 1T-CsYClO (Figure 3(b) → Figure 3(c)). Liquid water oxidises and exfoliates the 3R-M_xYClO phases but has no effect on the 2H-M_xYClO phases.[97]

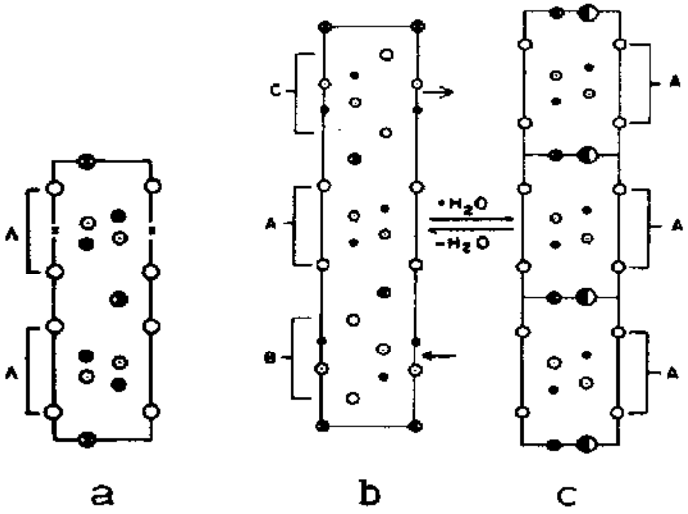


Figure 4. (110) projections of the 2H-M_xYClO (a), 3R-M_xYClO (b) and 1T-$M_x(H_2O)_yYClO$ (c) structures showing the proposed slab sliding process for the conversion of 3R-K_xYClO to 1T-$K_x(H_2O)yYClO$; ● – Y; ⊙ – O; O – Cl; ⊕ – M; ◐ – H_2O (reproduced by permission from Inorg. Chem., 24(1985)4120).

The only novel ternary chalcogenides to be described during 1985 are those of stoichiometry $M_4Re_6X_{13}$ (M = K–Cs; X = S, Se) reported by Bronger et al.[98] The materials successfully synthesised and characterised by XRD methods are listed in Table 6 together with relevant crystallographic parameters. The sulphides were obtained by reaction of M_2CO_3 with rhenium metal in a stream of

H_2S at 1073K; the selenides were prepared similarly using a stream of hydrogen charged with selenium; the mixed sulphide selenide was synthesised in like manner by combining both gas streams.[98]

Table 6. Crystallographic parameters for the isostructural series $M_4Re_6X_{13}$ (M = K-Cs; X = S,Se) which crystallises with monoclinic symmetry in space group C2/c.[98]

Compound	a/pm	b/pm	c/pm	β/°
$Rb_4Re_6S_{13}$	977.3	1658.4	1386.5	99.8
$Cs_4Re_6S_{13}$	1024.4	1779.2	1419.0	100.9
$Rb_2K_2Re_6S_{13}$	989.6	1654.3	1361.1	100.8
$K_4Re_6Se_{13}$	1716.7	1002.9	1229.3	91.4
$Rb_4Re_6Se_{13}$	1748.7	1002.4	1235.0	90.6
$Cs_4Re_6S_{9.45}Se_{3.55}$	1020.3	1751.1	1386.6	101.5

1.3.6 Ternary Halides

Compounds covered in this subsection are restricted to ternary halides containing both an alkali metal and either a transition metal or a lanthanide element; solvated materials are not considered. A smaller number of papers than is usual has been abstracted this year; the two major topics of interest - phase relationships and crystal structures - are still represented albeit at a much reduced level.

Phase relationships in the $KCl-RhCl_3$ system have been studied using dta and XRD methods.[99] Two intermediate phases were discovered; K_3RhCl_6 which undergoes an $\alpha \to \beta$ transformation at 743K before melting congruently at 1133K and $K_3Rh_2Cl_9$ which decomposes in a peritectic reaction at 1190K. Powder XRD data (d-values, intensities) were measured for both phases; unit cell parameters could not, however, be derived.[99]

Liquid structure in the $KCl-ZnCl_2$ system has been derived from X-ray diffraction data using the correlation method.[100] Analyses of the radial distribution functions of molten $KCl-ZnCl_2$(67/33 - K_2ZnCl_4; 50/50 - $KZnCl_3$; 33/67 - KZn_2Cl_5) and of molten $ZnCl_2$, indicated the existence of a tetrahedral $ZnCl_4$ unit in each of these systems.[100] Analogous structural analysis of molten $LiCl-AlCl_3$(50/50 - $LiAlCl_4$)[101] and of molten $NaCl-AlCl_3$(50/50 - $NaAlCl_4$)[102] confirmed the presence of the tetrahedral $AlCl_4$ unit in both systems. The M...Cl and Cl...Cl nearest neighbour distances for all six systems are collated in Table 7.

Table 7. Interatomic distances in molten KCl-$ZnCl_2$,[100] LiCl-$AlCl_3$[101] and NaCl-$AlCl_3$.[102]

	K_2ZnCl_4	$KZnCl_3$	K_2ZnCl_5	$ZnCl_2$	$LiAlCl_4$	$NaAlCl_4$
r(Zn...Cl)/pm	230.3	228.7	229.3	230.7	-	-
r(Al...Cl)/pm	-	-	-	-	215	213
r(Cl...Cl)/pm	376	376	376	376	350	348

Several novel ternary halides have been synthesised and structurally characterised using single crystal XRD methods;[103-109] they are listed in Table 8 together with pertinent crystallographic parameters. The three praseodynium derivatives, K_2PrX_5 (X = Br,I) and Rb_2PrCl_5 were prepared as part of an extensive investigation, coordinated by Meyer,[108] of the structural chemistry of M_2LnX_5 species. The other products (Table 9), however, were obtained as powders; XRD studies showed them to be isostructural to either Cs_2DyCl_5 or K_2PrCl_5, (Table 9).

Although the majority of the ternary halides were obtained under classical solid state conditions, $MTiCl_3$ (M = Rb, Cs)[104] and

Table 8. Crystallographic parameters for diverse ternary halides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	β/°	Ref
KSc_2F_7	orthorhombic	Cmmm	1064.3	654.0	403.0		103
$RbTiCl_3$	hexagonal	$P6_3/mmc$	711.7		600.0		104
$CsTiCl_3$	hexagonal	$P6_3/mmc$	730.2		605.3		104
$K_4Nb_6Br_{18}$	monoclinic	C2/m	1042.7	1722.2	1099.6	124.8	105
$Cs_7Co_4F_{15}$	monoclinic	$P2_1/c$	788.3	1096.6	1164.9	92.6	106
$Cs_7Ni_4F_{15}$	monoclinic	$P2_1/c$	787.2	1089.7	1149.5	92.7	106
K_2GdF_5	orthorhombic	Pnam	1081.4	662.3	738.9		107
K_2PrBr_5	orthorhombic	Pnma	1332.2	918.6	842.2		108
K_2PrI_5	orthorhombic	Pnma	1428.9	982.7	911.9		108
Rb_2PrCl_5	orthorhombic	Pnma	1311.0	894.3	818.1		108
KNd_2Cl_5	monoclinic	$P2_1/c$	894.5	785.2	1265.3	90.0	109

Table 9. Compounds of stoichiometry M_2LnX_5 synthesised by Meyer et al.[108]

Cs_2DyCl_5 -structure type (orthorhombic; Pbnm)

Rb_2LnCl_5 (Ln = Er, Tm, Lu)
$CsRbLnCl_5$ (Ln = Y, Tb-Lu)
Cs_2LnCl_5 (Ln = Y, Dy-Lu)

K_2PrCl_5 - structure type (orthorhombic; Pnma)

Cs_2LaCl_5
Rb_2PrCl_5
K_2LnBr_5 (Ln = La-Nd, Sm, Gd)
Rb_2LnBr_5 (Ln = La-Nd, Sm)
K_2LnI_5 (Ln = La-Nd)
Rb_2LnI_5 (Ln = La-Nd)

KNd_2Cl_5[109] were obtained under severely reducing conditions. $MTiCl_3$ (M = Rb, Cs)[104] were prepared by synproportionation of appropriate amounts of MCl, Ti and $TiCl_3$ in sealed Ta crucibles at 973K for 3 days; KNd_2Cl_5[109] was synthesised by treatment of $NdCl_3$ with liquid K. A novel preparative route to K_2TcF_6 - reaction of K_2TcBr_6 with AgF in 40% aqueous HF - has also been reported.[110]

An i.r. study[111] of K_2ReF_6 at 10 and 295K has confirmed the presence of trigonal distortion in the $ReF_6{}^{2-}$ anion. A ^{19}F n.m.r. study[112] of $KZnF_3$ has shown that contributions to the nuclear magnetic shielding of the ^{19}F nuclei arise from three sources; the closed shell electrons of the F^- ion under investigation, the closed shell electrons of the neighbouring ions and the inclusion of covalency in the predominantly ionic $Zn^{2+}...F^-$ bonding.

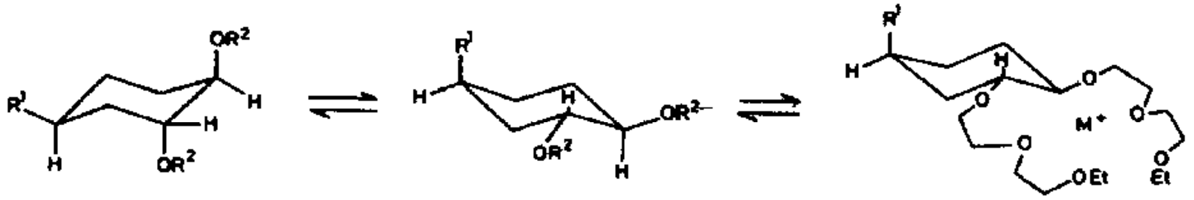
1.4 COMPOUNDS OF THE ALKALI METALS CONTAINING ORGANIC MOLECULES OR COMPLEX IONS

To provide a logical format for the presentation of the data abstracted for this section they are reviewed, if at all possible, in sub-divisions devoted to specialised subjects of current interest and significance. Inevitably some data cannot be thus categorised; these are considered in sub-divisions associated with the individual alkali metals. Since priorities have changed little during the past year, the format adopted for this section is identical to that used for the 1984 review.[113]

1.4.1 Complexes of Acyclic Lipophilic Ionophores

Ab initio MO calculations within the Hartree-Fock framework have been completed[114,115] for complexes of Na^+ and K^+ ions with the acyclic ligands 1,4,7,10-tetraaza- and 1,4,7,10-tetraoxadodecane and with the corresponding macrocyclic ligands 1,4,7,10-tetraaza- and 1,4,7,10-tetraoxacyclododecane(12C4). The general conformation of the ligands is predicted to remain the same on complexation; that is, the alternate form for the tetraaza- and the maxidentate form for the tetraoxa-ligands.[114,115] The calculations also show, however, that considerable input of energy is required to change the structures of the acyclic species from those of the free molecules to those of the complexed ligands.[115] A similar input of energy is not required for the macrocyclic species owing to their rigid prestrained conformations. Using these observations as a basis the remarkable stability of the complexes of macrocyclic ligands can be rationalised.[115]

To gain more information about the endothermic structure change on complexation, a series of conformationally biased pentaethyleneglycol diethyl ethers (30) has been synthesised by Raban et al[116] and their complexation of M^+ ions studied using low temperature ^{1}H-n.m.r. spectroscopy. The ionophores (30) exist as mixtures of conformers ax-(30) and eq-(30) which interconvert by ring reversal of the cyclohexane ring (Scheme 6). Since eq-(30), but not ax-(30), can achieve a conformation similar to that of 18C6 it was found to be much more effective at complexation.[116]

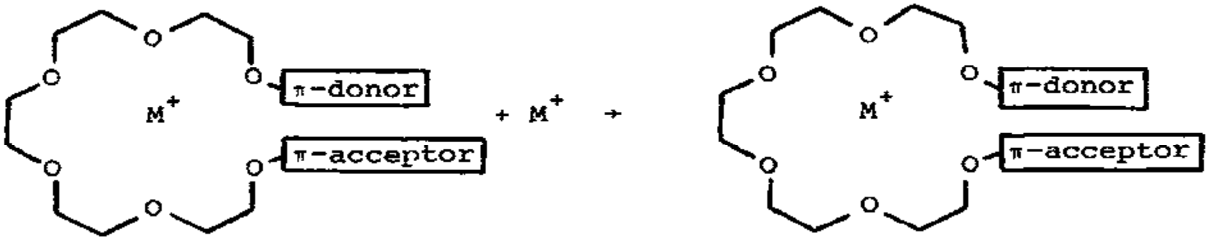


ax-(30) **eq-(30)** **eq-(30) M⁺**

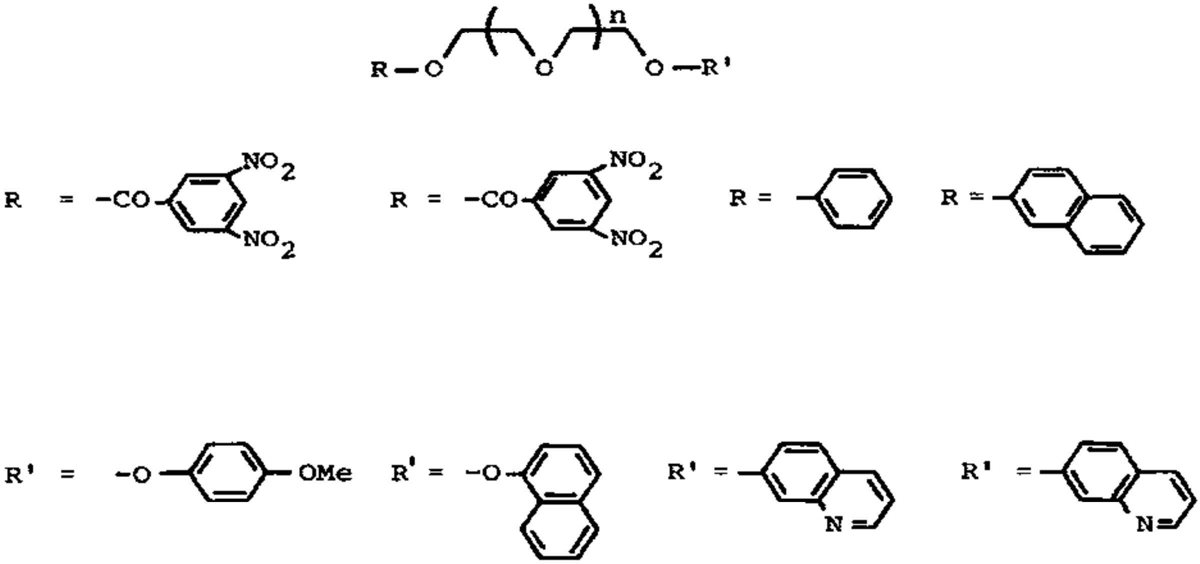
Scheme 6.

To try to promote the structure change Vogtle et al[117-119] and

Hiratani[120] have incorporated terminal π-electron donor and/or π-electron acceptor groups into various acyclic ionophores; it is intended that interaction between the π-systems of the aromatic rings will stabilise the structure required for complexation (Scheme 7). Such interaction can readily be studied using



Scheme 7.



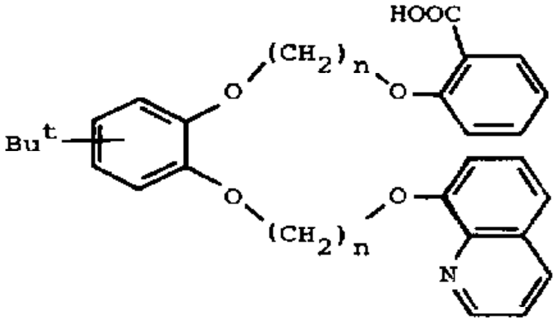
n = 2; (31)
n = 3; (32)
n = 4; (33)

n = 2; (34)
n = 3; (35)
n = 4; (36)

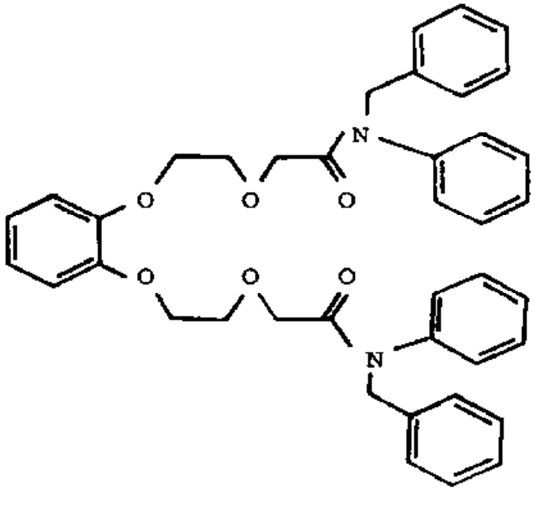
n = 3
(37)

n = 3
(38)

u.v.-visible spectroscopic methods.[117,120] Thus, Vogtle et al[117] have shown that addition of $MClO_4$ (M = Li-Cs) to CH_3CN solutions of the hexaoxa ionophores (33) or (36) causes a significant increase in absorption and a bathochromic shift of the charge transfer bands in the u.v.-visible spectrum, and that addition to solutions of the tetraoxa ionophores (31) or (34) results in a decrease in absorption and a hypsochromic shift.[117] The changes on complexation are such that some of these acyclic chromoionophores discern considerably and visually perceptibly between Na^+ and K^+ ions or between Na^+ and Li^+ ions.[117] Spectroscopic evidence which supports the formation of a stacked structure between terminal groups of the acyclic ionophores (39, 40) has been obtained by Hiratani[120] on addition to solutions of alkali metal salts, especially those of lithium, in non-polar solvents. The Li atom is thought to be located in a 6-fold coordination geometry provided by the four heteroatoms of the polyether chains, an oxygen of the carboxylic acid group and the nitrogen of the quinoline moiety.[120]



n = 2; (39)
n = 3; (40)



(41)

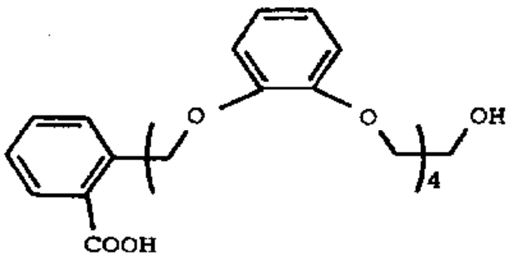
Structural evidence for interaction between terminal groups has been obtained by Vogtle et al[118] from a single crystal XRD study of $[(37)K]^+SCN^-, H_2O$ and of $[(38)K]^+SCN^-$.[118] The interaction is quite different in the two complexes; whereas the dihedral angle between the benzene and quinoline rings in the former is 83°, that between the naphthalene and quinoline rings in the latter is 1.1°.

In [(37)K]$^+$SCN$^-$,H_2O, the ligand wraps around the K atom such that four of the five polyether oxygens (276.8-298.4pm) and the quinoline nitrogen (285.2pm) act as coordinating centres in addition to the thiocyanate nitrogen (286.4pm) and water oxygen (276.8pm); the phenoxy group oxygen does not coordinate the cation owing to the failure of the benzene and quinoline groups to stack together. In [(38)K]$^+$SCN$^-$, all six heteroatoms of the ligand (r(K...O) = 276.6-288.5; 308.1pm; r(K...N) = 279.5pm), in addition to the thiocyanate nitrogen (288.8pm), ligate the K atom.[118]

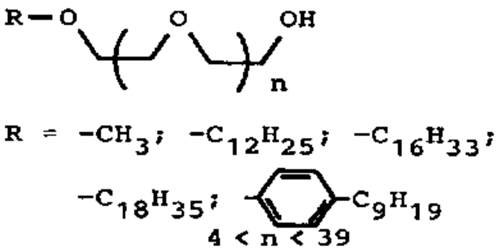
The synthesis and selectivity coefficients of a series of acyclic ionophores, typified by (41), have been reported by Vogtle et al.[119] Several, including (41) were found to exhibit a remarkable combination of high Ba^{2+} ion specificity and high lipophilicity and, hence, are attractive for analytical applications.

A novel synthetic acyclic ionophore with a single benzoic acid terminal group (42) has been reported.[121] Studies of the transport of Na^+ and K^+ ions through a dichloroethane liquid membrane in the presence of (42) indicate that this species has a higher selectivity for K^+ ions than any other ionophore described previously. This remarkably high selectivity is attributed to differences in solubility in dichloroethane.[121]

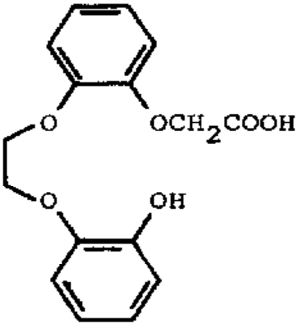
Thermodynamic parameters and stability constants for complex formation between a series of acyclic polyethers (43) and M^+ (M = Na-Cs) or M^{2+} (M = Ca-Ba) have been determined by calorimetric titration in CH_3OH.[122] With increase in the number of donor heteroatoms, the reaction enthalpies become more negative; the stability constants, however, change little owing to compensating changes in entropies.



(42)



(43)



(44)

The synthesis of [Zn[(44)$_2$K]$_2$] and [Zn[(44)$_2$Rb]$_2$] by reaction of zinc acetate, (44) and MBr (M = K,Rb) in ethanol has been reported.[123] These materials have very similar i.r. spectra to those of [Co[(44)$_2$K]$_2$] and [Co[(44)$_2$Rb]$_2$] which have been structurally characterised (see 1983 review[124]). Although the corresponding reaction with NH_4I in ethanol afforded [Zn[(44)$_2$NH$_4$]$_2$], the analogous reaction with cobalt(II) did not yield a product. It is thus suggested that subtle changes to the central (transition) metal and/or the ligand system may give 'tailor-made' complexes for selection of any required cation.[123]

The complexing properties of the naturally occuring acyclic ionophores, lysocellin[125] and monensin[126] have been studied using potentiometric and calorimetric methods, respectively. Complexation of M^+ (M = Na,K) and of M^{2+} (M = Mg,Ca) by lysocellin (AH) occurs according to Scheme 8; its Na^+/K^+ selectivity favours K^+, whereas its Mg^{2+}/Ca^{2+} selectivity favours Ca^{2+}.[125] Complexation of M^+ (M = Na,K) by monensin A and monensin B is such

$$AH + M^+ \rightleftharpoons AHM^+ \qquad A^- + M^{2+} \rightleftharpoons AM^+$$
$$A^- + M^+ \rightleftharpoons AM \qquad 2A^- + M^{2+} \rightleftharpoons A_2M$$

Scheme 8.

that monensin A is a more effective complexant than monensin B, similarly, monensin A exhibits a greater Na^+/K^+ selectivity than monensin B.[126] The observed differences are attributed to differences in entropic contributions to the binding free energy.

1.4.2 Crown Complexes

Once again research in the field of alkali and alkaline earth metal complexes of crowns and related macrocyclic ligands has a high publication profile. Consequently the topic has been divided into three subsections in which complexes of (i) 'classical' crown compounds and their substituted derivatives, (ii) lariat ethers, and (iii) novel macrocyclic ligands of unusual design, are discussed.

The complexation of Na^+ ($NaBPh_4$ or $NaPF_6$) by DB24C8[127] and by DB30C10[128] has been studied in CH_3NO_2 by ^{23}Na-n.m.r. spectroscopic methods. For the Na^+-DB24C8 mixtures,[127] the principal species in solution is the 1:1 complex. There is, however, some evidence for the formation of higher aggregates whose stoichiometry is plausibly n+1:n. An aggregation model based on this stoichiometry is proposed, the average number of crowns in the species varying from 1 to 3.8. For the Na^+-DB30C8 mixtures,[128] the major species in solution are the 1:1, 2:1 and 3:2 complexes. The characteristic ^{23}Na relaxation rates and chemical shifts of the complexes are compatible with a structure in which ion pairs are linked by the crowns.

Calorimetric and potentiometric methods have been used to study the complexation of Ba^{2+} by different crown ethers (15C5, 18C6), azacrown ethers (C21, C22 and C23) and cryptands (C211, C221, C222) in CH_3OH.[129] The macrocyclic effect, found for the reactions of crown ethers, was attributed to favourable entropic changes. The cryptate effect, on the other hand, was attributed to an increase in reaction enthalpies.

Crown (18C6, DB18C6) complexes of alkali metal hydroborates (MBH_4, MB_3H_8; M = Na,K) have been isolated from a variety of solvents (C_2H_5OH, CH_3OH, thf and water).[130] Characterisation of the products which included both solvated and unsolvated species was effected by chemical, and thermal (dta, tga, dtga) analyses as well as i.r. spectroscopy. Their solubilities in organic solvents was also assessed.

The crystal and molecular structures of the complexes, $[18C6Ba]^{2+}[(Bu^nO)_2PO_2]_2^-,H_2O$ (45),[131] $[DB36C12Li_2]^{2+}[OC_6H_2(NO_3)_3]_2^-,2H_2O$ (46),[132] $[B15C5Na]_2^+[Cu_2Cl_6]^{2-}$ (47),[133] $[DB18C6Na]_2^+[Cu_2Cl_6]^{2-}$ (48),[133] $K^+[12C4K]_6^+[Cu_4I_6]^{2-}[Cu_8I_{13}]^{5-}$ (49),[134] $[15C5K]_2^+[Cu_4I_6]^{2-}$ (50)[134] and $[DB24C8K]^+[Cu_3I_4]^-$ (51)[134] have been determined from single crystal XRD data. The Ba atom in the dibutylphosphate salt (45)[131] is located ~61pm above, and coordinated to each member of, the plane of the six heteroatoms of the 18C6 molecule (281-290pm); its nine-coordinate geometry is completed, on one side of the ring, by an oxygen of a dibutylphosphate anion (262pm), and on the other side by two oxygens, one from the second anion (267pm) and one from the water molecule (279pm).[131]

The two Li atoms in the structure (Figure 5) of the picrate salt (46)[132] are related by a centre of symmetry. They are four-coordinate, within a distorted trigonal bipyramidal geometry, to two crown oxygens (198.3, 223.4pm), to one water molecule (196.2pm) and to the phenoxide (193.6pm) and nitro group (206.7pm) oxygens of a picrate anion (Figure 5). The picrate anions are almost parallel to the catechol rings of the macrocycle with a minimum separation of 337pm.[132]

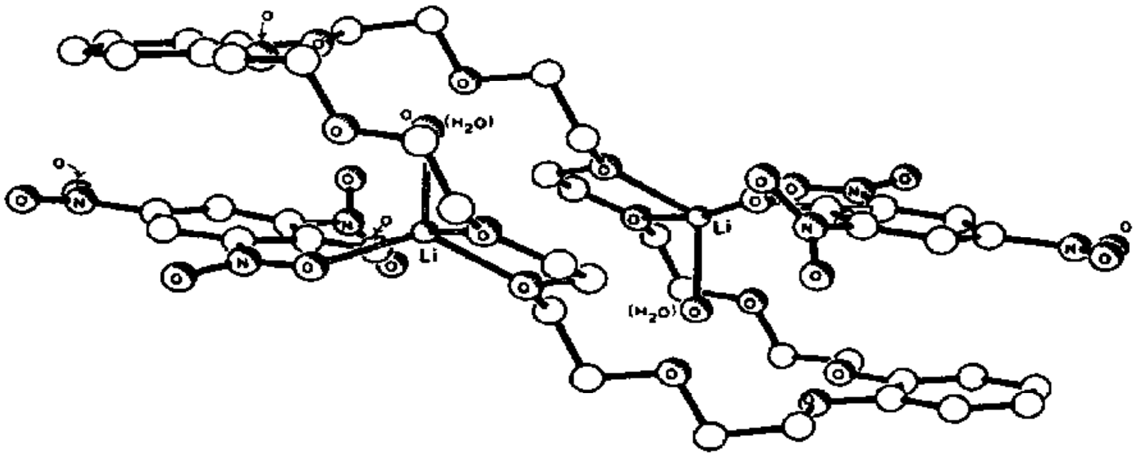


Figure 5. Molecular structure of $[\mathrm{DB36C12\,Li_2}]^{2+}\,[\mathrm{OC_6H_2(NO_3)_3}]_2^-$, $2H_2O$ (46) showing the Li atom coordination and the parallel stacking of the picrate and catechol rings (reproduced by permission from Polyhedron, 4(1985)567).

Markedly different structures are observed for the two copper(I) chloride complexes (47,48).[133] In both structures (Figures 6(a), 6(b))), the $Cu_2Cl_6^{2-}$ anion bridges two parallel centrosymmetrically related crown-cation moieties. In (47) it adopts a perpendicular configuration (Figure 6(a)); in (48) it adopts a parallel configuration (Figure 6(b)). The Na atom in (47) is coordinated by the five heteroatoms of the macrocyclic ring (242.2-251.3pm) and two chlorine atoms (290.5, 299.2pm); it lies ~96pm above the

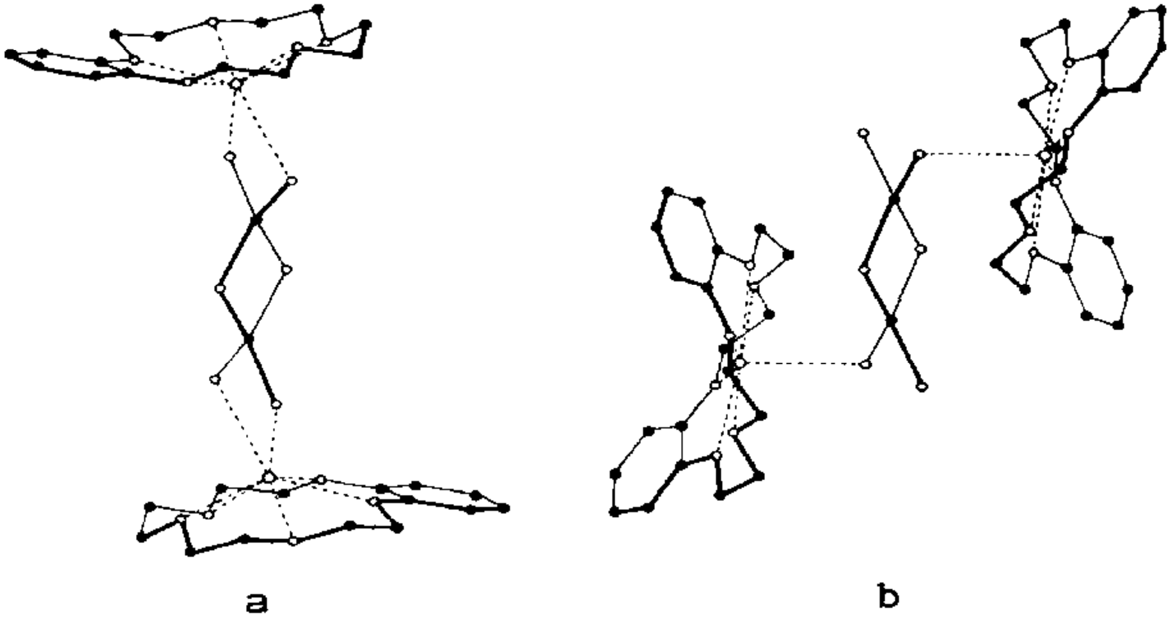


Figure 6. Molecular structures of (a) $[B15C5Na]_2^+[Cu_2Cl_6]^{2-}$ (47) and (b) $[DB18C6Na]_2^+[Cu_2Cl_6]^{2-}$ (48) (reproduced by permission from Inorg. Chim. Acta, 96(1985)21).

plane of the five heteroatoms of the crown ring (Figure 6(a)). That in (48), however, is coordinated by the six heteroatoms of the ring (263.9-271.9pm) and a single chlorine atom of the anion (283.4pm); it is located close to the centre of the crown lying only ~18pm above the plane formed by the six heteroatoms (Figure 6(b)).[133]

Unexpectedly different structural formats occur for the three copper(I) iodide complexes, (49,50,51). In (49) six K atoms, each coordinated to a 12C4 macrocycle, are positioned on faces of the $[Cu_8I_{13}]^{5-}$ clusters and in the voids between the $[Cu_4I_6]^{2-}$ and $[Cu_8I_{13}]^{5-}$ clusters. The seventh K atom separates the $[Cu_8I_{13}]^{5-}$ clusters at ionic distances ($r(K...I)_{av}$ = 376pm). In (50) the two K atoms, each coordinated to a 15C5 macrocycle, interact ionically with the iodine atoms of the polymeric Cu_4I_6 sheets; each K atom has three K...I distances of less than 385.2pm. In (51), the K atoms exhibit no involvement with the iodine atoms of the polymeric Cu_3I_4 chains; they interact solely with four of the eight heteroatoms of the DB24C8 macrocycle ($r(K...O) < 307$pm).[134]

The type of structure adopted by the copper(II) chloride and copper(I) iodide complexes, which is obviously crown ether dependent, is dictated by the extent to which the cation, when complexed to a crown ether of specific ligand (oxygen) content and cavity size can interact with the halogen. Thus, as the cavity size decreases from (48) to (47) the Na atom is progressively exposed, successively allowing access to one Cl atom in the DB18C6 complex (48) and then to two Cl atoms in the B15C5 complex (47). Similarly, the cavity of the DB24C8 molecule in (51) is large enough to encapsulate completely the K atom and prevent interaction with iodine whereas the cavities of the 15C5 and 12C4 molecules in (50) and (49) are too small to surround the K atom which, being thus exposed, interacts with iodine atoms.[134]

Stability constants and thermodynamic parameters for the reaction of crown ethers with alkali and alkaline earth metal cations have been determined in a variety of solvents using a plethora of experimental techniques.[135-138] Conflicting evidence has been obtained for the effects of salt concentration and counterion on the stability of $[18C6M]^+$ (M = Li-Cs) in both water and methanol using potentiometric and ^{23}Na-n.m.r. methods.[135] The stability constants obtained potentiometrically vary markedly with salt concentration and with counterion. The corresponding n.m.r. stability constants are virtually insensitive to change in both parameters. Resolution of the conflict is afforded in terms of the activity coefficients, γ_{ML^+}, γ_{M^+} and γ_L. Whereas the potentiometric stability constants are true concentration stability constants subject to the $\gamma_{ML^+}/\gamma_M \cdot \gamma_L$ variation the n.m.r. stability constants are hybrids between the concentration, K_c, and thermodynamic, K_t, constants which are related by the equation:

$$K_c = (\gamma_{M^+} \cdot \gamma_L / \gamma_{ML^+}) K_t \qquad \ldots(15)$$

The marked effect of salt concentration and counterion on the potentiometric stability constant is attributed to a large variation in γ_{ML^+}.[135]

Stability constants for the reaction of 15C5, 18C6, CH15C5, B15C5, DCH18C6 and DCH24C8 with M^+ (M = Na-Cs) and M^{2+} (M = Ca-Ba) have been determined in methanol by calorimetric titration;[136] depending on the macrocycle and the ion, 2:1, 1:1 and 1:2

complexes were formed. Similar data for the formation of 1:1 complexes of DB24C8 with M^+ (M = Na–Cs) have been determined in acetonitrile by conductometry.[137] The stability constants of complexes of 18C6 with M^+ (M = Li–Cs) and M^{2+} (M = Mg–Ba) have been assessed in glycerol using electrohydrodynamic mass spectrometry;[138] the mass spectral data uniquely reflect the effects of solvation and ion pairing in the formation of these complexes through the resolution of differently solvated and ion-paired species.

^{23}Na-n.m.r. techniques have been used by two groups of authors[139-141] to study aspects of the kinetics of the complexation-decomplexation reaction of Na^+ by crown ethers in a variety of solvents. Delville et al[139] have considered the $NaBPh_4$-DB24C8 system in nitromethane. At low concentrations, the exchange follows a unimolecular dissociative mechanism; at high concentrations, it obeys a bimolecular cation interchange mechanism. Popov et al have examined separately the influence of solvents[140] on the NaX (X = SCN, BPh_4)-18C6 system and the influence of counterions[141] on the NaX (X = BPh_4, SCN)-18C6 system in thf. In neat methanol, thf-methanol (60/40) and thf-propylene carbonate (80/20) the dissociative exchange mechanism is preferred; in neat propylene carbonate and thf-propylene carbonate (40/60), however, the bimolecular exchange mechanism predominates.[140] For $NaBPh_4$, the exchange is slow, the mechanism adopted being the dissociative one; for NaSCN, however, the exchange is rapid, the mechanism predominating being the bimolecular process.[141]

The mobilities of $[B18C6M]^+$ (M = Na–Cs) cations have been determined in various non-aqueous solvents using conductance methods.[142] Although apparently independent of the alkali metal, the mobilities do vary with the size of the crown ether, decreasing in the sequence:

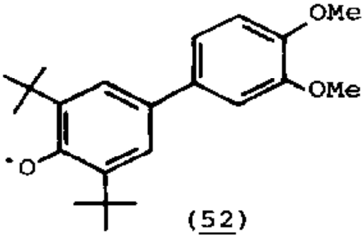
18C6 > B18C6 > DB18C6

The substituent effects on cation extraction and transport properties of a series of 4'-substituted B15C5 derivatives have been found to be significant and even comparable to the ring size effects.[143] For example, replacement of the nitro group in 4'-NO_2-B15C5 by an amino group to give 4'-NH_2-B15C5 leads to a similar increase in transport properties as does extension of the

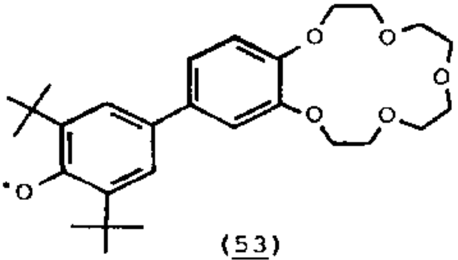
B15C5 ring in 4'-NO_2-B15C5 by a single -CH_2OCH_2- moiety to give 4'-NO_2-B18C6.

E.s.r. studies[144] of complex formation between the veratrole analogue (52) of 4'-phenoxyl-B15C5 (53) and alkali and alkaline earth metal salts in ethanol rigid matrices at 77K indicate the formation of 1:1 complexes for all metal cations studied and 2:1 complexes for K^+, Rb^+ and Cs^+ only. Comparison with previous data for complexes involving (53) suggests that the 2:1 complexes of (52) have a structure in which the aryloxyl skeletons stack over each other, the alkali metal cation being located between the two pairs of methoxy groups.[144]

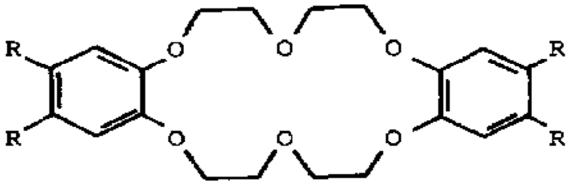
Complex formation between the tetrakis(phosphinyl)-substituted DB18C6 (54) and either M^+ (M = Li-Cs) or Co^{2+} ions or mixtures of these ions has been studied conductometrically in non-aqueous solvents.[145] The complex $[(54)K]^+Cl^-,2CoCl_2$ has been isolated from the mixed solutions; the K atom is thought to be located in the macrocycle and the Co atoms are thought to be coordinated by elements of the phosphinyl groups.[145]



(52)



(53)



R = $-CH_2P(O)Ph_2$

(54)

Solvent extraction of alkaline earth metal picrates with a series of ring-contracted and ring-enlarged crown ethers has been carried out to ascertain the effects of methylene chain length on cation binding ability.[146] Although both ring-contracted and ring-enlarged crown ethers exhibit reduced extractabilities for these cations, the effect is much more dramatic for the ring-contracted species.

1.4.3 Complexes of Lariat Ethers

Gokel et al[147,148] have reported the results of an extensive study of the alkali metal cation binding properties of diverse lariat ethers. The stability constants of the Na^+ complexes of a series of 12-, 15- and 18-membered ring nitrogen pivot lariat ethers indicate that strongest binding for Na^+ occurs when six oxygens are present in the lariat ether regardless of ring size, indicating that a flexible macrocycle is directed by the cation to envelop and solvate in the geometry most appropriate for the cation and not for the macrocycle.[147] The binding of M^+ (M = Li-K) by neutral and anionic forms of mono- and bi-bracchial carbon and nitrogen pivot lariat ethers has been surveyed using cyclic voltammetry techniques.[148] From the differences in potentials it was found that binding of the cations was enhanced from 15- to 13×10^6-fold upon electrochemical reduction. The binding enhancements, which differ in magnitude owing to steric constraints, are due to intramolecular ion pairing and are generally in the order:

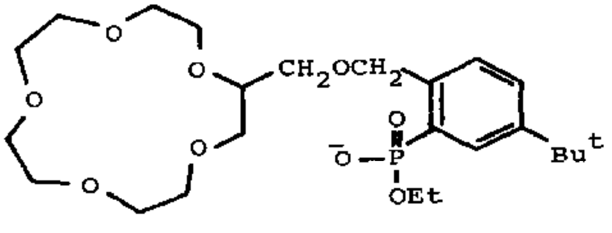
$Li^+ > Na^+ > K^+$

Participation of the pendant side chain of the 15C5 carbon pivot anionic lariat ether (<u>55</u>) in the complexation of Na^+, but not of Li^+ or K^+, in $CDCl_3$ has been demonstrated by ^1H-n.m.r. spectroscopic techniques.[149] The spectrum of the sodium salt exhibited an AB quartet (J_{AB} = 12Hz) centered at δ5.03 for the benzylic protons. In sharp contrast the benzylic proton resonance of the lithium and potassium derivatives appeared as broadened singlets centered at δ5.04 and δ5.18. Presumably Na^+ (diam. = 190pm) binds tightly within the cavity (diam. = 170-220pm) simultaneous coordination of the phosphonate function markedly restricting mobility of the side chain and hence of the two diastereotopic benzylic protons. Li^+ (diam. = 120pm) and K^+ (diam. = 266pm) however, are too small and too large, respectively, for strong interaction with the cavity. Hence coordination of these cations will be dominated by the phosphonate group and side chain mobility will not be lost.[149]

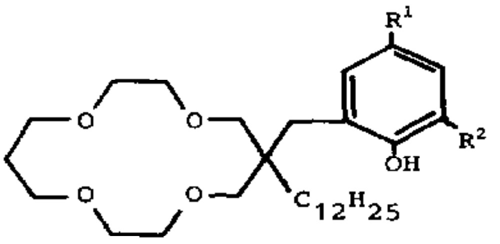
The alkali metal selectivity of lipophilic ring-enlarged carbon pivot lariat ethers incorporating either nitrophenol (eg. 56-59)[150] or carboxylic acid (eg. 60,61)[151] substituents in the side chain has been assessed using proton driven cation transport[150] or solvent extraction[151] methods by two independent groups. Japanese authors[150] have shown that membranes containing (57) act as an alkali metal cation pump the selectivity order being:

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

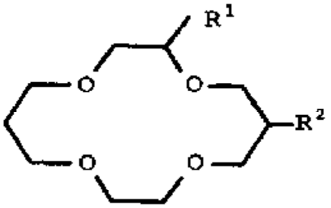
Whereas (58) and (59) exhibited similar membrane transport behaviour, but without the outstanding Li^+ selectivity, (56) did not transport any of the cations presumably owing to the high pK_a value of the phenol proton.[150] American authors[151] have observed that (60) and (61) exhibit the greatest Li^+ selectivity with respect to Na^+ of all the analogous 12C4, 13C4, 14C4, 15C4, B12C4, B14C4 and DB14C4 derivatives studied in competitive alkali metal cation solvent extraction experiments. Indeed, the Li^+/Na^+ selectivity ratios of 19-20 are said to be the highest yet achieved under these conditions.[151]

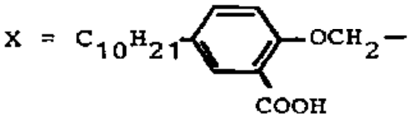


(55)



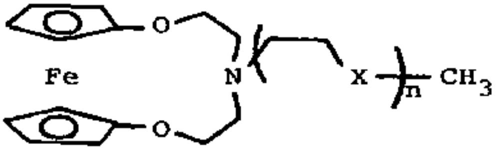
R^1	R^2	
H	H	(56)
NO_2	H	(57)
H	NO_2	(58)
NO_2	NO_2	(59)



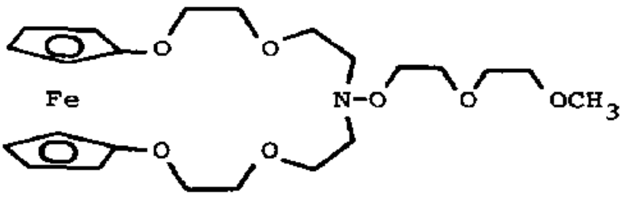


R^1	R^2	
X	H	(60)
H	X	(61)

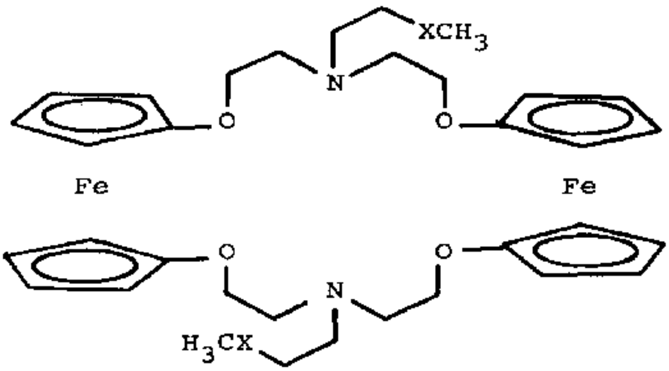
Novel mononuclear (62-66;[152] 69,[153] 70[153]) and dinuclear (67,68)[152] metallocenocrown ethers have been synthesised and their ability to extract alkali metal salts measured. All of the lariat ferrocenocrown ethers showed poor extractability although those bearing an alkoxy side chain (62,64,67) were more effective than those which contained an alkyl group (63,65,68) as a side arm.[152] Crystalline 1:1 complexes of $LiClO_4$ with (62) and (63) and of $NaClO_4$ with (62) were isolated.[152] The ferrocene and ruthenocene bis (crown ethers) (69,70) exhibit exclusive K^+ selective intramolecular sandwich-type complexation over either Na^+ or Cs^+.[153] This suggests that a well defined cavity exists between the cofacial amido-B15C5 units which provides an optimal spatial fit for the K^+ guest ion.[153]



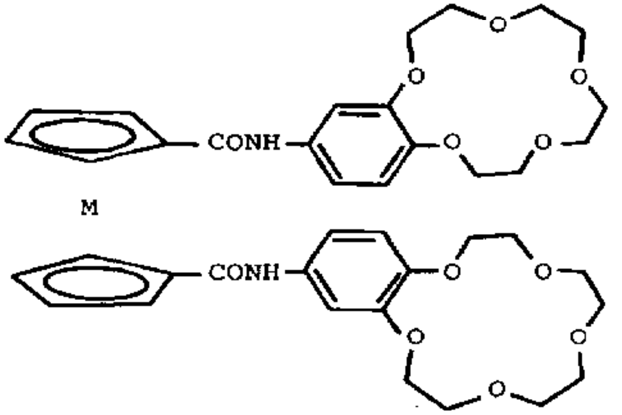
X = O ;n = 1 (62)
X = CH_2;n = 1 (63)
X = O ;n = 2 (64)
X = CH_2;n = 2 (65)



(66)



X = O (67)
X = CH_2 (68)

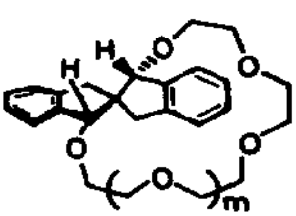


M = Fe (69)
M = Ru (70)

1.4.4 Complexes of Macrocyclic Polyethers of Novel Design

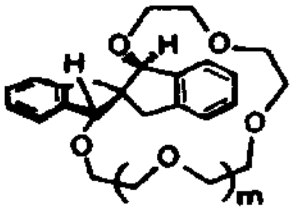
Fewer papers than is typical of earlier reviews have been abstracted for this subsection. Although the majority report the synthesis of traditionally designed macrocyclic polyethers[154-158] a number describe the preparation of novel complexants based on anisole spherands and related molecules.[159-163]

Four chiral crown ethers derived from (+)-trans-trans-2,2'-spirobiindan-1,1'-diol (71,72) and (+)-cis-trans-2,2'-spirobiindan-1,1'-diol (73,74) and the acyclic analogue (75) have been prepared and their abilities to extract alkali metal picrates investigated.[154] In comparison with 18C6 they are relatively



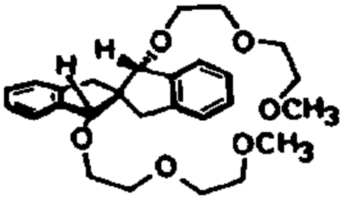
(71) m=2

(72) m=1



(73) m=2

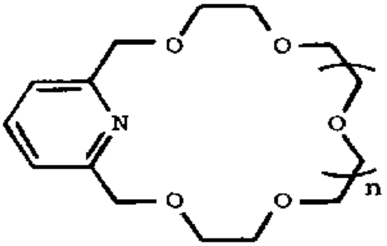
(74) m=1



(75)

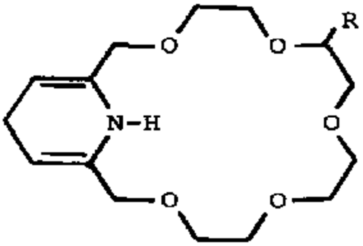
ineffective as extractants. The ligand with the greatest extractability (71) is ~30% as effective as 18C6 for Li-K, ~20% as effective for Rb^+ and ~6% as effective for Cs^+; the other ligands (72-75) are almost totally ineffective.[154]

Stability constants and thermodynamic parameters for complex formation between M^+ (M = Na-Cs) or M^{2+} (M = Ca-Ba) and several pyridinocrown ethers (76) have been determined by calorimetric titration in methanol.[155] The stability of these complexes is lower than that of the complexes formed by the corresponding crown ethers; when compared with complexes of other monosubstituted



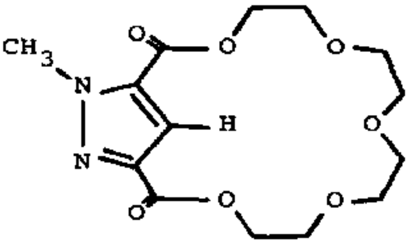
n = 1-3

(76)

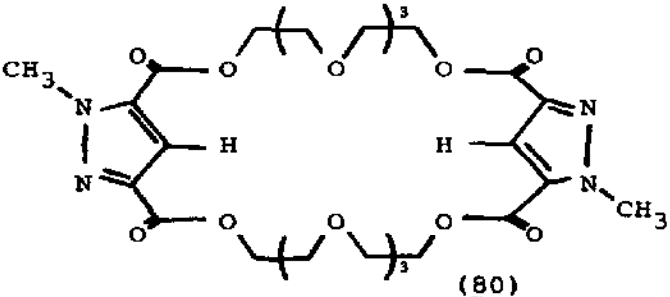


(77):R = H

(78):R = C_8H_{17}



(79)



(80)

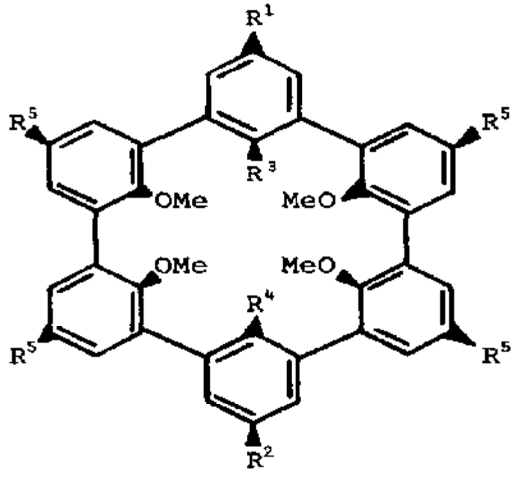
crown ethers, however, these complexes are far more stable.[155]

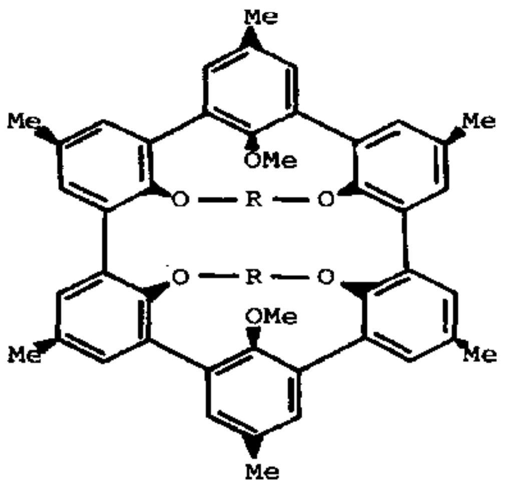
The alkali metal transport properties of the reduced pyridino- (77,78)[156] and pyrazolic crown ethers (79,80)[157] have been investigated independently. The proton-ionisable macrocycles (77,78)[156] were designed such that their binding of H^+ or M^+ can be controlled by adjustment of the pH of the solution. Their transport of M^+ across a $H_2O-CH_2Cl_2-H_2O$ membrane system was at the blank level for both (77) and (78) using neutral source solutions (pH = 6; ionisation of the proton did not occur). As the pH of the source solution was increased (pH >7; the proton is replaced by M^+), transport of M^+ increased, especially for (78). The difference in the ability of (77) and (78) to transport M^+ across the membrane system was attributed to the influence of the lipophilic C_8H_{17}-side chain. Partially selective transport of K^+ was observed in K^+/Na^+, K^+/Rb^+ and K^+/Cs^+ mixtures.[156] Of the two pyrazolic crown ethers (79,80),[157] (80) was clearly superior for transport of M^+ (M = K-Cs), they were equivalent for Na^+ and (79) was superior for Li^+; (80) exhibits selectivity for K^+ while (79) is most effective in transporting Li^+.[157]

Novel oligo benzo-condensed 18C6 ligands with a different gradation of lipophilicity and of molecular rigidity have been synthesised and their transport properties and ion selectivities for M^+ (M = Li-Cs) and M^{2+} (M = Mg-Ba) in bulk liquid membranes of differing composition have been determined.[158]

Cram et al[159] have described the synthesis of a series of anisole spherands (81-84; 87-88) and have reported the structural chemistry of several complexes with alkali metal salts, $[(81)Li]^+Cl^-$, $[(81)Na]^+CH_3SO_4^-$, $[(87)Li]^+FeCl_4^-$ and $[(88)Li]^+Cl^-$. In a separate communication;[160] they have published thermodynamic and kinetic parameters for the complexation of M^+ (M = Li-K) by (81), (87) and (88) in $CDCl_3$. Kollman et al[161] have complemented the experimental results with a theoretical study of the complexation of M^+ (M = Li-K) by similar anisole spherands (85,86). The complexants (81-84), which are constructed such that the orbitals of the unshared electron pairs of their oxygen atoms line an enforced cavity, strongly complex Li^+ and Na^+ but reject K^+, Ca^{2+} and Mg^{2+}.[159] Molecular mechanical calculations for the analogous complexants (85,86) and their complexes with M^+ (M = Li-K) confirm the high selectivity of (85) for Li^+ and Na^+ compared with that for K^+.[161] The difference between the energies of complexation of Na^+ and K^+ is dramatically larger with (85) - 172kJ.mol^{-1} - than with 18C6 - 33kJ.mol^{-1} - clearly showing why (85) has no tendency to bind K^+.[161]

Structural data for $[(81)Li]^+Cl^-$ and $[(81)Na]^+CH_3SO_4^-$ indicate that conformational reorganisation of the host does not occur on





(81); $R^1 = R^2 = R^5 =$ Me; $R^3 = R^4 =$ OMe
(82); $R^1 = R^3 =$ H; $R^2 = R^5 =$ Me; $R^4 =$ OMe
(83); $R^1 = R^2 = R^3 = R^4 =$ H; $R^5 =$ Me
(84); $R^1 = R^2 = R^5 =$ Me; $R^3 =$ OH; $R^4 =$ OMe
(85); $R^1 = R^2 = R^3 = R^4 = R^5 =$ OMe
(86); $R^1 = R^2 = R^3 = R^5 =$ H; $R^4 =$ OMe

(87); R =

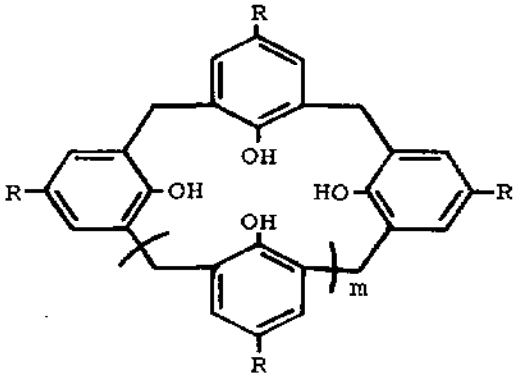

(88); R =


complexation.[159] The crystal structures of $[(87)Li]^+[FeCl_4]^-$ and $[(88)Li]^+Cl^-$ show the polycyclic hosts to be highly strained and to contain severe oxygen-oxygen compression.[159]

The thermodynamic and kinetic data obtained for complexation of Li^+ and Na^+ (as the picrates) in $CDCl_3$ by the spherands (81), (87) and (88) are compared with those for corresponding crowns, cryptands, hemispherands and acyclic polyethers.[160] When host-guest relationships are most complementary in any given host class the order for binding Li^+ and Na^+ (as the picrates) in $CDCl_3$ saturated with D_2O at 298K is:[160]

spherands > cryptands > hemispherands > crowns > acyclic polyethers

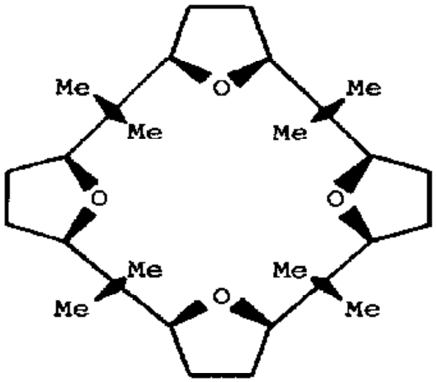
Cation transport from multiple alkali metal cation mixtures (MOH; M = Na-Cs) across a H_2O-organic solvent-H_2O bulk liquid membrane system using the series of p-alkylcalix[n]arenes (89) as carriers was coupled, in each case with a reverse flux of protons.[162] Although greatest selectivity for Cs^+ was found for the calix[4]arenes, the largest Cs^+ (as well as Na^+-Rb^+) flux was observed with the calix[6]arenes and calix[8]arenes, possibly owing to each calix[n]arene binding two cations. Decreasing the Cs:Rb ratio in the source phase results in decreasing selectivity for Cs^+ indicating the cation flux depends in part on the relative concentrations of the ions in the source phase.[162]



R = t-C_4H_9- or t-C_5H_{11}-

m = 1,3,5 (ie. n = 4,6,8)

(89)



(90)

The crystal and molecular structures of the lithium picrate complex of the 16C4-type tetramer of 2-isopropylidene(thf) (90) have been determined using single crystal XRD methods.[163] The Li atom is located close to the plane of the four heteroatoms of the macrocyclic ring, its five-fold coordination sphere being completed by the phenolic oxygen atom of the picrate anion; geometrical parameters are only available in miniprint form.[163]

1.4.5 Cryptates and Related Complexes

The majority of the papers abstracted for this subsection report structural data for diverse complexes;[164-170] the others describe some aspect of their solution chemistry.[171-173] ^{13}C- and ^{23}Na-

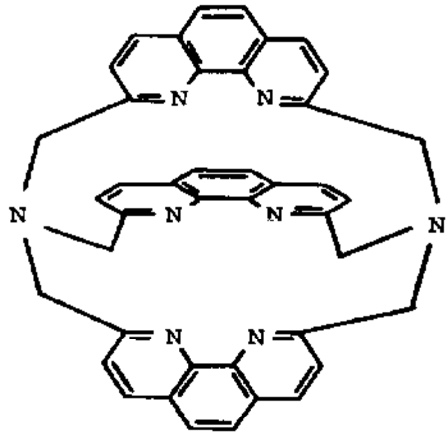
n.m.r. studies[171] of cation exchange between solvated and $[C211M]^+$ environments in water, dmso and dmf indicate that whereas $[C211Na]^+$ exists predominantly in the exclusive form (i.e., the cation is located in the centre of one of the poly(oxadiazacycloalkane) rings of the cryptand), $[C211Li]^+$ exists predominantly in the inclusive form (i.e., the cation resides in the centre of the cryptand's cavity). The data are discussed in terms of two sequential equilibria:

$$M^+ + C211 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{exclusive}}{[C211M]^+} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\text{inclusive}}{[C211M]^+} \qquad \ldots(16)$$

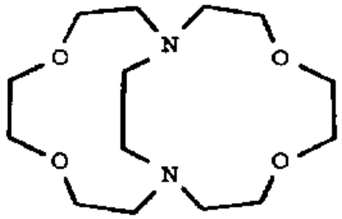
Dissociation rate constants and related thermodynamic parameters were calculated for $[C211Na]^+$.[171]

Danil de Namor et al have determined thermodynamic data for the complexation of M^+ (M = Li-Cs) by C222 in propylene carbonate and acetonitrile[172] and in nitromethane;[173] the results are compared with correspnding data in other dipolar aprotic solvents.

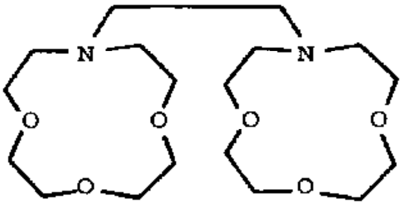
Single crystal XRD studies have been completed on C211,[164] C221[164,165] and C222[166] derivatives as well as on complexes of the cryptate analogues (91),[167] (92)[168,169] and (93).[170] In the cation of crystalline $[C211Mg(CH_2C(CH_3)_3)]^+[((CH_3)_3CCH_2)_3Mg]^-$, prepared by addition of C211 to dineopentyl magnesium,[164] C211



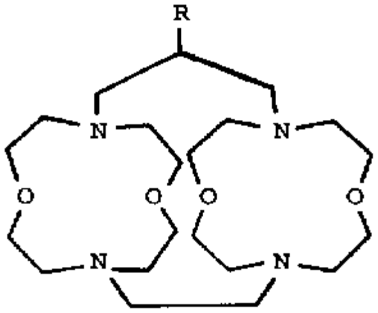
(91)



(92)



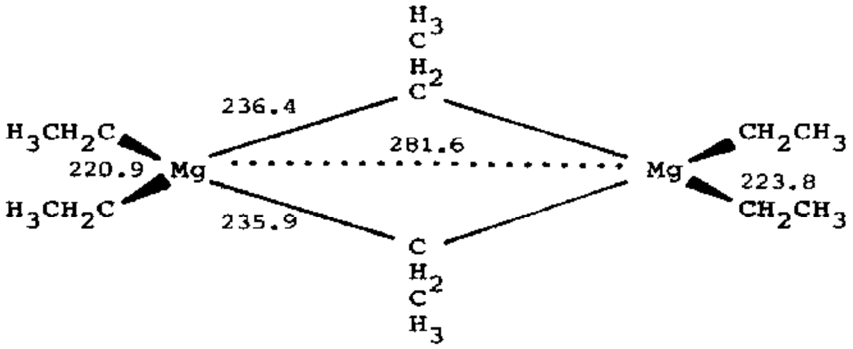
(93)



R = n-$C_{16}H_{33}$-
or $PhCH_2$-

(95)

uses all six heteroatoms to coordinate the Mg atom, the approximately pentagonal bipyramidal coordination geometry of which is completed by the neopentyl group carbon. In contrast, C221 in the cation of $[C221Mg(CH_2CH_3)]_2^+[(CH_3CH_2)_6Mg_2]^{2-}$, prepared by addition of C221 to diethylmagnesium,[164] only uses five of its seven heteroatoms to coordinate the Mg atom, the two oxygens of one of the cryptand bridges being considerably more remote; the six-fold coordination geometry of the Mg atom is completed by the ethyl group. In the anion of the neopentyl complex, the Mg atom is located in an essentially trigonal planar coordination sphere provided by the carbon atoms of three neopentyl groups [r(Mg...C) = 212.5, 224.0, 229.6pm, $\Sigma\theta$(CMgC) = 359.3°].[164] In the dianion of the ethyl complex (94), the two centrosymmetrically related Mg atoms, are surrounded by two bridging and two terminal ethyl



(94); distances/pm

groups in a pseudo-tetrahedral geometry.[164]

The molecular structure of $[C221Na]^+[W(CO)_5(O_2CH)]^-$ contains a C221 encapsulated Na^+ cation in which all seven heteroatoms of the cryptand coordinate the Na atom.[165] These interactions [r(Na...O) = 251.2-269.3pm; r(Na...N) = 274.2, 274.4pm] are, however, somewhat longer than those reported for isolated $[C221Na]^+$ cations owing to a novel strong contact ion pairing between the Na^+ cation and the formate's distal oxygen (238.8pm) which completes the cations eight-fold coordination geometry. Although the ion pairing persists for uncomplexed Na^+ ions in thf, the cryptand encapsulated species exists as a solvent separated or free ion pair in solution; similar solution behaviour is observed for $[C221Na]^+[W(CO)_5(O_2CCH_3)]^-$.[165] The geometry of the cation in $[C222Na]_2^+Te_4^{2-}$ is normal for C222 encapsulated Na^+ ions, with Na...O and Na...N distances in the range 245-306pm; there is no direct contact between anion and cation.[166]

The macrobicyclic ligand (91) which incorporates three 1,10-phenanthroline groups linked by nitrogen atoms acts in a similar manner to C222 readily enclosing alkali metal cations in its bicyclic cavity.[167] In the structure of $[(91)Na]^+Br^-,2CHCl_3$, the cation has a propeller-shaped geometry of approximately 3-fold symmetry in which the $N...Na^+...N$ linear bonds represent the shaft (277.4,280.5pm) and each planar phenanthroline group a blade of the propeller (267.7-273.1pm).[167]

Groth has followed his preliminary communication[174] on the structural characterisation of the complexes of (92) with MSCN (M = Li-K), first considered in the 1984 review,[175] with a more detailed description of the three structures.[168,169] In $[(92)Li^+]SCN^-,\frac{1}{2}H_2O$,[168] the Li atom is completely enclosed by the bicyclic ligand, being coordinated by all six heteroatoms. The rather large coordination number for Li is reflected by somewhat long bond distances [r(Li...N) = 220.5,221.0pm; r(Li...O) = 215.1-225.5pm]. There is no direct contact between cation and anion.[168] The structures of $[(92)Na]^+SCN^-$ and $[(92)K]^+SCN^-$ are almost identical with seven-coordinate alkali metal cations.[169] The cleft between the rings is opened up compared to the lithium complex permitting interaction with the nitrogen of the anion. The coordination bonds to Na^+ and K^+ vary between 246-260pm and 273-293pm, respectively.[169]

Groth[170] has also determined the crystal and molecular structure of [(93)K]$^+$SCN$^-$,1.5H_2O. It contains two crystallographically independent K atoms; they are both located in the cavity formed by the two monoazacrown units and are coordinated to the eight heteroatoms of the ligand with average K...O and K...N distances of 275.2 and 287.5pm, respectively.[170]

Lipophilic cage compounds containing two diazacrown units (95) have been shown to form extremely stable complexes with sodium salts;[176] they permit effective activation of hydrophilic and/or highly electronegative atoms in non-polar media.

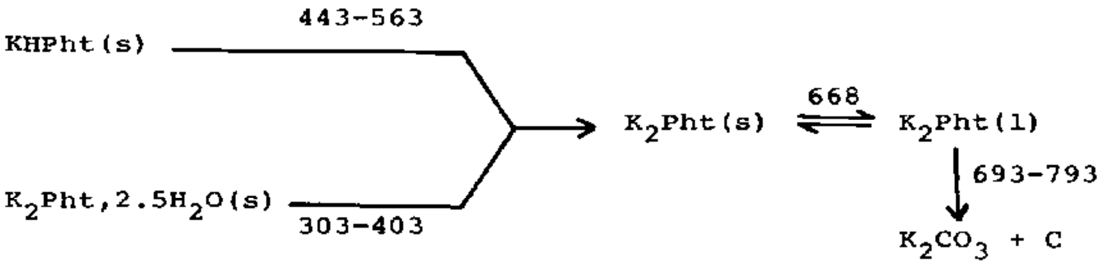
1.4.6 Salts of Carboxylic, Thiocarboxylic and Dithiocarbamic Acids

In a departure from the format adopted for earlier reviews, this subsection has been extended to include a discussion of the published results of the innovative research programme, coordinated by Gattow, on the chemistry of alkali and alkaline earth metal salts of dithiocarbamic acids. Again in contrast to earlier reviews, there is a paucity of abstracted papers describing alkali metal carboxylates and thiocarboxylates; although the reason for this reduction in activity is not clear, the biggest decrease has occured in structurally based papers.

The chemistry of metal formates, including alkali (Li-Cs) and alkaline earth metal (Mg-Ba) derivatives in aqueous and non-aqueous systems has been reviewed.[177] Crystallisation in the LiHCOO-KHCOO-H_2O system ($298 < T/K < 546$) has also been studied; at 298K, the hemihydrate, $KLi(HCOO)_2,0.5H_2O$, is produced but at 323K, the anhydrous formate, $KLi(HCOO)_2$, is obtained.[177]

Alkali metal (Li-K) and calcium complexes of monocarboxylate A^- (acetate, salicylate), dicarboxylate A^{2-} (malonate, maleate, succinate, malate, tartrate, phthalate, oxydiacetate) or amino acid HA (glycine, L-histidine) ligands have been studied potentiometrically.[178] The monocarboxylate ligands form [MA] and the dicarboxylate ligands [MA] and [M(HA)] species (charges omitted) with M^+ (M = Li-K) and Ca^{2+}. Glycine and L-histidine form $[MA]^+$ and $[M(HA)]^{2+}$ (and $[M(H_2A)]^{3+}$ for L-histidine) complexes with Ca^{2+}, whilst M^+ (M = Li-K) form only $[M(HA)]^+$ complexes with glycine.[178] Potentiometric studies of complex formation between M^+ (M = Li-Cs) and M^{2+} (M = Mg-Ba) and acetate ligands have yielded accurate thermodynamic parameters for several ionic strengths ($0.04 \leq I/mol.dm^{-3} \leq 1.00$) and at several temperatures ($283 \leq T/K \leq 318$).[179]

The thermal decomposition of anhydrous potassium hydrogen phthalate (KHPht) and of hydrated dipotassium phthalate ($K_2Pht,2.5H_2O$) has been shown to proceed via anhydrous dipotassium phthalate (K_2Pht) to potassium carbonate and carbon (Scheme 9).[180] In an oxidising atmosphere the organic decomposition products are oxidised with exothermic effects but



Scheme 9 ; T/K

in an inert atmosphere they undergo thermal decomposition to give volatile hydrocarbons and carbon.[180]

Structural data have been reported for three alkali metal carboxylates: disodium meso-tartrate,[181] potassium hydrogen (+) tartrate,[182] and trisodium D-2-phosphoglycerate hexahydrate.[183] Diverse alkali metal coordination spheres are observed. The Na atom in the meso-tartrate[181] is irregularly coordinated to six oxygens from one bidentate (237.8,245.8pm) and four monodentate (233.8-252.6pm) tartrate anions. Those in the D-2-phosphoglycerate[183] are crystallographically independent: Na(1) is surrounded by three water molecules and two carboxyl oxygens (229.7-245.4pm) in the form of a somewhat distorted tetragonal pyramid; Na(2) is coordinated by two water molecules, one terminal phosphate oxygen, one hydroxyl oxygen and one carboxyl oxygen (228.9-250.5pm) with a sixth more remote phosphate ester oxygen (285.0pm); Na(3) is surrounded by six water molecules (233.5-249.8pm) forming a distorted octahedron. Finally, the K atom in the (+)-tartrate[182] is located in an eight-fold coordination site of deformed cubic geometry generated by eight oxygens from the tartrate anions ($r(K...O)_{av}$ = 286.7pm).

Gattow et al[184-192] have reported the synthesis of a wide range of alkali and alkaline earth metal salts of diverse thiocarbamic acids. They have been characterised by chemical and thermoanalytical methods as well as by u.v.-visible, i.r., ^{1}H- and ^{13}C-n.m.r. and mass spectroscopy; in two instances, the potassium salt of N-formyldithiocarbamic acid,[185] and the dipotassium salt of 1,2-hydrazine bis(dithioformic acid),[192] single crystal XRD structural studies have been undertaken.

A crude sample of the monosodium salt of N-formyldithiocarbamic acid, $Na[S_2C{\cdot}NH{\cdot}CO{\cdot}H],nH_2O$ has been prepared[184] by reaction of formamide with CS_2 in the presence of NaH. Conversion to the free acid was effected by addition of HCl. Pure samples of $Na[S_2C{\cdot}NH{\cdot}CO{\cdot}H],H_2O$, $M[S_2C{\cdot}NH{\cdot}CO{\cdot}H]$ (M = K-Cs) and $Ba[S_2C{\cdot}NH{\cdot}CO{\cdot}H]_2{\cdot}2H_2O$ were then obtained[184] by treatment of the free acid with a solution of either the alkoxide (NaOEt; KO^tPr; $Ba(OMe)_2$) in the appropriate alcohol or the hydroxide ($RbOH,2H_2O$; $CsOH,H_2O$) in methanol. The crystal structure of $K[S_2C{\cdot}NH{\cdot}CO{\cdot}H]$[185] contains four crystallographically independent K atoms each of which is surrounded by seven sulphurs and two oxygens in a highly distorted geometry. In essence two different binuclear K atom coordination polyhedra are formed with five terminal sulphurs, two bridging sulphurs and two bridging oxygens; pertinent interatomic distances within the coordination polyhedra are collected in Table 10.

Table 10. Interatomic distances/pm. within the coordination polyhedra of $K[S_2C{\cdot}NH{\cdot}CO{\cdot}H]$[185]

K(n)	r(K(n)...S(terminal))	r(K(n)...S(bridging))	r(K(n)...O(bridging))
K(1)	326.6-376.8	350.6,414.6	270.4,273.6
K(2)	327.1-392.4	342.1,387.2	276.2,280.5
K(3)	330.5-398.0	343.9,398.0	274.4,282.8
K(4)	324.7-363.3	354.9,429.3	272.5,272.7

The corresponding N-methyl-N-formyldithiocarbamates, $M[S_2C{\cdot}NMe{\cdot}CO{\cdot}H]$ (M = Na-Cs) have been synthesised[186] either by reaction of N-methylformamide dissolved in thf with CS_2 in the presence of NaH or KOH or by addition of M_2SO_4 (M = Rb,Cs) to a CO_2-free aqueous solution of the barium salt previously obtained[186] by treatment of N-methylformamide in dmf with CS_2 in the presence of $Ba(OH)_2$.

The N-thioformyldithiocarbamates $Na[S_2C{\cdot}NH{\cdot}CS{\cdot}H],0.5H_2O$, $M[S_2C{\cdot}NH{\cdot}CS{\cdot}H]$ (M = K–Cs) and $Ba[S_2C{\cdot}NH{\cdot}CS{\cdot}H],3MeOCH_2CH_2OH$ have been prepared[187] by the metathetic reaction of $Bu^n{}_4N[S_2C{\cdot}NH{\cdot}CS{\cdot}H]$ with $MBPh_4$ (M = Na–Cs) or $Ba(BPh_4)_2$; the sodium salt was isolated from acetone, the other alkali metal and barium salts from $CH_3COCH_2CH_2OH$. The corresponding N-methyl-N-thioformyldithiocarbamates, $M[S_2C{\cdot}NMe{\cdot}CS{\cdot}H]$ (M = K–Cs), have been obtained[188] by reaction of N-methylthioformamide with CS_2 in the presence of MOH (M = K–Cs).

The disodium and dipotassium salts of the S-methyl ester of N-dithiomethylenedithiocarbazic acid, $M_2[S_2C{:}N{\cdot}NH{\cdot}CS{\cdot}SCH_3]$ (M = Na, K) have been synthesised[189] by reaction of dithiocarbazic acid with CS_2 in the presence of MH.

Treatment of hydrazine with CS_2 in the presence of MOH (M = Na, K) has yielded the trisodium salt of 1,2-hydrazine-bis(dithioformic acid), $Na_3[S_2C{\cdot}NH{\cdot}N{:}CS_2],7H_2O$,[190] as well as the disodium and dipotassium salts, $M_2[S_2C{\cdot}NH{\cdot}NH{\cdot}CS_2]$ (M = Na,K).[191] Single crystal XRD studies[192] of the dipotassium salt have shown that the K atom is surrounded by seven sulphurs (317.6–345.3pm) in an irregular seven-coordinate environment.

Mereiter et al[193] have determined the crystal and molecular structure of sodium diethyldithiocarbamate trihydrate, $Na[S_2C{\cdot}N(C_2H_5)_2],3H_2O$ at 175 and 295K. These data, together with earlier structural data for $Na[S_2C{\cdot}N(CH_2)_4],2H_2O$ and $Na[S_2C{\cdot}N(CH_3)_2],2H_2O$ and Raman spectroscopic data for all three salts have been considered in an attempt to understand the hydrogen bonding in the three sodium dialkyldithiocarbamate hydrates. The Na atom in $Na[S_2C{\cdot}N(C_2H_5)_2],3H_2O$ is located in a distorted octahedral coordination polyhedron generated by one sulphur atom {305.1pm(295K)/303.3pm(175K)} and five water molecules {234.1–249.2pm(295K)/233.3–246.9pm(175K)}.[193]

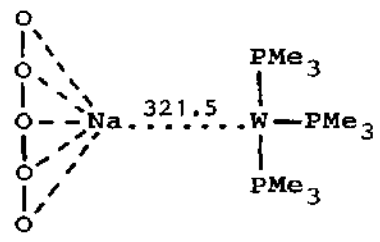
Gattow has also reported[194] the production of a series of alkali metal 1,2-ethanebis(trithiocarbonates), $M_2[S_2C{\cdot}S{\cdot}CH_2CH_2{\cdot}S{\cdot}CS_2]$ (M = Li–Cs), by reaction of the corresponding 1,2-ethanedithiolates with CS_2.

1.4.7 Heterobimetallic Complexes containing Alkali Metals

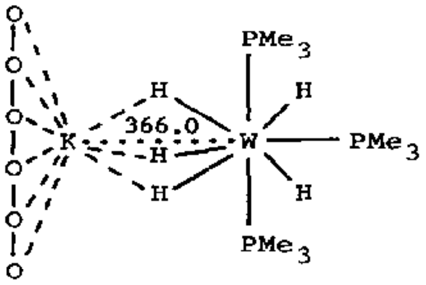
The synthesis of diverse heterobimetallic complexes has been reported during 1985; although the majority involve lithium as the alkali metal,[195-202] sodium[195] and potassium[195] derivatives have also been isolated. Their characterisation is generally based on structural identification by single crystal XRD methods;[195-201] the bridging ligands differ quite markedly ranging from H^-[195] through CH_3^-[196,197] and $C_6H_5^-$[198,199] to 2-$(Me_2NCH_2)C_6H_4^-$[200] and $Me_2PCH_2CH_2PH_2CH_2^-$.[201]

Treatment of $W(PMe_3)_3H_6$ with Bu^nLi, NaH or KH yields $W(PMe_3)_3H_5M$ (M = Li-K) or in the presence of the appropriate crown ethers, $[15C5Na]^+[W(PMe_3)_3H_5]^-$ (96) and $[18C6K]^+[W(PMe_3)_3H_5^-$ (97).[195] The crystal and molecular structures of (96), (97) and $[W(PMe_3)H_5Li]_4$ (98) have been determined;[195] they are shown schematically in Figure 7. Although that of (97) refined very satisfactorily (R = 2.33%) and it was possible to locate the hydrides, three of which bridge the K and W atoms, those of (96) and (98) did not refine as satisfactorily (R = 5.75% and 3.59%, respectively) owing to disorder, and the hydrides could not be located. Since the dispositions of the phosphine ligands around W in all three complexes relative to the alkali metals are similar, it is suggested that the hydrides of (96) may be located in similar positions to those of (97) and that some of the missing hydrides in (98) may bridge Li and W atoms. In both (96) and (97) the alkali metals are pulled out of the best planes defined by the heteroatoms (by 110pm for Na in (96); by 76pm for K in (97)) suggesting very strong interactions with the transition metal centres. Additional evidence for bridging hydrides in the

Figure 7. Schematic representations of the significant features of (96)-(103).

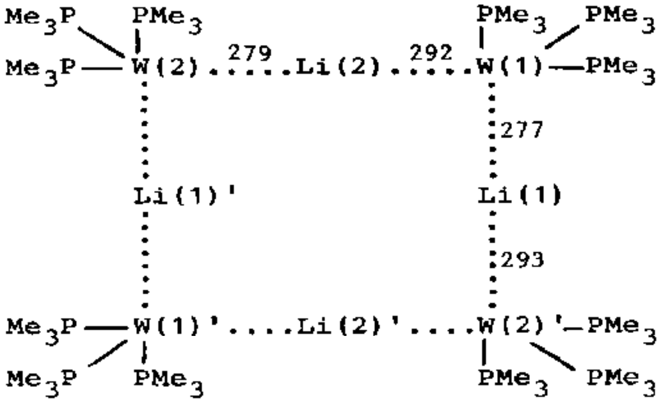


(96)



(97)

Figure 7 - continued



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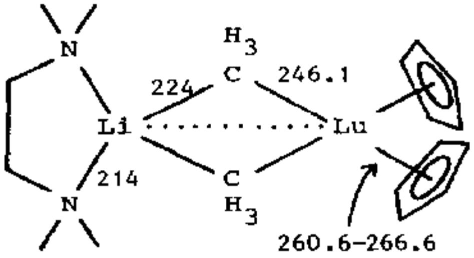

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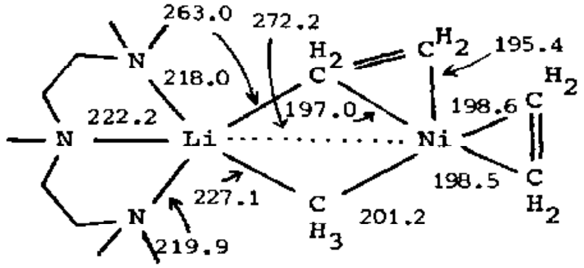

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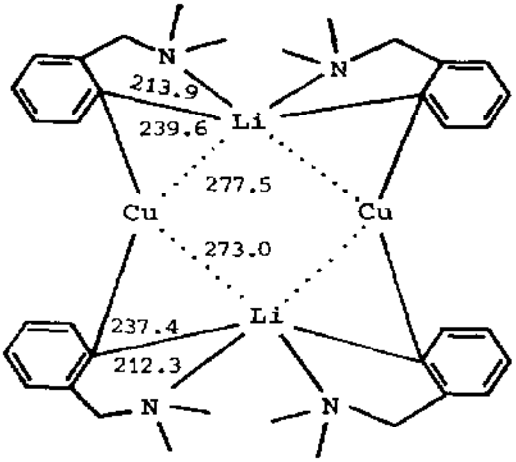

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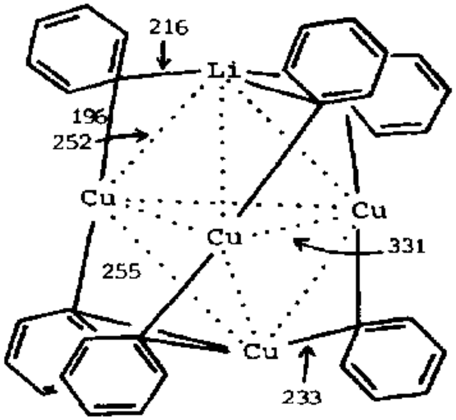
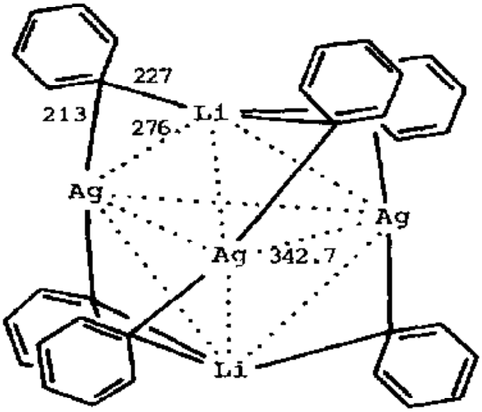




(102) Distances/pm. (103)

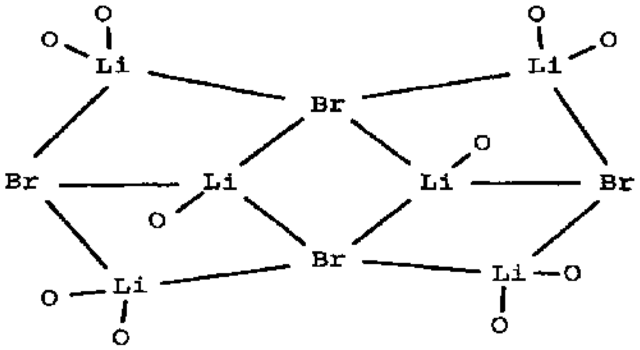
discrete centrosymmetric tetrameric Li_4W_4 ring of (98) is the alternating length of the Li-W vectors; it is suggested that hydrides bridge the shorter Li(1)...W(1) and Li(2)...W(2) contacts but not the longer Li(1)...W(2) and Li(2)...W(1) contacts ((98); Figure 7).[195]

The bismethyl bridged heterobimetallic $[(\eta^5\text{-}C_5H_5)_2Lu(\mu\text{-}CH_3)_2Li\text{-}(tmeda)]$ ((99); Figure 7) has been created by reaction of a 1:1:4 molar ratio of $LuCl_3$, NaC_5H_5 and $LiCH_3$ in ether containing tmeda.[196] Its structure has crystallographically imposed C_2-symmetry and consists of a $(\eta^5\text{-}C_5H_5)_2Lu$ moiety joined to a Li(tmeda) unit by two methyl bridges. The pseudo tetrahedral Li coordination sphere is thus composed of two carbon and two nitrogen atoms (Figure 7).[196]

Porschke et al[197] have prepared several members of the series of methyl bridged heterobimetallics $[(\pi\text{-ligand})_nNi(O)(\mu\text{-}CH_3)Li(n\text{-}donor)_m]$ where n-donor = tmeda, pmdta or thf and π-ligand = CO, C_2H_4 or cdt and have structurally characterised $[(\eta^2\text{-}C_2H_4)_2Ni(\mu\text{-}CH_3)Li(pmdta)]$ ((100); Figure 7). It consists of a $(\eta^2\text{-}C_2H_4)_2Ni$ moiety joined to a Li(pmdta) unit by a single methyl bridge. Thus the formal Li atom coordination geometry is distorted tetrahedral and is composed of one carbon and three nitrogen atoms. There is, however, also the possibility of weak bonding interactions between the Li atom and both the Ni atoms and an ethene carbon atom ((100);Figure 7). Porschke et al have also prepared and characterised three series of alkali metal (M = Li, Na) hydridotrialkylaluminates and gallates, $[M(n\text{-}donor)_m]^+[R_3Al\cdot H\cdot Ni(cdt)]^-$,[203] $[M(n\text{-}donor)_m]^+[R_3Al\cdot H\cdot Ni(\eta^2\text{-}C_2H_4)_2]^-$,[204] and $[M(n\text{-}donor)_m]^+[R_3Ga\cdot H\cdot Ni(\eta^2\text{-}C_2H_4)_2]^-$,[204] where n-donor = tmeda, pmdta or thf. For these complexes, in the absence of structural data, chemical and spectroscopic data suggest the presence of discrete cations in which the alkali metal is coordinated by solvent or amine molecules.[203,204]

The crystal and molecular structures of two Li-Cu clusters, $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2Cu_2Li_2]$[200] and $[Ph_6Cu_4Li]^-$[198] and of one Li-Ag cluster, $[Ph_6Ag_3Li_2]^-$[199] have been reported. In the centrosymmetric structure of $[\{2\text{-}(Me_2NCH_2)C_6H_4\}_2Cu_2Li_2]$((101); Figure 7)[200] each Li...Cu vector of the alternating Cu_2Li_2 planar ring is bridged by a $(2\text{-}Me_2NCH_2)C_6H_4$-ligand. The Li atoms are coordinated by two amine nitrogens and the two ipso-carbons of the benzene rings in a very distorted tetrahedral geometry; the Cu atoms are simply ligated by the two ipso-carbons of the benzene rings. The Li...Cu interatomic distance is too long for a strong bonding interaction ((101);Figure 7).

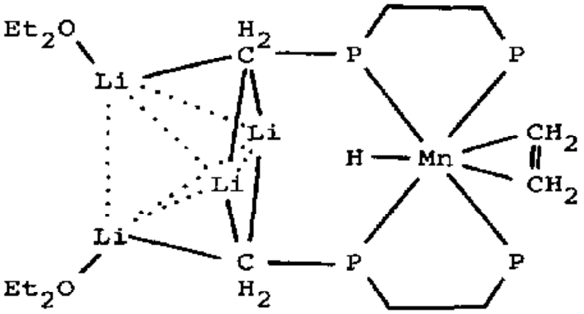
The $[Ph_6Cu_4Li]^-$ (102; Figure 7) and $[Ph_6Ag_3Li_2]^-$ (103; Figure 7) clusters, which were discovered in the structures of $[(Et_2O)_4Li]^+[Ph_6Cu_4Li]^-,2Et_2O$[198] and $[(Et_2O)_{10}Li_6Br_4]^{2+}$-$[Ph_6Ag_3Li_2]_2^-$[199] by Bau et al, have the same basic trigonal bipyramidal geometry, with the Li atoms occupying axial positions. The only crystallographic difference is the fact that $[Ph_6Cu_4Li]^-$, but not $[Ph_6Ag_3Li_2]^-$, is situated on a C_3 rotation axis. In both clusters, the six phenyl groups bridge the $M_{ax}...M_{eq}$ vectors in a perpendicular fashion, while the $M_{eq}...M_{eq}$ distances are non-bonding; this gives approximately trigonal and linear coordination polyhedra for the Li and Cu atoms, respectively (102,103; Figure 7). Although the structure of the $[(Et_2O)_4Li]^+$ cation in the copper complex[198] is unremarkable, that of the centrosymmetric $[(Et_2O)_{10}Li_6Br_4]^{2+}$ cation (104) in the silver complex[199] is worthy of comment. It consists of four edge-bridging Li atoms and two triply-bridging Li atoms surrounding a parallelogram made up of four Br atoms. Each edge-bridging Li atom is solvated by two ether molecules and each triply-bridging Li atom is solvated by a single ether molecule. Thus all six Li atoms are effectively located in distorted tetrahedral coordination sites.[199]



(104)

$r(Br...Br)_{av}$ = 388.4pm
$r(Li...Br)_{av}$ = 258 pm
$r(Li...Li)_{av}$ = 331 pm
$r(Li...O)_{av}$ = 194 pm

Interaction of [trans-MnH(η^2-C_2H_4)($Me_2PCH_2CH_2PMe_2$)$_2$] with tert-butyllithium leads to deprotonation of the chelating ligand and formation of a complex of stoichiometry $Li_4[MnH(\eta^2-C_2H_4)(CH_2(Me)PCH_2CH_2PMe_2)_2]_2,2Et_2O$ (105).[201] Its structure is based on a Li_4 tetrahedron which has a C_2 symmetry axis. Located abive each face of the tetrahedron is a CH_2 moiety which acts as a multicentre alkyl bridge (r(Li...C) = 220-236pm; r(Li...Li) = 246-269pm). Two of the Li atoms are also coordinated by ether molecules located along the C_3 symmetry axes of the tetrahedron (r(Li...O) = 205.3pm). The complex has overall 2-fold symmetry and the Mn(I) centre has pseudo octahedral geometry assuming the ethene molecule to occupy a single coordination site.[201]



(105)
[only one MnH(η^2-C_2H_4)($CH_2(Me)PCH_2CH_2PMe_2$)$_2$ moiety is shown]

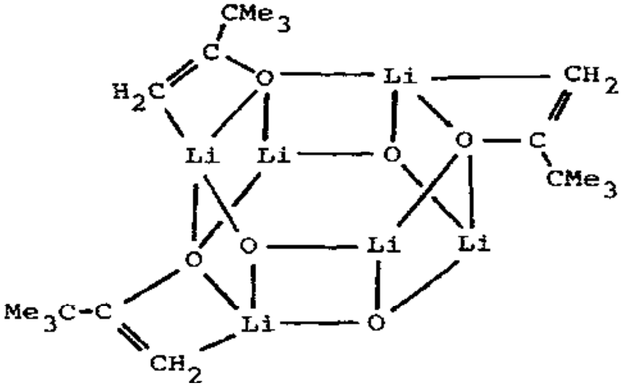
The first direct observation of resolved ^7Li-^1H coupling has been reported for the ligands in [(η^5-C_5Me_5)$IrH_2(SiMe_3)$Li(pmdta)] and [(η^5-C_5Me_5)IrH_3Li(pmdta)].[202] The complexes were synthesised by treatment of a mixture of [(η^5-C_5Me_5)IrH_3SiMe_3] or [(η^5-C_5Me_5)IrH_4] and pmdta with Bu^{t}Li in a minimum of hexane at 233K; the product was obtained in ~30% yield after 24 hours.[202]

1.4.8 Lithium Derivatives

As perceived for earlier reviews,[205] lithium chemistry continues to dominate this Chapter. The main thrust of activity can be subdivided into five broad subject areas: (i) theoretical analysis of small molecules, (ii) synthesis of novel heterobimetallic complexes, (iii) characterisation of oligomeric species, (iv) structural analysis of monomeric derivatives, and (v) organometallic chemistry. The first two topics are considered in subsections 1.3.2 and 1.4.7, respectively, while the next two are discussed in the present subsection; with the exception of novel structural data the last is not covered here since it is the subject of a separate annual review.

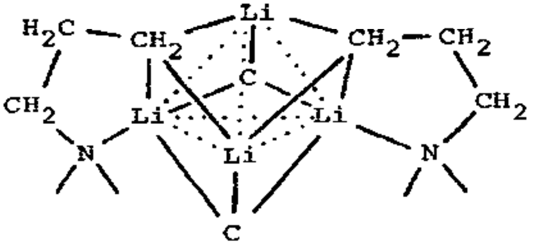
Lithium compounds have a tendency to oligomerise. The results of single crystal XRD studies have been published during 1985 for a single hexamer,[206] three tetramers,[207-209] and 11 dimers.[209-217] The structure of the unsolvated lithium enolate of tert-butyl methyl ketone (pinacolone) (106)[206] is based on an Li_6O_6 hexameric unit which is located at a crystallographic inversion centre and has approximate S_6 symmetry. Each Li atom is thus coordinated to three oxygens of separate enolate anions (eg. r(Li(2)...O) = 185.2-197.6pm). In contrast to the majority of structures of this type completion of the Li coordination polyhedron by a solvent molecule does not occur; instead the carbon atom of the methylene moiety is located such that a weak Li...C interaction occurs (eg. Li(2)...C(1) = 242.0pm).

Tetrameric Li_4C_4 and Li_4O_4 units are found in the structures of the lithium salt of 1-(dimethylamino)propane (107),[207] and of the lithium enolates of 2{(dimethylamino)methyl}acetophenone (108)[208] and methyl-3,3-dimethylbutanoate, thf solvate (109),[209] respectively. In (107)[207] the Li_4C_4 unit, which is very similar to that of ethyllithium, is located at a C_2 symmetry site. Each of the Li atoms is thus coordinated by three carbons of separate anions (r(Li(1)...C) = 225.2-228.3, r(Li(2)...C) = 225.5-227.9pm). Its distorted tetrahedral coordination sphere is completed by an intramolecularly bonded nitrogen of the dimethylamino moiety (r(Li(1)...N) = 207.1, r(Li(2)...N) = 206.5pm).[207] In (108),[208] the Li_4O_4 unit has $\bar{4}$ symmetry. The four crystallographically identical Li atoms are each surrounded by three oxygens (192.0, 196.0, 201.8pm) of separate enolate anions and an intramolecularly bonded nitrogen (211.6pm) of the dimethylamino moiety which is located on the C_3 axis of the Li_4 tetrahedron.[208] Clearly incorporation of a Lewis base into the enolate anion results in an oligomeric change from Li_6O_6 (for (106)) to Li_4O_4 (for (108)) and replacement of the weak Li...C(methylene) bond (in (106)) by the much stronger Li...N(dimethylamino) bond (in (108)). In (109),[209] the Li_4O_4 unit has no crystallographic symmetry;



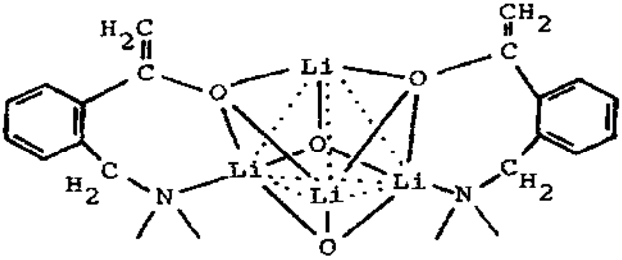
Three pinacolone enolate anions are omitted for clarity.

(106)



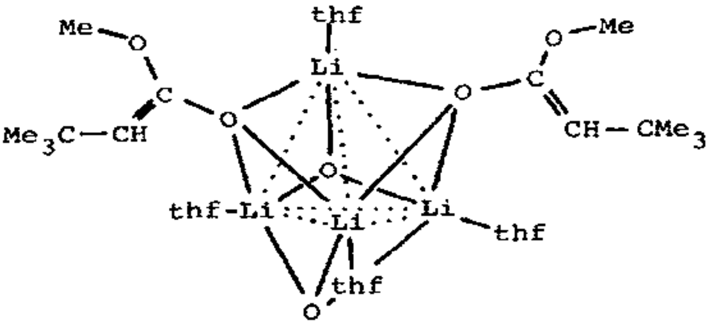
Two 1-(dimethylamino)propyl anions are omitted for clarity.

(107)



Two 2-[(dimethylamino)methyl]-acetophenone enolate anions are omitted for clarity.

(108)



Two methyl-3,3-dimethylbutanoate anions are omitted for clarity.

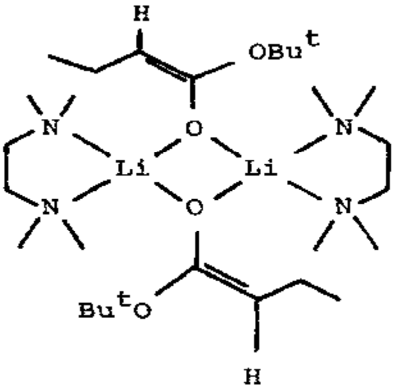
(109)

nonetheless, the twelve Li...O distances cover the relatively small range from 190 to 204pm. The fourth Li atom coordination site is occupied by the oxygen atom of a thf molecule.

Introduction of the bidentate chelating molecule tmeda into the structures of the lithium enolates of tert-butylpropionate, tmeda solvate (110)[209] and tert-butyl-2-methylpropionate tmeda solvate (111)[209] results in the formation of dimeric aggregates based on Li_2O_2 four-membered rings. In both structures, the Li_2O_2 unit has a crystallographic dyad axis and the tetrahedral coordination of the Li atom is achieved by bonding to the two nitrogens of the tmeda molecule; the Li...O distances in the two crystals vary from 190 to 195pm and the Li...N distances from 214.7 to 230.9pm.[209] A similar Li_2O_2 four-membered ring is found in the structure of the lithium enolate of 8-(dimethylamino)-8-heptafulvenolate, bis (thf) solvate (112).[210] It does not, however, have any symmetry, the four Li...O distances varying from 187.8 to 193.1pm. The tetrahedral coordination of each Li atom is completed by two thf molecules, for which the Li...O distances vary from 195.6 to 202.8pm.[210]

Although the structural core of $[Bu^t_2C{=}NLi,hmpa]_2$ (113)[211] is a centrosymmetric Li_2N_2 four-membered ring (192.3,194.8pm) comparable to the Li_2O_2 four-membered rings discussed above,[209-210] its Li atom coordination polyhedron differs markedly, being trigonal rather than tetrahedral. The third coordination site is filled by the oxygen of the hmpa molecule.[211] Molecular weight measurements show that in dilute benzene solution (~0.02M) (113) has an average degree of aggregation (n) of 1.12 suggesting a roughly 6:1 preponderance of monomer over dimer, but that on concentration (~0.04M) n increases to 1.33 which corresponds to a 2:1 ratio.[211]

Central Li_2S_2 four-membered rings have been found in the two dimeric lithium alkyl thiolates, $[\{(Me_3Si)_2CHS\}Li(thf)_2]_2$ (114)[212] and $[\{(Me_3Si)_3CS\}Li(thf)_{1.75}]_2$ (115).[212] Although the Li_2S_2 core in (114) is centrosymmetric (r(Li...S) = 243.9,245.0pm) that in (115) has no symmetry (r(Li...S) = 232.8-249.4pm). In both complexes, the Li atoms are four-coordinate with approximately tetrahedral geometry. In (114) one thf molecule is disordered; in (115) one thf is similarly disordered and a second loosely bound thf molecule, r(Li...O) = 246pm (cf. r(Li...O) = 191.8-196.1pm for the other thf molecules of (115) or = 193.5-211.6pm for the thf



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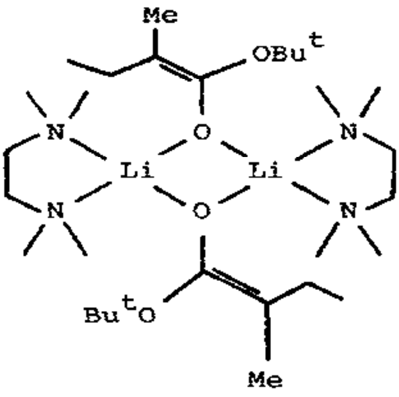

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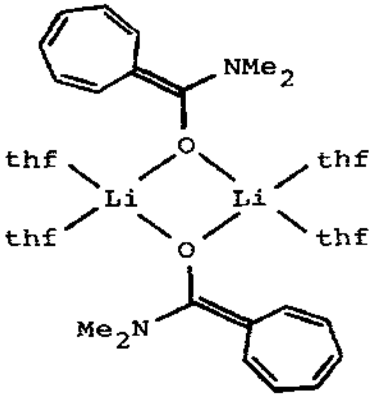

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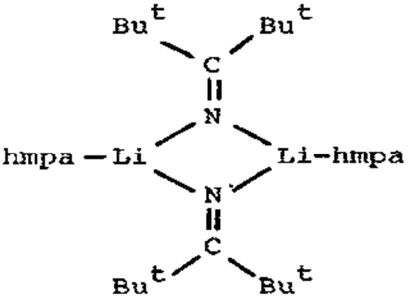

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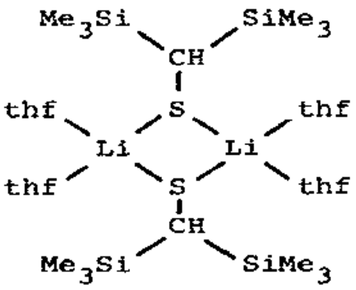

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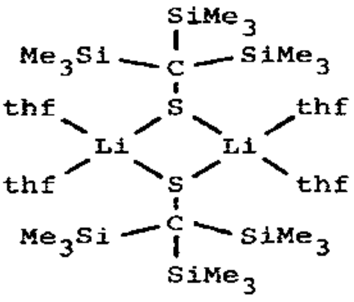
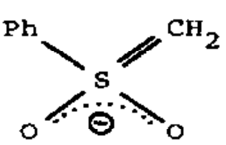


(115)

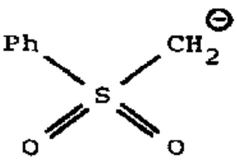
molecules of (114)), has only 50% occupancy.[212]

The crystal and molecular structures of five other dimeric species, $[CH_3{\cdot}C_6H_3N{\cdot}CH_2)Li(tmeda)]_2$ (116),[213] $[\{Ph{\cdot}(CH_2{:})SO_2\}Li(tmeda)]_2$ (117),[214] $[\{Ph{\cdot}(PhCH{:})SO_2\}Li(tmeda)]_2$ (118),[215] $[(Me_3Si)_3SiLi,1.5dme]_2$ (119),[216] and $[(Me_3C{\cdot}C{:}C{:}C{:}C{\cdot}CMe_3)Li_2(thf)]$ (120),[217] have been determined; not one of them contains a compact Li_2X_2 (X = non metal) central core. The centrosymmetric dimeric structure of (116)[213] contains two Li atoms each of which is surrounded by the two nitrogens (216.6, 230.7pm) of a chelating tmeda molecule, the α-carbon (235.1pm) of one pyridine molecule and the nitrogen (208.0pm) of the second pyridine molecule in a distorted tetrahedral configuration; this gives an eight-membered LiCCNLiCCN ring which adopts a stair like conformation. MNDO calculations for the corresponding ethylenediamine solvate confirm that this structure lies at a substantial energy minimum.[213]

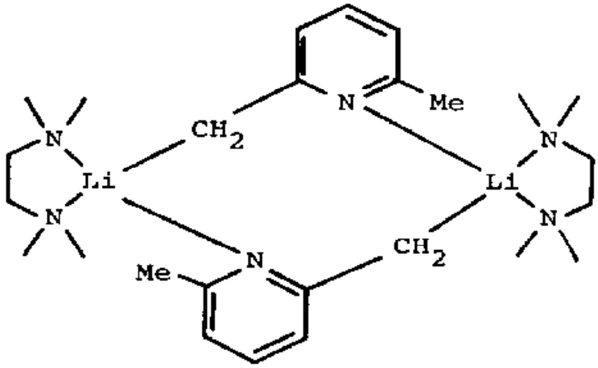
Two independent groups have described analogous dimeric structures for the (phenylsulphonyl)methyllithium-tmeda adduct (117)[214] and for the α-(phenylsulphonyl)benzyllithium-tmeda adduct (118).[215] The two Li atoms in each complex are coordinated by the two nitrogens ($r(Li...N)_{av}$ = 213.1 (117); 213.6pm (118)) of the chelating solvate molecule and two oxygens ($r(Li...O)_{av}$ = 188.6 (117); 189.0pm (118)) of different bridging sulphonyl carbanions in a distorted tetrahedral geometry; this gives an eight-membered LiOSOLiOSO ring for both complexes. The C...S interatomic distance (160.8 (117); 164.1pm (118)) in the carbanions[214,215] is appreciably shorter than that in sulphones (180.6pm) but similar to that in thioformaldehyde (161.08pm). This suggests the presence of a C=S double bond and the electronic configuration:



rather than



Low temperature (T = 153K) structural analysis of $[(Me_3Si)_3SiLi,1.5dme]_2$ (119),[216] synthesised from $(Me_3Si)_4Si$ and MeLi in dme, showed it to be composed of two $(Me_3Si)_3SiLi(dme)$ moieties centrosymmetrically connected by a bridging dme molecule.



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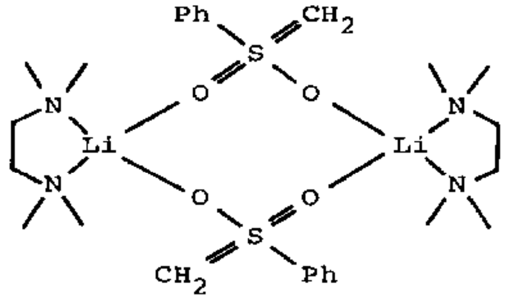

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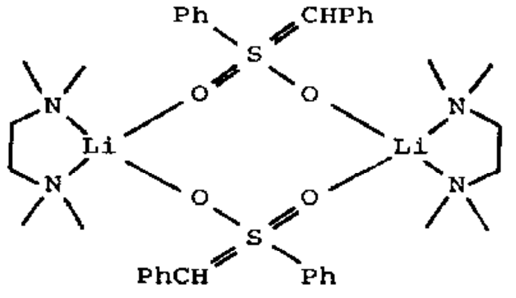

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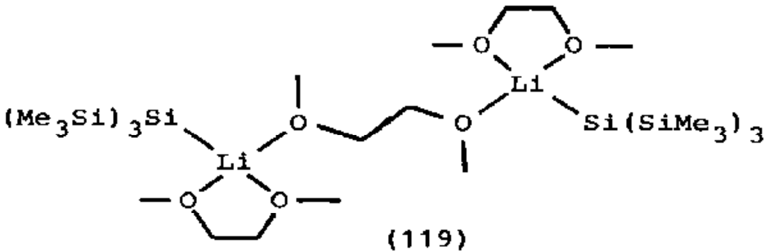

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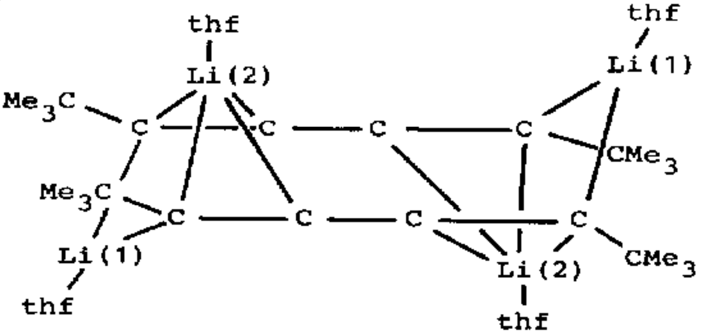
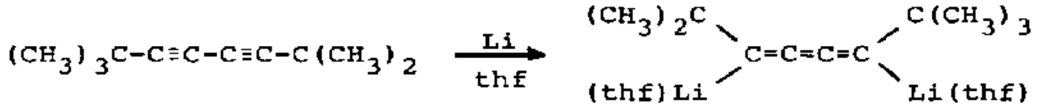


(120)

Each four-coordinate Li atom is surrounded by the two oxygens (199.3,200.3pm) of the chelating solvate molecule, one oxygen (200.3pm) of the bridging dme molecule and a silicon (263pm) in a distorted tetrahedral configuration.[216]

Addition of lithium metal to 2,2,7,7,-tetramethyl-3,5-octadiyne (121) in thf gave 3,6-dilithio-2,2,7,7-tetramethyl-3,4,5-octatriene as a crystalline bis(thf) adduct (120).[217] Structural analysis revealed (120) to have a dimeric cis-structure with two



$$(CH_3)_3C{-}C{\equiv}C{-}C{\equiv}C{-}C(CH_3)_2 \xrightarrow[\text{thf}]{\text{Li}} \underset{(\text{thf})Li}{\overset{(CH_3)_2C}{\diagdown}}C{=}C{=}C{=}C\underset{Li(\text{thf})}{\overset{C(CH_3)_3}{\diagup}} \quad \ldots(17)$$

different kinds of Li atom and a true butatriene geometry. Each Li(1) atom lies in a plane formed by and bridges the terminal carbons of the two butatriene moieties; its trigonal coordination sphere is completed by a thf oxygen. The two Li(2) atoms are located on either side of the plane formed by the two butatriene moieties each being coordinated to four separate carbons; their pseudo-square pyramidal coordination geometry is completed with a thf oxygen.[217] Model MNDO calculations (with and without solvation) agree remarkably well with experiment and help rationalise the choice of geometry.[217]

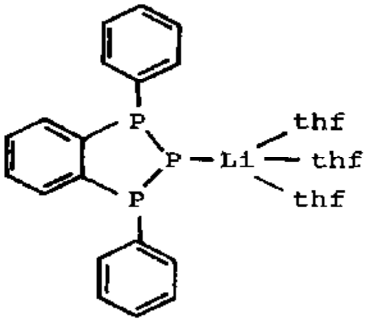
Multinuclear (^1H and ^7Li) n.m.r. studies of the aggregation and complexation of Bu^nLi in thf have yielded[218] the equilibrium parameters $\Delta H° = -(6.3\pm0.4)\,kJ\ mol^{-1}$ and $\Delta S° = -(58\pm2)\,J\ mol^{-1}K^{-1}$ for the tetramer-dimer equilibrium:

$$(Bu^nLi)_4,4thf + 4thf \rightleftharpoons 2\{(Bu^nLi)_2,4thf\} \qquad \ldots(18)$$

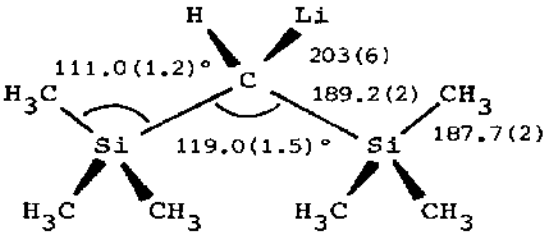
Quantitative line-shape analysis of temperature- and concentration -dependent ^{13}C-n.m.r. spectra of ^6Li- and ^{13}C-labelled Bu^nLi in thf have confirmed[219] that tetrameric and dimeric species are in dynamic equilibrium and have shown that exchange processes occur via this equilibrium. Similar data for $LiCHBr_2$ and $LiCH_2SC_6H_5$ indicate that these species exist in solution primarily as monomers and that exchange processes occur via a non-observed dimeric intermediate.[219]

Several monomeric lithium complexes have been structurally characterised. They fall into two categories: those with conventional σ-bonded ligands only and those containing η^n-bonded ligands. Of the former compounds, those examined in the solid state[220-222] by XRD methods exclusively contain four-coordinate (distorted tetrahedral) Li atoms, while that studied in the gas phase[223] by electron diffraction methods contains a singly coordinate Li atom.

Addition of pmdta to a suspension of PhLi in hexane/pentane mixtures affords the pmdta adduct of PhLi.[220] It is a monomeric organolithium, the Li atom being coordinated by an sp^2-hybridised carbon (214pm) of the phenyl group and the three nitrogens (213-215pm) of the tridentate chelating pmdta molecule.[220] Reaction of o-phenylenebis(lithium phosphide) with white phosphorus in thf yields the trisolvate of 2-lithio-2,3-dihydro-1,3-diphenyl-1H-benzotriphosphol (<u>122</u>).[221] The monomeric structure of (<u>122</u>) contains a Li atom coordinated by the central phosphorus (258.0pm) of the anion and the oxygens (190.7-195.9pm) of the three thf solvate molecules.[221] Treatment of MeOLi with ZnL_2,2MeOH (L = 1,3-bis(2-hydroxyphenyl-1,3-propanedione) in EtOH containing Et_4NCl yielded $Et_4N[LiL_2]$.[222] Structural analysis revealed a very simple monomeric anionic species in which the Li atom is surrounded by four oxygens (185-191pm) provided by two bidentate chelating propanedionate ligands. The bulky terminal groups of the β-diketone are thought to be essential to achieve monomeric Li complexation and isolation.[222]



(<u>122</u>)



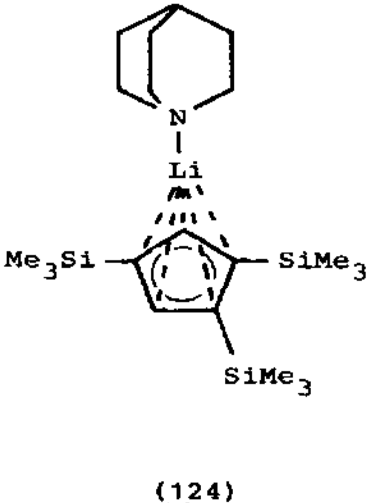
distances/pm

(<u>123</u>)

The electron diffraction data for $(Me_3Si)_2CHLi$ (<u>123</u>)[223] is consistent with a monomeric model; the presence of a small percentage of dimers or higher oligomers cannot, however, be excluded. Owing to the low scattering power of the Li atom and to the similarity of the Li...C and Si...C bond distances, the position of the Li atom could not be determined with high accuracy.[223]

Cyclopentadienyllithium is the classical example of a lithiated compound containing a η^n-bonded ligand. The i.r. and Raman spectra of crystalline C_5H_5M (M = Li-K) and the Raman spectra of thf solutions of C_5H_5M (M = Li,Na) have been obtained.[224] They are very similar to those of η^5-C_5H_5 complexes with predominantly ionic character of the metal-ligand bond; the polarity of this bond increases from solid state to solution environment.[224]

Structural confirmation of the presence of (η^5-C_5H_5)Li moieties in the 1:1 complexes of (η^5-1,2,4-$(Me_3Si)_3C_5H_2$)Li with quinuclidine and pmdta has been published.[225] The structure of [(η^5-1,2,4-$(Me_3Si)_3C_5H_2$)Li(CH$(CH_2CH_2)_3$N)] (<u>124</u>) contains two similar but crystallographically independent molecules in each unit cell. The two Li atoms are coordinated to the five carbons (r(Li(1)...C) = 213.7-217.1pm; r(Li(2)...C) = 215.1-222.2pm) of the cyclopentadienyl moiety and the single nitrogen (r(Li(1)...N) = 201.1pm; r(Li(2)...N) = 196.7pm) of the base.[225] Similarly, the structure of [(η^5-1,2,4-$(Me_3Si)_3C_5H_2$)Li(tmeda)] (<u>125</u>) contains two crystallographically distinct Li atoms. Their coordination



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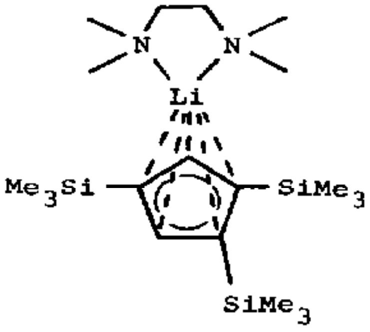
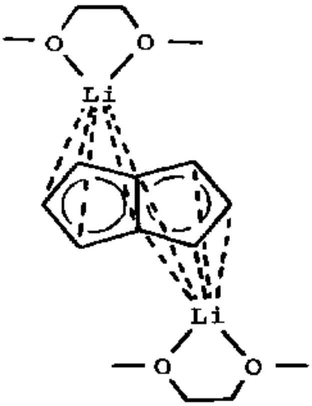


(<u>125</u>)

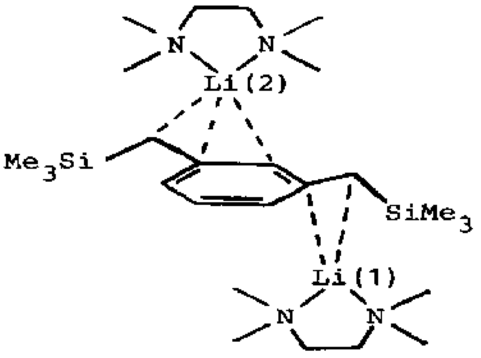


(<u>126</u>)

geometries are almost identical each atom interacting with the five carbons ($r(Li(1)...C) = 228.7-236.4pm$; $r(Li(2)...C) = 227.7-237.8pm$) of a cyclopentadienyl moiety and the two nitrogens ($r(Li(1)...N) = 211.6, 226.9pm$; $r(Li(2)...N) = 215.0, 220.6pm$) of a bidentate chelating tmeda molecule.[225]

(η^5-C_5H_5)Li coordination has also been observed in the structure of the bis(dme) adduct of dilithium pentalenide (126).[226] In agreement with the predictions of MNDO calculations, the Li atoms in (126) bridge opposite faces of the aromatic system, their seven-fold coordination polyhedra being completed by the two oxygens of the chelating dme molecule. The Li atoms are slightly closer to the peripheral carbons ($r(Li...C)_{av} = 222pm$) than to the bridgehead carbons ($r(Li...C)_{av} = 231pm$), the Li...O distance being typical at 201pm.[226]

η^2, η^3 and η^4-bonded ligands have been observed in the crystal structures of $[(1,3\text{-}(Me_3SiCH)_2C_6H_4)(Li(tmeda))_2]$ (127)[227] and the two polymorphs of $[(1,2\text{-}Ph_2C_8H_4)(Li(tmeda))_2]$ (128,129).[228] In (127),[227] there are two crystallographically distinct Li atoms.



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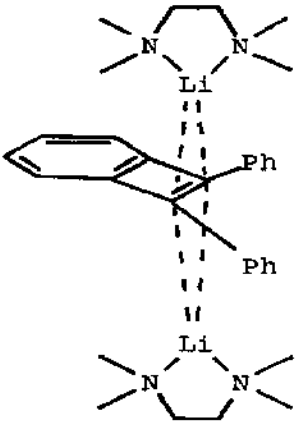
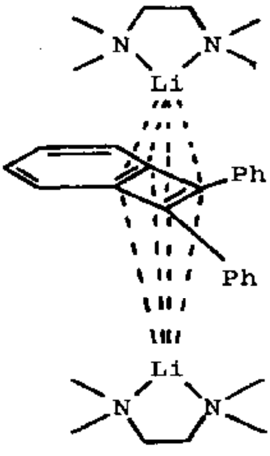
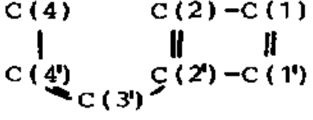


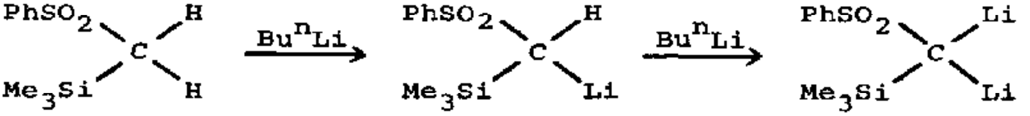




(128) (129)

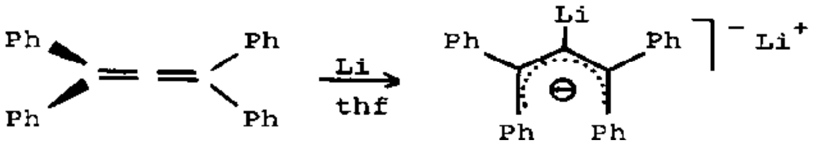
Li(1) is η^2-bonded to the hydrocarbyl moiety interacting through a carbon bearing a $SiMe_3$ group (214pm) and its adjacent aromatic carbon (230pm); Li(2) is η^3-bonded on the opposite side of the C_8 plane to the other carbon bearing a $SiMe_3$ group (214pm), and its nearest two aromatic carbons (226,244pm). The 4- and 5-fold coordination spheres of the two Li atoms are completed by the nitrogen atoms of the chelating tmeda molecules (r(Li(1)...N) = 201,208pm; r(Li(2)...N) = 206,208pm).[227] The two polymorphs of the bis(tmeda) solvate of dilithium 1,2-diphenylbenzocyclobutadienediide (128,129)[228] have pseudo C_2 symmetry the two Li atoms being found on opposite sides of the C_8 plane. In (128), the Li atom is η^2-bonded to two of the benzocyclobutadienediide carbons, the distances to C(1) and C(1') (214,220pm) being considerably shorter than those to C(2) and C(2') (266,269pm). In (129), the Li atom is η^4-bonded to four of the benzocyclobutadienediide carbons, the distances to C(1) and C(1') (223, 235pm) being similar to those to C(2) and C(2') (236,237pm). The 4- and 6-fold coordination polyhedra of the Li atoms in the two polymorphs are completed by the nitrogen atoms of the chelating tmeda molecule ($r(Li...N)_{av}$ = 204.4pm (in (128)), 194pm (in (129)).[228]

Five lithiated derivatives have been characterised using multinuclear (^{1}H-, ^{7}Li-, ^{13}C- and ^{29}Si-) n.m.r. techniques.[229-231] Low temperature data[229] for Ph_3SiLi, $Ph_2MeSiLi$ and $PhMe_2SiLi$ in dme, thf or 2-Methf indicate monomeric structures and at least a partial covalent contribution to the Li...Si bond. Dissociation of the Li...Si bond at higher temperatures or in more solvating media than the ethereal solvents used in this investigation cannot be excluded.[229] The novel dilithioalkylsulphone (131)[230] has been synthesised by stepwise lithiation of the trimethylsilylsulphone (130) with Bu^nLi:



(130) (131) ...(19)

Similarly, the novel tetraphenylpropenide (133)[231] has been prepared by reduction of tetraphenylallene (132) with highly active Li at low temperatures in thf:



(132) (133) ...(20)

The structure of (133), established by n.m.r. spectroscopic and chemical analysis, is that of an ionic allyllithium with C_{2v} symmetry, the second Li atom being covalently bonded to the central carbon atom.[231]

Two further papers describing diverse aspects of lithium (and heavier alkali metal) chemistry have been abstracted. Gattow and Schubert[232] have reported the preparation and characterisation of the alkali metal 1,2-ethanediothiolates, $M_2[SCH_2CH_2S]$ (M = Li-Cs). The Li salt was obtained by addition of a solution of Bu^nLi in hexane/thf mixtures to a solution of 1,2-ethanedithiol in thf; the Na and K salts were synthesised by dissolution of the alkali metal in ethanol followed by addition of a solution of 1,2-ethanedithiol in ethanol; the Rb and Cs salts were prepared by treatment of a suspension of the alkali metal in thf with a solution of 1,2-ethanedithiol in thf.[232] Bariyanga and Theophanides[233] have described complex formation between M^+ (M = Li,K) or M^{2+} (M = Mg,Ca,Ba) and guanosine in basic non-aqueous solution. Products of general formulae:

$M(guanosine)_n X_m, yH_2O, zC_2H_5OH$ (M = Li,Mg,Ca,Ba; n = 1,2,4;
X = Cl,Br,NO_3,ClO_4,OH; m = 1,2;
y = 0-6; z = 0-2).

$M(guanosine\text{-}H)(OH)_{n-1}, yH_2O$ (M = K,Ca,Ba; (guanosine-H) =
guanosine ionised at N_1, n = 1,2;
y = 1-3

have been characterised by their ^1H-n.m.r. and F.T.-i.r. spectra. In the non-ionised nucleoside complexes metal binding occurs through the guanine N(7) site and the anion is hydrogen bonded to the guanine N(1)H and NH_2 groups. In the ionised nucleoside complexes the metal binding is exclusively via the guanine O(6) site.

1.4.9 Sodium Derivatives

Of the six abstracted papers on sodium chemistry remaining after consideration of the specialised topics of current interest and significance, four[234-237] report the results of single crystal XRD structural studies; the others describe a soluble sodium reagent for the convenient synthesis of crystalline organosodium compounds[238] and the mechanism of sodium ion transport through solvated gramicidin, a transmembrane channel for alkali metal cations.[239]

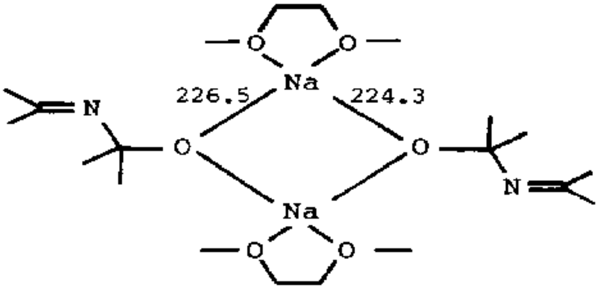
Schleyer et al[238] have shown that Bu^nNa, prepared via Bu^nLi and Bu^tONa by metal exchange and precipitation, is readily soluble in hexane after addition of solvating ligands such as tmeda or thf. The resulting solutions can be used (at low temperature) for homogeneous metallation of weak hydrocarbon acids; crystalline products suitable for X-ray analysis are often formed.[238]

Kim and Clementi,[239] in studying the energetics and hydration structures of solvated gramicidin, concluded that Na^+ moves along a helical path inside the channel while K^+ moves roughly linearly along the cylindrical axis of the channel. Both ions are thought to be capable of pushing a column of water through the channel owing to the small cross section of the latter.[239]

Nonasodium octa(p-toluenesulphonate)triiodide dihydrate (134),[234] sodium D-glucose-6-hydrogen phosphate(135),[235] trisodium fructose-1,6-diphosphate octahydrate (136)[236] and the bis(dme) adduct of sodium hexafluoropropanimine (137)[237] are the four sodium derivatives which have been structurally characterised. All nine Na atoms in (134)[234] are crystallographically distinct; when Na..O distances in the range 220-280pm are considered, coordination numbers of five (for Na(2), Na(4) and Na(6)), six (for Na(1), Na(3), Na(5), Na(7) and Na(9)) and seven (for Na(8)) are observed. Ligating oxygen atoms arise from monodentate and bidentate p-toluenesulphonate anions and water molecules; no Na...I interactions are found. Near regular coordination geometries arise when the ligating atoms come from different molecules; appreciable distortion occurs, however, when two oxygens are provided by a single anion.[234]

The two sugar derivatives were studied by Viswamitra et al.[235,236] In neither structure does a Na atom interact directly with any of the $\geqslant$P=O oxygens. That in (135)[235] is located in a monocapped trigonal prismatic coordination sphere provided by two phosphate hydroxyl oxygens (260,287pm), two phosphate ester oxygens (237,238pm) a ring oxygen (240pm) and two sugar hydroxyl oxygens (259,286pm). Two of those in (136)[236] - it contains a total of three crystallographically distinct Na atoms - are completely surrounded by water molecules (r(Na(1)...O) = 234.8-245.4pm; r(Na(2)...O) = 232.5-252.6pm) while the third, Na(3), interacts with one water molecule (232.2pm), one phosphate ester oxygen (261.2pm), a ring oxygen (245.2pm) and three sugar hydroxyl oxygens (237.9-244.9pm).

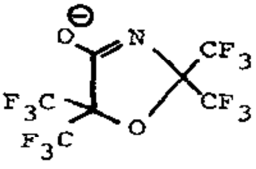
Structural analysis of (137),[237] prepared by reaction of NaSCN with hexafluoroacetone in a 1:2 molar ratio, has shown it to be based on a centrosymmetric Na_2O_2 ring, the oxygen being provided by the anion. The pseudo-tetrahedral Na coordination sphere is completed by the two oxygens of a chelating dme molecule.[237]



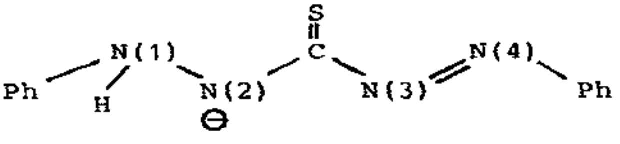
(137)

1.4.10 Potassium, Rubidium and Caesium Derivatives

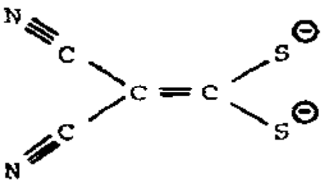
Although no papers describing the chemistry of rubidium or caesium compounds have been abstracted for this subsection, a limited number[237,240-243] almost exclusively reporting the results of single crystal XRD studies,[237,240-242] were found for potassium derivatives. A range of K atom coordination numbers, varying from 5 to 8 occur in the structures of the mono(dme) solvate of the monopotassium salt of tetrakis(trifluoromethyl)oxazolidine (138),[237] the monopotassium salt of 1,5-diphenyl-3-mercapto-formazanate (139),[240] the monohydrate of the dipotassium salt of 1,1-dicyanoethylene-2,2-dithiolate (140)[241] and in the dipotassium salt of 1,2-dithiole-3-thion-4,5-dithiolate (141).[242] The K atom in the (138) derivative is five-coordinate;[237] it is surrounded by two oxygens and one nitrogen of three separate anions and the two oxygen atoms of a chelating dme molecule. That in the (139) derivative is six-coordinate;[240] it is surrounded by three pairs of 'chelate'-type interactions originating in N(2) (279.3pm)/N(3) (305.2pm), N(4) (319.6pm)/S (315.0pm) and N(4) (330.5pm)/S (342.6 pm) combinations. The two K atoms in the (140) derivative are crystallographically related,[241] their seven-coordinate monocapped trigonal antiprismatic geometry is generated by three sulphurs (319.1-334.8pm), three nitrogens (291.7-312.4pm) and a single oxygen (272.7pm). The two K atoms in the (141) derivative are not only crystallographically related but are also located in a special position of the centrosymmetric Cmcm space group;[242] their eight coordinate distorted tetragonal antiprismatic geometry is formed by six relatively close exocyclic sulphurs (318.2-325.6pm) and two somewhat more remote cyclic sulphurs (374.8pm). This arrangement is consistent with the formal negative charge residing on the exocyclic sulphur atoms.[242]



(138)



(139)



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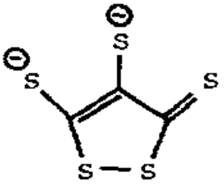
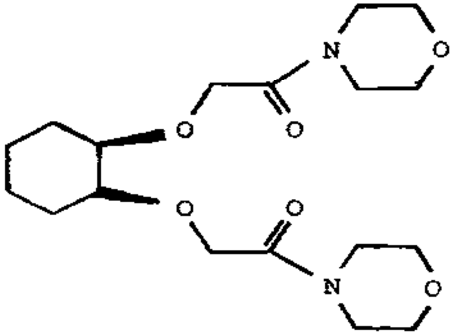


(141)

Finally, confirmation of the complexation of K$^+$ by cyclohexane-diacetamides (142) has been achieved using multinuclear (^{1}H and ^{13}C) n.m.r. spectroscopic methods;[243] thus far, such complexation has been observed neither by direct u.v. titration nor by picrate extraction methods.



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