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Chapter 1

ELEMENTS OF GROUP 1

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1.1 INTRODUCTION

The framework used in the 1978 Review[1] for reporting the chemistry of the elements of Groups I and II has also been adopted for the present review. Consequently, Chapters 1 and 2 are divided into sections covering topics, currently of interest and importance, in which the role of the metals is unique. For certain subjects (eg. cation solvation, molten salts, crown and cryptate complexes), the chemistry of the metals is closely interwoven; in these cases, the data abstracted are discussed once only in the relevant section of this Chapter.

The organometallic chemistry of lithium[2] and that of the heavier alkali metals (Na-Cs)[3] has been the subject of separate annual surveys for the year 1978; structural and spectroscopic studies, synthetic aspects and reaction chemistry are discussed in detail.

1.2 THE ELEMENTS

1.2.1 General Properties

The average cross sections for the $^{23}Na(n,p)^{23}Ne$ and $^{23}Na(n,\alpha)^{20}F$ reactions in a ^{235}U thermal fission reaction spectrum have been determined as 1.43 ± 0.02 mb and 0.53 ± 0.02 mb, respectively;[4] the data are based on $\bar{\sigma}_F = 0.705$ mb for the $^{27}Al(n,\alpha)^{24}Na$ monitor reaction.

The u.v. and visible spectra of Na_2, Na_3 and Na_4 clusters have been measured in inert gas (Kr or Xe) matrices;[5] analysis of the data has led to the electronic, geometrical and bonding properties of these clusters.

The structure factors of liquid sodium, potassium and caesium have been determined by X-ray and neutron diffraction methods.[6]

1.2.2 The Alkali Metals as Solvent Media

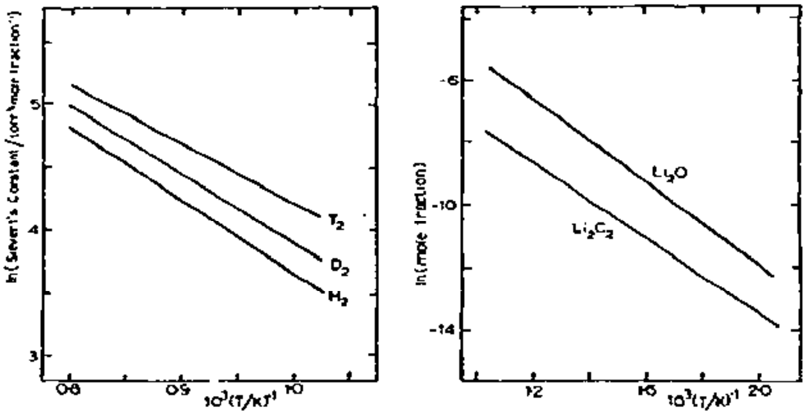
The role of liquid sodium as coolant in the fast breeder reactor, and that of liquid lithium as a candidate for use as coolant/tritium breeder in a deuterium-tritium-fuelled thermonuclear reactor, has maintained interest in the solution chemistry of these liquid metals. Phase relationships in liquid lithium-hydrogen isotope systems have been reported by three independent groups of authors;[7-10] in each case, the systems were studied by measuring hydrogen isotope partial pressures in equilibrium with Li-LiX (X=H, D or T) solutions. Veleckis[7] has shown that the monotectic temperatures of the liquid lithium-liquid LiX miscibility gap decrease from 967K (Li-LiH) through 963K (Li-LiD) to 961K (Li-LiT) and that for a given temperature the plateau pressures are in the order $p_{T_2} > p_{D_2} > p_{H_2}$. Smith et al.[8] have shown that the solubilities of the hydrogen isotopes in liquid lithium ($x_{LiX} < 0.1$) follow Sieverts Law (equation 1) where p_{X_2} is the equilibrium hydrogen

$$(p_{X_2})^{\frac{1}{2}} = K_s x_{LiX} \qquad \ldots (1)$$

isotope partial pressure above a solution of mole fraction, x_{LiX}, and K_s is the Sieverts constant. The temperature dependance of the individual solubilities can be expressed by equations (2) to (4). These data are summarised in Figure 1a. These authors[8]

Li-LiH ..... In $K_s = 9.842 - 6242/T$ $\quad 973 < T/K < 1273$ ... (2)
Li-LiD ..... In $K_s = 9.515 - 5644/T$ $\quad 973 < T/K < 1273$ ... (3)
Li-LiT ..... In $K_s = 9.226 - 5085/T$ $\quad 973 < T/K < 1273$ ... (4)

have also considered the mutual solubilities and isotopic exchange equilibria of H_2 and D_2 in lithium ($973<T/K<1173$). In the plateau region, the two isotopes could be treated as a single chemical species; in the dilute solution region, however, they dissolved independently of each other. Shpil'rain et al. have described a method[9] for calculating activity coefficients in these



(a) (b)

Figure 1. Solubility data for (a) LiX(X=H,D,T) in liquid lithium and (b) Li_2C_2 and Li_2O in liquid lithium.

systems under dilute solution conditions; they have applied it to hydrogen partial pressure data they have recently obtained[10] on the Li-LiH system using a hermetically sealed ampoule with a pressure sensing membrane.

The feasibility of the use of yttrium metal to extract tritium from liquid lithium at low concentrations has been considered;[11-13] on the basis of initial results and reasonable extrapolations it is concluded that yttrium can be used to extract tritium from lithium at concentrations as low as $x_{LiT}=10^{-6}$.

The solubilities of Li_2C_2[14] and of Li_2O[15] in liquid lithium have been measured at Argonne. The data are considerably lower than those previously reported and can be represented by equations (5) and (6), respectively; they are summarised in Figure 1b. Removal of Li_2C_2 and Li_2O from lithium to levels of 3 and 7 wppm respectively

$$\ln x_{Li_2C_2} = -1.440-5987/T \quad 455<T/K<1000 \qquad (5)$$

$$\ln x_{Li_2O} = 1.449-6668/T \quad 468<T/K<1007 \qquad (6)$$

(the solubilities at 473K) by cold trapping or filtration, an important aspect of compatibility problems of lithium in fusion reactors, should be feasible.

The solution chemistry of NaH in liquid sodium has been the subject of several papers.[16-21] A new technique,[16] which is said to be unique because of its applicability over a wide temperature range (423<T/K<973) has been developed to measure NaH levels in liquid sodium. It is based on an inert gas carrier method in which hydrogen is extracted from sodium into an inert gas through a thin nickel membrane; the hydrogen in the inert gas is determined by gas chromatography.

The interactions between NaH and Na_2O in liquid sodium have been considered in detail.[17-20] Ullmann et al.[17,18] have shown that the activities of both solutes decrease with increasing concentration of the reaction partner, thereby indicating formation of the hydroxide anion, OH^-. The free energy of the reaction (equation 7) was calculated to be $\Delta G^o(J\ mol^{-1}) = -(24{,}600 \pm 5{,}700) - (32 \pm 8.7)/T$,

$$O^{2-}(Na) + H^-(Na) \rightleftharpoons OH^-(Na) + 2e \qquad \ldots (7)$$

$623<T/K<773$.[17] In a complementary investigation, Maupre[19] has undertaken both a critical literature survey and an experimental study (using DTA, XRD and chemical analytical methods) of the sodium-rich corner of the Na-NaH-Na_2O-NaOH phase diagram. The results imply that the system is a reciprocal ternary system, the temperature of the stable pairs reversal (Na-NaOH at elevated temperature, NaH-Na_2O at low temperature) being 683K.

Maupre[19] has also shown that the Na-Na_2O-Na_2CO_3-C system is a reciprocal ternary system, the temperature of the stable pairs reversal (Na-Na_2CO_3 at elevated temperature, Na_2O-C at low temperature) being 963K.

The efficicacy of techniques for the removal of tritium,[21] iodine,[22] and caesium[23] from liquid sodium have been assessed. As in the case of lithium solutions, the most suitable getter for tritium in sodium was found to be yttrium.[21] The use of molten LiCl-NaCl-KCl to extract iodine from sodium has been shown to be feasible.[22] A cold trap, operating at 463K, containing reticulated vitreous carbon is effective in reducing fission product caesium activity in large sodium loop systems.[23].

The reactions of the oxides M_2O_3 (M=La,Pr,Nd,Gd) and Pr_6O_{11} with liquid lithium and of the oxides M_2O_3 (M=La,Pr,Nd,Sm,Gd,Tb,Dy) and Pr_6O_{11} with solutions of Li_3N in liquid lithium have been elucidated.[24] Whereas, La_2O_3 and Pr_2O_3 were stable to pure liquid lithium, Pr_6O_{11}, Nd_2O_3 and Gd_2O_3 reacted to form $LiMO_2$ (M=Pr,Nd,Gd). In the presence of Li_3N all oxides form the binary mononitride, MN.[24]

Reduction of Cu_2O and CuO by liquid potassium leads to copper metal with the formation of the oxides KCuO and K_4CuO_3, respectively.[25] Thermal analysis showed that Cu_2O reacts at 458K and that CuO reacts at 343K. The two ternary oxides were also observed as products of the solid state reactions of K_2O with Cu_2O and CuO.[25]

Reduction of UF_6 by both sodium and caesium metal has been studied.[26] Whereas with sodium β-Na_2UF_6 is formed, with caesium an unusual compound, which analyses as Cs_3UF_6 is formed. E.s.r. and u.v.-visible spectroscopic studies however, indicate the presence of U(IV) and free caesium in the lattice; the author thereby designates the compound $[Cs_2UF_6]Cs$.[26]

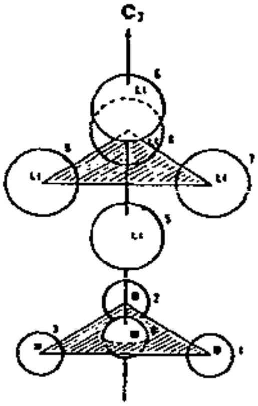
1.2.3 Metallic Solutions and Intermetallic Compounds

The structural properties of liquid Na-Cs solutions have been investigated using X-ray and neutron diffraction techniques.[27] The observation of appreciable concentration fluctuations is thought to be indicative of a tendency to phase separation in the liquid.[27] Neutron diffraction studies of liquid Na-K solutions have also been effected.[28] The presence of a negative excess volume in liquid Na-Rb and Na-Cs solutions has also been established.[29]

Thermodynamic data for Li-Mg,[30],Li-In,[31] Li-Tl,[31] Li-Sn,[32] Li-Pb,[33] Li-Bi[31] and Na-Ga[34] solutions have been evaluated using either calorimetric[30,31,33] or electrochemical[32,34] methods. The deviations from ideality observed in the lithium solutions were all attributed to the formation of associates in the solutions.[30-33] Furthermore, the results for the Na-Ga solutions are thought to be consistant with a pseudobinary alloy model based on partial compound formation in the solution; it is suggested that this compound may be Na_5Ga_8, the most stable compound in the solid state.[34]

Thermodynamic data available for ternary alkali metal solutions have been reviewed; special emphasis is put on the Na-K-Cs eutectic solution.[35]

X-ray and neutron powder diffraction data[36,37] show Li_5B_4, a totally metallic compound, to have a short range structure of rhombohedral (R3m) type with a=4.93Å and α=90° and a long range structure of b.c.c. ($I\bar{4}3m$) type with a=4.93Å. M.O. calculations[36]



(a)

Most stable energy states

State	Energy (eV)
D_{3h}. *four-boron cluster* (B–B = 1.32 Å)	
A_1'(2e)	−21.02
E' (4e)	−15.11
A_2''(2e)	−11.51
E' (4e)	−8.85
A_1'(—)	−8.68
D_{3h}. *five-lithium cluster* (Li–Li = 2.60 Å)	
A_2' (2e)	−8.69
A_2'' (2e)	−2.94
E' (1e)	+2.51

(b)

Figure 2. The atomic configuration (a) and the most stable energy states (b) of the four-boron and five-lithium clusters in the structure of Li_5B_4.

of the Li_5B_4 molecular unit (Figure 2a), based on the STO representation, have been undertaken; analysis of the most stable energy states calculated for the four-boron and five lithium clusters (Figure 2b) has shown that a partial electron transfer of ca. 0.35 e.u. from the E' energy level of the Li_5 cluster to the E' energy level of the B_4 cluster is necessary to stabilise the Li_5B_4 structure. The remaining 0.65 e.u. from the E' energy level of the Li_5 cluster are assumed to delocalise and to become 'free' electrons thereby giving rise to the metallic conducting properties.[36]

The crystal structures of Li_2In (orthorhombic, space group Cmcm, a=4.763, b=10.017, c=4.734Å) and of $Li_{13}In_3$ (cubic, space group Fd3m, a=13.556Å) have been determined.[38] Li_2In is isostructural with Li_2Ga whereas $Li_{13}In_3$ is an ordered variant of the body centred cubic package with isolated In atoms.

Phase relationships between Li_7Sn_2 and LiSn have been reinvestigated to determine the equilibrium conditions for the existence of $Li_{13}Sn_5$.[39] Three intermediate phases, $Li_{13}Sn_5$ (decomposes peritectically at 989K), Li_5Sn_2 (decomposes peritectically at 971K) and Li_7Sn_3 (decomposes peritectically at 781K) were found. X-ray diffraction studies of YLiSn (hexagonal, space group $P6_3mc$, a=9.296, c=7.346Å) have shown that lithium and tin atoms form a weakly distorted wurtzite type lattice, the yttrium atoms occupying the octahedral holes.[40]

The existence of the CsAu molecule has been established in a mass spectroscopic study of the vapour above the intermetallic compound.[41] The stability of CsAu ($D_{CsAu} \simeq 460 \pm 30$ kJ mol^{-1}) is determined mainly by an ionic bonding component, with caesium acting as donor and gold as acceptor.[41]

1.3 IONS AND ION PAIRS

Increasing interest in the spectroscopic and structural properties of ion pairs isolated in low temperature matrices has led to a change of emphasis in this section. Papers abstracted are no longer restricted to those in which cation solvation is described but also include those in which the chemistry of ion pairs both in solution and in low temperature matrices is discussed.

The invited papers presented at the symposium on 'Ions and Ion Pairs and their Role in Chemical Reactions' (Syracuse, N.Y., U.S.A., May-June 1978) have been published during the period of this Review.[42]

1.3.1 Cation Solvation in the Gas Phase

The elucidation of gas phase ion-molecule equilibria by sophisticated mass spectroscopic techniques has been reviewed;[43] the derivation of thermodynamic data for these clusters is emphasised and their relevance to general solution chemistry examined. Theoretical calculations of the electronic structure, equilibrium internuclear distances and dissociation energies of partially hydrated cations ($M(H_2O)^{n+}$, $M(H_2O)_x^{n+}$, $M(H_2O)(H_2O)^{n+}$, and $M(H_2O)_x(H_2O)^{n+}$, $M=Li^+$, Na^+, K^+, Be^{2+}, Mg^{2+}, Ca^{2+}) have been undertaken;[44] in particular, the influence of the cations on the hydrogen bonds between the water molecules has been assessed.

1.3.2 Cations and Ion Pairs in Solution

The application of alkali metal n.m.r. to the study of the immediate chemical environment of an alkali metal ion in solution has been reviewed,[45] the elucidation of ion-ion, ion-solvent and ion-ligand interactions is discussed.

Hydration of alkali metal cations in dilute aqueous solutions has been examined using neutron diffraction,[46] ultrasonic velocity and compressibility[47] and magnetic susceptibility[48] techniques. Analysis of the data from the neutron diffraction study of aqueous solutions of LiCl and of CsCl[46] indicated that (i) the coordination numbers for Li^+, Cs^+ and Cl^- are 4,8 and 6, respectively, (ii) the average ion...oxygen distances for Li^+ Cs^+ and Cl^- are 1.90 ± 0.05, 2.95 ± 0.10 and 3.10 ± 0.05Å, respectively and (iii) around the cations the water molecules adopt the configuration which permits orientation of one of the oxygen lone pair hybrids directly towards the cation.[46] The results of the ultrasonic studies of aqueous solutions of MCl (M=Li,Na,K,Rb,Cs) were interpreted by assuming that Li^+ ions act as structure makers, Rb^+ and Cs^+ ions act as structure breakers and Na^+ and K^+ ions interact but weakly with water molecules.

Hydration of M^+(M=Li,Na,K,Rb,Cs) in nitrobenzene, nitromethane and 2,2'-dichlorodiethylether has been studied[49] using $[(1,2\text{-}B_9C_2H_{11})_2\text{-}Co]^-$ anions as counterions for the extraction. For nitrobenzene, the organic phase hydration numbers decreased as follows: Li^+-6.5, Na^+-3.9, K^+-1.5, Rb^+-0.8, Cs^+-0.5. ^1H-n.m.r. data indicate that full dissociation of the salts occurs in the organic phase.[49]

Evidence for the existence of ion pairs in solutions of MI (M=Na,K,Rb,Cs) in n-alcohols,[50,51] MSCN and MNO_3 (M=Li,Na) in N,N'-dimethylacetamide,[52] $(COO)_2M_2$ in water[53] and CH_3COOLi[54] and

$CH_2ICOONa$[54,55] in water, methanol, and dioxane-water mixtures has been obtained. In a conductometric study of MI ion pairs in n-alcohols, Beronius[50,51] has shown that the structures of solvent separated ion-pairs (i) depend on the solvent[50] and (ii) influence their reactivities as nucleophilic reagents.[51] Ananthaswamy et al.[54] have concluded that in water, methanol and dioxane-water mixtures CH_3COOLi forms solvent separated ion pairs with an average size parameter of 6.69Å (the sum of the crystallographic radii is 1.87Å). In a similar experiment,[55] these authors have shown that the extent of participation of ion pairs in the reaction between $CH_2ICOONa$ and $Na_2S_2O_3$ in aqueous solution increases with ionic strength.

The formation of solvation complexes between the respective ion pairs and CH_3COOH molecules in solutions of, inter alia, LiCl, KCl, KBr in anhydrous acetic acid has been established;[56] comparison of the dipole moments of the solvation complexes with intrinsic dipole moments of the ion pairs yields structural information of the solvation complexes.

The effect of ethereal solvents on ion pairing and solvation phenomena of diphenylmethyl,[57,58] triphenylmethyl,[57,58] fluorenyl,[57] α-trimethylsilyl[57] and benzyl[57] alkali metal salts has been assessed using both variable temperature ^{13}C-n.m.r.[57] and u.v.-visible spectroscopy.[58] The data are interpreted assuming the formation of both contact and solvent separated ion pairs; there are, however, slight discrepancies in the detailed analyses of the two studies. The ion pair formation of some cyclic conjugated carbanions and nitranions has also been studied by absorption and fluorescence spectroscopy as a function of temperature, solvent and alkali metal ion.[59]

1.3.3 Ion Pairs in Low Temperature Matrices

Argon matrix isolation i.r. studies of KNO_3[60] and $NaPO_3$[61] ion pairs have been undertaken; with the air of ^{18}O enrichment, the two molecules are shown to have C_{2v} bidentate structures. The effect of hydration of $LiClO_4$ and $KClO_4$ ion pairs isolated in argon matrices has been followed using i.r. techniques;[62] the ClO_4^- ion is only very weakly distorted through interactions with water molecules, the complex retaining a bidentate structure.

The salt-molecule reaction technique has been used to synthesise MXF_2(X=Br,I),[63] MHIX(X=I,Cl,Br),[64] MHFX(X=F,Cl,Br,I)[65] and MFHCN[66] ion pairs in argon matrices (M^+_a is an alkali metal cation). I.r. spectroscopic studies indicate that whereas XF_2^-(X=Br,I), HF_2^- and HI_2^- have centrosymmetric $D_{\infty h}$ symmetry, HIX^-(X=Cl,Br) and HFX^- (X=Cl,Br,I) exist in a symmetric and an asymmetric form with the position of the M^+ ion determining which type of anion is formed. The MFHCN ion pair is the first example of a halogen cyanide anion to be isolated; attempts to synthesise other examples have been unsuccessful.

The interaction of CO with, inter alia, MF (M=Li,Na) and MF_2 (M=Mg,Ca,Sr,Ba) in argon matrices has been studied using i.r. spectroscopic techniques.[67] On formation of MF_n.CO complexes, the CO vibrational frequency is found to shift to higher values relative to free CO; within an isovalent group, the shifts are dependent on the metal's ionic radius.[67]

1.4 MOLTEN SALTS

Interest in the chemistry of molten salts has been maintained during the period of this Review; a surprising feature, however, is the proliferation in the number of molten salts studied.

1.4.1 Structural and Thermodynamic Properties

Analysis of the radial distribution functions derived from X-ray diffraction data has led to the structures of molten KCl (at 1173K)[68], K_2SO_4 (at 1423K)[69] and $2LiCl.MnCl_2$ (at 868K)[70] and $2KCl.MnCl_2$ (at 813K).[70] Comparison of the interionic distance in molten KCl[68] as derived experimentally (3.05Å) and by computer simulations with both rigid ion and shell models (2.95Å) shows remarkably good agreement. The coordination number at this interionic distance was evaluated as 4.1.[68] The most probable model for the short range order in molten K_2SO_4[69] is that of four nearest neighbour K^+ ions surrounding the SO_4^{2-} tetrahedron; one K^+ ion occupies a corner site, the other three occupy edge sites. The existence of a tetrahedral $MnCl_4^{2-}$ anion in molten $2MCl.MnCl_2$ (M=Li,K)[70,71] has been confirmed; it is surrounded by either 6 Li^+ or 5K^+ nearest neighbour cations. The presence of $MnCl_4^{2-}$ anions in NaCl-CsCl-$MnCl_2$ ternary melts has been invoked to interpret density[71] and electrical resistivity[72] measurements ($823<T/K<1323$).

Thermodynamic properties of MF-LnF_3 (M=Li,Na,K; Ln=Y,La,Yb; T=1360K)[73] and of MCl-YCl_3 (M=Li,Na,K,Rb,Cs; $998<T/K<1143$)[74] have been determined using thermochemical[73,74] and electrochemical[74] techniques. The results suggest that YF_6^{3-} and YbF_6^{3-} are important species in the mixtures of NaF and KF with YF_3 and YbF_3.[73] Similarly YCl_6^{3-} are thought to be important species in the mixtures of MCl (M=Na,K,Rb,Cs) with YCl_3; for the LiCl-YCl_3 system, however, the regular solution model fits quite well.[74] An analysis of the results of a potentiometric and vapour pressure study of the KCl-$AlCl_3$ system ($548<T/K<623$; $0.475<x_{KCl}<0.5$)[75] has shown that the acid-base properties of the solvent are best described by the equilibria (8) to (10)

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \quad \ldots (8)$$

$$3Al_2Cl_7^- \rightleftharpoons 2Al_3Cl_{10}^- + Cl^- \quad \ldots (9)$$

$$2Al_3Cl_{10}^- \rightleftharpoons 3Al_2Cl_6 + 2Cl^- \quad \ldots (10)$$

Raman studies of molten $SnCl_2$-$MAlCl_4$ (M=Li,Na,Cs; $0.0<x_{SnCl_2}<1.0$) gave no evidence for an interaction between $SnCl_2$ and $MAlCl_4$. Evidence for the dissociation of polymeric $SnCl_2$ into monomeric units by the $AlCl_4^-$ species was, however, obtained.[76]

1.4.2 Solution Properties

The solvent properties of a wide range of molten salts have been studied; although halides[77-81] and nitrates[82-89] predominate as reaction media, some data have been obtained for nitrites,[90] bisulphites,[91] and acetates.[92]

The anodic dissolution characteristics of Ni, Mo and 304 stainless steel have been examined in pure and Li_2S saturated LiCl-KCl eutectic melt;[77] it is found that the metals corrode more readily in the Li_2S saturated melt than in pure LiCl-KCl.

The reduction of $TiCl_4$ in various alkali metal chloride solutions (LiCl-CsCl, LiCl-KCl-$BaCl_2$, NaCl-$CaCl_2$-$BaCl_2$, LiCl-KCl-CsCl-$BaCl_2$) has been studied.[78] It is possible to stabilise certain oxidation states by complexation; the greater the ionic radius of the alkali metal cation, the more effective the complexation.

Electrooxidation of S in NaCl-$AlCl_3$ solutions has been found to be complex because of concentration and temperature effects;[79] it proceeds from S_8 to SCl_3^+ and involves S_8^+ $(S_{16})^{2+}$, S_8^{2+} and SCl^+ as intermediates. The chemistry of Mg(II) in basic KCl-$AlCl_3$

solutions has been shown to be based on the complex equilibrium (11); in acidic solutions, however, it is shown to exist as Mg^{2+}.[80]

$$MgCl_4^{2-} \rightleftharpoons MgCl_3^- + Cl^- \qquad \ldots (11)$$

The oxidation of PbS has been investigated in molten $KCl-PbCl_2$.[81] The reaction is complex occurring in two steps, the first of which is a reversible two electron transfer.

The kinetic stability of the NO_3^- ion in $LiNO_3$,[82] $NaNO_3$[83] and KNO_3[84] has been assessed by chronopotentiometric[82,83] and Raman[84] spectroscopic methods.

The electrode reaction mechanisms for several $M/MO/CO_3^{2-}/CO_2/O_2$ (M is a transition metal) electrodes in fused KNO_3(623K) have been elucidated.[85] Co,Ni,Pd, and Pt undergo oxidation (equation 12); Fe,Zn,Ag,Ta and Cu undergo reduction (equation 13) although a more

$$M + CO_3^{2-} \rightleftharpoons MO + CO_2 + 2e \qquad \ldots (12)$$

$$MO + CO_3^{2-} \rightleftharpoons M + CO_2 + O_2 + 2e \qquad \ldots (13)$$

complex oxide may be involved in some cases. The difference in behaviour is attributed to the different crystal field stabilisation energies of the carbonato-complexes formed by the metal ions; these complexes are thought to be the critical species in the electrode reaction.[85]

$Cu(NO_3)_2.3H_2O$ has been successfully dehydrated at 413K in $LiNO_3-KNO_3$ molten eutectic.[86] At higher temperatures (~573K) it acted as a Lux-Flood acid precipitating CuO (equation 14). With KI, it reacted at 413K to form CuI (equation 15) but at 453K a

$$Cu(NO_3)_2 \rightarrow CuO + 2NO_2 + \tfrac{1}{2}O_2 \qquad \ldots (14)$$

mixture of CuI and CuO was formed (equation 16). With powdered Ag,

$$Cu(NO_3)_2 + 2I^- \rightarrow CuI + 2NO_3^- + \tfrac{1}{2}I_2 \qquad \ldots (15)$$

$$Cu(NO_3)_2 + I^- \rightarrow CuO + NO_3^- + NO_2 + \tfrac{1}{2}I_2 \qquad \ldots (16)$$

a violent reaction (equation 17) occurred at 433K.[86]

$$Cu(NO_3)_2 + Ag \rightarrow CuO + AgNO_3 + NO_2 \qquad \ldots (17)$$

The conditions for the formation of $CdCl^+$ and $CdCl_2$ in molten KNO_3-$Ca(NO_3)_2$ solutions[87] and of AgI, AgI_2^- and Ag_2I^+ in molten KNO_3-$Ba(NO_3)_2$ solutions[88] have been delineated.

The solubility of Na_2CO_3 and K_2CO_3 in molten $NaNO_3/KNO_3$ eutectic ($523<T/K<613$) has been determined;[89] values of the Gibbs free energy, enthalpy and eutropy of solution have been calculated from the results.

Reactions of a number of lead compounds in molten $NaNO_2$-KNO_2 eutectic have been examined and the temperatures and stoichiometries of the reactions established.[90] The thermal decomposition of lead nitrate (equation 18) is the key reaction, this compound apparently

$$Pb(NO_2)_2 \rightarrow PbO + NO_2 + NO \qquad \ldots \text{(18)}$$

being formed from $Pb(NO_3)_2$ and $PbCl_2$ by anion exchange and from Pb_3O_4 on removal of Pb(II) cations. Pb(IV) as oxide or oxyanion oxidises nitrite to nitrate (equation 19), while PbO and metallic

$$PbO_2 + NO_2^- \rightarrow PbO + NO_3^- \qquad \ldots \text{(19)}$$

Pb are relatively unreactive at temperatures below 673K.[90]

The reactions of a number of metals with molten $NaHSO_4$-$KHSO_4$ eutectic have been studied at 473K.[91] Al, V and Au did not react with the melt; Na,Mg,Mn and Zn reacted to form H_2; Co,Ni,Cu,Ag, Sn,Hg and Pb produced SO_2 and H_2O; while Ti,Cr,Fe and Cd produced H_2, H_2O and SO_2. With the exception of Na, Cu, Ag and Zn, which dissolved completely in the melt, reactions were generally slow, owing to the formation of a protective coating on the metal surface.[91]

The CH_3COOLi-CH_3COONa-CH_3COOK molten salt eutectic has been shown to be sufficiently basic to ionise aromatic amine indicators of $pK_a = 15$;[92] typically, solutions of methyl p-hydroxybenzoate reacted to form methylacetate, methanol, phenol, anisole and CO_2.

1.5 SIMPLE COMPOUNDS OF THE ALKALI METALS

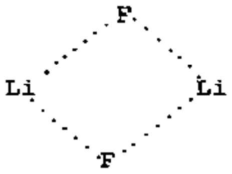
In this section, recent developments in the chemistry of the simple binary and ternary compounds of the alkali metals are discussed. There is a general paucity of information for the binary compounds, but a plethora of data for the ternary compounds. To avoid unnecessary duplication with other chapters of this review, the range of ternary compounds considered is restricted to those containing both an alkali metal and a transition metal.

1.5.1 Binary Compounds

Owing to the small number of papers abstracted for this section, the chemistry of the binary compounds will be considered as a whole rather than in a series of subsections as in the previous review.

Theoretical calculations have been undertaken for MH and MH^+ (M=Na,K).[93] A theoretical analysis of the reaction of excited Li atoms with H_2 has also been effected;[94] the geometry of the system was restricted to that with C_{2v} symmetry. The relative stabilities of the isomers MCN and MNC (M=Li,Na) have been assessed using ab initio calculations;[95] for both cations, the most stable configurations are computed to be the isocyanides, MNC.

Several papers[96-105] describing the physicochemical properties of molecular dimers, principally those of the alkali metal halides, have been published during the period of this review. Theoretical calculations of the molecular geometries and dimerisation energies of the dimers, Li_2F_2, Li_2H_2, Na_2H_2 (Be_2H_4, Li_4 and H_4) have been undertaken.[96] An electron diffraction study[97] of gaseous LiF at 1360K has given the internuclear distances r(Li...F)=1.746Å, r(F...F)=2.76Å and the mean amplitudes of the vibrations of pairs of nuclei l(Li...F)=0.102Å, l(F...F)=0.21Å, in the Li_2F_2 dimer.[97] It is concluded that the molecule (1) has D_{2h} symmetry.



(1)

UPS data for monomers and dimers of LiX(X=Cl,Br,I) have been recorded in the vapour phase using a molecular beam technique;[98] the spectra have been interpreted with the aid of ab initio SCF calculations.

The average molar mass (81.0±4.6) of the vapour above NaCl at 1273K has been determined by a transpiration method ($1153<T/K<1382$);[99,100] it is interpreted as corresponding to a dimer content of 38±8% in the vapour. The enthalpy of dimerisation of NaCl (equation 20) has been calculated to be $\Delta H_r^\circ(298K) = -(211.7\pm5.0)\,kJmol^{-1}$. This

$$2NaCl(g) \rightleftharpoons Na_2Cl_2\ (g) \qquad \ldots(20)$$

value is in fair agreement with that obtained by Schafer and Wagner (-200.8kJmol^{-1}) in a comprehensive mass spectroscopic-Knudsen cell study of gas phase complexes in the systems MCl-ScCl$_3$ (M=Li,[101] Na[102], K[103], Rb[104], Cs[105]). The thermochemical data derived from this study are collated in Table 1; it is interesting to note that the less stable dimers give rise to more stable complexes.[101-5]

Table 1. Thermochemical data (ΔH_r^o(298K)/kJ.mol^{-1} and ΔS_r^o(298K)/Jmol^{-1}deg^{-1}) for gas phase complexes in the systems MCl-ScCl$_3$ (M=Li,Na,K,Rb,Cs)[101-5]

Reaction	Alkali Metal	ΔH_r^o	ΔS_r^o
$2MCl(g) \rightleftharpoons M_2Cl_2(g)$	Li	-212.1	-
	Na	-200.8	-
	K	-187.9	-
	Rb	-174.1	-126.8
	Cs	-172.0	-132.2
$LiCl(g)+Li_2Cl_2(g) \rightleftharpoons Li_3Cl_3(g)$	-	-211.3	-
$2ScCl_3(g) \rightleftharpoons Sc_2Cl_6(g)$	-	-200.0	-139.7
$ScCl_3(g) + Sc_2Cl_6(g) \rightleftharpoons Sc_3Cl_9(g)$	-	-211.3	-
$MCl(g) + ScCl_3(g) \rightleftharpoons MScCl_4(g)$	Li	-237.2	-146.9
	Na	-242.7	-149.4
$\frac{1}{2}M_2Cl_2(g)+\frac{1}{2}Sc_2Cl_6(g) \rightleftharpoons MScCl_4(g)$	Li	-32.6	-3.8
	Na	-41.4	-8.4
	K	-46.9	+3.8
	Rb	-45.2	-2.5
	Cs	-47.7	+3.3
$2LiScCl_4(g) \rightleftharpoons Li_2Sc_2Cl_8(g)$	-	-163.6	-141.8

The standard enthalpies of formation of MCl(M=Rb,Cs) have been redetermined[106] from new enthalpy of solution data: ΔH_f^o(RbCl, c, 298.15K)=-(435.203±0.159)kJ mol^{-1}; ΔH_f^o (CsCl, c, 298.15K) = -(442.291 ± 0.159)kJmol^{-1}.

A neutron diffraction study of $NaBr.2H_2O$ has been undertaken[107] at 295K to examine the coordination of the water molecules and the hydrogen bonding. The dihydrate crystallises with monoclinic symmetry, space group $P2_1/c$, $a=6.575$, $b=10.456$, $c=6.776$Å, $\beta=113.38^\circ$.

The polylithium organic compound C_2Li_6 has been obtained in 99% purity (equation 21) using Knudsen effusion techniques.[108] Reactions

$$12Li + Hg(C_2H_5)_2 \longrightarrow 2C_2Li_6 + Hg \qquad \ldots(21)$$

of lithium with Et_2Hg, Et_4Sn, Et_4Pb, Me_2Hg, CH_2IHgI $(CF_3)_2Hg$ and $(C_2H_3$ $(C_2H_3)_4Sn$ have also been studied; invariably a mixture of products including C_2H_5Li, C_2Li_6, C_2Li_4 and C_2Li_2 was obtained.[108]

A novel method for the preparation of crystalline Li_3N has been described;[109] it is obtained by precipitation from a dilute solution of lithium in liquid sodium. The crystal chemistry of Li_3N has also been discussed.[110] Crystalline samples of MP (M=Na,K) have been prepared by reaction of the elements in sealed glass ampoules at 725 and 765K, respectively.[111] Relevant unit cell parameters are collected in Table 2, together with those for Cs_2S_2 which has been prepared by ammono thermal synthesis ($T\sim572K$, $2<p/kbar<3$).[112]

Table 2. Unit Cell Parameters for NaP,[111] KP,[111] Cs_2S_2[112]

Compound	Symmetry	Space Group	a/Å	b/Å	c/Å
NaP	orthorhombic	$P2_12_12_1$	6.038	5.643	10.142
KP	orthorhombic	$P2_12_12_1$	6.500	6.016	11.288
Cs_2S_2	orthorhombic	Immm	6.992	9.615	5.232

KNSO has been prepared (equation 22).[113] It darkens on heating

$$KOt\text{-}Bu + Me_3SiNSO \rightarrow KNSO + Me_3SiOt\text{-}Bu \qquad \ldots(22)$$

to 408K and melts at 463 to a bubbling orange liquid, explodes on ignition and ignites on contact with water. It is soluble in benzene solutions of 18C6; evaporation of the solution gives a 1:1 crown complex as a white crystalline solid, m.pt. 423-426K(decomp).[113]

A model for the large scale structure of NaOH aqueous glasses has been proposed;[114] it involves very small clusters of hydrated Na^+ and OH^- ions (with an internal structure similar to that in concentrated NaOH crystalline hydrates such as $NaOH.4H_2O$) embedded in a matrix of 'ice-like' excess water. This model is used to interpret the overall radiation chemistry of alkaline glasses.[114]

1.5.2 Ternary oxides and chalcogenides

For the reasons outlined earlier, the only ternary compounds considered in this section are those containing both an alkali metal and a transition metal. Several novel oxides[115-25] and selenides[126] have been prepared; although the former were obtained by classical solid state methods, the latter were synthesised in fusion reactions of alkali metal carbonates with selenium and copper. The crystallographic properties of these materials are summarised in Table 3. The data for Na_4CoO_3 and $Na_{10}Co_3O_9$ are of particular interest. Single crystals of these materials have been independently prepared by two groups of authors,[121-4] and investigated by X-ray diffraction methods. Unfortunately their analysis of the X-ray data show marked inconsistencies; there are differences in unit cell parameters and, in the case of Na_4CoO_3, even the symmetry of the crystal habit differs. Nonetheless, the two groups of authors describe similar molecular arrangements, the crystals being built up of Na^+ cations and discrete CoO_3^{4-} or $Co_4O_9^{10-}$ anions with an approximately trigonal planar arrangement of oxygen atoms about the cobalt atoms in both anions.[121-4]

The structure of $Na_2Ti_9O_{19}$ has been analysed using high resolution electron microscopy.[116] It consists of TiO_2-bronze type units interleaved with bridging TiO_6 octahedra and contains two types of hole sufficiently large for the Na^+ cation; the chemical composition of the material requires that these holes be fully occupied.[116] An electron microscope study of vacuum annealed $LiFe_5O_8$ crystals has also been undertaken.[127] Although the stable phase was expected to be the tetragonal γ-$LiFe_5O_8$, electron diffraction patterns for this phase were absent. Instead, the major part of the samples was identified as having the disordered spinel structure, presumably lithium deficient lithium ferrite; a number of iron oxide crystal structures (β-Fe_2O_3, γ-Fe_2O_3) were also identified.

Evidence from a comprehensive study (DTA,DSC,XRD, etc.) of the polymorphic behaviour in $K_2Cr_2O_7$ indicates that it is extremely sensitive to the provenance of the sample.[128]

Several investigations of the physicochemical properties of the vanadium[117,118,129] and tungsten bronzes[130,131] have been effected. Treatment of solid V_2O_5 with an acetonitrile solution of LiI at room temperature affords a series of bronzes, $Li_xV_2O_5 (0<x<1.0)$;[117] these products are quite distinct from those with the same composition but prepared at $T>673K$. The structures of these bronzes

Table 3. Crystallographic parameters for a number of ternary oxides and selenides

Compound	Symmetry	Space Group	a/Å	b/Å	c/Å	α/°	β/°	γ/°	Ref.
$Li_2Ti_3O_7$	orthorhombic	Pbnm	5.016	9.543	2.945	-	-	-	115
$Na_2Ti_9O_{19}$	monoclinic	C2/m	12.2	3.78	15.3	-	98	-	116
δ-$Li_xV_2O_5$	orthorhombic	-	11.272	4.971	3.389	-	-	-	117
ε-$Li_xV_2O_5$	orthorhombic	-	11.335	4.683	3.589	-	-	-	117
β-$Na_xV_2O_5$	monoclinic	C2/m	16.435	3.612	10.086	-	109.61	-	118
$K_2Cr_3O_{10}$	monoclinic	$P2_1/n$	7.618	17.791	7.354	-	99.20	-	119
$NaMo_4O_{10}$	tetragonal	P4/mbm	9.559	-	2.860	-	-	-	120
Na_4CoO_3	monoclinic	Cc	10.995	5.749	8.130	-	113.96	-	121
Na_4CoO_3	triclinic	P1	8.14	6.22	5.75	117.5	89.9	111.2	122 123
$Na_{10}Co_4O_9$	triclinic	$P\bar{1}$	8.540	8.452	11.343	93.49	105.63	121.16	121
$Na_{10}Co_4O_9$	triclinic	$P\bar{1}$	12.18	8.52	8.32	119.96	87.89	116.75	124
$4KNbO_3,KF$	monoclinic	$P2_1/n$	5.106	11.817	11.867	-	92.98	-	125
$Rb_3Cu_8Se_6$	monoclinic	C2/m	18.458	4.010	10.212	-	104.44	-	126
$Cs_3Cu_8Se_6$	monoclinic	C2/m	19.076	4.078	10.449	-	106.04	-	126

appear to be closely related to that of V_2O_5; relevant unit cell parameters for δ-LiV_2O_5 and ε-LiV_2O_5 are included in Table 3. Magnetic susceptibility and DSC data for the bronzes are also reported.[117] The homogeneity ranges of the β-$Na_xV_2O_5$ and χ-$Na_{2+2x}V_6O_{16}$ bronzes have been studied by e.p.r. and i.r. spectroscopy.[129] The relationship between the crystal structure and electrical properties of the β-$Na_xV_2O_5$ bronze has been examined.[118] The structure of β-$Na_xV_2O_5$ is based on a V–O framework; the Na^+ cations lie in 2 rows in tunnels within this framework (Figure 3). With increasing sodium content the Na^+ sites are gradually filled until at $x=0.33$ the occupational probability is 50%. X-ray diffuse scattering studies have shown that at $x<0.33$, the Na^+ cations occur in clusters, rather than being randomly distributed among the possible sites in the tunnel structure, and that the crystal contains regions where the electron concentration is fixed at a value corresponding to $x=0.33$. This picture provides a basis for the interrupted strand model of electronic transport in which β-$Na_xV_2O_5$ is regarded as a material with (i) one-dimensional metallic character originating from the delocalised states arranged in a linear chain along the tunnel axis and (ii) semiconductive nature due to localisation of electrons.[118]

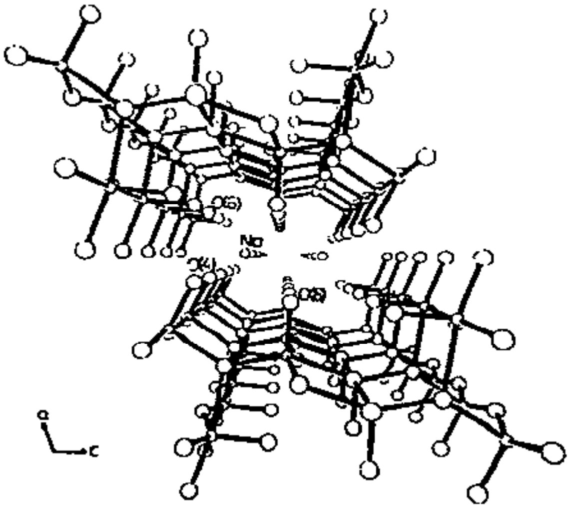


Figure 3. Perspective view of the tunnel structure of β-$Na_xV_2O_5$. (Reproduced by permission from Bull.Chem.Soc.Jpn., 52(1979)1315)

The reduction of the K_xWO_3 (x=0.33, 0.57) bronzes in a stream of hydrogen (at 943, 1013K)[130] and their solubility in aqueous K_2WO_4 solutions (298,323K)[131] have been investigated. Reduction of $K_{0.33}WO_3$ occurs via $K_{0.57}WO_3$, K_2WO_4 being formed as a side-product; the reduction products of $K_{0.57}WO_3$ are K_2WO_4 and α-W.[130] Whereas $K_{0.33}WO_3$ dissolves in aqueous K_2WO_4 solutions with enrichment of the solution in K_2WO_4, $K_{0.57}WO_3$ dissolves without decomposition.[131]

Phase relationships in the M_2O-VO_2-V_2O_5 (M=Rb,Cs) systems have been delineated.[132] One compound ($Rb_{0.9}V_4O_9$) was found in the rubidium system and four compounds ($Cs_{0.4}V_3O_7$, CsV_4O_9, $Cs_2V_4O_9$ and $Cs_3V_5O_{14}$) in the caesium system.

The vibrational properties of MVO_3(M=K,Rb,Cs)[133] and of $NaGdO_2$[134] have been determined and compared with theoretically derived data. The magnetic properties of M_2FeO_4 (M=K,Rb,Cs)[135] and of $NaCeS_2$[136] have also been elucidated. The electrical conductivity of a number of lithium compounds with the NaCl-type structure (Li_6WO_6, β-Li_4WO_5, γ-Li_4MoO_5, Li_6TeO_6, Li_4VO_5) has been measured.[137] The differences between the conductivities of the various compounds is relatively small. The conductivities of β-Li_4WO_5, γ-Li_4MoO_5 and Li_4UO_5; which have ordered NaCl-type structures are slightly lower than those in Li_6WO_6 and Li_6TeO_6 which deviate from the NaCl-type structure by having 1/6 of the lithium ions in tetrahedral holes and 1/7 of the oxygen sites unoccupied, respectively. The conductivity of the structurally unrelated Li_6UO_6 has also been determined; it is of a similar order.[137]

A mass spectroscopic study (T=833K) of the $LiReO_4$-$CsReO_4$ system ($0.3<x_{LiReO_4}<1$) has shown the existence of $LiReO_4$, $CsReO_4$, $(LiReO_4)_2$ $(CsReO_4)_2$ and $LiCs(ReO_4)_2$ in the gas phase.[138]

1.5.3 Ternary Halides

A considerable research effort has been applied to the elucidation of the chemistry of these compounds, particularly their structural and spectroscopic properties, during the period of the review. Phase relationships in the NaCl-$PdCl_2$,[139] MBr-$CdBr_2$(M=K,Rb,Cs),[140] MF-DyF_3 (M=Rb,Cs),[141] KCl-MCl_3 (M=Gd,Dy),[142] CsCl-MCl_3 (M=Pr,Dy, Er,Yb),[142] systems have been determined using TA DTA and XRD techniques. Although Na_2PdCl_4[139] and $MCdBr_3$ and M_2CdBr_4 (M=K,Rb, Cs)[140] are the only ternary halides formed in the systems containing transition metals, a plethora of compounds are formed in the systems containing lanthanide metals;[141,142] these include compounds of stoichiometry A_3MX_6, A_2MX_5, AM_2X_7 and AM_3X_{10}. X-ray powder diffraction data are quoted for all these compounds[139-42] together with thermodynamic data for those of stoichiometry A_3MCl_6 and AM_2Cl_7.[143] Thermodynamic data have also been obtained for $LiZrF_5$, Li_2ZrF_6, and $LiZr_2F_9$[144] and for K_2WCl_6, M_2WBr_6 (M=K,Rb,Cs) and K_2ReX_6 (X=Cl,Br).[145]

Numerous single crystal XRD studies of the structures of ternary halides have been undertaken;[146-59] crystallographic data are collected in Table 4. Of the tungsten bronze like M_xVF_3 (M=K, Rb,Cs) compounds, K_xVF_3 and Rb_xVF_3 are slightly distorted from hexagonal and are orthorhombic; Cs_xVF_3, however, does not exhibit any distortion from hexagonal symmetry.[146] β-$RbCrCl_3$ has been shown to undergo a transition to γ-$RbCrCl_3$ at 201K; the structural determination for γ-$RbCrCl_3$ (at 100K) shows it to have a slightly distorted hexagonal perovskite structure which is related to the β-phase.[149] $KCuF_3$ has also been shown to have a distorted perovskite structure; the electron density distribution in crystals of $KCuF_3$ has been studied in great detail in an attempt to ascertain the origin of the Jahn-Teller distortion in this material.[160]

The structural chemistry of the spinel-type chlorides, Li_2MCl_4 (M=Mg,Mn,Fe,Cd) has been studied by DTA, far i.r., Raman and XRD techniques.[161] The vibrational spectra indicate that 1:1 ordering on the octahedral sites does not occur. Both DTA and XRD show that the spinels undergo a reversible phase transition to a high temperature cubic defect structure at 808K (Li_2MgCl_4) 733K (Li_2MnCl_4) and 658K (Li_2CdCl_4). The high temperature structure (eg. Li_2MgCl_4, a_o=5.291Å) has a cubic unit cell constant approximately half that of the spinel lattice (eg. Li_2MgCl_4, a_o= 10.411Å).[161] Single crystal, neutron diffraction studies of Rb_2CrCl_4 at 77 and 5.5K[162] have shown that the microscopic origin of the ferromagnetic exchange of this compound is due to the displacement of the Cl atoms in the basal plane by 0.16Å from the midpoint of the line joining adjacent Cr atoms. This gives tetragonally elongated $CrCl_6$ units with principal axes alternately along (011) and (0$\bar{1}$1) of the D_{2h}^{18} (Cmca) unit cell.[162] Single crystal neutron diffraction data have been collected for Rb_2ZnBr_4 at 373, 300 and 4.2K;[163] these temperatures correspond to the three phases: the normal high temperature phase, the incommensurate phase (355>T/K>200) and the phase with a tripled c-axis, respectively. The basic structure type is that of β-K_2SO_4 in

Table 4 Crystallographic parameters for a number of ternary halides

Compound	symmetry	space group	a/Å	b/Å	c/Å	β/°	Ref.
$K_{0.25}VF_3$	orthorhombic		12.895	7.398	7.533	–	146
$Rb_{0.25}VF_3$	orthorhombic		12.904	7.411	7.550	–	146
$Cs_{0.25}VF_3$	hexagonal		14.994	–	7.646	–	146
$K_{0.54}(Mn,Fe)F_3$	tetragonal	$P4_2bc$	12.768	–	8.002	–	147
$Cs_{0.2}(Zn,Fe)F_3$	monoclinic	$P2_1$	7.474	7.636	7.461	120.0	148
γ-$RbCrF_3$	monoclinic	C2	12.109	6.962	12.438	93.94	149
$CsCrI_3$	hexagonal	$P6_3mc$	8.132	–	6.946	–	150
$KTiF_4$	orthorhombic	Pcmn	7.944	7.750	12.195	–	151
$NaCrF_4$	monoclinic	$P2_1/c$	7.862	5.328	7.406	101.65	152
Rb_2MnBr_4	tetragonal	I4/mmm	5.37	–	17.32	–	153
Rb_2FeI_4	monoclinic	$P2_1$	7.705	8.182	10.341	109.87	154
K_2ZnCl_4	orthorhombic	$Pna2_1$	26.778	12.402	7.256	–	155
K_2RuCl_6	cubic	Fm3m	9.737	–	–	–	156
δ-Na_2UF_6	hexagonal	P3	6.112	–	7.240	–	157
$Rb_2Au_2Br_6$	monoclinic	I2/m	8.52	7.243	11.210	101.24	158
$Rb_3Au_3Cl_8$	monoclinic	C2/c	12.02	7.522	18.29	97.62	158
$K_4Ru_2Cl_{10}O$	tetragonal	I4/mmm	7.097	–	17.015	–	157
$Li_2Th_5F_{22},LiOH$	tetragonal	$P42_12$	11.307	–	6.390	–	159

space group Pcmn; the variation in structure in the three phases is considered in terms of the thermal vibrations of the crystal lattice.[163]

Cousson et al.[159] have established that the compound they previously defined as $LiTh_2F_9$[164] is, in reality, $Li_2Th_5F_{22}.LiOH$; the formula of the crystal used to measure X-ray diffraction intensities was determined by fast γ-ray spectroscopy. Pauling[165] has criticised the assignment by Cousson et al.[166] of the Li^+ ions in Li_3ThF_7 since two of the three crystallographically different Li^+ ions are only 2.03Å apart - less than the smallest reported

Li...Li distance in any ionic compound (Li_2O, r(Li...Li) =2.31Å). Pauling postulates that either the space group is incorrect or the Li^+ ions occupy a larger number of equivalent positions with some randomness.[165]

A series of compounds with the formulae $ABCMCl_6$ and A_2CMCl_6 (A,B,C=K,Rb,Cs; C=Li,Na; R=lanthanide) have been prepared and characterised by XRD techniques.[167] These compounds, known as chloroelpasolites, are all cubic with a_o values ranging from 10.055 (for $RbKLiScCl_6$) to 10.842Å (for $CsRbNaNdCl_6$).[167]

A Mössbauer study of $NaFeF_3$ has been undertaken ($4.2<T/K<293$) to elucidate the magnetic properties of this material. The results of a comprehensive study ($77<T/K<448$) of the far i.r. spectra of $CsCuCl_3$ have been reported;[169] the spectral change due to the phase transition has been interpreted on the basis of the structural distortion of the crystal.

The X-ray L_{III} absorption edge structure of Re in Cs_2ReCl_6 has been measured and an analysis of the data attempted in terms of M.O. theory.[170] Finally, ^{35}Cl n.q.r. studies of $NaAuCl_4.2H_2O$ have been effected as a function of temperature (77,195,273K) and pressures ($P>550$ MPa); the data are used to elucidate the electronic effects within the complex.[171]

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

Interest in the chemistry of complexes formed by alkali and alkaline earth metals with both acyclic and cyclic polyether compounds and with cryptands has been maintained during 1979. Consequently this section of the review has subdivisions relating to each of these complex types as well as to the individual alkali metals. In the latter subdivisions, data pertinent to several alkali metals are discussed once only, in the subdivision relating to the lightest metal considered.

1.6.1 Acyclic Polyether Complexes

The complexation of alkali and alkaline earth metals by acyclic neutral ligands, principally acyclic polyethers stiffened by rigid terminal groups containing donor atoms (e.g. aromatic donor end groups) has been reviewed by Vogtle and Weber;[172] comparison of the resultant complexes with analogous derivatives of both naturally occurring acyclic ionophoric antibiotics and crown compounds is undertaken.

It has been established[173] in a ^{23}Na n.m.r. study of the interaction of Na^+ with the ionophoric antibiotic, Lasolocid X-537A, in the presence of biogenic amines (serotonin bimaleate, 3-hydroxytyramine or L-norepinephrine) that the cation competes with the biogenic amine for binding to Lasolocid X-537A. Stability constants for both Na^+ and amine complexes with Lasolocid X-537A are quoted.[173]

Yanagida et al. have reported[174] the crystal structure of heptaethylene glycol-$Sr(SCN)_2$, a complex of a simple linear polyether. The Sr^{2+} cation (see Figure 4) is coordinated by eight oxygen atoms from the heptaethylene glycol moiety, r(Sr...O) = 2.56-2.73Å, and a nitrogen atom, from one of the SCN^- anions, r(Sr...N) = 2.57Å; the coordination polyhedron is quite irregular.

The formation of alkali metal and alkaline metal complexes of simple glycols (mono- di- tri- and tetraethyleneglycol), in both water and isopropanol, has been investigated using conductometric methods.[175] Molecular interactions in alkali metal halide-acetamide-glycol (mono-di-tri- and tetraethyleneglycol) systems have also been studied using ^{1}H n.m.r. spectroscopic techniques;[176] it is concluded that an increase in the number of oxyethylene units in a glycol molecule leads to enhancement of the electrostatic interaction of MX with acetamide.

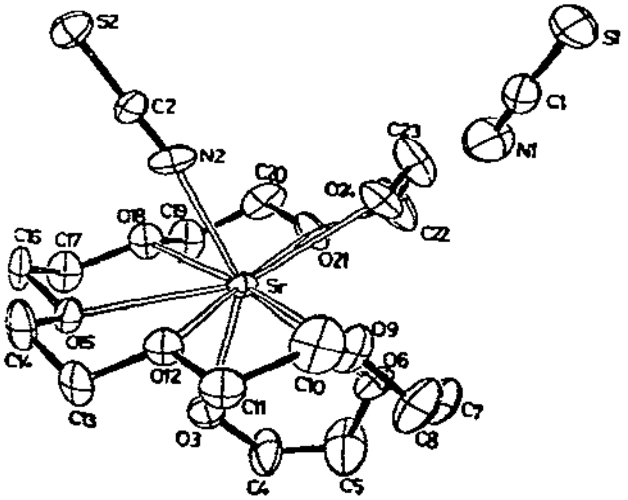
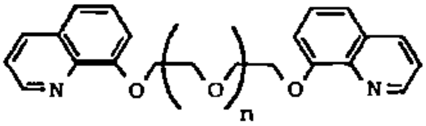
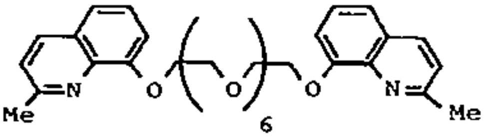


Figure 4. The molecular structure of heptaethylene glycol-$Sr(SCN)_2$ (Reproduced by permission from Bull.Chem.Soc.Jpn., 52(1979) 1209).

Saenger et al.[177-182] have reported the results of a comprehensive structural study of a number of complexes formed by acyclic polyethers containing aromatic donor end groups (2) to (6); they are the 1:1 complexes of RbI with (2),(3),(4) and (5) and the 2:1 complex of KSCN with (6). The molecular geometries of these complexes differ markedly. In (2).RbI,[177] Rb^+ is coordinated



(2) n=1
(3) n=3
(5) n=6



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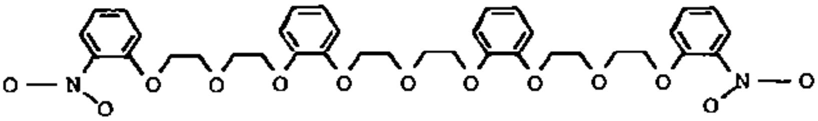


(6)

to all five heteroatoms of the ligand, r(Rb...N) = 2.97Å, r(Rb...O) =3.07.3.17Å and to two symmetry related anions, r(Rb...I)=3.69, 3.90Å; the ligand wraps around Rb^+ in a circular manner with the quinoline planes tilted like the wings of a butterfly (dihedral angle = 66.8°). The effect of methylation of (3) (giving (4)) on the coordination geometry of these complexes is seen in the structures of (3).RbI[178] and (4).RbI.[179] Whereas Rb^+ in (3).RbI is coordinated solely by the seven heteroatoms of the ligand, r(Rb...N) =2.93, 2.96Å, r(Rb...O) = 2.88-3.08Å, which adopts a helical chiral configuration by changing one C-O torsional angle from trans to gauche, that in (4). RbI is coordinated to the anion, r(Rb...I) = 3.63Å, as well as to all seven heteroatoms of the ligand, r(Rb...N) = 3.04, 3.11Å, r(Rb...O) = 2.84-3.12Å, which forms a helical structure with the heterocycles stacked parallel to each other, 3.4Å apart.[179]

By studying the complexes of the larger polyethers (5) and (6), Saenger et al.[180-2] have established that these complexes can adopt one of two structures: the polyether can wrap spherically around the cation and thus shield it from the anion, as in (5).RbI[180,182] or the polyether can adopt a S-shaped arrangement with each loop coordinating a cation, which is still bound to an anion for geometric reasons as in (6).2KSN.[181] These structures are shown in detail in Figure 5. In (5).RbI (Figure 5a,5b) all the heteroatoms of the ligand lie approximately on the surface of a sphere of radius 3.07Å giving a 10-coordinate Rb^+ ion, r(Rb...N)= 3.20, 3.37, r(Rb...O) = 2.96-3.15Å.[180,182] In (6).2KSCN, (Figure 5c) the polyether chains form one S loop around each K^+SCN^- ion pair coordinating the K^+ ion by three nitro oxygen atoms, r(K...O) = 3.11, 3.18Å, and five ether oxygen atoms, r(K...O) = 2.68-3.30Å. The 10-fold K^+ coordination sphere is completed by both the nitrogen and sulphur atoms of the anion, r(K...N(S)) = 3.26, 3.39Å. (The two SCN^- ions are twofold disordered, such that the S and N atoms overlap).[181]

The influence of aromatic donor end groups on the thermodynamics and kinetics of alkali metal ion complex formation have also been elucidated.[183]

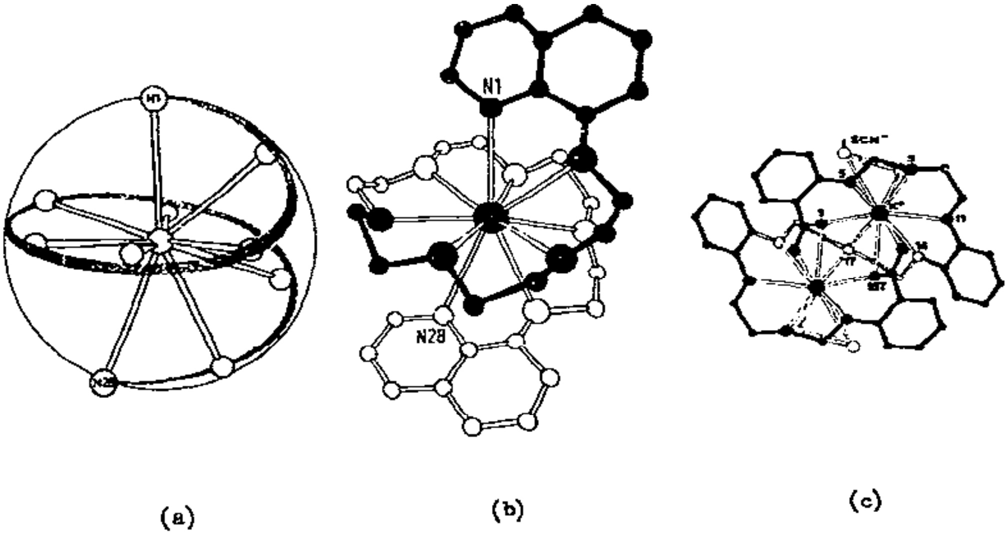


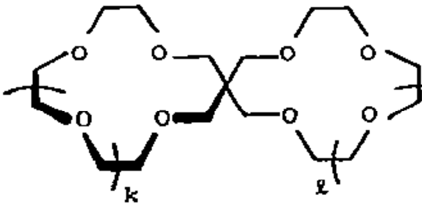
Figure 5. Coordination of alkali metal cations by very long linear polyethers: (a,b) spherical mononuclear Rb^+ complex of (5) and (c) S-shaped binuclear K^+ complex of (6) (Reproduced by permission from Angew.Chem.Int.Ed.Engl., 18 (1979) 226,227)

1.6.2 Crown Complexes

A large number of papers describing aspects of the complexation of alkali metals and of alkaline earth metals by crown ethers, have been published recently; two topics appear to be of particular interest: (i) the design of new crown ethers and the assessment of their complexing ability, and (ii) the structural properties of the crown ether complexes so formed.

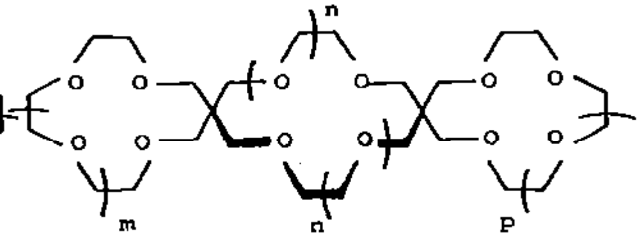
Using space filling models, Vogtle et al. have shown that small crown ethers (and cryptands) just fit into the conical lipophilic cavity of γ-cyclodextrin.[184] The model considerations also show that crown complexes, though much more rigid, should also be capable of being accommodated in the γ-cyclodextrin cavity. Indeed, reaction of aqueous solutions, typically of the 12C4.LiSCN complex with aqueous solutions of γ-cyclodextrin at room temperature leads to crystallisation of "cascade complexes" with 1:1 stoichiometry.

Of the several new designs of crown ethers capable of complexing alkali and alkaline earth metal cations,[185-191] the multi-loop crown ethers, produced by Weber,[185] are the most novel. These ligands, typically (7) and (8), contain several rings, which have tailor made cavity sizes and donor properties, coupled by spiro C-atoms; they have been shown to be generally useful as hosts for the joint incorporation of several cations. Examples of the other new macrocyclic ligand systems include (9),[186] (10),[187] (11),[188] (12),[189] (13)[190] (14)[191]; their abilities to complex metal cations including both alkali metal and alkaline earth metal cations has been surveyed. The macrocyclic Schiff bases, (13) and (14) are produced by metal (Ca^{2+}, Sr^{2+}, Ba^{2+}) induced template syntheses. In the absence of the cations, the macrocycles are formed in either very small yield or not at all; alkali metal cations and Mg^{2+} are ineffective in promoting the synthesis of the macrocycles.



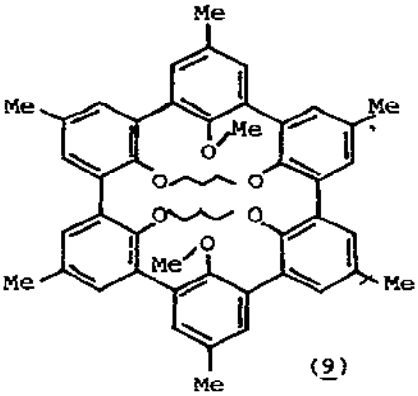
(7a) k=ℓ=1
(7b) k=ℓ=2
(7c) k=3, ℓ=1

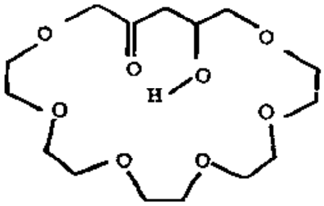
(7)



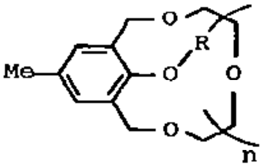
(8a) m=3,n=2,p=3
(8b) m=2,n=3,p=2

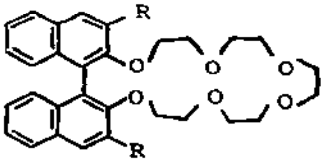
(8)


(9)


(10)

(11)

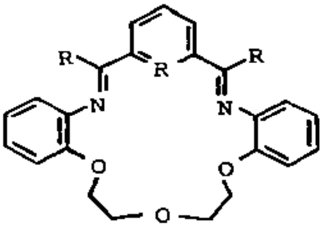

n=2,3,4. R=Me,CH_2OMe,H.

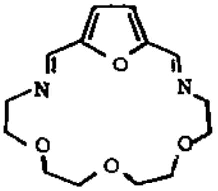

(12)

R=CH_2OH, CH_2Cl, CN.

The use of caesium salts in the synthesis of crown ethers[192] and of macrocyclic lactones[193] has also been reported.

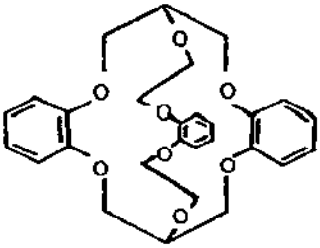
(13)


R = H, Me


(14)

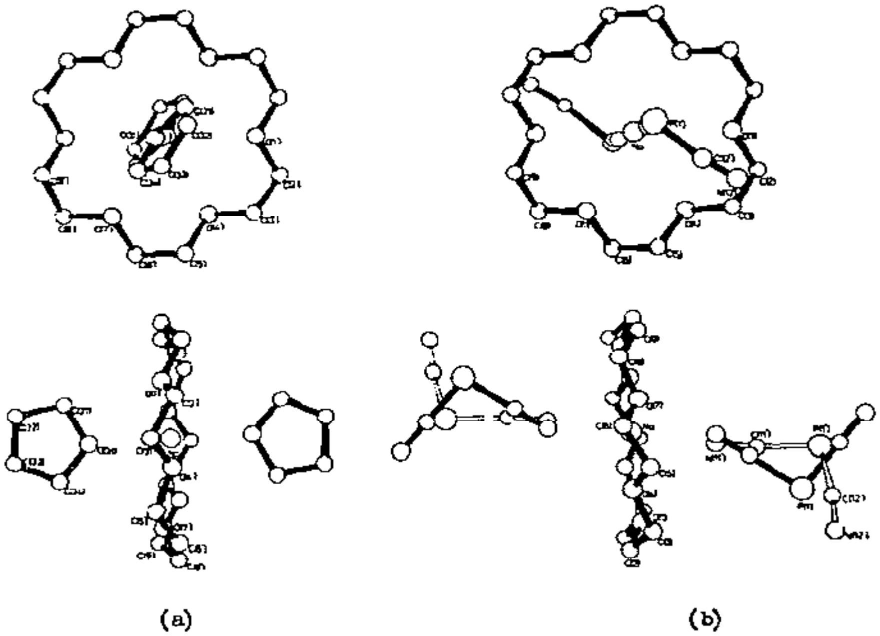
Structural studies have been undertaken on the simple crown ether complexes, $(15C5)_2.BaBr_2.2H_2O$,[194] $(18C6)_2.K_2MoO_4.5H_2O$,[195] $18C6.K_2Mo_6O_{19}.H_2O$,[196] $18C6.NaP(CN)_2.THF$,[197] $18C6.NaP(CN)_3Br.2THF$,[198] $DB30C10.RbNCS.H_2O$,[199] $DB30C10.2NaNCS$[200] and the bridged crown ether complex, (15)$.KCl.nH_2O$.[201]

The crystal structure of $(15C5)_2.BaBr_2.2H_2O$[194] is built up of $[(15C5)_2Ba]^{2+}$ cations with a D_{5d} sandwich structure and $[Br_4(H_2O)_4]^{4-}$ complex anions in which the Br^- ions are connected by H_2O molecules through hydrogen bonding.


(15)

The two K^+ ions in $(18C6)_2.K_2MoO_4.5H_2O$ are in crystallographically distinct positions.[195] One is coordinated to the heteroatoms of an 18C6 molecule and two water molecules whereas the other is coordinated to a second 18C6 molecule, one water molecule and the MoO_4^{2-} anion; both K^+ ions are displaced from the mean oxygen planes of the 18C6 molecules by 0.92 and 0.78Å, respectively. The structure of $(18C6)_2.K_2Mo_6O_{19}.H_2O$ is somewhat simpler;[196] it is based on a sandwich structure composed of a $Mo_6O_{19}^{2-}$ anion located between two $[18C6.K]^+$ crown complex cations. The sandwich structures connect through a water molecule; the latter is strongly bonded to two K^+ ions by an ion-dipole interaction.[196]

The X-ray structure analysis of $18C6.NaP(CN)_2.THF$[197] shows that comparable positively (Figure 6a) and negatively (Figure 6b) charged units are present in the crystal. They are each formed from a sodium ion surrounded by a crown ether, r(Na...O) = 2.71-2.79Å, with two further ligands in the apical positions, namely two O-coordinated THF molecules, r(Na...O) = 2.36Å, or two N-coordinated dicyanophosphide ions, r(Na...N) = 2.44,2.48Å. The latter randomly populate two different sites with occupation factors of 0.42 and 0.58 (Figure 6b, lower view). In both the cation and anion, the ligand atoms surround Na^+ in an almost hexagonal bipyramidal arrangement; as a result of the alternating deviations of the heteroatoms from the mean NaO_6 plane it is clearly distorted into a scalenohedron.[197] $18C6.NaP(CN)_3Br.2THF$[198] contains an almost identical cationic arrangement to that in the dicyanophosphide derivative. The anion, however, exists as a dimeric species with pseudo-octahedral geometry at the phosphorus atom; the octahedron is formed by three facial cyano groups, two bridging halogen atoms, and the lone pair of

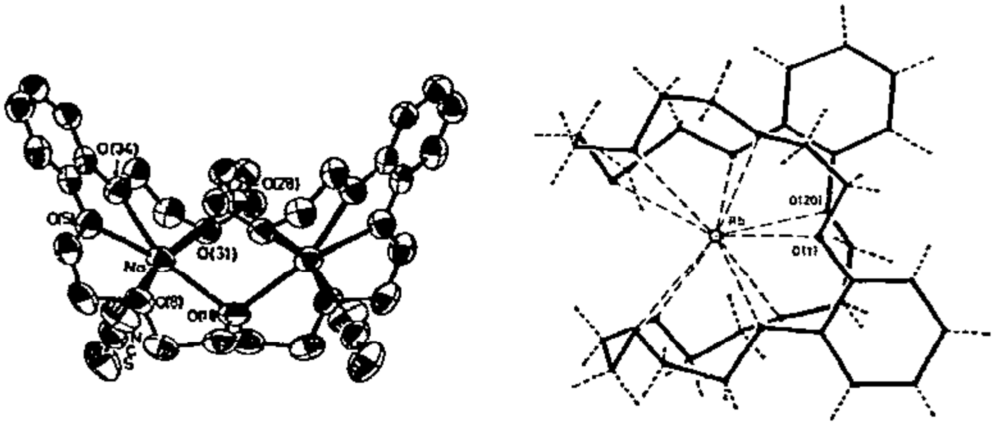

(a)

(b)

Figure 6. The positive (a) and negative (b) molecular units in the structure of 18C6.NaP(CN)$_2$.THF. (Reproduced by permission from Angew. Chem. Int. Ed. Engl., 18(1979)934)

electrons.[198]

The difference in structure between the DB30C10 complexes of NaSCN and of RbSCN is quite marked; whereas DB30C10 complexes with two Na$^+$ cations, it only complexes one Rb$^+$ cation forming DB30C10.(NaSCN)$_2$.H$_2$O[199] and DB30C10, RbSCN.H$_2$O,[200] respectively. In the case of the case of the sodium derivative (Figure 7a) each ligand complexes with two Na$^+$ cations, r(Na...O) = 2.40-2.59Å, and each cation is also coordinated to one isothiocyanate anion through the nitrogen atom, r(Na...N) = 2.36Å. The two halves of the complex are related by a crystallographic 2-fold rotation axis which passes through two oxygen atoms O(11) and O(28) of the ligand; these atoms bridge the cations which are 3.94Å apart. The nitrogen and bridging oxygen O(28) form the apices of an approximately pentagonal bipyramidal arrangement around the Na$^+$ ion.[199] For the Rubidium derivative (Figure 7b) the ligand envelopes a single Rb$^+$ cation, r(Rb...O) = 2.96-3.19Å, and the anion is remote from the cation forming infinite chains with the water molecule.[200]



(a) (b)

Figure 7. The coordination by DB30C10 around (a) Na^+ in the binuclear complex DB30C10.$(NaSCN)_2.H_2O$ and (b) Rb^+ in the mononuclear complex DB30C10.bSCN.H_2O. (Reproduced by permission from (a) J.Chem.Soc.Dalton Trans., (1979) 1831, (b) Acta Crystallogr., B35(1979)330)

The crystal structure of the complex formed by KCl with the bridged macrocyclic polyether (15), (15).KCl.$nH_2O(n{\sim}5)$, is built up of discrete cations containing K^+ coordinated only by the encapsulating ligand (Figure 8) with the Cl^- ions and water molecules occupying disordered sites in columns.[201] All eight oxygen atoms of the ligand are coordinated to the K^+, r(K...O)=2.68-2.74Å, the four in the bridge, O(4) O(7) O(14) and O(17) and two catechol oxygen atoms, O(1) and O(20) form a ring almost coplanar with K^+, while the other two oxygen atoms O(28) and O(35) on ring B are 2.4Å from this plane on the same side of the K^+ ion (Figure 8). This ion has no neighbours within 3.65Å on the other side and is not coordinated by solvent or anion.[201]

Interaction between B15C5 and Na^+, K^+ and Ba^{2+}[202] and between DB30C10 and Na^+, K^+ and Cs^+[203] have been studied in a number of solvents using ^{1}H[202], ^{13}C[202,203], ^{23}Na[203], and ^{133}Cs[203] n.m.r. techniques. In the B15C5 study,[202] it is deduced that K^+ ions

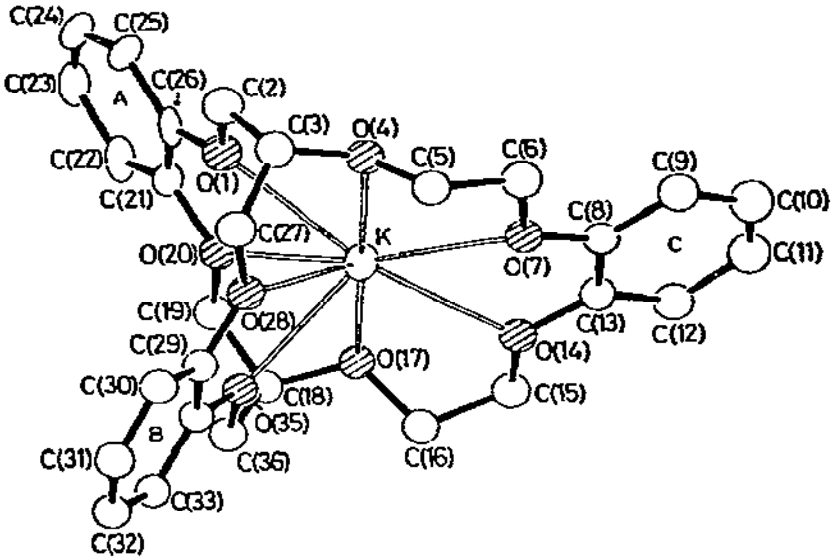


Figure 8. The molecular structure of ($\underline{15}$).K^+ in ($\underline{15}$).KCl.nH_2O (Reproduced by permission from J.Chem.Soc.Commun., (1979) 486)

adopt a sandwich structure in solution and that Ba^{2+} forms a 1:1 complex in which solvent effects play a considerable role. In the DB30C10 study,[203] it was shown that whereas K^+ and Cs^+ form 1:1 complexes, Na^+ forms three complexes with stoichiometries Na_2L Na_3L_2 and NaL. It is also reported that the data support the existence of a 'wrap-around' structure for the 1:1 Cs^+: DB30C10 complex in solution.[203]

The extraction of a number of alkali metals[204] and alkaline earth metal picrates[205,206] from aqueous solutions into benzene[204-6] or chloroform[206] in the presence of 15C5,[204-5] 18C6,[204-5] or DB18C6[205-6] has been investigated; the data are interpreted in terms of the ionic radii of the cation and the stability of the crown complex in the aqueous phase. The association constants for the formation of complexes between the 4-tert-butyl and 3,5-ditert-butyl derivatives of DB18C6 and alkali metal cations in CH_3OH, CH_3CN and DMSO have also been determined.[207] The results are compared to those for DB18C6 and it is shown that complex formation is affected by steric factors and by the physicochemical properties of the solvent as well as the relative size of the polyether cavity and the cation diameter.

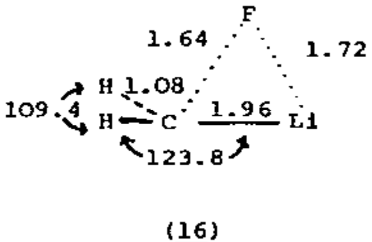
1.6.3 Cryptates and Related Complexes

Surprisingly few papers describing the chemistry of cryptates and related complexes have been published during the period of the review. The effect of C222 on the partition of alkali metal cations (Li^+, Na^+, K^+, Rb^+, Cs^+) between water and CH_3OH has been assessed;[208] it alters the cation transfer selectivity by factors of up to 10^7. The solvent extraction of ion pair complexes of a number of cryptates of Na^+, K^+ and Cs^+ have been investigated;[209] cryptands studied include C22, C211, C221, C222 and C222B. Conditions for extraction and separation of the alkali metal cations at low concentrations have been established.[209]

1.6.4 Lithium Derivatives

Although there are a vast number of publications dealing with lithium chemistry, those abstracted for this review are relatively few in number, emphasis being placed on the inorganic chemistry of lithium; the organometallic chemistry of lithium, which accounts for the majority of these papers, is ignored since it is reviewed in detail elsewhere.[2]

Molecular orbital calculations have been undertaken on the molecules CH_2FLi,[210] CLi_2CH_2,[211] the methyl lithium cluster species[212] $Li_4(CH_3)_3^+$, $Li_4(CH_3)_2^+$, $Li_4(CH_3)^+$, $Li_2(CH_3)^+$, $Li(CH_3)^+$ and $Li_2(CH_3)_2$ and the $H_2C...Li^+$ system.[213] Complete geometry optimisation of a variety of possible structures for the carbenoid, CH_2FLi, showed the most stable structure to have a peculiar umbrella-shaped ('inverted carbon') structure, (16), and $CH_2Li^+F^-$ ion pair character.[210] The results of a recent ^{13}C-n.m.r. spectroscopic investigation of 1-lithio, 1-bromocyclopropane CH_2BrLi[214] at 173K in THF appear to be



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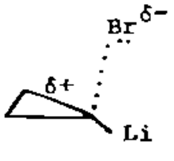

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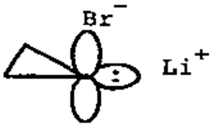
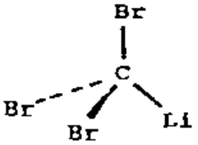


(18)

distances/Å; angles/°

in accord with this theoretical observation, the n.m.r. data suggesting considerable weakening of the C-Br bond (17) or even rehybridisation (18). In a similar ^{13}C-n.m.r. study of Br_3CLi at 173K in THF,[215] the results indicate the presence of three species: (a) Br_3CLi with highly polarised Br→C bonds (19) (b) Br_3CLi distorted as a result of stepwise release of LiBr, (20), (21), and (c) Br_2C (22).



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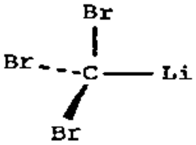

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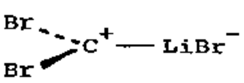

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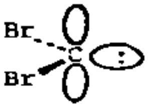
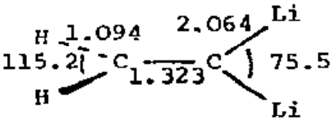


(22)

Application of SCF MO theory to $CLi_2{=}CH_2$ predicts the twisted triplet structure (23) to be the ground state, followed energetically by the planar triplet (24, 5.0kJ), twisted singlet (25, 118.8kJ) and planar singlet (26, 122.6kJ).[211] Calculations of the complex



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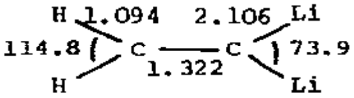

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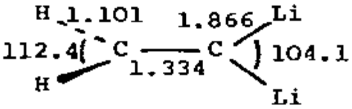

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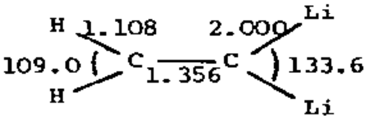


(26)

distances/Å, angles/°

formed by Li^+ with CH_2 were restricted to a geometry based on a Li^+ ion situated on the z-axis which bisects the HCH angle (101°) with r(C...H) = 1.125, r(C...Li) = 4.03 atomic units.[213]

^{13}C, ^{7}Li and ^{6}Li n.m.r. studies of n-propyl lithium in hydrocarbon solvents have shown that the n-propyl tetramers and hexamers undergo fast intra-aggregate carbon-lithium bond exchange to at least 193K and inter-aggregate exchange at higher temperatures.[216] Complexes of n- and s-butyl lithium with THF, $(CH_3)_2O$ and $(CH_3)_3N$ have been studied ($173 < T/K < 293$) using i.r. techniques.[217] The complexation is much stronger for n-butyl lithium, the strength of the interaction decreasing with ligand in the order THF > $(CH_3)_2O$ > $(CH_3)_3N$.

An X-ray crystal study of $(LiN{=}Ct\text{-}Bu_2)_2$ has revealed a 'folded chair' arrangement of its metal atoms held together by triply bridging methyleneamino groups.[218] During refinement of the hexameric structure (Figure 9) alternative positions (3A and 3B) were found for one of the three lithium atoms in the asymmetric unit; these were assigned site occupation factors of 0.5 and correspond to two possible orientations of the Li_6-rings. The $t\text{-}Bu_2C{=}N$ ligands bridge the six smaller of the eight triangular faces of the Li_6-rings, oriented so that the ligand NCC_2 planes are perpendicular to the Li_3 faces. Details of the molecular

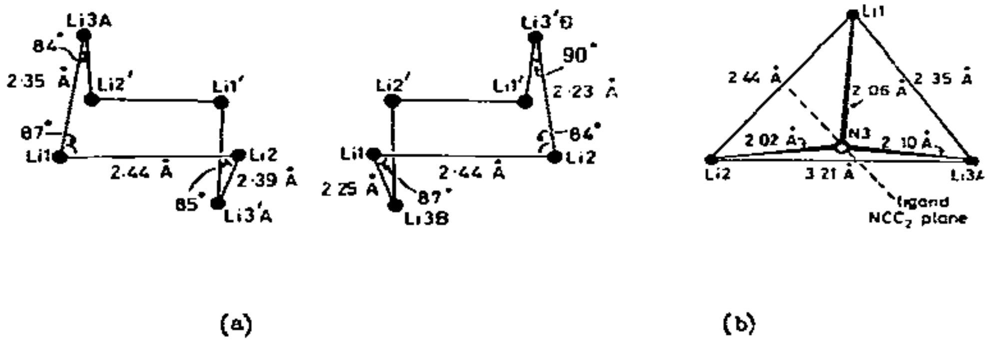


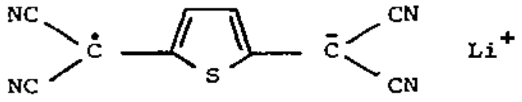
Figure 9. The two possible orientations of the Li_6 ring (a) and the type of bridging of an Li_3 face by a μ^3-methyleneamino group (b) that occurs in $(LiN{=}Ct\text{-}Bu_2)_2$ showing interatomic distances and angles. (Reproduced by permission from J.Chem.Soc.Chem.Commun., (1979) 943)

geometries of the Li_6-rings and of the Li_3N-bridging units are given in Figure 9.[218]

$M[S_2C.N(CN)_2]$, M = Li-Cs, have been prepared by reaction of $M[N(CN)_2]$ with CS_2 in DMF.[219] The products have been characterised by i.r. and u.v.-visible spectroscopic techniques. The salts (Li^+, Na^+, K^+) of thio-2-violuric acid have also been prepared and characterised by physicochemical techniques.[220]

The synthesis, crystal structure and thermal decomposition of lithium glutarate, hydrogenglutarate dioxouranate(VI) tetrahydrate have been described.[221] It was isolated from the glutaric acid-uranyl nitrate-lithium hydroxide system at pH4.4. The geometry around the Li^+ ion is tetrahedral with one monodentate glutarato ligand and three water molecules, whereas that of the uranium is approximately hexagonal bipyramidal. On heating, dehydration occurs at 363-433K, followed by transformation into a mixture of uranium and lithium glutarates at 473-543K. Finally decomposition to $Li_2U_2O_7$ occurs between 613 and 973K.[221]

The radical anion (27) has been synthesised by slow addition of (28) in CH_2Cl_2 to anhydrous LiI in CH_3CN under argon.[222] It is a blue-black crystalline solid; its electrical and complexing properties have been compared with those of the TCNQ analogue.[222]



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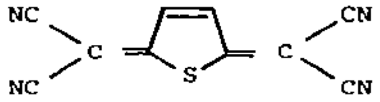
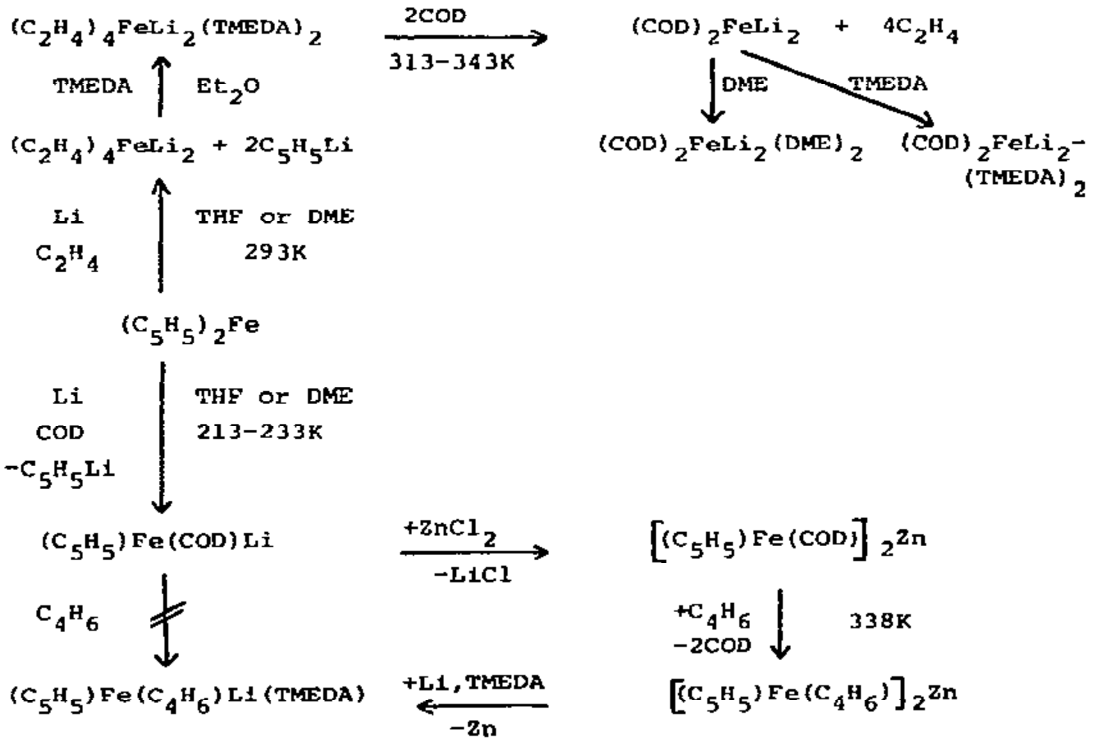


(28)

The complexing properties of both β-diketones[223] and biuret[224] to the alkali metal cations have been evaluated. The correlation between the experimental results and the theoretically derived stabilisation energies for the 1:1 and 1:2 biuret complexes is noted.[224]

Structural analyses of the $[Li(THF)_3]^+$ and $[Na(THF)_2]^+$ salts of the binuclear iron acyl monoanion, $[Fe_2(CO)_5(C(O)R)(\mu_2\text{-}PPh_2)_2]^-$ (R=Ph,Me) have been carried out.[225] The occurrence of tight ion pairing between the alkali metal and the acyloxygen atom is found in both salts. The Li^+ ion possesses a nearly regular tetrahedral arrangement of one acyl and three THF oxygen atoms, while the Na^+ ion has a highly distorted square-pyramidal environment comprised of the acyl oxygen, two carbonyl oxygens from symmetry related monoanions and two THF oxygen atoms.[225]

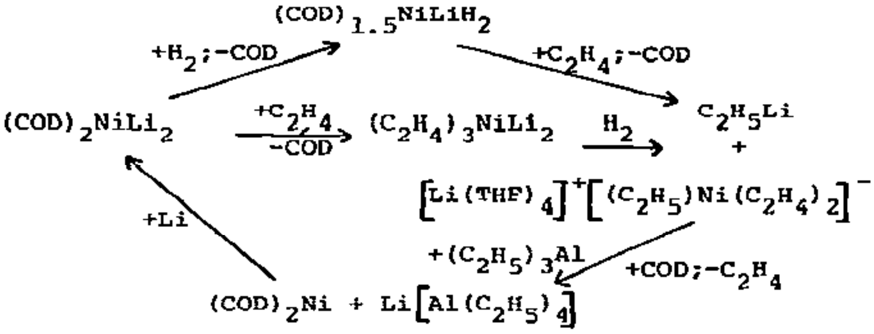
The synthesis of a number of bimetallic systems involving either lithium[226-233] or sodium[230] have been reported. Jonas et al. have described the preparation of some iron-lithium moieties according to Scheme 1.[226,227] They have also obtained the nickel-lithium derivative, of 1,5,9-cyclododecatriene, $[Ni(C_{12}H_{17}NiLi)_2]$-$(THF)_4$,[228] and have described the nickel(0) induced synthesis of



Scheme 1

COD = η^4-1,5-cyclooctadiene TMEDA = tetramethylethylenediamine.

ethyllithium from Li, H_2 and C_2H_4 using the nickel-lithium intermediates, $[COD_{1.5}NiLi_2H_2](THF)_x$ or $(C_2H_4)_3NiLi_2$ according to Scheme 2.[229]

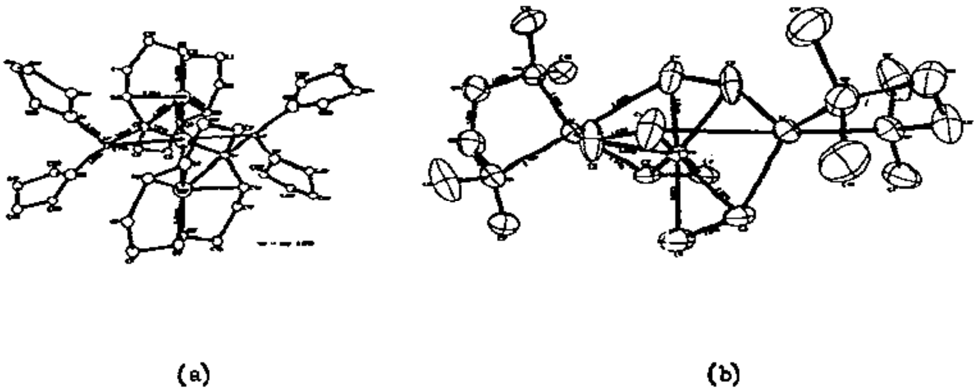


Scheme 2

Floriani et al. have shown that reduction of [N,N'-ethylenebis-(salicylideniminato)] cobalt(II), Co(salen), with Li and Na metal in THF, affords the bimetallic systems, [(Co(salen))NaTHF] and $[(Co(salen))Li(THF)_{1.5}]$. Blenkers et al.[231] and van Koten et al.[232-3] have independently described the preparation of Group 1B (Cu,Ag,Au)-lithium bimetallic systems of the type $Ar_4M_2Li_2$ by treatment of aryllithium compounds with either the appropriate aryl-Group 1B metal moiety[231-2] or the appropriate Group 1B metal halide (Cu or Ag) or halide phosphine complex (Br Au PPh_3).[232]

The crystal structures of several of these products, viz, $[(C_2H_4)_4FeLi_2(TMEDA)_2]$ (Figure 10a),[226] $[Ni(C_{12}H_{17}NiLi)_2(THF)_4]$, (Figure 10b),[228] $[(Co(salen))Li(THF)_{1.5}]$ (Figures 11a, 11b),[230] and $[(Co(salen))_2Na_2(THF)_2]$ (Figure 11c)[230] have been elucidated. The figures are generally self explanatory. In the structure of $[(Co(salen))Li(THF)_{1.5}]$, however, there are two different molecular complexes, $[(Co(salen))Li(THF)_2]$ and $[(Co(salen))_2Li_2(THF)_2]$ in a 2:1 ratio; these are shown in Figures, 11a and 11b, respectively.

Cryoscopic,[231] ^1H-and ^{13}C-n.m.r. spectroscopic[231-3] and ^{197}Au-Mössbauer data[232] for the $Ar_4M_2Li_2$ (M=Cu,Ag,Au) compounds, indicate that their structure in solution consists of aryl groups bridging one Group 1B metal and one lithium atom of a trans-M_2Li_2 core. Evidence is put forward for 3-centre 2-electron ArMLi bonding[233] and the observed interaggregate exchange between the tetranuclear



(a) (b)

Figure 10. Molecular structures of the bimetallic complexes (a) $[(C_2H_4)_4FeLi_2(TMEDA)_2]$ and (b) $[Ni(C_{12}H_{17}NiLi)_2(THF)_4]$, showing interatomic distances (in Å). (Reproduced by permission from Angew.Chem.Int.Ed.Engl., 18(1979) 550, 487)

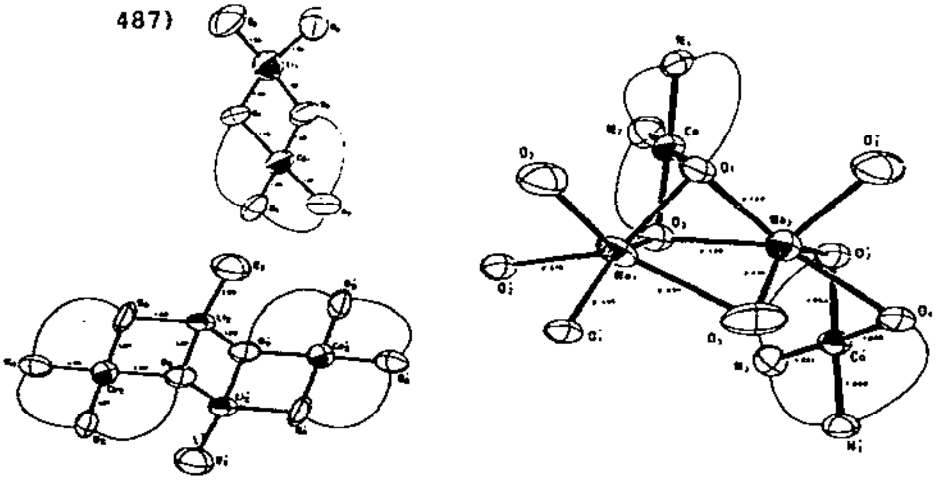


Figure 11. Partial drawings of the bimetallic complexes (a) $[(Co(salen))-Li(THF)_2]$, (b) $[(Co(salen))_2Li_2(THF)_2]$ and (c) $[(Co(salen))_2-Na_2(THF)_2]$ showing interatomic distances (in Å) for the coordination polyhedra around Li, Na and Co. The organic parts of the ligands are omitted for clarity. (Reproduced by permission from Inorg.Chem., 18(1979) 3469).

species is discussed in terms of an associative mechanism involving the formation of an octanuclear intermediate.[232]

1.6.5 Sodium Derivatives

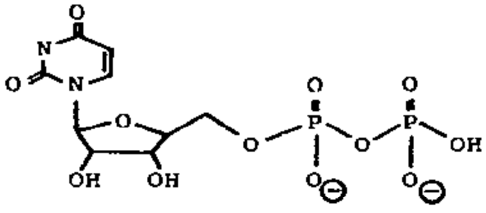
The crystal structures of the two sodium salts, sodium anilinemethanesulphonate monohydrate,[234] and disodium dihydrogen 1-hydroxyethylidenediphosphonate tetrahydrate[235] have been elucidated. The Na^+ cation in the sulphonate is in a distorted octahedral coordination sphere of oxygen atoms, furnished by two monodentate, r(Na...O) = 2.38, 2.46Å and one bidentate r(Na...O) = 2.38, 2.70Å sulphonate groups and two water molecules, r(Na...O) = 2.36, 2.42Å.[234] The diphosphonate contains two crystallographically distinguishable Na^+ cations; the coordination about Na(1), provided by the hydroxyl oxygen, r(Na...O)=2.45Å, two phosphate oxygen atoms from opposite ends of the same diphosphonate anion, r(Na...O) = 2.43, 2.45Å and three water oxygen atoms, r(Na...O) = 2.30-2.36Å, is nearly octahedral while the coordination about Na(2), provided by the same two phosphate oxygen atoms, r(Na...O) = 2.39, 2.86Å and three water oxygen atoms, r(Na...O) = 2.30-2.45Å, is approximately square pyramidal.[235]

Low temperature ^{13}C n.m.r. spectra of sodium salts of 2,4-pentanedione, 2,4-hexanedione, 3-methyl-2,4-pentanedione and 3-ethyl-2,4-pentanedione have been recorded;[236] resonances attributable to ZZ, EZ and ZE diastereoisomers or topomers were distinguishable at the temperatures at which the spectra were measured.

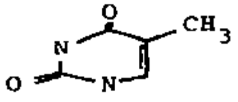
1.6.6 Potassium Derivatives

All the papers abstracted for this section describe the crystal and molecular structures of a diverse series of potassium salts.[238-243] The most contentious is that published by Pluth and Smith;[237] they have undertaken an accurate X-ray structure analysis of two crystals of dehydrated K^+-exchanged zeolite A and found no evidence for the supposed zero-coordinate K atom proposed by Seff et al.[244] Instead two small electron density peaks were observed opposite four oxygen atoms. The peak assigned to 0.5 atom of K(6) (0.5, 0.24, 0.24) is displaced into the main cage at ca. 2.8 and 3.0Å to two pairs of oxygen atoms. The peak assigned to 0.15 atom of K(7) (0.175, 0,0) is displaced into the sodalite cage at ca.3.0Å to four oxygen atoms. The other potassium atoms are 6.3K (1) (0.23, 0.23, 0.23), 3K(2) (0,0.47, 0.47) and 1.5K (4,5) (0.16, 0.16, 0.16). All K atoms lie within 3Å of several framework oxygen atoms, and although their coordinations are unusual, there is no evidence for zero coordination. An electron microprobe analysis yielded 11.8 Al and 12.2 Si per cell.[237]

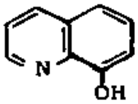
Six-coordinate K^+ ions have been observed in the dipotassium salt of uridine 5'-diphosphate trihydrate,[238] potassium thyminate trihydrate[239] and potassium quinolin-8-olate quinolin-8-ol (1/1).[240] There are significant differences in the six-fold coordination



uridine 5'-diphosphate



thyminic acid



quinolin-8-ol

spheres of the four non-equivalent K^+ ions in the uridine 5'-diphosphate;[238] K(1) is coordinated by two O(2) atoms of the uracil, r(K...O)=2.78, 2.84Å and the oxygen atoms of four water molecules, r(K...O)=2.83-2.88Å, while K(2), K(3) and K(4) are coordinated by oxygen atoms of the α and β phosphate groups, r(K...O) = 2.58-3.15Å. The K^+ coordination in the thyminate is distorted trigonal prismatic;[239] the six oxygen atoms, r(K...O)= 2.8Å (average), are provided by five water molecules and a thyminate anion. The 1/1 quinolin-8-olate-quinolin-8-ol adduct structure[240] consists of centrosymmetrical dimers, in which each K^+ ion is six-coordinated by a chelating anion, r(K...O) = 2.65Å, r(K...N)=2.82Å and by two chelated neutral molecules, r(K...O)=2.71, 2.78Å, r(K...N)=2.95, 3.00Å, the oxygen and the nitrogen atoms of the latter molecules being shared with the other K^+ ion in the dimer.[240]

In the crystals of the 1/2 quinolin-8-olate-quinolin-8-ol adduct, the K^+ ions are 7-coordinate, approximately in a pentagonal bipyramid, within the centrosymmetrical dimeric molecular structure.[240] The equatorial plane is formed by two nearly parallel chelating molecules, r(K...O)=2.76,2.84Å, r(K...N)=2.89Å, and by the nitrogen of the chelating anion, r(K...N)=2.89Å, the oxygen of which forms one apex of the bipyramid, r(K...O)=2.76Å. The other apex is occupied by a nitrogen atom of a neutral ligand in the other half of the dimer, r(K...N)=3.17Å. 7-coordinate K^+ has also been observed in the dicyandiamide adduct of the monopotassium salt of cyanamide[241] and in potassium methanehydroxysulphonate.[242] In the cyanamide derivative,[241] the monocapped trigonal prismatic geometry comprises three anion nitrile nitrogen atoms, two dimer nitrile nitrogen atoms and two dimer imino nitrogen atoms with r(K...N)=2.78-3.16Å. The K^+ coordination geometry in the sulphonate salt is approximately pentagonal pyramidal with r(K...O) =2.76-2.92Å.[242]

Potassium hydrogen bis(dibromoacetate)[243] comprises well defined dimeric anions, $H(Br_2CHCOO)_2^-$, and K^+ ions with 6+2 coordination provided by four non-bridging oxygen atoms, r(K...O)=2.76, 2.85Å, and four bridging oxygen atoms, r(K...O)=3.01, 3.89Å.

1.6.7 Rubidium and Caesium Derivatives

$Rb_2(TCNQ)_3$ has been shown to be isostructural with $Cs_2(TCNQ)_3$ in an X-ray crystallographic study at 113K.[245] The Rb^+ cations lie in linear arrays perpendicular to (010) and are surrounded by edge-sharing cubes of eight nitrogen atoms, $r(Rb...N_t)$=3.01Å, $r(Rb...N_b)$=3.26Å (N_t and N_b refer to terminal and bridging nitrogen atoms, respectively).

The rubidium salt of the recently identified fluoroxysulphate anion, $FOSO_3^-$,[246] and the rubidium and caesium salts of bis(trifluoromethanesulphonyl)methane[247] have been characterised by single crystal X-ray diffraction techniques. In the fluoroxysulphate derivative, each Rb^+ cation is coordinated to nine oxygen atoms, r(Rb...O)=2.96-3.30Å, and two fluorine atoms, r(Rb...F)=3.17,3.26Å.[246] The two salts of bis(trifluoromethanesulphonyl)methane have been shown to be isomorphous; the coordination geometry of the cation is highly irregular with seven oxygen atoms, r(Rb...O)=2.85-3.45Å and one carbon atom r(Rb...C)=3.62Å coming from six different anions.[247]

The reported synthesis of the caesium salts of CO_2F^- and of $CO_2F_2^{2-}$ has been challenged;[248] a careful re-examination of the reported reactions of CO_2 and NO_2F with CsF and of Cs_2O with COF_2 was singularly unsuccessful.

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