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Chapter 1

ELEMENTS OF GROUP 1

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1.1 INTRODUCTION

The widespread use of the alkali metals as simple counter-cations complicates the definition of the limits of the literature search pertinent to this review. In general, only those data relevant to a number of broad subject groups, in which the role of the alkali metals is unique, have been abstracted. Consequently the format of this Chapter is such that the chemistry of these elements is considered collectively in sections which reflect topics presently of interest and importance.

For certain subjects (eg. cation solvation, molten salts, crown and cryptate complexes), the chemistry of the Group I and II metals is closely interwoven; in these cases, the data abstracted are discussed once only in the relevant section in this Chapter.

The organometallic chemistry of lithium[1] and that of the heavier alkali metals (Na - Cs)[2] has been the subject of separate annual surveys for the year 1977; structural and spectroscopic studies, preparative techniques and chemical characteristics are discussed in detail.

1.2 THE ELEMENTS

1.2.1 General Properties

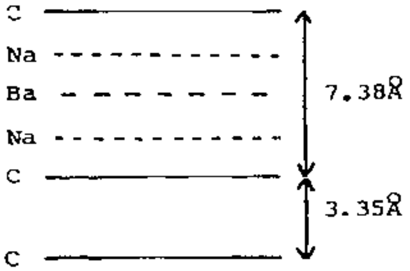
The lattice parameter (a_o) of potassium has been determined ($279 \leqslant T/K \leqslant 333$) by neutron scattering spectrometry;[3] the value quoted at 273K is 5.32691 ± 0.00034Å.

Theoretical calculations of the equilibrium geometries and electronic structures of the dimers, Li_2[4,5] and Be_2[4] and of the trimers, Li_3, Li_2Na, Na_3, Na_2K, K_3 and Cs_3,[6] have been effected using a variety of models; the trimers are most stable in the linear symmetric configuration.[6]

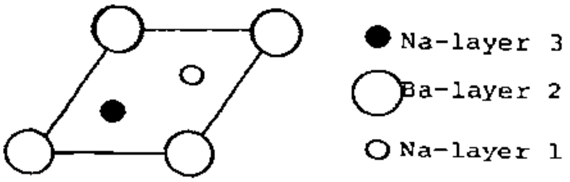
The major products of the reaction of lithium vapour with benzene and with halobenzenes are polylithiated compounds;[7] nevertheless measurable quantities of multi-substituted benzenes, $C_6H_{6-n}Li_n$ ($1 \leqslant n \leqslant 3$) are produced. Experiments under extreme reaction conditions give evidence for the production of small quantities of lithium substituted species with cyclohexene and cyclohexane structures.

Margrave et al.[8-10] have undertaken matrix isolation studies of the reactions of lithium atoms with H_2O,[8] NH_3,[8] SiF_4,[9] UF_4[10] and UF_6[10] and of the heavier alkali metals (Na,K,Cs) with UF_4 and UF_6;[10] the products of the reactions have been characterised by e.s.r.[8,9] and i.r.[10] spectroscopy. Whereas 1:1 and 1:2 molecular complexes are formed in the Li:H_2O system, the Li:NH_3 system only exhibits a 1:1 complex; the stability of the complexes is attributed to the sharing of the Lewis base lone pair electrons with lithium.[8] Diamagnetic silicon difluoride and a paramagnetic species, either the silicon difluoride diradical or the silicon difluoride anion, are formed in the Li:SiF_4 system.[9] MUF_n (M = Li,Na,K,Cs,$4 \leqslant n \leqslant 7$) moieties are formed in the reactions of the alkali metal atoms with UF_4 and UF_6.[10]

A new type of graphite intercalation compound containing both sodium and barium has been prepared;[11] several different stages of intercalation were observed. X-ray diffraction analysis of the second stage compound (the one richest in metal with C/(Na+Ba) = 7 or 8) is consistent with an intercalated triple metallic layer consisting of a sheet of barium atoms sandwiched between two outer sheets of sodium (1); furthermore, this intercalated sub-layer is hexagonal and parallel to that of the graphite (2).



(1)



(2)

The reactivity of C_8K towards organic substrates has been investigated in detail;[12] it undergoes reaction by both one- and two-electron processes. The reaction of weak protic acids (e.g. H_2O,ROH) with C_8K proceeds both *via* simple deprotonation of the acid to give a partially reduced graphite, and by reduction leading to hydrogen formation. Study of the products formed on reaction of alkyl halides with C_8K shows that one-electron transfer is an important reaction pathway for reductions with C_8K. The acid-base chemistry of the corresponding rubidium and caesium intercalates was shown to be similar to that for C_8K.[12]

1.2.2 The Alkali Metals as Solvent Media

Several papers, in which aspects of the solution chemistry of both lithium[13,14] and sodium[15,16] are described, have been published; interest in these topics is maintained by their relevance to nuclear reactor technology. Reaction between Li_3N and excess Li_2C_2 in liquid lithium at 673K gave crystalline Li_2NCN.[13,1 This reaction is of considerable importance since the NCN^{2-} anion is thought to be the first example of a covalently bonded polyatomic anion stable in the presence of liquid lithium. The product, which was also formed (but as a powder) in the high temperature (873K) solid state reaction between Li_3N and Li_2C_2,[14] was characterised by single crystal X-ray diffraction techniques. Modified preparative routes to crystalline Li_3N (obtained from Li-Na solutions by reaction with gaseous nitrogen at 673K) and to Li_2C_2 (obtained by a reaction at 873K of liquid lithium with graphite) are also described in detail.[14]

The solubility of NaH in liquid sodium has been determined by resistivity techniques.[15] When the results are combined with data from equilibrium pressure-composition isotherms, solubility equation (1) is obtained.

$$\log_{10}(\text{mol \% H}) = 4.82 - 3600/T \qquad 613 \leqslant T/K \leqslant 673 \qquad (1)$$

These results corroborate the composite solubility equation (2) formulated in a recent review.[17]

$$\log_{10}(\text{mol \% H}) = 4.44 - 3380/T \qquad 453 \leqslant T/K \leqslant 673 \qquad (2)$$

The overall phase relationships in the sodium, NaH, NaOH, Na_2O system have been elucidated by studying, as a function of composition, the variation in the equilibrium pressure of hydrogen over sodium solutionsin the presence of these salts.[16] The isothermal sections (633, 673, 723K) of the pseudo-quaternary system so derived indicate that the two liquid phases, i.e. metallic and hydroxide, can coexist in either the presence or absence of either of the two solid phases, i.e. NaH and Na_2O. An unusual feature of the data is that the solid solution based on Na_2O is very extensive at the higher temperatures but is quite restricted at 633K.[16]

The electrical resistivity of solutions of NaH ($613 < T/K < 703$) and of Na_2O (T = 673K) in liquid sodium has also been determined.[15] The relative increase in the resistivity of the sodium caused by the two solutes is thought to reflect the difference in size of the solvated anions.

1.2.3 Metallic Solutions and Intermetallic Compounds

A survey[18] of the formulae of binary intermetallic compounds has shown that the vast majority contain not more than five atoms and can be classified as one of the following nine types: A_4B, A_3B, A_2B, A_3B_2, AB, A_2B_3, AB_2, AB_3 and AB_4. In most of these compounds the number of valence electrons per molecule is an even number, not exceeding 16. A surprising observation is the frequent occurrence of A_xB_y and A_yB_x intermetallics in an A-B system; typical examples are: Na_2Au, $AuNa_2$; Na_3Sn, $NaSn_3$; Be_2Ta, $BeTa_2$; Sr_3Ag_2, Sr_2Ag_3. The minimum internuclear distance in AB intermetallics with $CsC\ell$-type structure has also been reviewed.[19]

Lithium rich ($1.00 \geq x_{Li} \geq 0.40$) phases have been studied in the Li-B phase system using density, electrical resistance and hall coefficient measurements.[20] The data were analysed on the assumption that the alloys contained lithium and two lithium-rich phases, Li_3B and Li_5B_4. A crystal structure has been proposed for Li_5B_4.[21] It is rhombohedral, R3m, with a = 4.93Å, α = 90° but it is disordered in such a way that its long range symmetry is b.c.c., $I\bar{4}3m$, with a = 4.93Å. Within the short range order, four boron atoms form trigonal planar clusters; the lithium atoms cluster in trigonal bipyramids with five atoms at the vertices (c.f. the configuration found in the low temperature hexagonal structure of lithium).

The thermodynamic properties of the Na-Tℓ,[22] Li-Sb[23] and Li-Bi[23] systems have been evaluated. Those of the Na-Tℓ system have been interpreted satisfactorily using the model of associated solutions; the compound NaTℓ has the main influence on the thermodynamics of the system.[22] The Gibbs free energy of formation (ΔG_f^o) and corresponding enthalpies (ΔH_f^o) and entropies (ΔS_f^o) for intermetallic phases in the Li-Sb and Li-Bi systems have been determined.[23] Values (at 673K) are quoted in Table 1.

Table 1. Thermodynamic Parameters for Li_2Sb, Li_3Sb, LiBi and Li_3Bi at 673K[23]

	Li_2Sb	Li_3Sb	LiBi	Li_3Bi
$\Delta G_f^o/kJ.mol^{-1}$	-176.0	-260.1	-76.0	-215.3
$\Delta H_f^o/kJ.mol^{-1}$	-220.4	-325.2	-108.9	-293.5
$\Delta S_f^o/J.K^{-1}.mol^{-1}$	-66	-97	-49	-116

The stoichiometry ranges for $Li_{3+\delta}X$ (X = Sb or Bi) have also been investigated; whereas that for $Li_{3+\delta}Sb$ is very narrow, that for $Li_{3+\delta}Bi$ is fairly large ($\Delta\delta$ = 0.22), predominantly on the lithium deficit side.[23]

An analysis of the thermodynamic properties of liquid Na-Sn solutions ($523 \leqslant T/K \leqslant 723$, $0.0 \leqslant x_{Na} \leqslant 0.3$) indicates that the solutions are strongly ordered and of partial ionic character.[24] ^7Li and ^{115}In Knight shifts and the electrical resistivity of a number of Li-In solutions ($1.0 \geqslant x_{Li} \geqslant 0.0$) indicate the possible formation of a loosely bound Li_3In compound in the liquid phase.[25] The electrical resistivity of Na-Sr solutions ($373 \leqslant T/K \leqslant 773$, $1.00 \geqslant x_{Na} \geqslant 0.62$) has also been investigated;[26] there is no indication of the formation of any compounds in this system.

1.3 CATIONIC SOLVATION

Cationic solvation both in the gas phase and in solution is only of peripheral interest to the inorganic chemist. Consequently, for this section of the review the papers abstracted were restricted to those in which structural or spectroscopic aspects of the subject are discussed.

1.3.1 Solvation in the Gas Phase

The equilibrium geometries and electronic structures of the monoligand clusters, $Li(H_2O)^+$, $Li(NH_3)^+$ and LiN_2^+ have been assessed using a FSGO model.[27] For LiN_2^+, the perpendicular complex is predicted to be more stable than the linear one. The predicted geometries of the other two moieties are as expected, the binding energies of the Li...O and Li...N bonds being in good agreement with other theoretical estimates.[27]

Gas phase binding energies of Li^+ to a number of simple Lewis bases have been determined by ion-cyclotron resonance spectroscopy.[28] The strength of the Lewis bases increase in the order: $H_2O < H_2CO < HCN < C_6H_6 < MeOH < Me_2O < NH_3 < MeNH_2 < Me_3N < Me_2NH$. The observation of a non-regular methyl substitution effect on the binding energies for methyl substituted ammonia derivatives is unusual. An even more pronounced inversion was noted, however, for the interaction of these Lewis bases with the more complex acids $cpNi^+$ and BMe_3. The binding energies of a number of Lewis acids to NH_3 were also determined.[28] The strength of the Lewis acids vary in the order: $H^+ > CH_3^+ > cpNi^+ > Li^+ > K^+ > BMe_3$. Similar, but less extensive, conclusions were reached in a high pressure mass spectrometric study of the thermochemical properties of alkali metal cations solvated by NH_3.[29] Investigation of the equilibria (3) led to the enthalpies and entropies of the clustering reactions.

$$M^+(NH_3)_n + NH_3 \rightleftharpoons M^+(NH_3)_{n+1} \qquad (3)$$

Comparison of the data for the monoligand clusters with similar data for H_2O clusters, shows that NH_3 bonds more strongly than H_2O for all alkali metal ions. Furthermore, the relative bond strength of NH_3 to the various alkali metal cations varies inversely with their size. In the ammonia clusters, Li^+ and Na^+ display a tendency for a preferred first solvation shell coordination number of 4; a similar tendency is not observed for K^+ and Rb^+.[29]

Standard free energies of equilibria (4) have been computed

$$M^+(H_2O)_n + H_2O \rightleftharpoons M^+(H_2O)_{n+1} \qquad (4)$$

using the liquid drop theory.[30] Using generally accepted ionic radii[31] (Li^+, 0.68; Na^+, 0.97; K^+, 1.33; Rb^+, 1.47; Cs^+, 1.67Å), values are obtained which agree reasonably well with experiment, especially for $n > 3$. If, however, the ionic radius is computed as an empirical parameter (Na^+, 0.98; K^+, 1.75; Rb^+, 2.00; Cs^+, 2.35Å) then a near perfect fit is obtained for all values of n for Na^+ to Cs^+.[30]

1.3.2 Solvation in Solution

The use of ^{23}Na n.m.r. spectroscopy in solvation studies has been reviewed.[32] It affords direct insight into solvation and ion-pairing phenomena, by giving access to, inter alia, binding constants, reorientational correlation times and the microdynamics of the sodium coordination shell.

A new model for hydration of electrolytes has been developed[33] from which it is possible to predict hydration numbers for the electrolyte from vapour pressure measurements; the theory has been applied to $KC\ell$ solutions. Thermodynamic parameters of aqueous electrolytes have been calculated by two groups of authors using simple electrostatic models.[34,35] Extension of one of the models[35] to include non-aqueous solvents shows that the first solvation layer of an ion in a non-polar solvent is no smaller than that in a polar solvent.

Solvation of ions in water has been the subject of both i.r.[36] and n.m.r.[37] studies of the glasses formed from aqueous electrolyte solutions. Low temperature i.r. studies[36] of glasses formed from solutions using dilute solutions of HOD in D_2O as solvent has shown that the spectroscopic properties of H_2O molecules bound to the cations are dominated by the other H_2O molecules to which each is hydrogen-bonded. The results of ^{2}H n.m.r. experiments[37] in the liquid and glassy states of concentrated aqueous solutions of $LiC\ell$ in D_2O (concn. range: $LiC\ell$:D_2O varies from 3.5 to 6.3) have been interpreted to show that the solutions have similar structures to the corresponding glasses. Small clusters of $Li^+(H_2O)_4C\ell^-$ are thought to exist with excess water incorporated interstitially and having dynamic properties remarkably similar to those of bulk water.

Preferential solvation of electrolytes in H_2O-cosolvent systems has been investigated using both nuclear magnetic relaxation[38-40] (^{1}H, ^{23}Na and ^{87}Rb) and n.m.r. chemical shift (^{133}Cs) techniques. Preferential incorporation of H_2O into the cation's solvation sphere is indicated for Na^+ in H_2O-MeOH,[38] K^+ in H_2O-MeOH,[39,40] Rb^+ in H_2O-MeOH,[38-40] Rb^+ in H_2O-DMF,[38] Cs^+ in H_2O-DMF[41] and Mg^{2+} in H_2O-MeOH[39,40] mixed solvent systems. Evidence for significant incorporation of DMSO, from H_2O-DMSO mixed solvent systems, into the solvation sphere of Na^+[38] has also been obtained. Structural features of solutions of alkali metal chlorides (M = Li,Na,K,Rb,Cs) in the H_2O-DMSO mixed solvent system have also been elucidated using e.m.f. techniques;[42] the data suggest there is considerable incorporation of DMSO molecules into the solvation shells of Li^+.

^1H n.m.r. studies of the solvation of Mg^{2+} in MeOH and in MeOH-cosolvent mixtures has shown that strongly basic solvents such as DMF and DMSO progressively displace MeOH molecules from the Mg^{2+} cation solvation shell.[43]

A new method for the determination of the solvation number of Na^+ in non-aqueous polar solvents, has been presented.[44] It is based on the distribution of a donor solvent between two liquid phases - benzene (or cyclohexane) containing $Na[AlEt_4]$ and the donor solvent. The distribution is strongly affected by solvation with the salt; a solvation number of 6 is obtained with THF, DMSO, pyridine and dimethoxyethane.

The influence of N-substitution on the solvation interaction of amides with alkali- and alkaline earth-metal ions has been studied using ^7Li ^9Be and ^{23}Na n.m.r. techniques.[45] The observed shifts were discussed in terms of the donor abilities of the solvents.

The interactions, in polar aprotic solvents, of alkali metal thiocyanates have been studied using both n.m.r.[46]and vibrational spectroscopic[47] techniques. Analysis of the results of ^7Li and ^{15}N n.m.r. studies[46] of the association of Li^+ with SCN^- in DMF, THF, ether and dimethylcarbonate indicates that a free ion - ion pair equilibrium occurs in DMF and a free ion - ion pair - dimerization quilibrium occurs in ether and dimethylcarbonate; in all three solvents N-bonded species are formed. In THF, however, equilibrium between ion pairs, dimers and S-bonded species occurs. The occurrence of Li...S interactions in THF is attributed to its higher dielectric constant with respect to the other solvents.[46] I.r. and Raman spectra of the ion pairs MNCS (M = Li,Na,K,Rb,Cs) in DMF have been measured;[47] force constant calculations have been undertaken using a solvated ion pair model.

1.4 MOLTEN SALTS

Recent interest in the field of molten salts has centered on their structural characteristics and on their solution chemistry (particularly that of $LiC\ell$-$KC\ell$, $NaC\ell$-$A\ell C\ell_3$ and $LiNO_3$-KNO_3 mixtures). The spectroscopic properties (i.r., Raman, e.s.r. and n.m.r.) of molten salts have been reviewed.[48]

1.4.1 Structural and Thermodynamic Properties

The development of X-ray diffraction techniques for the study of high temperature liquids has resulted in structural analyses for molten halides,[49-52] sulphates[53] and nitrates;[54] the analysis is based on the derivation of the radial distribution functions for the liquid from X-ray diffraction data. Two groups of Russian authors[49,50] have established that the structure of molten individual alkali metal halides, at temperatures close to their melting points, is not homogeneous but can be described in terms of a cluster model. The short range order in the clusters is reminiscent of the ionic packing in the corresponding crystals, i.e. $NaC\ell$- or $CsC\ell$-type. Russian workers[51] have also studied the structures of molten binary mixtures of alkali metal halides e.g. $NaC\ell$-$KC\ell$, KI-CsI. Their analysis of the X-ray diffraction data indicates that the ions are randomly distributed in these melts. Molten $LiC\ell$, $PbC\ell_2$ and their mixtures have been examined in detail by a group of Japanese authors.[52] The Li^+ cations in molten $LiC\ell$ are coordinated by four $C\ell^-$ anions at a Li...Cℓ peak position of 2.40Å. Addition of $LiC\ell$ to molten $PbC\ell_2$ leads to a decrease in the coordination of the lead atoms, from 8 (for pure $PbC\ell_2$) to 6 (for $LiC\ell$, $PbC\ell_2$); there is little evidence for the presence of the rigid pyramidal $PbC\ell_3^-$ anion in these solutions.[52]

The Japanese authors have also undertaken structural analysis of the molten alkali metal sulphates, Li_2SO_4, Na_2SO_4 and their mixtures[53] and of the molten alkali metal nitrates.[54] The existence of the tetrahedral SO_4^{2-} and trigonal planar NO_3^- ions in these melts has been demonstrated. A close packed arrangement of SO_4^{2-} ions seems to be the configuration realised in molten Li_2SO_4. In molten Na_2SO_4, Na^+ ions probably occupy a position intermediate between the edge and face sites of the SO_4^{2-} ion.[53] Molten MNO_3 (M = Na,K,Rb,Cs) may have a diamond- (or zinc blende-) like arrangement of NO_3^- anions and M^+ cations with 25% random vacancies, whereas $LiNO_3$ could have a simple cubic-(or $NaC\ell$-)type arrangement of ions.[54] Appropriate M...O, M...S and M...N distances are quoted for all sulphates and nitrates studied.

Thermodynamic parameters for the molten alkali metal nitrates have been derived from P-V-T relationships ($500 \leq T/K \leq 800$, $p \leq 1400$ kbar). Thermodynamic properties of liquid mixtures of AF(A = Li,Na,K) with BF_2(B = Mg,Sr,Ba)[57] and with AlF_3[58] and of ABr(A = Na,K) with BBr_2(B = Ca,Sr,Ba)[59] have been derived from calorimetric[57,58] and e.m.f. measurements,[59] respectively. Enthalpies of formation of the solid phases, $AMgF_3$ (A = Na,K) and $A_3A\ell F_6$ (A = Li,Na,K) are included in Table 2. In the case of the fluoroaluminates the $A\ell F_6^{3-}$ ion is thought to exist in the liquid mixture.[58] Thermodynamic properties of the $KC\ell-AgC\ell$,[60] $LiC\ell-ZnC\ell_2$,[61] $NaC\ell-YC\ell_3$,[62] and $MC\ell-GdC\ell_3$ (M = Na,K,Cs)[63] molten salt mixtures have also been investigated.

Table 2. Enthalpies of formation (ΔH_f^o) for a number of ternary fluorides

$AF + MgF_2$ $AMgF_3$			$3AF + A\ell F_3$ $A_3A\ell F_6$		
Fluoride	T/K	ΔH_f^o/kJ.mol^{-1}	Fluoride	T/K	ΔH_f^o/kJ.mol^{-1}
			$Li_3A\ell F_6$	298	-19.08
$NaMgF_3$	1300	-12.1	$Na_3A\ell F_6$	298	-74.22
$KMgF_3$	1130	-22.6	$K_3A\ell F_6$	298	-118.0

1.4.2. Solution Properties

The behaviour of hydrogen in LiF-NaF-KF molten eutectic mixtures has been investigated.[64] Whilst studying the diffusion coefficient and the solubility of hydrogen in the melt (723 ⩽ T/K ⩽ 923), the production of CH_4, presumably by reaction of hydrogen with carbon impurity in the molten mixture, was observed.

A number of reactions have been studied in the $LiC\ell-KC\ell$ eutectic molten salt.[65-68] Interpretation of electronic absorption spectra[65] has shown the dominant telluride species present in this medium (and $LiF-BeF_2$ molten salt mixtures) to be the Te^- ion, formed presumably via reaction (5); the presence of higher tellurides

$$Li_2Te(c) + \tfrac{1}{2}Te_2(g) \rightarrow 2Li^+(soln.) + 2Te^-(soln.) \qquad (5)$$

such as Te_3^- is also suggested. Hydrolysis of Cr(III) in $LiC\ell-KC\ell$ mixtures occurs via a 3-stage process.[66] The initial stage involves reversible hydrolysis to form $[CrC\ell_3(OH)]^{3-}$; this is followed by a slower polymerisation reaction to form a bridged species such as $[C\ell_5Cr-O-CrC\ell_5]^{6-}$. The process culminates in irreversible formation of an insoluble chromium (III) oxychloride phase. Redox reactions of Cr(III)/Cr(II), Fe(III)/Fe(II), Cu(II)/Cu(I), Pt(IV)/

Pt(II) and Eu(III)/Eu(II) have been studied at n-type semiconducting SnO_2 electrodes in LiCℓ-KCℓ melts. (T = 723K).[67] The reactions are found to be reversible, indicating no effect of electron depletion on the electron transfer kinetics. The solubility of Li_2S and the solubility product of FeS have been determined in LiCℓ-KCℓ melts ($673 \leqslant T/K \leqslant 773$).[68] During operation of the cells at relatively high S^{2-} concentrations, the complex phases Li_2FeS_2 and $LiK_6Fe_{24}S_{26}C\ell$ are formed; these phases are shown to have marginal stabilities in this melt.[68]

Aspects of the chemistry of sulphur,[69] selenium[70] and tellurium[71] in solution in NaCℓ-$A\ell C\ell_3$ melts have been elucidated. In an electronic absorption spectrophotometric study[69] of the oxidation of sulphur by chlorine in these melts, four different cationic sulphur species were observed; the most probable formulations for these moieties are S^{4+}, S^{2+}, S_2^{2+} and S_4^{2+} (ie. sulphur in oxidation states IV, II, I and ½). The electrochemistry of selenium,[70] $SeC\ell_4$[70] and $TeC\ell_4$[71] in NaCℓ-$A\ell C\ell_3$ melts has been investigated by a variety of techniques. Selenium can be reduced in both basic and acidic melts by a single 2 electron step to selenide which exists in the melt as either AℓSeCℓ or $A\ell SeC\ell_2^-$ (or the analogous solvated species, $A\ell_2SeC\ell_5^-$ or $A\ell_2SeC\ell_6^{2-}$) depending on the acidity.[70] The Se-Se(IV) oxidation mechanism is dependent on melt acidity. In acid melts oxidation occurs in a single 4-electron step; in basic melts, however, it occurs in 2-electron steps via Se(II). Reduction of Se(IV) to Se always occurred in a single 4-electron step. In a study of $SeC\ell_4$ solutions it was found that two Se(IV) species exist in the melt, $SeC\ell_6^{2-}$ and $SeC\ell_5^-$, linked by the acidity dependent equilibrium (6). Tellurium(IV) exists in NaCℓ-$A\ell C\ell_3$

$$SeC\ell_5^- + C\ell^- \rightleftharpoons SeC\ell_6^{2-} \qquad (6)$$

melts as $TeC\ell_3^+$.[71] Reduction of this species is dependent on the acidity ofthe melt. In the most basic melts, reduction to Te occurs via a soluble Te(II) species, i.e. via two 2-electron steps; in more acidic melts, however, reduction occurs via a 4-electron step. Elemental tellurium undergoes a complexation reaction with Te(IV) to form Te_4^{2+}. The mechanism of this reaction has been investigated in detail; it is thought to occur via reactions (7) and (8).[71]

$$TeC\ell_3^+ + Te \longrightarrow 2TeC\ell^+ + C\ell^- \quad (7)$$

$$TeC\ell^+ + 3Te \longrightarrow Te_4^{2+} + C\ell^- \quad (8)$$

The electrochemical reduction scheme of Cr(III) at a glassy carbon electrode in $NaC\ell$-$A\ell C\ell_3$ solutions has been established:[72] it occurs in two successive steps (to Cr(II) and Cr metal, respectively). The results also indicated that a reversible chemical step, in which an electroactive species was produced, preceded the electron transfer; the exact identity of this step could not be ascertained.[72]

The i.r. emission spectra of the $A\ell C\ell_4^-$ ion in $MC\ell$ (M = Li,Na,K)-$A\ell C\ell_3$ melts have been reported.[73]

Several features of the chemistry of nitrite and nitrate molten salts have been investigated.[74-79] Controversy still surrounds the nature of the basic species in these melts. Further data on this problem has now been obtained, however, by studying equilibrium (9) in a $NaNO_2$-KNO_2 eutectic medium.[74] Experiments in glass,

$$NO_2^- + O_2^{2-} \rightleftharpoons NO_3^- + O^{2-} \quad (9)$$

zirconium and platinum containers point to the strong possibility of the formation of peroxynitrate anions in the medium.

The behaviour of Co, Ni and Cu (in nitrite melts)[75] and of Co,[76] Pt,[77] Ag[78] and Ca[79] (in nitrate melts) has been examined. Co(III) (as $Na_3[Co(NO_2)_6]$ or $[Co(NH_3)_6]C\ell_3$) reacts with both $LiNO_2$-KNO_2 eutectic[75] and $LiNO_3$-KNO_3 eutectic,[76] ultimately producing Co_3O_4. In the nitrite melts, reaction occurred via the more stable complex, $K_3[Co(NO_2)_6]$, whereas in the nitrate melts, the intermediate products included CoO (from the nitro-complex) and $CoC\ell_2$ and $NH_4C\ell$ (from the ammino-complex); the Co(II) moieties are readily oxidised to Co_3O_4 by the nitrate melt. Electronic absorption spectra of the solutions formed on dissolving $CuSO_4$ and $NiC\ell_2$ in $LiNO_2$-KNO_2 eutectic at 393K indicate the formation of moieties containing both nitro- and nitrito- ligands (i.e. $[Cu(NO_2)_4(ONO)_2]^{4-}$ and $[Ni(NO_2)_3(ONO)_3]^{4-}$). At higher temperatures the cations are precipitated as the oxides by Lux-Flood acid-base reactions with the medium. The preoxidised platinum electrode has been shown to respond to the presence of CO_2 and of CO_3^{2-} in pure $NaNO_3$ or KNO_3 at 623K;[77] the electrode reaction (10) was established. The solubility equilibrium (11) of Ag_2O in molten

$$Pt + CO_3^{2-} \longrightarrow PtO + CO_2 + 2e \tag{10}$$

$$\tfrac{1}{2}Ag_2O(c) + \tfrac{1}{2}H_2O(soln.) \rightleftharpoons Ag^+(soln.) + OH^-(soln.) \tag{11}$$

$LiNO_3$-KNO_3 $(0.30 \leqslant x_{LiNO_3} \leqslant 0.59;\ 415 \leqslant T/K \leqslant 525)$ in the presence of water at controlled activity, has been investigated by e.m.f. methods.[78] Electrochemical and calorimetric studies of the behaviour of calcium in molten nitrates ($LiNO_3$, KNO_3 and their mixtures) have shown that a protective surface film (probably oxide) is generated on the metal, which prevents further reaction.[79] In the presence of halide impurity salts, however, reaction (12)

$$14Ca + 6NO_3^- \longrightarrow 14CaO + 2N_2 + N_2O + 3O^{2-} \tag{12}$$

occurred quite readily; it is assumed that the protective film is depassivated by the displacement of NO_3^- ions by X^- ions.[79]

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; that which has been published, however, is mainly associated with oxides and halides. The range of ternary compounds considered is restricted to avoid unnecessary duplication with other chapters of this review; thus, the majority of the data abstracted for this sub-section describe the chemistry of ternary oxides, chalcogenides, hydrides and halides containing alkali- and either alkaline earth- or transition-metals.

1.5.1 Hydrides

Theorectical calculations have been undertaken for NaH,[80,81] KH[81] and the pathways associated with the formation and dissociation of Li_2H.[82] Using a minimal basis INDO method, developed for molecules containing elements from Na to Cℓ, molecular parameters for NaH (as well as Na_2, NaF and NaCℓ) have been computed.[80]

Unfortunately these molecules are predicted to have lower bond lengths than experimentally determined; the magnitude and variation in dipole moment, however, is correctly predicted. The extent of interaction between ionic and covalent configurations of NaH and KH has also been assessed.[81] Analysis of reaction (13) has revealed extensive charge transfer intermediates of the type $Li_2^+ ... H^-$ and

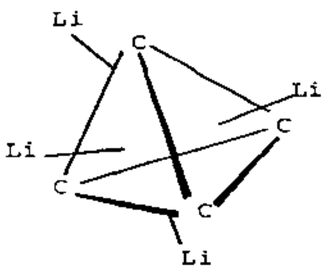
$$H + Li_2 \rightleftharpoons Li_2H \rightleftharpoons LiH + Li \qquad (13)$$

$Li^+ ... LiH^-$.[82] Calculations of a number of parameters of isotopic LiH crystals (^6LiH, ^7LiH, ^6LiD and ^7LiD) have also been effected.[83]

The reaction (in THF) of LiH and NaH with representative trialkylboranes (Et_3B, $n\text{-}Bu_3B$, $i\text{-}Bu_3B$, $sec\text{-}Bu_3B$) of increasing steric requirements has been examined in detail.[84] It proceeds in 1:1 stoichiometry; the products of the reaction, alkali metal trialkylborohydrides have been characterised by chemical analysis, i.r. and ^{11}B n.m.r. spectroscopy. The rate of the reaction is strongly influenced by the steric requirements of the trialkylborane; furthermore NaH exhibits greater reactivity than LiH in these reactions.

1.5.2 Carbides, nitrides, cyanides, etc.

A monomeric substance of empirical formula C_4Li_4 has been obtained by irradiation of Li_2C_2 in liquid NH_3 at 228K.[85] The white powder, which is sensitive to air and moisture, decomposes slowly at room temperature but is stable under argon at 253K. ^{13}C n.m.r. and field-desorption mass spectra are compatible with a derivative of the long-sought species tetrahedrane. Ab initio M.O. calculations on isolated C_4Li_4 isomers show the face-centered structure (3), with Li atoms on the faces of a tetrahedron of C



(3)

atoms, to be more favourable than other structures of high symmetry. This structure is reminiscent of the X-ray structure of Me_4Li_4.[85]

The free energy and entropy of formation of Li_3N ($\Delta G^o_f(Li_3N,c,298.15K) = -(128.6 \pm 1.10)kJ.mol.^{-1}$, $\Delta S^o_f(Li_3N,c,298.15K) = -(120.46 \pm 0.54)J.K.^{-1} mol.^{-1}$) have been derived[86] from a study ($5 \leq T/K \leq 350$) of the heat capacity of a well characterised sample of Li_3N using recently determined enthalpy data ($\Delta H^o_f(Li_3N, c,298.15K) = -(164.56 \pm 1.09)kJ.mol.^{-1}$).[87] Structural and chemical aspects of a number of alkali metal azides MN_3 (M = Li,Na,K,Rb,Cs) have been elucidated from studies of their magnetic[88] and thermochemical properties.[89]

The room temperature crystal structure of $NaCN,2H_2O$ has been refined.[90] It is monoclinic, $P2_1/a$, a = 6.622, b = 10.561, c = 6.064Å, β = 103.06°. The results are generally in agreement with those of a recent 150K study,[91] except that the CN groups appear to be partially disordered at room temperature. High pressure Raman spectra of NaCN and KCN have been measured;[92] characterisation of the various polymorphs of these compounds was readily achieved using this spectroscopic technique. A computer simulation of the molecular dynamics of liquid KCN has also been carried out;[93] good agreement between computed and experimentally determined thermodynamic data has been obtained.

In a study of the alkali metal salts of cyanamide (H_2NCN), the crystal structures of Li_2NCN[94,95] (tetragonal, I4/mmm, a = 3.687, c = 8.668Å) and of NaHNCN[96] (orthorhombic, Pbcm, a = 3.531, b = 10.358, c = 6.486Å) have been determined. In Li_2NCN, the Li^+ cation is surrounded by four nitrogen atoms in a distorted tetrahedral environment (r(Li...N) = 2.068Å). The larger Na^+ cation, in NaHNCN is surrounded by four nitrile-nitrogen atoms (r(Li...N) = 2.495, 2.693) and 2 ammino-nitrogen atoms (r(Li...N) = 2.483) in a pseudo-octahedral arrangement.

1.5.3 Oxides

Simon and his coworkers[97,98] have continued their studies of alkali metal suboxides. Partial oxidation of Rb–Cs alloys leads to the formation of ternary suboxides.[97] $Rb_7Cs_{11}O_3$ has been prepared by reacting stoichiometric amounts of the elements; oxygen is introduced by thermal decomposition of mercury oxide. It forms needle-shaped metallic crystals of violet-bronze colour melting at 251K. Single crystal (183K) studies have shown that the compound crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 32.281, b = 21.877, c = 9.025Å, and z = 4. It contains clusters of composition $Cs_{11}O_3$, which also occur in the caesium suboxides. The Rb atoms are arranged in close-packed wavy sheets filling the space between columns of $Cs_{11}O_3$ clusters. The chemical bonding within the clusters is predominantly ionic, whereas bonding between the clusters and the Rb atoms is purely metallic.[97] The electrical resistance of the binary suboxides, Rb_6O, Rb_9O_2, Cs_7O and $Cs_{11}O_3$ has been determined ($1.6 \leqslant T/K \leqslant 350$) by means of a contactless eddy current method;[98] the resistivities of the suboxides are ca. 50% greater than those of the pure metals. Metastable species obtained by quenching of the melts exhibited irreversible resistivity-temperature behaviour, which is thought to be indicative of a complex ordering process leading to the crystalline phases.[98]

The chemical behaviour of tritium produced by ${}^6Li(n,\alpha){}^3H$ in Li_2O, containing trace quantities of LiOH and Li_2CO_3, has been examined by observing the tritiated species (HTO, HT, T_2, CH_3T) released from the target over the temperature range, $373 \leqslant T/K \leqslant 873$.[99] The tritium is thought to be stabilised initially as LiOT in the solid phase; as the temperature is increased it is then released, predominantly via reaction (14). Temperature dependent

$$LiOT(c) + LiOH(c) \xrightarrow{673K} Li_2O(c) + HTO(g) \qquad (14)$$

($298 \leqslant T/K \leqslant 673$) X-ray analysis of K_2O and of Rb_2O has confirmed the fact that for both oxides there is only one crystallographic form, the f.c.c. antifluorite type.[100]

1.5.4 Halides

The ionic radii of alkali metal halides[101,102] (and of alkaline earth metal halides[101] and chalcogenides[102]) have been considered by two groups of authors. An empirical soft-sphere model for ionic crystals has been developed;[101] it is proposed that internuclear distances (d) are related to soft sphere radii for cations and anions (M and X, respectively) by equation (15) where k is a constant characteristic of the class of compound. Internuclear

$$d^k = M^k + X^k \qquad (15)$$

distances in Groups I and II metal halide crystals (for which $k = 5/3$) are reproduced with remarkable accuracy (±0.003Å). It is interesting to note that soft sphere radii for the metal ions are identical to metallic radii for 12 coordination.[101] A theoretical analysisof short range interactions in binary crystals has also been undertaken.[102] Ionic radii and internuclear distances in Group I metal halides and Group II metal chalcogenides have been calculated. The ionic radii derived, agree closely with experimental values from electron density measurements. They are additive in that they produce internuclear distances which agree well with observed values (±0.10Å). The calculated radii differ from Pauling's values in being larger for cations and smaller for anions by ca. 0.25Å.[102]

A theoretical study of the energies of solution and association for univalent substitutional anion impurities (e.g. F^-,Br^-,I^-) in crystals of alkali metal chlorides (MCℓ; M = Li,Na,K,Rb) has been undertaken.[103] The calculated data are discussed with respect to ion size, polarisation effects and the diffusional properties of the univalent impurity in the host crystal. The electrical conductivity and heat capacity of single crystals of LiF, NaCℓ, NaBr and KCℓ have been investigated near their melting points.[104] Premelting surface phenomena, commencing about 6K below the bulk melting points, were observed in both properties, although no premelting effects (to within at most 0.5K) were identified within the crystal bulk.

Mass spectroscopic studies of the vapour phase over LiF[105] and over RbI[106] have been the subject of separate investigations. Although monomers, dimers and trimers were observed in the LiF system, only monomeric and dimeric moieties were identified in the RbI system. Thermodynamic data for the formation of vapour phase RbI and Rb_2I_2 were also determined.[106]

Heat capacities of $RbHF_2$ and of $CsHF_2$ have been measured ($5 \leqslant T/K \leqslant 533$);[107] thermodynamic data for the various phase transitions in these compounds are quoted.

Matrix isolation studies of the reactions of alkali metal halide molecules with H_2O,[108] NH_3,[109] UF_4[110] and UF_6[110] have been undertaken; i.r. spectroscopic techniques were used to identify and characterise the products. Analysis of the MX-H_2O system[108] indicates that a pyramidal structure is formed in which the metal cationis bound to oxygen of H_2O and that the anion sits as a counterion at the base of the pyramid and interacts through hydrogen bonds to the water molecule. On the other hand, it is proposed that the product of the $MX-NH_3$ system[109] has a structure of the form $NH_3M^+.X^-$ with the interaction involving the attraction of the alkali metal cation to the nitrogen lone pair; a hydrogen bonding interaction is not indicated. Cocondensation in the $MF-UF_4$ and $MF-UF_6$ systems led to the ternary products MUF_n $(4 \leqslant n \leqslant 7)$.[110]

The double salts, $KCl,K_2Mo_2O_7$ and $KBr,K_2Mo_2O_7$, have been crystallised from molten 1:1 mixtures of KCl or KBr with $K_2Mo_2O_7$.[111] $CsX,Cs_2Mo_2O_7$ (X = Cl or Br) can also be prepared in the same way. These compounds are decomposed by both water and liquid NH_3. Their Raman and i.r. spectra have been assigned assuming the $Mo_2O_7^{2-}$ ion to have D_{3d} or D_{3h} symmetry. A single crystal structure determination of $KBr,K_2Mo_2O_7$, (hexagonal, $P6_3/mmc$, a = 6.017, c = 15.624Å) has also been undertaken.[112]

Single crystal structural analysis of the complex salt $NaCl,2H_2O_2,4Na_2SO_4$ (tetragonal, P4/mnc, a = 10.53, c = 8.42Å) has shown the coordination of one of the Na^+ ions to be unusual.[113] Although eight ofthe nine Na^+ ions possess the expected distorted octahedral coordination (five oxygen atoms, r(Na...O) range from 2.25 to 2.65Å and one chlorine atom, r(Na...Cl) = 3.016Å), the other has a coordination number of eight - a tetragonal prismatic array of oxygen atoms, r(Na...O) = 2.565Å - not hitherto reported for Na^+ ions in such simple compounds. The crystal and molecular structure of the NaBr complex of monensin (orthorhombic, $P2_12_12_1$, a = 16.618, b = 18.702, c = 12.923Å) have also been examined.[114] In this compound, the Na^+ ions are coordinated to six oxygen atoms in a distorted octahedral fashion at distances ranging from 2.349 to 2.503Å.

The free energies of interaction of MCl (M = Li,Na,Cs) with glycine[115] and of NaCl with a number of α-ω amino acids[116] have been calculated from e.m.f. measurements on appropriate cells with transference at 298.15K.

1.5.5 Ternary Hydrides

Hartree-Fock-Roothaan theoretical calculations for the ternary hydrides $LiBeH_3$,[117] $LiBH_4$[118] and $LiAlH_4$[119] have been undertaken; energetic, geometric and force characteristics and electron density distributions have been determined.

Phase relationships in the Li-Rh-H,[120] Li-Ir-H[121] and Li-Pt-H[122] systems have been characterised. In addition to LiH, the compounds which exist in the rhodium and iridium systems are the intermetallics LiRh and LiIr and the ternary halides Li_4MH_4 (M = Rh,Ir), Li_4RhH_5 and Li_4IrH_6. Li_4MH_4 were prepared by heating stoichiometric ratios of LiH and Rh (or Ir) in an inert atmosphere. In the presence of hydrogen, Li_4MH_4 absorb hydrogen to form the higher hydrides. X-ray powder diffraction studies indicate Li_4RhH_4 is tetragonal, the other three are orthorhombic.[120,121] Reaction of LiH with platinum at 873K under hydrogen atmospheres, has produced a ternary hydride (and corresponding deuteride) with limiting phase composition, $LiPtH_{0.66}$.[122] The structure of this material, studied by X-ray and neutron diffraction techniques, has been shown to be based on a sheetwise ordered hexagonal close packing of lithium and platinum (in alternate sheets) in which hydrogen atoms occupy tetrahedral holes (hexagonal, P3m1, a = 2.728, c = 4.226Å).[122]

1.5.6 Ternary Oxides and Chalcogenides

For reasons noted previously, the only ternary oxides considered in this section are those containing both alkali- and transition-metals. The preparation of a vast number of these compounds[123-140] has been reported, principally by Hoppe and his co-workers. In general classical solid state reactions (e.g. high temperature reactions between alkali metal oxides, carbonates or nitrates with transition metal oxides) were used as preparative routes. The tetratitanates, $M_2Ti_4O_9$ (M = Li,Na,K,Rb,Cs), however, were prepared by reaction of the $MC\ell$ with $T\ell_2Ti_4O_9$ at 733K under vacuum, the volatility of $T\ell C\ell$ favouring the reaction (16).[123]

$$2MC\ell + T\ell_2Ti_4O_9 \longrightarrow M_2Ti_4O_9 + 2T\ell C\ell \qquad (16)$$

The most salient features of the chemistry of the ternary oxides are their crystallographic properties; these are summarised in Table 3. The single crystal X-ray diffraction study of α-K_2CrO_4[126] was undertaken to assess the electron density distribution in this material. The effective charges of the atoms were estimated to be Cr +0.1, O -0.5, K +1.0; the neutralised charges of the chromium and oxygen atoms indicate a significant contribution of the 3d atomic orbitals of the chromium atoms to the Cr – O bonding orbitals.[126]

The structures of molten Na_2WO_4 (1033K)[141] and $Na_2W_2O_7$ (1083K)[142] have been investigated by analysis of the radial distribution

Table 3 Crystallographic parameters for a number of ternary oxides

Compound	symmetry	space group	a/Å	b/Å	c/Å	α/°	β/°	γ/°	Reference
$Li_2Ti_4O_9$	monoclinic	C2/m	15.89	3.84	12.06	-	105.7	-	123
$Na_2Ti_4O_9$	monoclinic	C2/m	17.38	3.784	11.99	-	106.2	-	123
$K_2Ti_4O_9$	monoclinic	C2/m	18.25	3.791	12.01	-	106.4	-	123
$Rb_2Ti_4O_9$	monoclinic	C2/m	18.92	3.797	12.05	-	106.2	-	123
$Cs_2Ti_4O_9$	monoclinic	C2/m	20.16	3.789	12.03	-	107.0	-	123
$Rb_8Nb_{22}O_{59}$	rhombohedral*	$R\bar{3}m$	7.53	-	43.39	-	-	-	124
$Cs_8Nb_{22}O_{59}$	rhombohedral*	$R\bar{3}m$	7.53	-	43.02	-	-	-	124
$RbTaO_3$	monoclinic	C2/m	9.58	8.50	8.13	-	94.8	-	125
α-K_2CrO_4	orthorhombic	Pnma	7.662	5.919	10.391	-	-	-	126
$K_2W_4O_{13}$	trigonal	$P\bar{3}$	15.566	-	3.846	-	-	-	127
$Rb_{0.3}WO_3$	hexagonal	$P6_3/mcm$	7.3875	-	7.5589	-	-	-	128
$Na_{14}Mn_2O_9$†	trigonal	$P\bar{3}$	6.66	-	9.35	-	-	-	129
$K_6Mn_2O_6$	monoclinic	$P2_1/a$	6.76	11.39	6.63	-	96.9	-	130
Na_5FeO_4	orthorhombic	Pbca	10.33	5.97	18.08	-	-	-	131
$Na_8Fe_2O_7$	monoclinic	$P2_1/c$	8.70	11.01	10.09	-	107.6	-	132
$K_6Fe_2O_6$	monoclinic	$P2_1/a$	7.13	11.12	6.51	-	102.3	-	130

Table 3 continued

Compound	symmetry	space group	a/Å	b/Å	c/Å	α/°	β/°	γ/°	Reference
$Na_{14}Fe_6O_{16}$	triclinic	$P\bar{1}$	11.42	8.27	5.95	109.3	87.7	111.4	133
$Na_4Fe_2O_5$	monoclinic	$P2_1/n$	11.87	5.67	9.17	-	104.5	-	134
KRu_4O_8	tetragonal	$I4/m$	9.88	-	3.12	-	-	-	135
Rb_2ZnO_2	monoclinic	$P2_1/c$	9.55	6.33	15.91	-	118.6	-	136
Cs_2ZnO_2	monoclinic	$P2_1/c$	9.85	6.61	16.26	-	116.8	-	136
$K_2Zn_6O_7$	tetragonal	$P4_2nm$	10.91	-	3.32	-	-	-	137
$Na_{14}Cd_2O_9$ †	trigonal	$P\bar{3}$	6.75	-	9.43	-	-	-	138
Li_2UO_4	orthorhombic	Pnma	10.547	6.065	5.134	-	-	-	139
K_2AmO_4	tetragonal	$I4/mmm$	4.286	-	13.05	-	-	-	140
Rb_2AmO_4	tetragonal	$I4/mmm$	4.316	-	13.71	-	-	-	140
Cs_2AmO_4	tetragonal	$I4/mmm$	4.364	-	14.65	-	-	-	140

*These materials were indexed assuming a hexagonal triple cell

†These materials represent the most cation-rich ternary oxides of the alkali metals

functions derived from X-ray scattered intensity data. Molten Na_2WO_4 is thought to be composed of Na atoms and WO_4 tetrahedra;[141] coexistence ofWO_4 tetrahedra and WO_6 octahedra in molten $Na_2W_2O_7$ is considered plausible.[142]

Several investigations of the vanadium[143-145] and tungsten bronzes[128,146] have been effected. X-ray diffraction analysis of the phase equilibria in the Li-V-O system[143] has defined the limiting composition of the θ-type lithium vanadium bronzes, $Li_xV_5O_{12\mp y}$ and the region of $Li_xV_2O_{3+y}$ solid solutions. Similar studies of the Na-V-O system[144] have resulted in the identification of a new series of ρ'-type sodium vanadium brones, $Na_{1+x}V_5O_{13}$ and the definition ofthe limiting compositions of the κ-type sodium vanadium bronzes, $Na_{2+2x}V_6O_{16-2y}$. The thermal stabilities of the ρ'-type and κ-type bronzes have been ascertained in both air and argon.[144] Electrochemical studies of the K-V-O system[145] have delineated the region of the ψ-type bronzes, $K_2V_{8-x}O_{21-y}$, φ-type bronzes, $K_xV_2O_5$ and of potassium hypovanadate, $K_2V_3O_7$.

The crystal structures of the rubidium tungsten bronze, $Rb_{0.30}WO_3$[128] and the potassium ruthenium bronze, KRu_4O_8,[135] have been examined; relevant details are included in Table 3. Polymorphism in the alkali metal tungsten bronzes, M_xWO_3 (M = Li,Na,K, Rb) has been investigated as a function of pressure.[146] No evidence for phase changes were observed for Na_xWO_3 and Rb_xWO_3; in contrast, Li_xWO_3 and K_xWO_3 show properties which may indicate some sort of transition.

Phase relationships in the Cs-U-O system have been investigated;[147] ten crystallographically distinct caesium uranates have been defined. Thermodynamic data for this system have also been examined in detail.

Enthalpies of formation of K_3CrO_4[148] and of Li_2ZrO_3, Li_4ZrO_4 and Li_8ZrO_6[149] have been determined from calorimetric and mass spectroscopic measurements, respectively; the data are summarised in Table 4.

Table 4 Enthalpies of formation of a number of ternary oxides

Oxide	K_3CrO_4[148]	Li_2ZrO_3[149]	Li_4ZrO_4[149]	Li_8ZrO_6[149]
$\Delta H_f^O(298.15K)/kJ.mol^{-1}$	-1548.1	-1755.6	-2364.0	-3562.3

Thermal analysis of a number of anhydrous ternary oxides of general formulae AMO_2, A_2MO_3 and $A_2M_3O_4$[150] and of the isostructural dihydrates, $LiMO_4$, $2H_2O$ (M = Tc,Re)[151] have been effected.

A small number of ternary chalcogenides have been prepared recently. $MCrS_8$ (M = K,Rb,Cs) were obtained by reaction of chromium powder with the corresponding alkali metal carbonate in a current of dry H_2S at ca 1320K;[152] M_6HgX_4 (M = K,Rb; X = S,Se) were formed in the high temperature (613K) solid state reaction of the appropriate sulphides or selenides.[153] Unit cell parameters for both sets of compounds are collected in Table 5. The magnetic and electrical properties of polycrystalline samples of $Na_{1-x}VX_2$ (X = S,Se) have been measured as a function of temperature.[154] The stoichiometric compounds are semiconductors with localised magnetic moments of the $V^{3+}(d^2)$ ions; they undergo a clear paramagnetic-antiferromagnetic phase transition at ca 50K with a simultaneous first order cooperative Jahn-Teller lattic distortion. The non-stoichiometric compounds are metallic and exhibit several anomalies in their magnetic and electric behaviour.[154]

Table 5 Crystallographic parameters for a number of ternary sulphides and selenides

Compound	Symmetry	Space Group	a/Å	b/Å	c/Å	β/°	Reference
KCr_5S_8	monoclinic	C2/m	17.798	3.447	8.598	105.00	152
$RbCr_5S_8$	monoclinic	C2/m	17.835	3.452	8.654	104.74	152
$CsCr_5S_8$	monoclinic	C2/m	17.915	3.464	8.732	104.62	152
K_6HgS_4	hexagonal	$P6_3mc$	9.98	-	7.65	-	153
K_6HgSe_4	hexagonal	$P6_3mc$	10.3	-	7.88	-	153
Rb_6HgS_4	hexagonal	$P6_3mc$	10.3	-	7.94	-	153
Rb_6HgSe_4	hexagonal	$P6_3mc$	10.7	-	8.19	-	153

1.5.7 Ternary Halides

The only ternary halides considered for this section are those containing alkali metals and either alkaline earth, transition or lanthanide metals; the major interests in these compounds have been of a crystallographic and spectroscopic nature. The pseudobinary phase diagrams of the $NaC\ell-Nb_3C\ell_8$,[155] $RbI-CrI_2$,[156] $CsC\ell-FeC\ell_3$,[157] $NaF-ZnF_2$,[158] $MF-PrF_4$ (M = Na,K,Rb,Cs),[159] $KF-DyF_3$,[160] and $LiF-TbF_4$[159] systems have been investigated using d.t.a. and X-ray crystallographic techniques. The only compounds observed in the systems containing transition elements were $Na_7Nb_3C\ell_{15}$ (d. peritectically, 863K),[155] $RbCrI_3$ (m.p. 773K),[156] $CsFeC\ell_4$ (m.p. 655K), $Cs_3FeC\ell_6$ (d. peritectically, 754K), $Cs_3Fe_2C\ell_9$ (d. peritectically, 544K)[157] and $NaZnF_3$ (m.p. 1056K).[158] A plethora of compounds was identified in the systems containing lanthanide metals; they include K_3PrF_7, M_2PrF_6 (M = Na,K,Rb,Cs), $M_7Pr_6F_{31}$ (M = Na,K), $MPrF_5$ (M = Rb,Cs), $Rb_2Pr_3F_{14}$,[159] K_3DyF_6, K_2DyF_5, $KDyF_4$, KDy_2F_7, KDy_3F_{10},[160] Li_4TbF_8 and Li_2TbF_6.[159] Crystallographic data for these compounds, where available, are collected with those for a number of other ternary halides in Table 6. The effect of pressure ($1 \leqslant p/\text{kbar} \leqslant 28$) on the structure of the mixed valence ternary chloride, $CsAuC\ell_3$, has been studied using neutron diffraction techniques;[165] no clear transformation in structure was observed.

Polarised Raman spectra of single crystals of $RbCdX_3$ (X = Cℓ,Br),[166] $CsMgC\ell_3$[167] and $CsNiC\ell_3$[168] and far i.r. reflection spectra of single crystals of $CsMgC\ell_3$,[167] $CsCaC\ell_3$[167] and $CsNiC\ell_3$[168] have been examined. A normal coordinate analysis of the data for $CsMgC\ell_3$ and $CsCaC\ell_3$ indicates that some covalent character exists in the Mg-Cℓ and Ca-Cℓ bonds.[167]

E.p.r. studies of crystals of $CsMgC\ell_3$, $CsMgBr_3$ and $CsCdBr_3$ doped with Cr(III) ions, have shown that there is an extraordinary tendency of Cr(III) ions to form exchange coupled pairs (even at Cr(III) concentrations of 1 in 1000).[169] The host materials have the linear chain $CsNiC\ell_3$ structure; the pairs consist of two Cr(III) ions located in Mg or Cd sites situated on either side of a vacant Mg or Cd site (Figure 1a). The stability of the Cr(III)-vacancy-Cr(III) system appears to result from the charge compensation requirement of a linear chain $CsNiC\ell_3$ lattice. The formation of Cr(III)-vacancy-Cr(III) pairs in $CsMX_3$ crystals is dramatically reduced by the presence of Li^+, Na^+ or In^{3+}. The

Table 6. Crystallographic parameters for a number of ternary halides

Compound	Symmetry	Space Group	a/Å	b/Å	c/Å	α/°	β/°	γ/°	Reference
$RbCrC\ell_3$(295K)	monoclinic	C2/m	12.224	7.040	6.250	-	93.34	-	161
$CsCrC\ell_3$(60K)	monoclinic	C2/m	12.523	7.152	6.171	-	91.38	-	161
$RbCrI_3$	triclinic	$P\bar{1}$	8.047	8.057	7.261	90.38	95.69	120.70	156
$CsCrF_4$	hexagonal	$P\bar{6}2m$	9.650	-	3.857	-	-	-	162
$Rb_3Mn_2C\ell_7$	tetragonal	I4/mmm	5.08	-	26.14	-	-	-	163
Rb_2MnF_5,H_2O	orthorhombic	Cmcm	9.383	8.214	8.348	-	-	-	164
Cs_2MnF_5,H_2O	orthorhombic	Cmmm	9.727	8.686	4.254	-	-	-	164
$Cs_3Fe_2C\ell_9$	hexagonal	$P6_3$/mmc	7.235	-	17.780	-	-	-	157
$CsAuC\ell_3$	tetragonal	I4/mmm	7.495	-	10.880	-	-	-	165
$RbCdC\ell_3$	orthorhombic	Pnma	8.949	4.026	14.93	-	-	-	166
K_3PrF_7	cubic	-	9.23	-	-	-	-	-	159
Rb_2PrF_6	orthorhombic	-	6.906	11.92	7.532	-	-	-	159
$Na_7Pr_6F_{31}$	hexagonal	-	14.47	-	9.63	-	-	-	159
$K_7Pr_6F_{31}$	hexagonal	-	15.09	-	10.27	-	-	-	159
K_3DyF_6(L.T.)	monoclinic	$P2_1$/m	6.381	6.590	9.131	-	90.76	-	160
K_3DyF_6(H.T.)	cubic	Fm3m	9.201	-	-	-	-	-	160
K_2DyF_5	orthorhombic	$Pna2_1$	10.762	6.597	7.300	-	-	-	160
$KDyF_4$	hexagonal	-	14.143	-	10.151	-	-	-	160
α-KDy_2F_7(LT)	monoclinic	C2	14.430	8.071	12.077	-	125.53	-	160
β-KDy_2F_7(HT)	cubic	Fm3m	11.438	-	-	-	-	-	160
KDy_3F_{10}	cubic	Fm3m	11.616	-	-	-	-	-	160
Li_4TbF_8	orthorhombic	Pnma	9.68	9.70	5.70	-	-	-	159

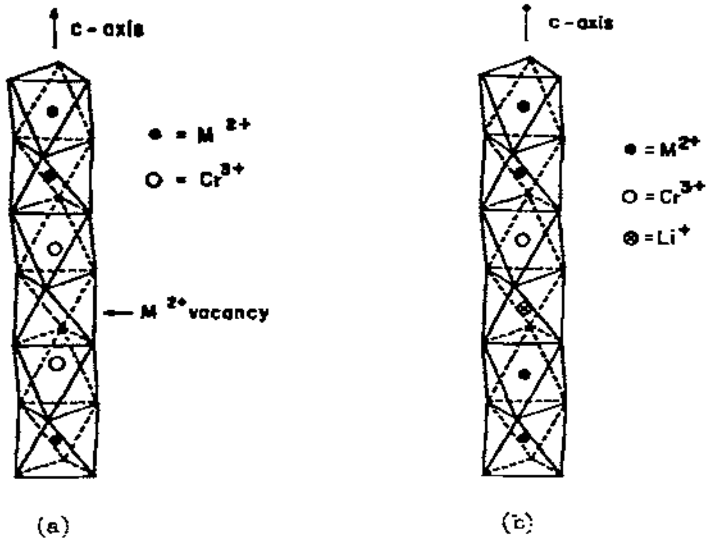


Figure 1. Perspective views of a $[MX_3^-]_n$ chain showing (a) the proposed structure of the Cr(III)-Cr(III) pair and (b) the proposed structure of the Cr(III)-Li(I) centre. The corners of the octahedra are occupied by halide ions. Reproduced by permission from J. Am. Chem. Soc., 100 (1978) 469.

presence of the small monovalent ions is thought to provide an alternative mode by which the Cr ions can be incorporated into the $CsMX_3$ lattice. It seems likely that a Cr(III) and a Li(I) ion enter adjacent metal ion sites within the same $[MX_3^-]_n$ chain (Figure 1b). The presence of In(III) ions is thought to lead to a decrease in Cr(III)-vacancy-Cr(III) pairs because of the formation of mixed Cr(III)-vacancy-In(III) pairs as well as homonuclear pairs.[169]

The thermal stabilities of $K_2ZrC\ell_6$,[170] $K_2HfC\ell_6$,[170] $MNbC\ell_6$ (M = Na,K,Rb,Cs),[171,172] $MTaC\ell_6$ (M = Na,K,Rb,Cs)[171,172] and $MTcBr_6$ (M = K,Rb,Cs)[173] have been examined. Fluorination of complexes in the MF-UF_4 (M = Rb,Cs) systems has been studied.[174] In all cases, U(VI) was formed, usually as M_2UF_8; oxidation of M_3UF_7, however, yielded M_3UF_9.

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

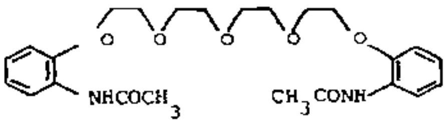
To simplify the text in this Section, noncyclic polyether complexes, crown complexes and cryptates are considered in special subdivisions. The majority of the data, however, are discussed in subdivisions devoted to derivatives of the individual alkali metals. For those data pertinent to several alkali metals, they are described once only in the subdivision of the lightest metal considered.

1.6.1 Non-cyclic Polyether Complexes

Recent investigations of the chemistry of the crown complexes of alkali- and alkaline earth-metal salts has generated interest in the possibility in the formation of analogous non-cyclic polyether complexes. Several papers[175-184] describing the preparation and characterisation of such complexes both in solution and in the solid phase have been published during 1978.

Comprehensive ^1H n.m.r. studies of the interaction of noncyclic poly(oxyethylene) derivatives, i.e. polyethylene glycols, $H(OCH_2CH_2)_nOH$ ($1 \leqslant n \leqslant 8$) and their dimethyl ether derivatives, so-called "glymes", $Me(OCH_2CH_2)_nOMe$, ($3 \leqslant n \leqslant 8$), with alkali and alkaline earth metal thiocyanates have been undertaken by Yamagida *et al*. in d_4-methanol,[175] d_2-water,[175] d_6-acetone[176] and d_3-acetonitrile.[176] In d_4-methanol solutions the ethylene proton signal of hexa-ethylene glycol ($n = 6$) was affected by addition of Na^+ or Ca^{2+}, that of heptaethylene glycol ($n = 7$) was affected by addition of Na^+, K^+, Rb^+, Cs^+, Sr^{2+} or Ba^{2+} and that of octaethyleneglycol ($n = 8$) was affected by the addition of K^+, Rb^+, Cs^+, Sr^{2+} or Ba^{2+}; neither Li^+ nor Mg^{2+} altered the ^1H n.m.r. signals of any of the glycols studied.[175] Similar observations were made for solutions of glycols in water.[175] The changes in the spectra on addition of the cations were assumed to be a manifestation of a complexation interaction between the cation and the polyether derivative. Similarly, in d_6-acetone and d_3- acetonitrile solutions,[176] interpretation of the ^1H n.m.r. spectra indicate specific complexations of tetraethylene glycol ($n = 4$) with Mg^{2+}, hexaethylene glycol with Na^+ and Ca^{2+} and heptaethyleneglycol with K^+. No specific interaction was detected for Rb^+ and Cs^+ in these solvents.[176] I.r. and ^1H n.m.r. studies of the tetraphenylborates of complexes of poly(oxyalkylene) derivatives, i.e. non-cyclic polyethers with the recurrent - $CHRCH_2O$ - unit, with Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} have indicated similar complexation interactions.[177] The thermodynamics for the complexation of Na^+ (from

$NaC\ell O_4$) by (4) in pyridine solution have been determined by ^{23}Na n.m.r. spectroscopic techniques.[178] A strong complex is formed ($\Delta h_f^o = -71 kJ.mol^{-1}$, $\Delta S_f^o = -201 J.K^{-1}mol^{-1}$) in which the



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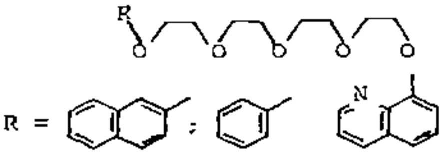
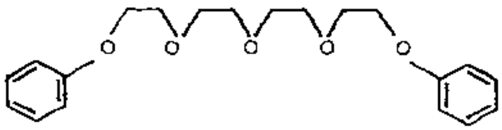


(5)

interaction is best described as a wrapping of the heptadentate ligandaround the Na^+ cation.

In a careful study of the crystallisation of noncyclic polyether complexes of alkali and alkaline earth metal thiocyanates, Vogtle et al[179,180] have concluded that it is not necessary for the polyether to bear two rigid donor end groups, e.g. (4), for crystallisation of such complexes. Crystalline complexes of polyethers with a single donor end e.g. (5) have been produced with alkali and alkaline earth metal salts.[179] It is thought that the chain segment adjacent to the donor group can enclose the cation in a planar fashion. Careful crystallisation experiments have also shown that polyethers bearing two donor free but rigid aryl groups at their ends and containing at least five ether oxygen atoms e.g. (6) give crystalline complexes, especially with



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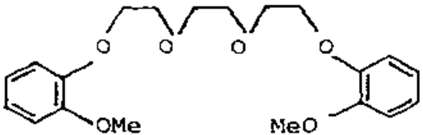
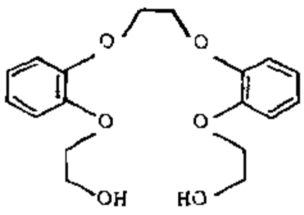


(7)

alkaline earth metals.[180] The crystallisation of 1:1 complexes of simple "glymes" with these salts has been claimed by Yanagida et al; however, few experimental details are quoted.[176]

The crystal structures of four examples of complexes formed by noncyclic polyethers with two rigid donor end groups have been published;[181-183] they are the 1:1 complexes of NaSCN with (7),[181] of NaSCN with (8),[182] of potassium picrate with (9)[183] and the 1:2 complex of KSCN with (8).[182] The open chain polyethers and anions provide the coordination for the sodium cations in NaSCN.(7) and NaSCN.(8). In NaSCN.(7) the cation is coordinated by all



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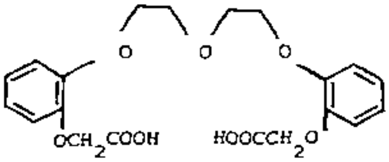
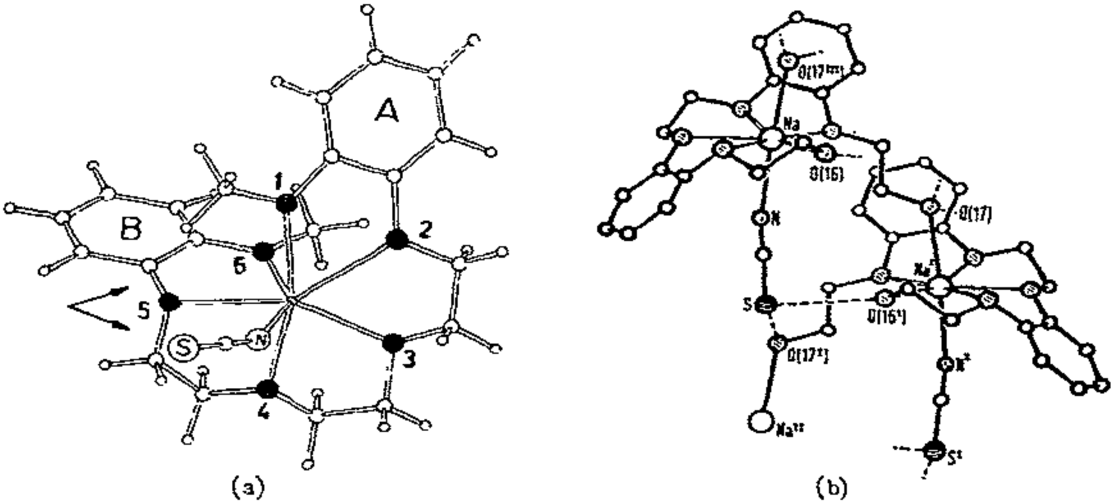


(9)

six oxygen atoms, (r(Na...O) = 2.33-2.54Å), and the nitrogen atom ofthe thiocyanate ion, (r(Na...N) = 2.33Å) (Figure 2a).[181] Starting with one oxyanisole residue the polyether ligand is wrapped around the Na^+ ion in a planar annular structure with C-O torsion angles trans and ethylenedioxy C-C angles gauche. To avoid a collision between the two oxyanisole residues, the two C-O bonds near the second oxyanisole residue are gauche, giving rise to a helical ligand structure with the normals to the phenyl rings forming an angle of 116°. NaSCN.(8) contains two independent Na^+ cations (Figure 2b) which are almost identically bound.[182] All the oxygens of the noncyclic polyether bind to Na^+ ions; five of the oxygen atoms of one ligand form the equatorial plane of a pentagonal bipyramid and the sixth (diol) oxygen atom is coordinated to a symmetry related sodium ion. Seven coordination of each Na^+



(a) (b)

Figure 2 The coordination spheres of the Na^+ cations in (a) NaSCN.(7) and (b) NaSCN.(8). Reproduced by permission from (a) Acta. Cryst., B34 (1978) 2752, (b) J. Chem. Soc. Chem. commun., (1978) 1001.

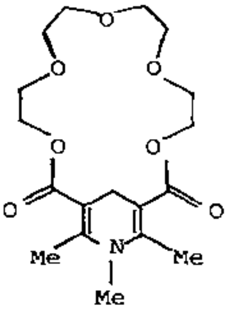
ion is completed in one apical position by the nitrogen atom of the NCS^- ion and in the other by the diol oxygen atom of another symmetry-related ligand, thus forming two independent chains of molecules along the glide planes parallel to the c-axis (Figure 2b).

The crystal structure of $K[C_6H_2(NO_2)_3O]$.(9) shows the complex cation to be dimeric; the two monomeric units are held together by a centrosymmetric bridge formed by two bridging carbonyl oxygen atoms.[183] The K^+ ions are eight-coordinate, the two carbonyl and five ether oxygen atoms of the noncyclic polyether carboxylic acid forming, with the bridging carbonyl oxygen of the symmetry related ligand, a shallow helix around each K^+ ion, r(K...O) = 2.729–2.903. The coordination of the two independent K^+ ions in the structure of the solvated species $[KSCN.(8)_2]_2.CHCl_3$ is established by two polyether ligands; five oxygen atoms from each ligand complete the 10-coordination of the K^+ ions which are not coordinated by the anions or further oxygen atoms from other ligands.[182]

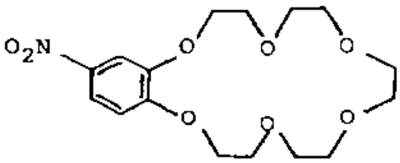
A tetraglyme coordination complex of potassium, bis (tetraglyme) potassium biphenyl, has been crystallised by slow cooling of a solution of potassium biphenyl in tetraglyme.[184] The crystal structure of this moiety, determined by X-ray methods at 120K, shows that the ten oxygen atoms of the two tetraglyme molecules spherically surround each K^+ ion, such as to give a solvent separated ion pair structure. The magnetic properties of this material have also been examined in detail.[184]

1.6.2 Crown Complexes

Interest in crown and related complexes of alkali- and alkaline earth-metal cations has been maintained during the period of this review. A new class of crown ethers containing or attached to 1,4-dihydropyridine rings have been synthesised; the crown ether



(10)



(11)

1,4-dihydropyridine (10) complexes with $NaC\ell O_4$ and forms crystals containing a molecule of acetone, $NaC\ell O_4.(10), Me_2CO$.[185] Single crystal X-ray diffraction analysis has established that the Na^+ ion is located in a pseudo-pentagonal bipyramidal coordination sphere. The five equatorial positions are occupied by the five oxygen atoms of the crown ether ring; the coordination is completed by the carbonyl oxygen of the acetone molecule and by the perchlorate anion.

Crystallographic investigations of complexes of B15C5,[186] of B18C6[187,188] and its 4-nitro-derivative (11),[189] and of DB24C8[190] have been undertaken. Huml et al[188,189] have examined the effect of nitro-substitution in the 4-position of the benzene ring of B18C6 on the structural properties of RbNCS.B18C6. The unsubstituted complex forms a centrosymmetric sandwich-type dimer with the Rb^+ ions in centrosymmetrically related positions separated by two anions.[188] Thus, each cation in the dimer is bound by the ion-dipole interaction with six oxygen atoms of the crown ether ring, r(Rb...O) = 2.913-3.132Å (the distance of the ion from the weighted mean plane of oxygen atoms is 1.24Å) and by electrostatic interaction with two NCS^- ions, r(Rb...N) = 3.05Å.[188] The 4-nitro substituted complex has a monomeric structure.[189] The Rb^+ ion is bound by an ion-dipole interaction with the six oxygen atoms of the crown ether ring, r(Rb...O) = 2.96-3.08Å (the distance of the ion from the weighted mean plane of oxygen atoms is 1.17Å) and by electrostatic interaction with the nitrogen atom of the NCS^- anion and one oxygen atom of the nitrogroup of the centrosymmetrically related macrocycle, r(Rb...O) = 3.09Å. The second oxygen atom of the nitrogroup is slightly more remote from the Rb^+ ion, r(Rb...O) = 3.81Å.[189]

The crystal structures of $Mg(NCS)_2.B15C5$,[186] $Ca(NCS)_2.B15C5.MeOH$,[186] $Ca(NCS)_2.B15C5.H_2O$,[186] $Sr(C\ell O_4)_2.B18C6.(H_2O)_3$[187] $Ba(C\ell O_4)_2.B18C6.(H_2O)_2$[187] and $Ba(C\ell O_4)_2.DB24C8$[190] have been determined by Truter *et al*. The coordination of the Mg^{2+} ion is a pentagonal bipyramid with the nitrogen atoms of the NCS^- anions in axial positions.[186] The Ca^{2+} ion in the methanol complex has irregular eight coordination which includes the five ether oxygen atoms, the two NCS^- nitrogen atoms and the oxygen atom of the methanol molecule.[186] The coordination of the Ca^{2+} ion in the analogous hydrate, is identical with that of the methanol complex with the water oxygen replacing the methanol oxygen atom.[186] In the strontium compound, there are separate perchlorate ions and complex cations having strontium in nine-coordination by six oxygen atoms from the crown ether ring, two water oxygen atoms on one side of the ring and one water oxygen atom on the other.[187] In the barium compounds,[187,190] the cations are coordinated by ten oxygen atoms. For the B18C6 complex, the coordination sphere consists of six oxygen atoms from the crown ether ring, two water oxygen atoms and one oxygen atom from a perchlorate ion on one side of the ring and one oxygen atom from the second perchlorate ion on the other side of the ring.[187] For the DB24C8 complex, the coordination is built up by the eight oxygen atoms of the crown ether ring, which cradles but does not enclose the cation, and by two perchlorate ions, one unidentate and one possibly bidentate.[190]

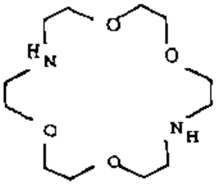
Solution ^1H n.m.r. spectra of the crown ethers B15C5 and B21C7 as free ligands and in mixtures with alkali metal iodides or thiocyanates have been measured.[191] An empirical explanation of the effect of complexation on the spectra is given in terms of electric field effect, ring current variations and specific ion pairing. The stabilities of a number of complexes formed between alkali metal cations (M = Na,K,Rb,Cs) and crown ethers (B15C6, B18C6, DCH18C6, DB18C6) has been studied in methanol and in acetonitrile using polarographic techniques.[192] The character of the solvent was found to be an important factor in view of its ability to solvate the cation.[192]

The distribution of alkali metal picrates (M = Na,K,Rb,Cs) between water and benzene[193] and of alkali metal halides (M = Na,K) between water and a number of protic solvents[194] has been investigated in the presence of 18C6 and DB18C6 or DCH18C6, respectively. The overall equilibrium constants for the partition of the picrates pass through a maximum at K^+;[193] this observation mirrors the correlation between the stability of the complex and the size of the cation. The order of extractability of the halides was found to be $F^- > I^- > Br^- > C\ell^-$, apparently reflecting the efficacy of the solvation of the ions by the protic solvents.[194] Ultrasonic absorption studies of the kinetics of the complexation of Sr^{2+} and Ba^{2+} with 15C5 and 18C6 crown ethers in aqueous solution have also been undertaken.[195]

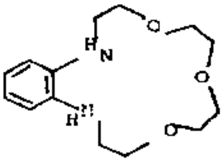
The effect of crown ethers, 18C6 and DCH18C6, on the rate of reaction of MeOK with 1-chloro-2,4-dinitrobenzene has been assessed in several methanol-benzene mixtures.[196] It is inferred that the observed variations in rate are derived from the ability of the crown ethers to dissociate ion pairs.[196] The influence of cation binding ($M = Li,Na,K$) on the photochemistry of 4-valeroyl-substitued DB18C6 has been investigated;[197] the effect is moderately specific for K^+ions.

In a study of the cation binding properties of crown ether acetals (compounds related to crown ethers in which one (or more) of the $-OCH_2CH_2-$ groups is replaced by an $-OCHR-$ group), the effect of alkali metal cations on the hydrolysis of $\overline{OCHMe(OCH_2CH_2)_nOCH_2CH_2}$, $0 \leqslant n \leqslant 5$, has been ascertained.[198] Although the ions have no real effect for $n \leqslant 3$, large reductions in rate are observed by acetals containing 17- and 20-membered rings, $n = 4,5$. These observations are thought to be consistent with selective cation binding and a resultant lowering of the basicity of the acetal oxygen atoms.[198]

The complexing abilities of a series of crown compounds, in which one ether function has been replaced by -NR- e.g. (<u>12</u>) and (<u>13</u>), have been examined.[199] The effects of replacing one or two ether functions by -NH-, increasing ring size in nitrogen crowns and change in the imino function -NR- ($R = H$, ^{n}Pr or $COCH_2CH_2CO_2H$) were all investigated. Although possible, it was generally found more difficult to prepare sodium iodide complexes of these nitrogen crowns than of crown ethers, and replacement of -O- by -NH- in crown ethers resulted in a reduction of extracting power.[199]



(<u>12</u>)



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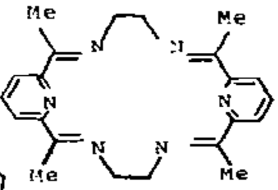
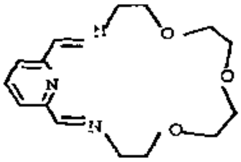


(<u>14</u>)

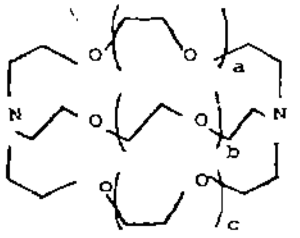


(<u>15</u>)

The synthesis of alkaline earth metal complexes of the unusual macrocycles (<u>14</u>) and (<u>15</u>) has been reported.[200,201] Single crystal X-ray diffraction studies of $SrC\ell_2.(14),2H_2O$[200] have shown the Sr^{2+} ion to be 8-coordinate, the six nitrogen atoms of the macrocycle defining the equatorial girdle, $r(Sr...N) = 2.71-2.74Å$, and the halide ions occupying the axial positions, $r(Sr...C\ell) = 2.93$Å. The X-ray structures of $Ca(NCS)_2.(15)$ and $Sr(NCS)_2.(15),H_2O$ have also been determined.[201] While the metal ions in both complexes are found to be coordinated to the macrocyclic ligand, the smaller Ca^{2+} is located much more within the cavity of the macrocycle compared to Sr^{2+}. Thus the Ca^{2+} ion lies in the mean plane of the macrocycle oxygen and nitrogen atoms whereas the Sr^{2+} is displaced by 0.53Å from this plane. Both metals appear to be equally disposed to the nitrogen and oxygen atoms of the macrocycle. The presence of six donor atoms in the macrocycle together with two N-bonded NCS ions gives Ca^{2+} a coordination number of eight while the coordination of Sr^{2+} is increased to nine by a water molecule.[201]

1.6.3 Cryptates and Related Complexes

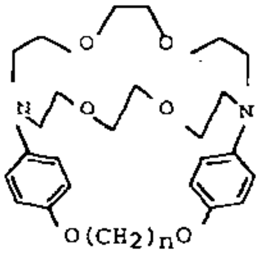
Cryptate formation in non-aqueous solvents has been studied by Schneider *et al.*[202,203] Stability constants of the complexes formed by cryptands (16)-(18), i.e. C211, C221 and C222, with K^+ have been determined in methanol and several aprotic polar solvents as a function of temperature.[202] Free energies, enthalpies and entropies of complexation have been computed from the experimental data. The rates of dissociation of a variety of alkali metal cryptates have been measured in methanol.[203] These have been combined with the measured stability constants to give corresponding formation rates. The pronounced selectivity of the cryptands for alkali metal cations is found to be reflected entirely in the rates, with the formation rate increasing monotonically with increasing cation size. For a given cation, the formation rates increase with increasing cryptand size.[203] The crystal structures of two alkali metal ion cryptates NaNCS.C221 and KNCS.C221 have been determined.[204] In both compounds the alkali metal cation is held inside the molecular cavity of the bicyclic ligand by ion-



	a	b	c	
(16)	1	0	0	C211
(17)	1	1	0	C221
(18)	1	1	1	C222

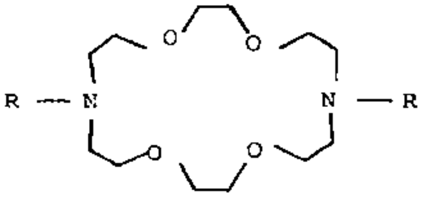
dipole interactions. In the sodium cryptate the cation is not coordinated by any other donor atoms and is thus seven-coordinate. In the potassium derivative, however, the cation also interacts with the NCS^- ion giving it an eight-fold coordination sphere.[204]

The gradation of the ion selectivity of macrocyclic ligands through conformational changes produced by homologous bridges has been studied for alkali-(M = Na,K) and alkaline earth-(M = Sr,Ba) metal ions in $MeOH$-H_2O solutions at 293K.[205] The complexation constants for (19) are almost independent of n and are low compared with those for (20). Values are close to those for (21); in (19) and (21) steric restraints seem to inhibit a perfect donor participation of the triply bonded N atoms. On the other hand, compounds (22) and (23) seemed to be sterically less strained; although they exhibit lower complexation constants than (20), they coordinate much more strongly than conformationally restricted bridged ligands (19).[205]



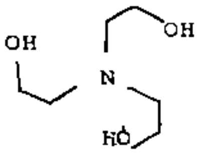
$2 \leqslant n \leqslant 6$

(19)

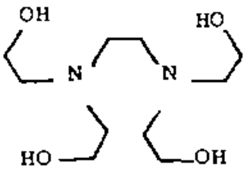


(20) R = Me
(21) R = CH_2CMe_3
(22) R = CH_2Ph
(23) R = $CH_2Ph(4\text{-}OMe)$

Crystalline complexes of alkali- and alkaline earth-metal cations with branched glycols such as the tripod ligand (24), e.g. $NaC\ell O_4.(24)$ and $Ca(NCS)_2.(24)_2$, the tetrapod ligand (25), e.g. $Ca(NCS)_2.(25)$, and the pentapod ligand (26), e.g. $BaI_2.(26)$,



(24)



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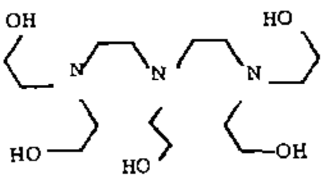
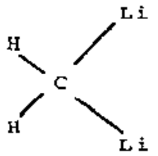


(26)

have been prepared and characterised; the data are compared with those of simpler ligand systems.[206]

1.6.4 Lithium Derivatives

The results of several ab initio MO calculations on small organolithium moieties have been presented;[207-211] the majority describe the structural properties and stabilisation energies of oligomers of dilithiomethane, CH_2Li_2. When solvent-free methyl lithium is heated to 523K, methane is lost and CH_2Li_2 remains as a light brown amorphous, presumably polymeric, powder. This moiety has not been studied to any significant extent physically, and its structure is unknown. Recent calculations by Pople and Schleyer[207] on CH_2Li_2 monomer have revealed remarkable features: the cis-planar form (27) is found to be only 8-40kJ.mol^{-1} less stable than the "tetrahedral" (C_{2v}) geometry (28). The authors conclude that because of their π-acceptor and σ-donor character, electropositive substituents, especially lithium, are particularly effective in stabilising the planar arrangements.[207] In an extension of these calculations, Laidig and Schaefer[208] have shown that the lowest energy singlet and triplet states of both planar and tetrahedral CH_2Li_2 are almost degenerate; structural parameters for all four states are quoted in detail.[208] As a further step in investigating the structure of polymeric CH_2Li_2, Pople and Schleyer,[209] have presented the results of a study of the dimer, $(CH_2Li_2)_2$. Two types of dimer structures were considered. In the first, designated



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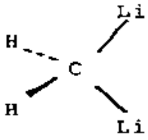

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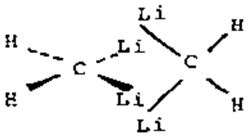

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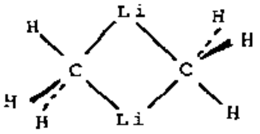


(30)

"head to tail", the Li atoms of one molecule interact with the hydrogens of the other; in the second, designated "head to head", the four lithium atoms are adjacent. Of the many structures considered, (29) with four lithium atoms bridging two perpendicular CH_2 units (i.e. two perpendicular planar CH_2Li_2 monomers) was shown to have the most stable geometry for $(CH_2Li_2)_2$.

Pople and Schleyer[210] have also examined the methyl-lithium dimer $(CH_3Li)_2$. Five geometries were optimised in the calculations; the C_{2h} structure (30) was found to be the most stable conformation. The results of these calculations were used to ascertain a mechanism for the inversion of alkyl-lithiums; a possible inversion transition state was considered to be the C_s structure, derived from (30), in which one methyl group is constrained to lie in a plane bisecting the Li-C-Li angle.[210] Streitwieser[211] has developed an electrostatic model of the methyl-lithium tetramer $(CH_3Li)_4$. A collection of four positive and four negative point charges arranged as two interpenetrating tetrahedra, subject to Coulombic forces alone, has a minimum energy at a ratio of the two tetrahedra sides of 0.783, a value consistent with the observed Li-Li to C-C distance ratio of 0.73 in the structure of $(CH_3Li)_4$.[211]

Methyl-lithium tetramer and N,N,N',N'-tetramethylethylenediamine (tmeda) react to form $(CH_3Li)_4(tmeda)_2$.[212] A single crystal X-ray diffraction study of this material shows that the methyl-lithium tetramers persist. These units show almost ideal Td symmetry and are linked through Li-tmeda-Li bridges. Significant interatomic distances are: r(Li-Li) = 2.56Å, r(C-Li) = 2.25Å.

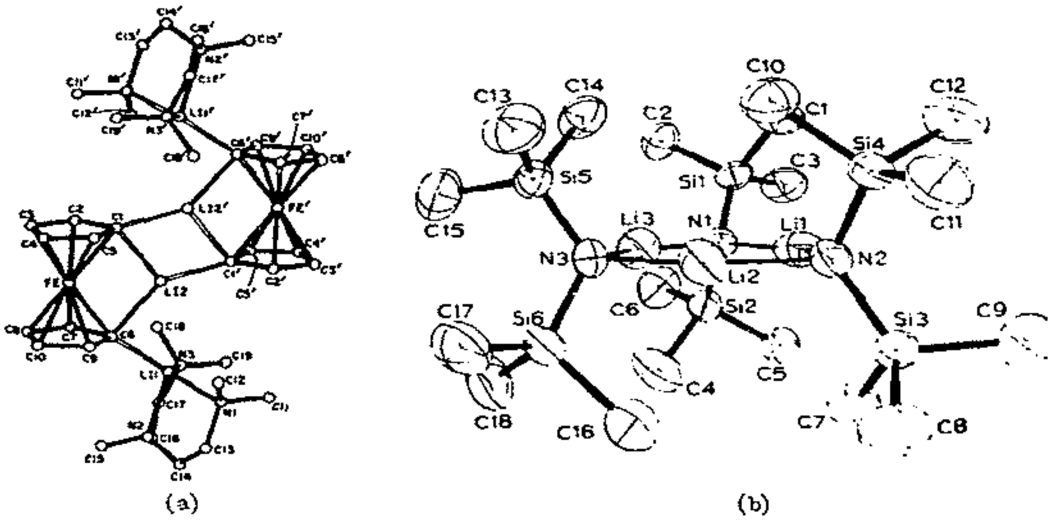
^1H n.m.r. spectra of ether and pentane solutions of lithium di(n-butyl)cuprate with n-butyl-lithium have been examined as a function of temperature.[213] In ether, the spectra are consistent with a dimeric 1:1 RCu:RLi complex, $(R_2CuLi)_2$ and a monomeric 1:3 complex, R_4CuLi_3, while in pentane trimeric 1:1 and dimeric 1:2 complexes are proposed, $(R_2CuLi)_3$ and $(R_3CuLi_2)_2$, respectively. Structures, based on metal octahedral and tetrahedral aggregates are proposed for these complexes; although speculative, they do form an internally consistent picture which is supported by chemical evidence. The influence of tri-n-butylphosphine and LiI on the solution ^1H n.m.r. spectra of certain lithium organocuprates has also been studied.[213] The ^{13}C n.m.r. spectra of $(CH_3)CCH_2CH = CHCH_2\text{-}M$ and of $(CH_3)_3CCH_2CH = C(CH_3)CH_2\text{-}M$ (M = Li,Na,K,Rb,Cs) have been measured in several solvents.[214] It is concluded that all these compounds are delocalised ionic compounds with the charge favouring the α-position over the γ-position.

The kinetics of the disproportionation of $(\text{azobenzene})^{-}....Li^{+}$ ion pairs[215] and of the formation of the dimers of the alkali metal salts (M = Li,Na,K,Cs) of diphenylethylene radical anions[216] have been studied by polargraphic and flash photolysis techniques, respectively. The chelating properties of biuret,[217] 1,4-diazabutadienes[218] and 1,2-semidiones[219] for alkali metal salts have been the subject of both theoretical[217] and experimental studies.[218,219] A series of N,N-dimethylformamide, N-methylformamide and N,N,N',N'-tetramethylurea solvates of a number of alkali metal salts have been prepared;[220] characterisation of the hygroscopic products has been effected by chemical analysis and i.r. spectroscopy. Coordination is thought to occur through the oxygen atom of the solvate molecule.[220]

The crystal and molecular structures of the monohydrate[221] and monomethanol solvate[222] of lithium hydrogen phthalate have been examined by single crystal X-ray diffraction methods. Two crystallographically distinct Li^+ ions exist in each structure. All four Li^+ ions are 4-coordinate, their distorted tetrahedral environments being composed of oxygen atoms from both the anions and the solvate molecules.[221,222]

The reaction of ferrocene with n-butyl-lithium-pentamethyldiethylenetriamine (1:3 molar ratio) results in a dilithicated ferrocene derivative.[223] The molecular structure of this complex, which contains only one triamine ligand per two lithium atoms and has the empirical formula $(h^5\text{-}C_5H_4)_2Fe(N_3C_9H_{23})Li_2$, has been determined in the solid state and has been found to be dimeric, crystallographic symmetry $\bar{1}$, with the lithium atoms in the two types of environment (Figure 3a). All three pentamethyldiethylenetriamine nitrogen atoms are coordinated to one of the unique Li atoms while the second unsolvated Li atom bridges between one carbon atom of a cyclopentadienyl ring from each ferrocene monomer to form the dimer. A four-centre electron-deficient bridge group is thus observed consisting of the two unsolvated lithium atoms and two carbon atoms from two different ferrocenyl groups (Figure 3(a)). The Li-Fe distance is short, 2.67Å, and is ascribed to bonding between the ferrocene e_g molecular orbital and the unsolvated lithium atom.[223]

The crystal structure of the trimeric N-lithiohexamethyldisilazane $[LiN(SiMe_3)_2]_3$ has been determined from single crystal X-ray diffraction data.[224] The compound exists in a trimeric configuration with a planar Li_3N_3 ring (Figure 3(b)); the average Li-N distance is 2.00Å and the ring angles are N-Li-N = 147°, Li-N-Li = 92°.



(a) (b)

Figure 3. Molecular structures of (a) $[(h^5\text{-}C_5H_4)_2Fe(N_3C_9H_{23})Li_2]_2$ and (b) $[LiN(SiMe_3)_2]_3$. Reproduced with permission from (a) J. Am. Chem. Soc., 100 (1978) 6382 and (b) J. Organomet. Chem., 157 (1978) 229.

1.6.5 Sodium Derivatives

In biological systems, the interactions between macromolecules and their surrounding ionic media are of great importance; the results of several diverse investigations of these phenomena, mainly involving Na^+ cations, have been published recently.[225-229] X537A (Lasalocid), an ionophore antibiotic of the monensin series reacts with various metal ions giving complex salts which are highly soluble in organic solvents.[225] A sodium - X537A - water (2:2:2) complex has been crystallised from 95% ethanol. The structure of the complex, which appears to be an intermediate in the monomer to dimer transition that accompanies ion capture and transport, consists of two sodium and two water molecules enclosed by both X537A ions. Six of the seven oxygen atoms coordinated to one sodium ion are contributed by both X537A ions; a water molecule provides the seventh site. The other sodium ion is coordinated to four oxygen atoms of a single X537A ion and both water molecules.[225] The behaviour, in $CDCl_3$ solution, of the free acid X537A and of its sodium (and thallium) salts, has been ascertained from ^{13}C n.m.r. measurements.[226] The spectra indicate that the sodium salt exists as a dimer in $CDCl_3$ solution, while the free acid is present as the monomer.

^1H n.m.r. spectra of the alkali metal salts of 5'-guanosine monophospate in concentrated D_2O solutions show that Na^+,K^+,Rb^+ form slowly exchanging ordered structures with the nucleotide, whereas Li^+ and Cs^+ provide little or no evidence for structure formation.[227] Alkali metal ion (Na^+,Cs^+) binding to aggregates of amphiphilic compounds has been studied by ^{23}Na and ^{133}Cs n.m.r. techniques.[228] Counterion binding does not change appreciably with the alkyl chain length but varies very sensitively with the polar head group. The interaction between Na^+ ions and poly-(methacrylic acid) in aqueous solution have been examined using ^{23}Na n.m.r. techniques.[229] Both carboxylate and carboxylic acid groups are thought to be involved in the ion binding. The results are compared with those of the Na^+-poly(acrylic acid) system and marked differences are found between the two polyanions.

The crystal structures of a number of sodium salts of organic moieties, sodium uridine-5'-O-methylphosphate.CH_3OH,[230] sodium 5,6-dihydro-2-thiouracil-6-sulphonate.H_2O,[231] and disodium malonate.H_2O,[232] have been determined by single crystal X-ray diffraction methods. Whereas the Na^+ ion is five coordinate in the uridine derivative, r(Na...O) = 2.31 to 2.41Å, with contact to a sixth oxygen atom at 3.21Å, the Na^+ ions in the thiouracil derivative, r(Na...O) = 2.36 to 2.49Å, and in the malonate salt, r(Na...O) = 2.29 to 2.58Å are six coordinate. The coordination geometry of Na^+ ion in the uridine derivative is ill-defined, but that in the other two salts is distorted octahedral.

Stability constants of alkali metal (Na,K,Rb,Cs) complexes of organic acids (phenol, o-cresol, p-bromophenol, butyric and caproic acids) have been determined by potentiometric pH titration in aqueous solutions.[233] The stability constants increase with increasing pKa of the organic acid.

A THF solution of sodium N,N'-ethylenebis(salicylideniminato)-cobaltate, Na[Co(salen)] reacts reversibly with CO giving a mono-carbonylic species, Na[Co(salen)CO], rapidly evolving under a CO atmosphere to a compound containing $Na[Co(CO)_4]$ as a complexed ion pair, $[(Co(salen))_2NaCo(CO)_4THF]$.[234] The structure of this material (Figure 4) has been solved by single crystal X-ray diffraction methods.[234] Its most interesting feature is the fact that it is a complex of Na^+ octahedrally surrounded by six oxygen atoms, r(Na...O) = 2.38 to 2.46Å, provided by two Co(salen) groups, acting as bidentate chelating ligands, THF and $Co(CO)_4^-$ bonded to

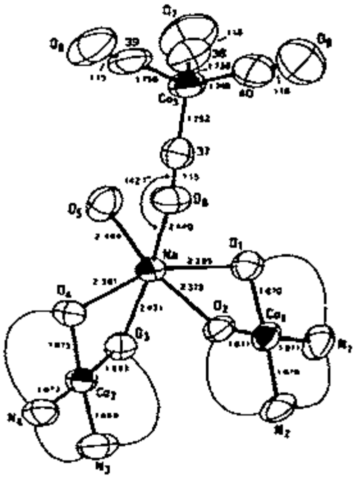


Figure 4. A partial view of the $[(Co(salen))_2NaCo(CO)_4THF]$ molecule, showing a selection of bond distances involving mainly Na and Co atoms. Reproduced with permission from Inorg. Chem. 17 (1978) 3002.

Na^+ through one of the carbonylic oxygen atoms (Figure 4). The $Co(CO)_4^-$ unit has essentially an undistorted tetrahedral symmetry.[234]

A novel method for the location of supercage Na^+ ions and water molecules in hydrated NaX zeolite using X-ray powder diffraction methods has been developed.[235] The procedure utilises microdensitometrically collected photographic intensity data. These are prepared for input into normal programs for crystal structure solution by a routine for unscrambling multi-indexed reflections, which use a heavy atom method based on the zeolite framework sites. The results are compared with those of earlier workers. Two additional Na^+ sites (designated IV and V) have been found; the octahedral coordination of these sites clearly indicate the presence of $[Na(H_2O)_6]^+$ cations.[235]

1.6.6 Potassium and Rubidium Derivatives

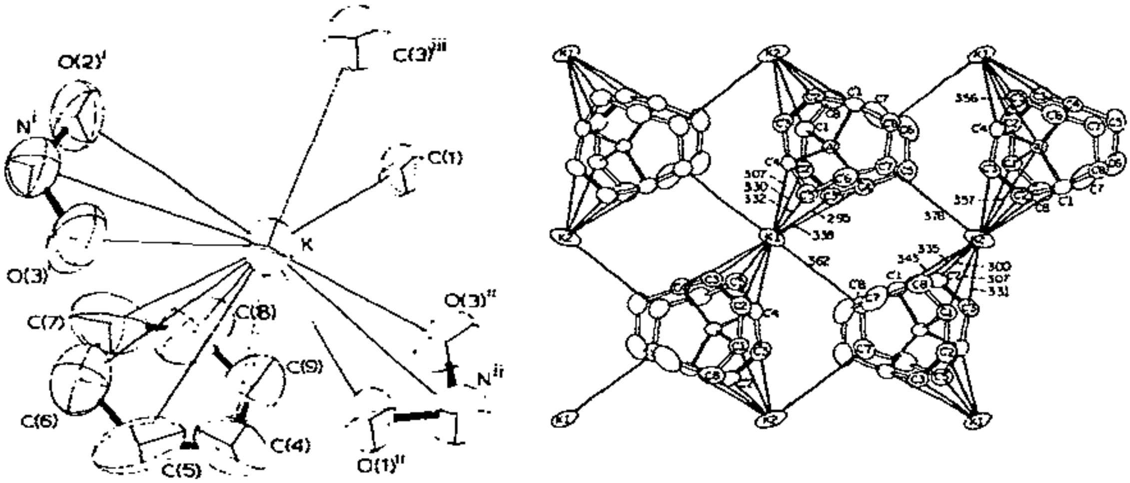
The crystal structures of three potassium salts of complex organic acids have been determined by X-ray diffraction methods.[236-238] Five coordinate potassium, (five oxygen atoms, $r(K...O) = 2.64-2.88$, in a distorted square based pyramidal geometry) is found in potassium benzilate.[236] The potassium ion in potassium hydrogen furan-3-4-dicarboxylate is surrounded by seven oxygen atoms r(K...O) = 2.65 to 3.02Å, and by an eighth at a longer separation, r(K...O) = 3.25Å; the coordination geometry is that of a bicapped trigonal prism.[237] The two crystallographically distinct K^+ ions in the monopotassium salt of 2H-1,2,6-thiadiazine-3,4(4H,6H)-dione-1,1-dioxide monohydrate have seven and eight coordination.[238] K(1) is surrounded by eight atoms (two nitrogen atoms, r(K...N) = 2.91Å and six oxygen atoms, r(K...O) = 2.80 to 2.86Å) which form a distorted hendecahedron; K(2) is at the centre of a monocapped face of a trigonal prism formed by seven oxygen atoms, r(K...O) = 2.80 to 2.94Å.[238]

Crystallographic studies have been undertaken of 7,7,8,8-TCNQ complexes of both K^+ and Rb^+. The 1:1 K^+:TCNQ complex contains a K^+ cation surrounded by eight nitrogen atoms in a cubic arrangement, r(K...N) = 2.86 to 2.97Å.[239] A similar arrangement is found for the Rb^+ cation in the 2:3 Rb^+:TCNQ complex; the cations are surrounded by a distorted cube of eight nitrogen atoms, r(Rb...N) = 2.89 to 3.40Å.[240]

The effect of DCH18C6 and C222 on the kinetics of the protonation of potassium anthracenide by ethanol in THF has been ascertained;[241] the studies emphasize the important role played by contact ion-pair formation.

The reactions of potassium salts e.g. $KBPh_4$, $KC\ell O_4$ with N-donor ligands such as 1,10-phenanthroline and 2,2'-bipyridine has been examined in dry acetone.[242] 3:1 phenanthroline:K^+ adducts ($K(phen)_3BPh_4$, $K(phen)_3C\ell O_4$) and a 1:1 bipyridine:K^+ adduct ($K(bipy)BPh_4$) have been isolated; these products have been characterised by analysis and i.r. and Raman spectroscopy.[242]

The synthesis of $M[A\ell(CH_3)_6NO_3]$ (M^+ = K,Rb,Cs) has been accomplished by addition of stoichiometric ratios of $(CH_3)_3A\ell$ to the corresponding nitrate in benzene.[243] $K[A\ell(CH_3)_3NO_3],C_6H_6$ was obtained by the addition of DB18C6 to the liquid, $K[A\ell_2(CH_3)_6NO_3]$, $7.0C_6H_6$. The crystal structures of $K[A\ell_2(CH_3)_6NO_3]$ and of $K[A\ell(CH_3)_3NO_3],C_6H_6$ have been determined from single crystal X-ray diffraction data. In the dialuminium complex, the nitrate ion bridges the two $(CH_3)_3A\ell$ units together via separate oxygen atoms. There are two formula units in the asymmetric unit and the two independent K^+ ions differ markedly in their environments; K(1) is surrounded by five methyl groups, r(K...C) = 3.18-3.44Å, one bidentate, r(K...O) = 2.92,3.11Å, and one monodentate nitrate ligand, r(K...O) = 2.82Å, whereas K(2) is surrounded by five methyl groups, r(K...C) = 3.11-3.44Å, and a single bidentate nitrate ligand, r(K...O) = 2.80, 2.98Å. The environment of the K^+ ion in the benzene adduct is somewhat more unusual (Figure 5a): the cation is symmetrically disposed over the benzene molecule, r(K...C) = 3.29 to 3.46Å, with two bidentate nitrate groups, r(K...O) = 2.75 to 3.04Å and two methyl units, r(K...C) = 2.27, 2.28 completing the coordination sphere.



(a) (b)

Figure 5. The coordination spheres around the potassium ions in (a) $K[Al(CH_3)_3NO_3].C_6H_6$ and (b) $K[(C_8H_{12})_2Al]$. Reproduced with permission form (a) J. Organomet. Chem., 155 (1978) 1, (b) J. Organomet. Chem., 152 (1978) 367.

1,3-cyclooctadiene reacts with $(CH_3)_3Al$ and potassium in THF to give potassium bis(3,8-cis-cyclooctenyl)aluminate, $K[(C_8H_{12})_2Al]$. The structureof the complex was determined using single crystal X-ray diffractometer techniques. The two crystallographically distinct K^+ ions (Figure 5b) are centrosymmetrically sandwiched between two bis(3,8-cis-cyclooctenyl)aluminate groups, each group providing five carbon atoms for the pseudo-pentagonal prismatic coordination spheres, r(K(1)...C) = 2.95-3.38, r(K(2) ...C) = 3.00-3.43Å.

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