Chapter 1

ELEMENTS OF GROUP 1

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1.1 INTRODUCTION

As for the 1980 review,[1] the papers abstracted for this and the
next Chapter of the present review, have been restricted to those
containing some facet of alkali or alkaline earth metal chemistry
in which the role of the metal is unique; the application of these
metals as simple counter cations is not considered.   The data
abstracted are such that they are best discussed in a number of
subject topics currently of interest and importance; Chapters 1 and
2 are subdivided accordingly.   For certain topics, (e.g., molten
salts, polyether and cryptate complexes) the chemistry of the two
groups of metals is closely interwoven; in these cases, the data
abstracted are discussed once only in the appropriate section of
this Chapter.

1.2 THE ELEMENTS

The application of lithium and of sodium in energy production and
storage technology continually stimulates interest in the chemistry
of these metals, their solutions and their intermetallic compounds.
Chemical aspects of the role of liquid sodium as coolant in the
fast breeder reactor and that of liquid lithium as a candidate for
use as coolant/tritium breeder in the thermonuclear reactor were
considered at the second international conference on 'Liquid Metal
Technology in Energy Production' (April 1980, Richland, Wa., U.S.A.).
Subjects covered for both liquid metals included corrosion and
mass transfer, containment material compatibility and structural
integrity, impurity monitoring and control together with basic
physical chemistry.   Similarly, the development of battery systems
using lithium and sodium based electrodes has led to a large number
of papers, primarily in the Journal of the Electrochemical Society,
in which facets of the chemistry of these metals and of their
intermetallic compounds are described.   Systems which are
considered include low temperature lithium-thionyl chloride or
sulphuryl chloride cells and moderate temperature lithium or
sodium-transition metal oxide or chalcogenide cells; aspects of
chemistry covered include electrode-electrolyte compatibility
studies, alkali metal incorporation in transition metal oxides or
chalcogenides and the introduction of novel electrode materials
constructed from Zintl phases based on lithium or sodium.

Since the majority of the papers published in these two fields
are technologically oriented, they are of only peripheral interest

to the average inorganic chemist and hence will not be considered in detail. The specialist reader is referred to the Proceedings of the Conference[2] and the appropriate volume of the Journal of the Electrochemical Society.[3] There are, however, a number of papers of more general interest; these have been abstracted and are reviewed, as appropriate, in the following subsections.

1.2.1 General Properties

A linear semi-empirical relationship has been shown to hold between the electron affinity of the alkali metals and the ionisation enthalpy of the neighbouring alkaline earth metal.[4] Using this relationship, the electron affinity of francium has been calculated as 45.4 ± 0.2 kJ.mol^{-1}.[4]

Three papers have been published during the period of this Report in which the combustion of alkali metals is considered.[5-7] The relative behaviour of sodium and of potassium has been studied.[5] Although theoretical analyses based on presently availabl kinetic data predict that potassium burns faster than sodium, it was observed experimentally that the two metals burned at similar rates.[5]

A novel method for the analysis of the combustion residues of a sodium fire have been proposed.[6] By hydrolysing the residues, equations (1)-(3), titrating the NaOH so formed and simultaneously

$$Na + H_2O \longrightarrow NaOH + \tfrac{1}{2}H_2 \qquad \qquad ...(1)$$

$$Na_2O + H_2O \longrightarrow 2NaOH \qquad \qquad ...(2)$$

$$Na_2O_2 + H_2O \longrightarrow 2NaOH + \tfrac{1}{2}O_2 \qquad \qquad ...(3)$$

measuring the volume of gases evolved and the $H_2:O_2$ ratio, their exact composition can be determined. The method has been tested on commercial sodium, Na_2O and Na_2O_2 and has been applied successfully to various sodium fires. It is recognised that the presence of NaO_2 may be a potential source of error. Thermodynamic calculations[7] of the composition of the gas phase in equilibrium with burning sodium, however, suggest that NaO_2 cannot be formed in equilibrium with Na and Na_2O or Na_2O_2 and hence it will not be present in combustion residues obtained at normal pressure.

In a related study, the kinetics of alkali metal (Li, Na, K, Cs)

ionisation in an atmospheric pressure $CO/O_2/N_2$ flame of known temperature (T=1930K) have been redetermined[8] using an r.f. resonance method.[9]
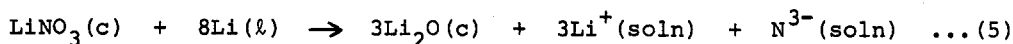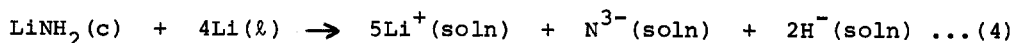
The feasibility of the preparation of high purity silicon by reaction of sodium with SiF_4 has been demonstrated.[10] The reaction is commercially attractive in view of the relatively inexpensive starting materials, SiF_4 being obtained from H_2SiF_6 by precipitation and decomposition of Na_2SiF_6.

The existence of $Li(NH_3)_4$ has been postulated from the results of a study of the $Li-NH_3$ diagram.[11] It is thought to melt congruently forming eutectics with solid NH_3 (at 88.80K) and with solid lithium (at 88.91K); although the eutectic compositions are unknown at present it seems likely that they are very close to $x_{Li}=0.2$, the stoichiometric composition of $Li(NH_3)_4$.
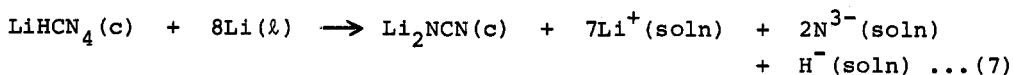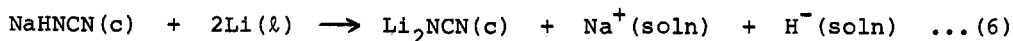
1.2.2 The Alkali Metals as Solvent Media

The solvent properties of liquid lithium and of liquid sodium have been the subject of two reviews.[12,13] In both papers, it is emphasised that the major difference between the two solvents lies in the dominant reactive species: in liquid lithium it is dissolved nitrogen (Li_3N), but in liquid sodium it is dissolved oxygen (Na_2O). Thus, whereas transition metals readily form binary or ternary oxides in liquid sodium, in liquid lithium, they form corresponding nitrides. Indeed, the formation of oxides in liquid lithium is restricted to the lanthanide elements and, even then, only in the absence of Li_3N.

The solution chemistry of liquid lithium has been extensively studied[12-19] during the past year. A summary of chemical interactions between non-metals dissolved in liquid lithium has been presented.[12] Whereas hydrogen (LiH) reacts with neither nitrogen (Li_3N) nor carbon (Li_2C_2), reaction between Li_3N and Li_2C_2 occurs at 673K to form Li_2NCN. Similarly Li_3N reacts with silicon ($Li_{22}Si_5$) to form an, as yet, unidentified ternary nitride, but not with germanium ($Li_{22}Ge_5$). In an attempt to extend and corroborate these observations, the stabilities of a number of salts of heteronuclear polyatomic anions ($LiNH_2$, $LiNO_3$, NaHNCN and $LiHCN_4$) towards lithium has been ascertained at 750K using a resistivity technique to monitor the species formed in solution.[14] Whereas $LiNH_2$ and $LiNO_3$ undergo complete dissociation, equations (4) and (5), NaHNCN and $LiHCN_4$ only undergo partial dissociation,

$$LiNH_2(c) + 4Li(\ell) \rightarrow 5Li^+(soln) + N^{3-}(soln) + 2H^-(soln) \quad ...(4)$$

$$LiNO_3(c) + 8Li(\ell) \rightarrow 3Li_2O(c) + 3Li^+(soln) + N^{3-}(soln) \quad ...(5)$$

equation (6) and (7), Li_2NCN being formed as a stable product.[14]

$$NaHNCN(c) + 2Li(\ell) \longrightarrow Li_2NCN(c) + Na^+(soln) + H^-(soln) \quad ...(6)$$

$$LiHCN_4(c) + 8Li(\ell) \longrightarrow Li_2NCN(c) + 7Li^+(soln) + 2N^{3-}(soln)$$
$$+ H^-(soln) \quad ...(7)$$

A number of these experimental observations have been theoretically corroborated in a thermochemical analysis ($500 \leqslant T/K \leqslant 1500$) of the Li-O-H, Li-O-C and Li-N-C systems.[15] Metallurgical phase diagrams reveal that the compounds LiOH, Li_2CO_3 and LiCN cannot coexist with lithium and that interactions between Li_2O, LiH and Li_2C_2 will be negligible. Conversely, Li_2NCN has been shown to be stable to liquid lithium and hence strong interaction is expected to occur between Li_3N and Li_2C_2.[15]

Nitride formation has been observed to be the primary feature of corrosion of several transition metals in liquid lithium.[13,16,17] The corrosion of titanium, zirconium, vanadium, niobium and tantalum plates immersed in static lithium containing high Li_3N concentrations has been studied at 923K;[13] X-ray powder diffraction analysis of the corroded surfaces showed the formation of binary or ternary nitrides. Resistivity studies of the reaction of chromium plates with Li_3N dissolved in liquid lithium have shown that at $T \geqslant 773K$ and at $x_N \geqslant 0.0005$, Li_3N attacks the chromium to produce a surface deposit which is tentatively suggested to be a ternary lithium-chromium-nitride.[16] Preliminary compatibility studies between AlSl 316 stainless steel plates and liquid lithium at 923K correlated a slight increase in plate weight with a reduction of the nitrogen content of the liquid metal.[17]

The stability of boron nitride towards lithium has been ascertained using an electrochemical method;[18] reaction was observed to occur with the formation of Li_3N and an unidentified lithium boride.

The solubilities of silicon ($0.00 \leqslant x_{Si} \leqslant 0.0165$) and of germanium ($0.00 \leqslant x_{Ge} \leqslant 0.0872$) in liquid lithium have been determined by the

resistivity technique;[19] they can be represented, in part, by
equations (8) and (9).   X-ray powder diffraction studies show
that the compounds $Li_{22}Si_5$ and $Li_{22}Ge_5$ precipitate from dilute

$$\ln x_{Si} = 5.548 - 6775/T \qquad 500 \leqslant T/K \leqslant 700 \qquad \ldots (8)$$

$$\ln x_{Ge} = 5.459 - 6630/T \qquad 530 \leqslant T/K \leqslant 715 \qquad \ldots (9)$$

solutions of silicon and of germanium in liquid lithium.   The
resulting point of $Li_{22}Ge_5$ (934K) and the lithium-rich eutectic
horizontal (453.5K) have been established by thermal methods and
used to augment the Li-Ge phase diagram $(0.00 \leqslant x_{Ge} \leqslant 0.20)$.[19]

   Results have been reported for sodium solutions containing a
number of diverse solutes, including non-metals,[20,21] metals[22] and
metal oxides.[23]   The kinetics of the decomposition of NaOH in
liquid sodium, equation (10), have been determined $(573 \leqslant T/K \leqslant 773)$

$$2Na(\ell) + NaOH(soln) \rightleftharpoons Na_2O(soln) + NaH(soln) \qquad \ldots (10)$$
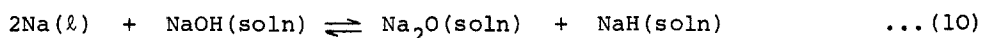
by monitoring the variation in concentration of the dissolved
decomposition products using electrochemical oxygen and hydrogen
meters.[20]   The kinetics of the gettering of dissolved oxygen
(by uranium foil) and of dissolved hydrogen (by yttrium foil) have
been determined similarly.[20]   Equilibrium measurements on the
Na-U-O system have been used to derive thermodynamic data for the
formation of Na_3UO_4, the ternary oxide in equilibrium with UO_2
and sodium containing dissolved oxygen; the data are reported in
section 1.4.4.[20]

   In an independent, yet complementary investigation, the
solubility of UO_2 (and of PuO_2) in liquid sodium has been determined
experimentally $(948 \leqslant T/K \leqslant 1083)$.[23]   The results exhibit considerable
scatter and appear to be dependent on the oxygen content of the
sodium; at 1073K and an oxygen concentration of <1 wppm O, a
maximum solubility value of 0.06 wppm UO_2 (0.02 wppm PuO_2) is
quoted.   It is tacitly assumed that $UO_2(PuO_2)$ is the soluble
species.   As pointed out earlier, however, $Na_3UO_4(Na_3PuO_4)$ is also
present as a solid phase in this system and may be the soluble
species especially at higher oxygen concentrations.   This
duplicity of dissolved species is probably responsible for the
observed scatter in the data and their dependence on oxygen

concentration.[23]

Preliminary compatibility studies have also been effected between commercially available UO_2 ceramics and liquid sodium;[24] no deterioration of the UO_2 was observed, even after 100 hours immersion in sodium at 1173K. Comparative studies were undertaken on ceramics based on ThO_2, MgO and Al_2O_3.[24] Whereas ThO_2, like UO_2, did not appear affected after 100 hours exposure at 1173K, the MgO- and Al_2O_3-based ceramics exhibited discoloration of the surface and marked deterioration in structural integrity.

Electrochemical studies of carbon activity in liquid sodium solutions (T=913K) strongly suggest that carbon dissolves as C_2 units and in accordance with Henry's Law.[21] The results also give an approximate value (16 wppm C) for carbon solubility in sodium with respect to graphite at 913K. Similar studies have also shown that the carbon formed (together with hydrogen and methane) as a product of the reaction of mineral oil with liquid sodium readily dissolves in the liquid metal increasing its carbon activity.[21]

The solubility of iron in liquid sodium containing very low levels of oxygen has been determined by a radio-tracer technique;[22] it can be represented by equation (11). Preliminary solubility

$$\log S(\text{wppm Fe}) \ = \ 4.720 - 4116/T \qquad 658 \leqslant T/K \leqslant 997 \qquad \ldots (11)$$

data have also been reported for manganese in liquid lithium;[22] they lie in the range from 0.1 to 10 wppm Mn ($623 \leqslant T/K \leqslant 923$). As in the case of $UO_2(PuO_2)$ the solubility data for both iron and manganese are susceptible to the presence of oxygen in the liquid sodium. They increase markedly with increase in oxygen concentration, presumably owing to the formation of more soluble oxygenated species.[22]

1.2.3 Metallic Solutions

Chemical short range ordering (i.e., pseudo compound formation) in liquid phase binary metallic solutions has been studied in a number of laboratories.[25-30] Thermodynamic investigations of liquid Li-Ag,[25] Li-Pb,[25] Na-Hg,[26] and Na-Tl[27] solutions have provided evidence for ordering in these systems. The excess stabilities of Li-Ag and of Li-Pb solutions exhibit maxima at $Li_{0.5}Ag_{0.5}$ and $Li_{0.80}Pb_{0.20}$.[25] Similar maxima occur in the heat

capacities of liquid Na-Hg[26] and of Na-Tl[27] solutions at $Na_{0.33}Hg_{0.67}$ and $Na_{0.50}Tl_{0.50}$; the compositions at which these maxima occur can be correlated with the stoichiometries of the intermetallic compounds, LiAg, $Li_{22}Pb_5$, $NaHg_2$ and NaTl. The thermodynamic properties of the Na-Hg solutions were measured not only as a function of temperature and composition but also as a function of pressure. In principle, all the thermodynamic properties of a liquid binary metal solution A_xB_{1-x} can be determined using this method, providing they are known for the pure components A and B.

Entropy data for liquid Na-Pb solutions, which exhibit anomalous behaviour at $Na_{0.8}Pb_{0.2}$ have been successfully calculated using the theory of the entropy of mixing of compound-forming liquid solutions on the basis of the pseudobinary mixture of hard spheres model.[28]

The origin of the short range ordering phenomenon, is thought to be ionic in nature. Indeed, theoretical studies of M-Au (M = Li, Na, K, Rb, Cs) liquid solutions have been undertaken[29] using a tight-binding model which includes short range order and charge transfer in a self-consistent way. The model accounts satisfactorily for both the metallic conductivity of $Li_{0.50}Au_{0.50}$ and the ionic conductivity of $Cs_{0.50}Au_{0.50}$. Transfer of electronic charge from potassium to sodium has even been shown to be a possibility in Na-K liquid solutions.[30]

1.2.4 Intermetallic Compounds

Wen and Huggins[31,32] have undertaken a comprehensive emf study of the thermodynamic properties of the intermetallic compounds formed in the Li-Ga[31] and Li-Sn[32] systems; materials such as these are presently being considered for use as either reactants or mixed conducting matrices in lithium-based battery electrodes. Coulombic titration curves showed that three compounds exist in the Li-Ga system (nominal compositions Li_2Ga, Li_3Ga_2, LiGa) and that six compounds exist in the Li-Sn system (nominal compositions $Li_{22}Sn_5$, Li_7Sn_2, $Li_{13}Sn_5$, Li_5Sn_2, Li_7Sn_3 and LiSn). Thermodynamic data for the intermediate phases are collected in Table 1. The existence of Li_2Ga, Li_3Ga_2 and LiGa was further substantiated by X-ray powder diffraction analysis. Evidence for Li_5Ga_4 was not obtained in either the coulombic or the structural study.[31] Schafer et al,[33] however, have prepared single crystals of this material; X-ray diffraction studies indicate that it has a structure intermediate

Table 1.   Thermodynamic data (688K) for the intermediate phases
            in the Li-Ga[31] and Li-Sn[32] systems.

Phase	$-\Delta H_f^{\circ}$(X,c,688K) kJ mol^{-1}	$-\Delta S_f^{\circ}$(X,c,688K) J K^{-1}mol^{-1}	$-\Delta G_f^{\circ}$(X,c,688K) kJ mol^{-1}
Li_2Ga	-	-	62
Li_3Ga_2	-	-	115
$LiGa$	-	-	51
$Li_{22}Sn_5$	220	75.6	168.0
Li_7Sn_2	197	63.1	153.6
$Li_{13}Sn_5$	165	52.8	128.7
Li_5Sn_2	159	49.7	124.8
Li_7Sn_3	151	47.7	118.2
$LiSn$	70	25.8	52.2

between those of LiGa and Li_3Ga_2 (Figure 1).
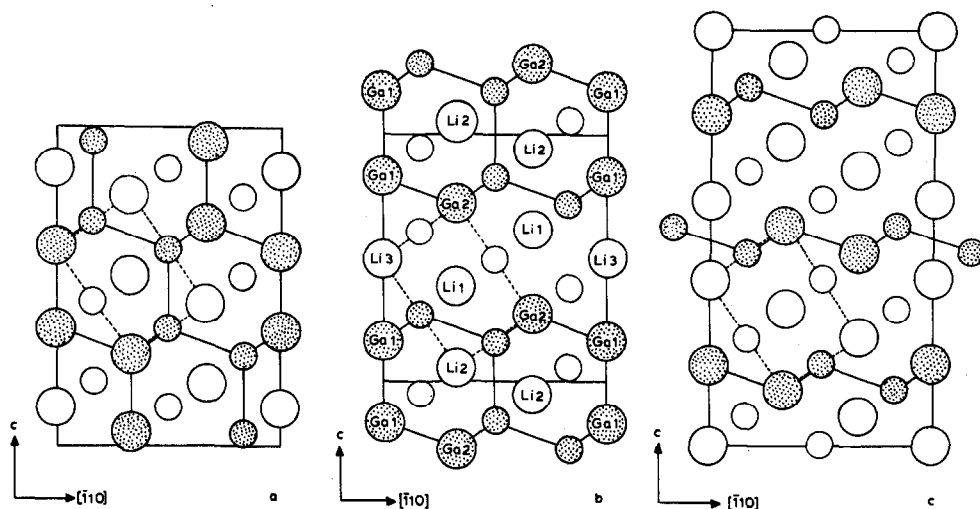

Figure 1.   Projection onto the (110) plane of the unit cells of
             (a) LiGa (in a pseudo-rhombohedral setting), (b) Li_5Ga_4
             and (c) Li_3Ga_2 (reproduced by permission from
             Z. anorg. allg. Chem., 474(1981)221).

Table 2. Unit cell parameters for binary and ternary intermetallic phases.

Phase	Symmetry	Space Group	a/pm	b/pm	c/pm	$\beta/°$	Reference
Li_2Ga	orthorhombic	Cmcm	456.2	954.2	436.4	-	31
Li_3Ga_2	rhombohedral	R3m	436.7	-	1389.6	-	31
LiGa	cubic	(NaTl)	621.3	-	-	-	31
Li_5Ga_4	hexagonal	$P\bar{3}m1$	437.5	-	825.7	-	33
$RbGa_3$	tetragonal	$I\bar{4}m2$	631.5	-	1500.0	-	34
$RbGa_7$	monoclinic	C2/m	1143.2	660.3	1025.9	111.85	35
$\alpha-Li_2ZnGe$	cubic	(Li_3Bi)	614.8	-	-	-	36
$\beta-Li_2ZnGe$	hexagonal	$P\bar{3}m1$	432.6	-	1647.0	-	36
$Rb_4Au_7Sn_2$	rhombohedral	$R\bar{3}m$	680.1	-	2909.0	-	37

Phase transitions in Li_2ZnGe have been studied by X-ray diffraction and d.t.a. methods.[36] The transition from $\beta-Li_2ZnGe$ (hexagonal-Na_3As structure) to $\alpha-Li_2ZnGe$ (cubic-Li_3Bi structure) occurs at 775K with ΔH^O_{trans}=4.5 kJ mol^{-1}; $\alpha-Li_2ZnGe$ melts at 1058K with ΔH^O_m=39.9 kJ mol^{-1}. Pertinent crystallographic data are included in Table 2, together with unit cell parameters for $Rb_4Au_7Sn_2$.[37]

Fascinating observations have been made when Zintl phases have been extracted into ethylene diamine containing the cryptate, C222.[38-40] [119]Sn-n.m.r. studies of the solutions resulting from contact of Na_xSn alloys ($1 \leqslant x \leqslant 2$) with ethylenediamine in both the presence and absence of C222 indicate the presence of the naked cluster, Sn_4^{2-}. Similarly Na-Sn-Tl, Na-Sn-Ge and Na-Sn-Te alloys give rise to the heteroatomic naked clusters, $TlSn_8^{5-}$, nido-$Sn_{9-x}Ge_x^{4-}$ ($0 \leqslant x \leqslant 9$) and $SnTe_4^{4-}$, respectively. The complexes are thought to be polyhedral cluster anions, with the exception of $SnTe_4^{4-}$ which appears to be a classical Sn-centred tetrahedral tellurostannate anion.[38] The fluxional behaviour of Sn_4^{2-} in solution has been predicted from ab initio calculations.[39] Extraction of KSn_2 with ethylenediamine containing C222 gave, inter alia, black plate-shaped crystals which analysed as $[K(C222)]_2.Sn_4.en$; $[Na(C222)]_2.Ge_4$ has also been synthesised.[40] Single crystal X-ray diffraction studies have shown the salts to contain the complex cryptate cation $[M(C222)]^+$ and the 18-electron, tetrahedral cluster

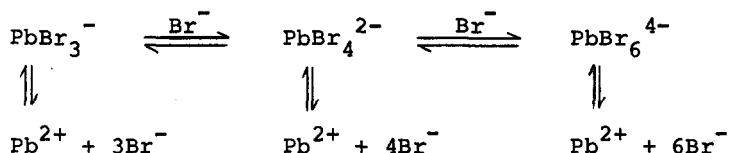anions, Sn_4^{2-} and Ge_4^{2-}.[40]

1.3 MOLTEN SALTS

Recent interest in molten salt chemistry has centred on their structural characteristics and on the behaviour of dissolved solutes.   The change of emphasis noted in the previous Report[41] has been maintained, there being a higher number of papers extracted for the solution properties subsection vis-a-vis the structural and thermodynamic properties subsection.

1.3.1   Structural and Thermodynamic Properties

The structure of molten NaCl has been reinvestigated using X-ray diffraction methods.[42]   The first peak position in the radial distribution curve occurs at 273pm.   This value is consistent with that (275pm) obtained in an earlier X-ray diffraction analysis[43] and the summation of the cation and anion radii (276pm); it is inferred that the value (260pm) obtained by neutron diffraction methods[44] is low and should not be used as evidence of coincidence with the computer-simulation calculations.

Thermodynamic parameters of NaCl-KCl,[45] NaCl-AlCl$_3$,[46] NaCl-NiCl$_2$,[47] KCl-CdCl$_2$,[48] MBr (M=K,Rb,Cs)-PbBr$_2$[49] and LiI-NdI$_3$[50] molten salt mixtures have been determined by vapour phase,[45,46,50] calorimetric[48] and electrochemical[46,47,49] methods.   With the exception of the NaCl-KCl mixtures, the thermodynamic data have been used to derive structural characteristics.   Substantial evidence is provided for the stabilisation and structural ordering of the NaCl-AlCl$_3$,[46] NaCl-NiCl$_2$[47] and KCl-CdCl$_2$[48] melts near the stoichiometric compositions NaAlCl$_4$, Na$_2$NiCl$_4$ and KCdCl$_3$, respectively; a model based on alkali metal cations and discrete complex anions has been proposed for these systems.[47]

The results for the MBr-PbBr$_2$ system[49] indicate that a number of complex ions, including PbBr$_4^{2-}$, PbBr$_6^{4-}$ and possibly PbBr$_3^-$, are present in the melts and that a series of equilibria exist as shown in scheme 1:

$$PbBr_3^- \underset{}{\overset{Br^-}{\rightleftharpoons}} PbBr_4^{2-} \underset{}{\overset{Br^-}{\rightleftharpoons}} PbBr_6^{4-}$$

$$\updownarrow \qquad\qquad \updownarrow \qquad\qquad \updownarrow$$

$$Pb^{2+} + 3Br^- \qquad Pb^{2+} + 4Br^- \qquad Pb^{2+} + 6Br^-$$
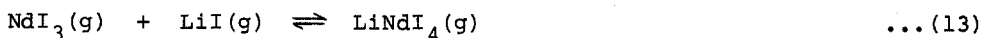
Scheme 1

Similarly, the results for the LiI-NdI$_3$ system[50] indicate that iodine is present in three different anionic environments - terminal, bridged and free - under equilibrium conditions, equation (12).

$$2[NdI_6]^{3-} \rightleftharpoons [Nd_2I_{11}]^{5-} + I^- \qquad \ldots(12)$$
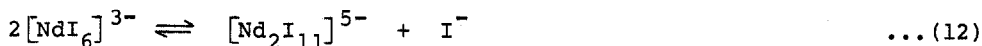
Different species are present in the gas phase equilibrium, equation (13), above these liquids.

$$NdI_3(g) + LiI(g) \rightleftharpoons LiNdI_4(g) \qquad \ldots(13)$$

The salient features of the thermodynamic analysis of the NaCl-KCl system[45] are the small negative deviations from ideality observed in the liquid state and the large positive deviations from ideality in the solid state; the latter are attributed to the strain energy which arises from the difference in radii between Na$^+$ and K$^+$.[45]

Raman spectra have been recorded for Li$_2$SO$_4$,[51,52] Na$_2$SO$_4$,[51] Na$_2$CO$_3$,[51] K$_2$CO$_3$,[51] NaClO$_3$[51] melts and for Li$_2$SO$_4$-K$_2$SO$_4$,[51,52] Li$_2$CO$_3$-K$_2$CO$_3$[51] and NaClO$_3$-AgClO$_3$[51] molten mixtures as a function of temperature and, where appropriate, composition. The symmetric stretching frequencies (ν_1) of the anions in these melts have been combined with literature data for other oxyanions and have been correlated with the polarizing power and polarizability of the cation.[51] The asymmetric stretching frequency (ν_3) of the SO$_4$$^{2-}$ anion is split in Li$_2$SO$_4$ and Li$_2$SO$_4$-K$_2$SO$_4$ melts, indicating the presence of structures with C$_{3v}$ and C$_s$, rather than T$_d$, symmetry;[52] these findings are in agreement with models proposed from X-ray diffraction studies.[53]

Pressure-composition-temperature data have been collected for the LiCl-LiH system by measuring equilibrium hydrogen pressures in a Sievert's apparatus.[54] The system follows Sievert's Law:

$$p_{H_2}^{\frac{1}{2}} = k \cdot x_{LiH}/x_{LiCl} \qquad \ldots(14)$$
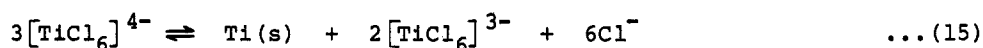
for compositions below 10 mol % LiH.[54]

1.3.2   Solution Properties

The solvent properties of a wide range of molten salts have been studied; although halides and nitrates predominate as reaction media,

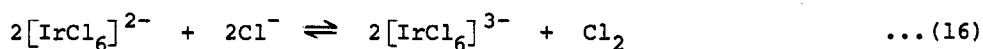some data have been reported for carbonates, sulphates and pyrosulphates.

Solubility data for NiO and Co_3O_4 in molten NaCl (1100K) have been determined[55] by coulombic titration of the respective chlorides ($NiCl_2$, $CoCl_2$) with electrochemically generated oxide ion. Analysis of the data is complicated by competitive reactions which result in the formation of Na_2O_2, $NaNiO_2$ and $NaCoO_2$.[55]

Electronic absorption spectroscopic studies of the coordination chemistry of titanium halides in LiCl-KCl eutectic ($658 \leqslant T/K \leqslant 1185$)[56] and NaCl-KCl eutectic containing varying amounts of KF ($963 \leqslant T/K \leqslant 1023$)[57] have been undertaken. In LiCl-KCl melts, Ti(III) ions are present in an octahedral $[TiCl_6]^{3-}$-tetrahedral $[TiCl_4]^-$ coordination equilibrium, the equilibrium favouring $[TiCl_4]^-$ at elevated temperatures. Although Ti(II) ions are octahedrally coordinated $[TiCl_6]^{4-}$ in this solvent a disproportionation equilibrium, equation (15), is established as evidenced by the

$$3[TiCl_6]^{4-} \rightleftharpoons Ti(s) + 2[TiCl_6]^{3-} + 6Cl^- \qquad \ldots(15)$$

formation of a metallic film. In NaCl-KCl melts, Ti(III) ions form tetragonally distorted octahedral $[TiCl_6]^{3-}$ complexes with $\sim D_{4h}$ symmetry. As the concentration of KF is increased, mixed coordination species $[TiCl_xF_{6-x}]^{3-}$ are obtained until at KF:Ti(III) ratios in excess of 100, the trigonally distorted octahedral $[TiF_6]^{3-}$ complex with $\sim D_3$ symmetry is formed.[57]

Chlorination of iridium in molten KCl or LiCl-KCl eutectic leads to a mixture of $[IrCl_6]^{3-}$ and $[IrCl_6]^{2-}$ in the ratio Ir(III):Ir(IV) = 2:1;[58] this is thought to be indicative of the establishment of an intramolecular redox equilibrium, equation (16).

$$2[IrCl_6]^{2-} + 2Cl^- \rightleftharpoons 2[IrCl_6]^{3-} + Cl_2 \qquad \ldots(16)$$

Reactions of FeS electrodes in LiCl-KCl melts of varying composition (673K)[59] and in LiF-LiCl-LiBr (0.22-0.31-0.47) molten salt (700K)[60] have been elucidated by a combination of phase studies, cyclic voltammetry and emf measurements. In LiCl-KCl melts,[59] six electrochemical and four chemical reactions were established; they involved the formation of either Li_2FeS_2 or $LiK_6Fe_{24}S_{26}Cl$. The experiments using LiF-LiCl-LiBr as solvent were undertaken to ascertain the free energy of formation of

Li_2FeS_2;[60] $\Delta G_f^O(Li_2FeS_2,c,700K) = -524.9$ kJ mol^{-1} - this is
equivalent to a free energy of formation from Li_2S and FeS of
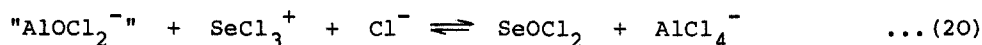-1.9 kJ mol^{-1} at 700K.[60]

The deposition characteristics of gadolinium from LiF-LiCl-GdF$_3$
(0.18-0.80-0.02), LiF-BaF$_2$-GdF$_3$ (0.75-0.10-0.15) and LiF-GdF$_3$
(0.75-0.25) electrolytes have been evaluated.[61]   The morphology
of the deposited gadolinium differed with the electrolyte, plate-
like, block-like and needle-like crystals being obtained from the
three molten salts, respectively.[61]

The corrosion behaviour of platinum, gold, tin oxide and glassy
carbon electrodes immersed in LiCl-KCl eutectic at 723K has been
assessed by electrochemical characterisationof the UO_2^{2+}/UO_2^+
couple using normal pulse polarography.[62]   Whereas platinum and gold
electrodes corroded in the melt, tin oxide and glassy carbon
electrodes were inert.   The structural integrity of vanadium-
titanium-aluminium-molybdenum (0.90-0.08-0.01-0.01) alloy electrodes
immersed in molten LiCl-KCl eutectic has also been ascertained.[63]

Several features of the chemistry of chloroaluminate melts have been
elucidated.[56,64-70]   The solubility of NaCl in NaCl-AlCl$_3$ melts
at 448K has been found to be $x_{NaCl} = 0.50209$ by potentiometric
measurements with chlorine/chloride electrodes.[64]   Furthermore in
the pCl range of 3.885-5.034, the measured potential of these
electrodes could be rationalised by a combination of three reactions,
equations (17)-(19).[64]   Solution   of SeCl$_4$ in this melt in the pCl

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \qquad\qquad pK = 7.052 \qquad\qquad ...(17)$$

$$3Al_2Cl_7^- \rightleftharpoons 2Al_3Cl_{10}^- + Cl^- \qquad\qquad pK = 6.9 \qquad\qquad ...(18)$$

$$2Al_3Cl_{10}^- \rightleftharpoons 3Al_2Cl_6 + 2Cl^- \qquad\qquad pK = 14 \qquad\qquad ...(19)$$

range 1.183-4.662 leads to SeCl$_3^+$.[64]   Under basic conditions
(pCl < 2.58) and in the presence of oxide impurity (formulated as
"AlOCl$_2^-$") SeCl$_3^+$ reacts to form SeOCl$_2$ (equation (20)).   Under
acidic conditions (pCl > 2.58) no reaction occurs, the oxide

$$\text{"AlOCl}_2^-\text{"} + SeCl_3^+ + Cl^- \rightleftharpoons SeOCl_2 + AlCl_4^- \qquad\qquad ...(20)$$
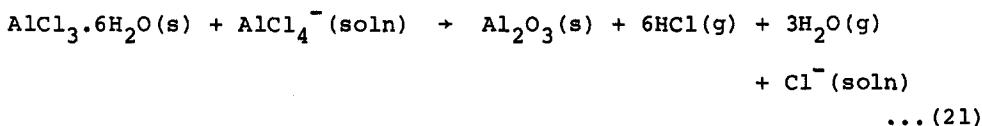
impurity existing in the form of the oxochloroaluminium compound.[64]
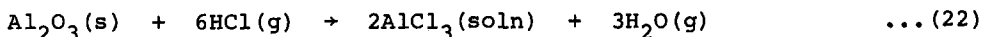Electronic absorption spectroscopic studies of the coordination

chemistry of titanium halides in KCl-AlCl$_3$ melts (1.00 $\leqslant$ x$_{AlCl_3}$ $\leqslant$ 0.49; 471$\leqslant$ T/K $\leqslant$ 894) have been effected.[56]   Although Ti(III) ions are octahedrally coordinated $[TiCl_6]^{3-}$ in pure AlCl$_3$ and in KCl-AlCl$_3$ melts with x$_{AlCl_3}$ $\geqslant$0.67, octahedral $[TiCl_6]^{3-}$-tetrahedral $[TiCl_4]^{-}$ coordination equilibria are established at lower AlCl$_3$ contents.   Ti(II) ions adopt octahedral coordination $[TiCl_6]^{4-}$ in AlCl$_3$ and in KCl-AlCl$_3$ melts with x$_{AlCl_3}$ $\geqslant$0.51.   The situation is complicated, however, by a disproportionation equilibrium which occurs for x$_{AlCl_3}$ $\leqslant$ 0.6 and which culminates at x$_{AlCl_3}$ = 0.49 where Ti(II) ions are unstable and the spectrum of Ti(III) ions in an octahedral-tetrahedral coordination equilibrium is obtained.[56]

Oxidation reactions of aluminium,[65,66] sulphur[67] and iodine[68] have been studied in NaCl-AlCl$_3$ melts.   The kinetics of the oxidation of aluminium to AlCl$_3$ in equimolar NaCl-AlCl$_3$ melt (620 $\leqslant$ T/K $\leqslant$ 780) using PbCl$_2$, CdCl$_2$ or CuCl$_2$ have been shown to be first order.[65]   In the presence of chlorine gas the halogen carrier (e.g. PbCl$_2$) can be recovered in good yield.[66]   U.v.-visible and e.s.r. spectroscopic studies (405 $\leqslant$ T/K $\leqslant$ 523) of the electro-oxidation of sulphur in acidic NaCl-AlCl$_3$ (0.37-0.63) melts clearly show[67] that the oxidation of S$_8$ to SCl$_3^{+}$ is very complex;suggested intermediates included diverse polymeric sulphur cations and SCl$_2$.[67] Resonance Raman and u.v.-visible spectroscopic studies, together with thin layer coulometry, have shown[68] that whereas oxidation of iodine to ICl proceeds via I$_2^{+}$ in acidic NaCl-AlCl$_3$ (0.37-0.63) melts, oxidation in basic NaCl-AlCl$_3$ (0.50-0.50) melts leads directly to ICl.

Low temperature (373 $\leqslant$ T/K $\leqslant$ 393) dehydration of AlCl$_3$,6H$_2$O in MCl-AlCl$_3$ (M = Li,Na,K) melts is not possible owing to the thermal decomposition of the hexahydrate into Al$_2$O$_3$, equation (21).[69] At higher temperatures (673 $\leqslant$ T/K $\leqslant$ 773), however, the alumina so

$$AlCl_3.6H_2O(s) + AlCl_4^{-}(soln) \rightarrow Al_2O_3(s) + 6HCl(g) + 3H_2O(g)$$
$$+ Cl^{-}(soln)$$
$$...(21)$$

formed is reactive to overpressures of HCl and readily forms the anhydrous chloride, equation (22).

$$Al_2O_3(s) + 6HCl(g) \rightarrow 2AlCl_3(soln) + 3H_2O(g) \qquad ...(22)$$
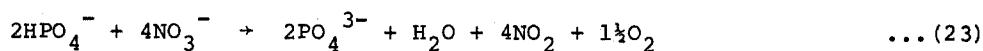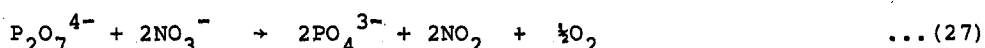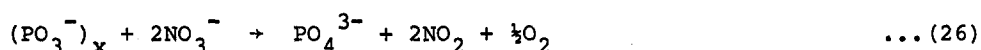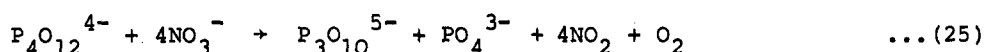
Electrodeposition and dissolution processes occuring on aluminium surfaces submerged in $LiCl-AlCl_3$ (0.5075-0.4925) molten salts have been elucidated.[70] The major surface product, LiAl, is formed predominantly by a deposition process rather than an implantation mechanism. Similar studies were also conducted using $NaCl-AlCl_3$ (0.5025-0.4975) melts;[70] unfortunately the role of dissolved oxygen species in this melt complicates the interpretation of the deposition and dissolution data.

The application of chloroantimonates as molten salt solvents has also been investigated.[71,72] The solubility of antimony metal in molten $CsCl-SbCl_3$ ($0.00 \leqslant x_{CsCl} \leqslant 0.80$; $678 \leqslant T/K \leqslant 915$) has been determined.[71] Isothermal solubility data pass through a maximum at $x_{CsCl} \sim 0.3$. It is postulated that this behaviour is due to the formation of chlorophilic and chlorophobic species. Whereas both species are thought to exist in melts rich in $SbCl_3$, the chloro-philic species is stabilised in melts rich in $CsCl$.[71]

Electronic absorption spectra of solutions of a number of transition metal chlorides (MCl_3 (M = Ti,V,Cr,Fe) and MCl_2 (M = Mn, Co,Ni)) have been studied[72] in $KCl-SbCl_3$ (0.08-0.92) melts and compared with similar data for $SbCl_3$ melts. The predominant coordination geometry observed is octahedral; it is only in the case of Mn(II) and Co(II) that tetrahedral coordination geometries are observed. The Co(II) system exhibits an octahedral-tetrahedral coordination equilibrium which is dependent on the chloride content of the melt.[72]

The solution chemistry of molten nitrates has been the subject of several papers; solvents considered include KNO_3,[73] $LiNO_3-KNO_3$ eutectic,[74,75] equimolar $NaNO_3-KNO_3$,[76,77] $NaNO_3-Ba(NO_3)_2$ eutectic[78] and $KNO_3-Ba(NO_3)_2$ eutectic.[79] Cryoscopic studies[73] of solutions of diverse phosphates in molten KNO_3 suggest that whereas the polyanions $P_3O_{10}^{5-}$ and $P_3O_9^{3-}$ are stable, the simple phosphates and classical metaphosphates dissociate with the formation of the stable PO_4^{3-} anion, and in some cases, $P_3O_{10}^{5-}$ or $P_3O_9^{3-}$. The reactive phosphates appear to act as Lux-Flood acids abstracting O^{2-} from NO_3^- forming PO_4^{3-}, NO_2 and O_2, equations (23)-(27).[73]

$$2HPO_4^- + 4NO_3^- \rightarrow 2PO_4^{3-} + H_2O + 4NO_2 + 1\tfrac{1}{2}O_2 \qquad \ldots(23)$$

$$P_4O_{12}^{4-} + 2NO_3^- \rightarrow P_3O_9^{3-} + PO_4^{3-} + 2NO_2 + \tfrac{1}{2}O_2 \qquad \ldots(24)$$

$$P_4O_{12}^{4-} + 4NO_3^- \rightarrow P_3O_{10}^{5-} + PO_4^{3-} + 4NO_2 + O_2 \qquad \ldots(25)$$

$$(PO_3^-)_x + 2NO_3^- \rightarrow PO_4^{3-} + 2NO_2 + \tfrac{1}{2}O_2 \qquad \ldots(26)$$

$$P_2O_7^{4-} + 2NO_3^- \rightarrow 2PO_4^{3-} + 2NO_2 + \tfrac{1}{2}O_2 \qquad \ldots(27)$$

Electronic absorption spectroscopic studies[74] of the solutions formed by dissolution of TiF_3 and of $Co(NO_3)_2$ in molten $LiNO_3$-KNO_3 eutectic containing KF indicate the formation of the tetrahedral complexes, $[TiF_4]^-$ and $[CoF_4]^{2-}$. Similar studies[75] of molten $LiNO_3$-KNO_3 eutectic containing KN_3 and either Co(II), Ni(II) or Cu(II) salts gave evidence for the formation of transition metal azido complexes.

Thermodynamic parameters of diverse equilibria pertaining in molten $NaNO_3$-KNO_3,[76,77] and in molten MNO_3-$Ba(NO_3)_2$ (M = Na,K)[78,79] have been evaluated. Stability constants for $[Ca(IO_3)]^+$, $[Ca(IO_3)_2]$, $[Ag(MoO_4)]^-$, $[Ag_2MoO_4]$ and $[Ag(MoO_4)_2]^{3-}$ and thermodynamic data for the associated equilibria have been determined in molten equimolar $NaNO_3$-KNO_3 ($523 < T/K < 613$) by Holmberg et al. from potentiometric and solubility measurements.[76,77] A continuous range of solid solutions $[(Ag_xNa_{1-x})_2MoO_4]$ ($1 < x < 0.4$) was observed at 553K; these solids can be considered to be regular cationic substitutional solutions with an interaction parameter of 9.6 ± 0.5 kJ mol^{-1}.[77] Gupta et al.[78] have evaluated thermodynamic parameters of the formation of CdI^+ and of CdI_2 in molten KNO_3-$Ba(NO_3)_2$ (0.876-0.124) eutectic ($568 < T/K < 608$) and of the equilibrium between $AgCl_2^-$, $AgBr_2^-$ and $AgClBr^-$ (equation (28)) in molten $NaNO_3$-$Ba(NO_3)_2$ (0.942-0.058) eutectic ($623 < T/K < 673$) from

$$AgCl_2^- + AgBr_2^- \rightleftharpoons 2AgClBr^- \qquad \ldots(28)$$

concentration cell emf data. The equilibrium constant for equation (28) corresponds to a slight stabilisation of the mixed complex.

The kinetics of the CO_2/O_2 reaction in molten Li_2CO_3-K_2CO_3 eutectic have been elucidated[79] using an electrolytic cell containing porous NiO electrodes; the reported reaction orders are complex and do not correlate with any of the proposed reaction mechanisms.

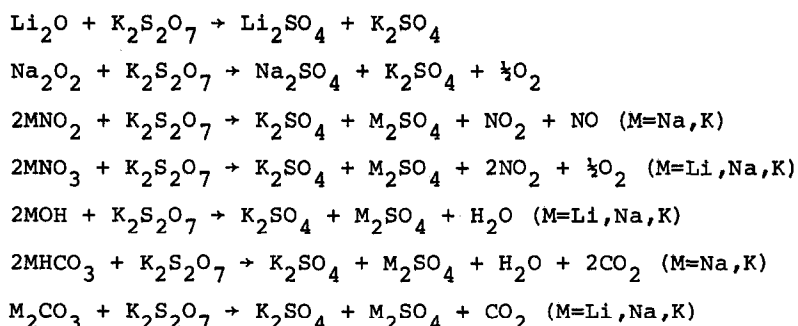Solubility data for NiO and CoO in molten Na_2SO_4 (1200K) have

been measured by coulombic titration of $NiSO_4$ and $CoSO_4$ with electrochemically generated oxide ion.[55]   Analysis of the data was complicated by competitive reactions leading to the formation of Na_2O_2, $NaNiO_2$ and $NaCoO_2$.

Anion-cation interactions in molten equimolar Na_2SO_4-K_2SO_4 have been investigated using both electronic and vibrational spectroscopic methods.[80]   Addition of Al^{3+} ions to this melt results in the formation of a bidentate (C_{2v}) and a monodentate (C_{3v}) species. In the latter case, the Al^{3+} ion may also interact with a contiguous sulphate ion in a similar fashion to form a bridging C_{2v} species. Addition of Li^+ ions to the melt only produces the monodentate (C_{3v}) sulphate species.   Solutions of Cr(III), Fe(III) and Ni(II) ions have also been considered.   Whereas Cr(III) ions are octahedrally coordinated by bidentate sulphato anions forming $[Cr(SO_4)_3]^{3-}$ complexes, Fe(III) ions form tetrahedrally coordinated $[Fe(SO_4)_4]^{5-}$ complexes containing monodentate sulphato anions; the situation for Ni(II) ions is complex, an octahedral $[Ni(SO_4)_3]^{4-}$-tetrahedral $[Ni(SO_4)_4]^{6-}$ coordination equilibrium being established.[80]

Electrochemical studies[81] of molten Na_2SO_4 have shown that the dominant oxidant is the $S_2O_7^{2-}$ ion.   Dissolved oxygen and SO_2 can also act as oxidants but their contributions are limited by their very low solubilities in molten Na_2SO_4.

A group of Australian workers,[82,83] have investigated the reactions of a number of oxygen-containing salts with molten $K_2S_2O_7$; investigatory techniques used in the study included mass spectroscopy of the vapour over the molten salt, Raman spectroscopy of quenched samples, thermogravimetry and chemical analysis.   The reactions are summarised in Scheme 2; they are all Lux-Flood acid-base reactions in which the pyrosulphate anion abstracts an oxide anion from the oxyanions to form the sulphate anion.[82,83]

Phase relationships in the $Li_2S_2O_7$-$Na_2S_2O_7$-$K_2S_2O_7$ ternary system have been investigated.[84]   Solubility limits have been established for $Li_2S_2O_7$, $Na_2S_2O_7$, $K_2S_2O_7$, $LiKS_2O_7$ and $NaKS_2O_7$ and the existence of two quasi-binary systems, $Li_2S_2O_7$-$NaKS_2O_7$ and $LiKS_2O_7$-$NaKS_2O_7$ has been ascertained.[84]
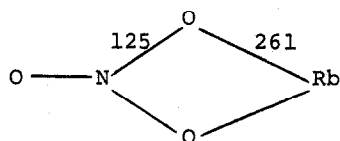
$$Li_2O + K_2S_2O_7 \rightarrow Li_2SO_4 + K_2SO_4$$

$$Na_2O_2 + K_2S_2O_7 \rightarrow Na_2SO_4 + K_2SO_4 + \tfrac{1}{2}O_2$$

$$2MNO_2 + K_2S_2O_7 \rightarrow K_2SO_4 + M_2SO_4 + NO_2 + NO \quad (M=Na,K)$$

$$2MNO_3 + K_2S_2O_7 \rightarrow K_2SO_4 + M_2SO_4 + 2NO_2 + \tfrac{1}{2}O_2 \quad (M=Li,Na,K)$$

$$2MOH + K_2S_2O_7 \rightarrow K_2SO_4 + M_2SO_4 + H_2O \quad (M=Li,Na,K)$$

$$2MHCO_3 + K_2S_2O_7 \rightarrow K_2SO_4 + M_2SO_4 + H_2O + 2CO_2 \quad (M=Na,K)$$

$$M_2CO_3 + K_2S_2O_7 \rightarrow K_2SO_4 + M_2SO_4 + CO_2 \quad (M=Li,Na,K)$$

Scheme 2

1.4   SIMPLE COMPOUNDS OF THE ALKALI METALS

Data abstracted for this section are primarily associated with recent advances in the chemistry of simple binary and ternary compounds containing an alkali metal; by the very nature of these materials, structural and thermodynamic data predominate.   In contrast to previous Reports, however, ion pairs are also included in this section.

1.4.1   Ion Pairs

Ion pairs have been investigated both in the gas phase[85-87] and in low temperature matrices.[88-91]   Gas phase structures of $Rb^+[NO_3]^-$,[85] $Cs^+[NO_3]^-$,[86] and $Na^+[PO_3]^-$[87] have been elucidated by a group of Russian authors using electron diffraction methods. The diffraction data were considered within the context of the three most probable equilibrium geometries, all of which assumed D_{3h} symmetry for the anion: (a) a triangular pyramidal configuration with C_{3v} symmetry (b) a planar C_{2v} symmetry configuration with the Cs^+ cation in an axial monodentate arrangement and (c) a planar C_{2v} symmetryconfiguration with the Cs^+ cation in a dihedral bidentate arrangement.   For all three ion pairs (1 - 3) the experimental data were consistent with geometry (c).   Although bond distances could be determined with reasonable accuracy, bond angles could not be measured owing to the limitation of the experimental data and technique; structural data are included on the diagrams.   Ab initio calculations of the equilibrium geometry of the $Li^+[PO_3]^-$ ion pair have also been undertaken.[92]   The difference in energy between the more stable configurations (b) and (c) was found to be very small ($< 17kJ\ mol^{-1}$)

(1)   (2)
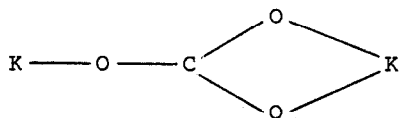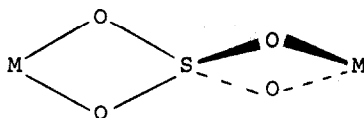

(3)   distances/pm.

and it is suggested that the moiety is non-rigid with respect to migration of the cation around the anion.[92]

I.r. studies of $M_2^+[CO_3]^{2-}$ (M=K,Rb,Cs),[88] $M_2^+[SO_4]^{2-}$ (M=K,Rb,Cs)[89] and $Cs^+[PF_4]^-$,[90] isolated in various cryogenic matrices, have been completed. Analysis of the data indicate that $K_2^+[CO_3]^{2-}$ has a C_{2v} structure (4),[88] and that $M_2^+[SO_4]^{2-}$ has a D_{2d} structure (5).[89]

(4)   (5)

The equilibrium geometry of $Cs^+[PF_4]^-$ is more complex, the anion adopting a folded square C_{2v} structure for the anion (c.f. isoelectronic SF_4) with the Cs^+ cation in an axial monodentate arrangement.[90] The salt-molecule reaction technique used to prepare $Cs^+[PF_4]^-$ has also been successfully used in the preparation of $Cs^+[PF_3Cl]^-$ and $Cs^+[PF_2Cl_2]^-$; the synthesis of $Cs^+[PFCl_3]^-$ and of $Cs^+[PCl_4]^-$ has not been achieved using this method, thereby supporting the suggestion that PCl_3 is a weaker Lewis acid than PF_3.[90]

In a fascinating study[91] of the reductive coupling of CO_2 by lithium atoms to give lithium oxalate, both $Li^+[CO_2]^-$ and $Li_2^+[CO_2]^{2-}$ ion pairs have been detected as reactive intermediates by i.r. matrix isolation spectroscopy. The results support scheme 3 as the mechanism of the dimerisation process which leads to oxalate formation.[91]

$$Li + CO_2 \rightarrow Li^+[CO_2]^-$$

$$Li^+[CO_2]^- + Li \rightarrow Li_2^+[CO_2]^{2-}$$

$$Li_2^+[CO_2]^{2-} + CO_2 \rightarrow Li_2C_2O_4$$

Scheme 3

1.4.2 Binary Compounds

There is a general paucity of data for binary compounds. Furthermore, those which are available are somewhat fragmented, relating to a number of diverse materials.

Ab initio calculations of the equilibrium geometries of the Li_2F_2 dimer[93] and of the $(LiH)_n$ ($2 \leqslant n \leqslant 8$) oligomers[94] have been undertaken. The geometry of Li_2F_2, which has D_{2h} symmetry, is best described by the results obtained using the DZRS basis set; on the other hand, the most realistic vibrational properties of this dimer were obtained using the DZHD basis set.[93] The equilibrium structures for $(LiH)_n$ oligomers with odd values of n were found to be planar cyclic with D_{nh} molecular geometry; those for $(LiH)_n$ oligomers with even values of n, however, were found to be three-dimensional precursors of the crystal structure. Stability calculations for these molecules confirm the strong tendency of LiH to oligomerise.[94]

Rotational constants and cohesive energies of alkali metal hydrides, MH (M=Li,Na,K,Rb,Cs) have been computed[95] by replacing Woodcock's generalised pair potential with a combination of Morse-Kratzer potentials; the computed values are in accordance with available thermochemical data.

Various crystal properties of the alkali metal halides with the NaCl structure, MX (M=Li,Na,K,Rb; X=F,Cl,Br,I) have been evaluated using either the Born model formulation[96] (crystal binding energies) or Woodcock's generalised pair interaction potential energy function[97]

(compressibilities and thermal expansion coefficients).

The vapourisation thermodynamics of NaI, equations (29,30),

$$NaI(s) \rightleftharpoons NaI(g) \qquad \Delta H^O(298.15K) = 203 \text{ kJ mol}^{-1} \quad ...(29)$$

$$2NaI(s) \rightleftharpoons Na_2I_2(g) \qquad \Delta H^O(298.15K) = 236 \text{ kJ mol}^{-1} \quad ...(30)$$

have been derived from measurements of the vapour density of the saturated vapour over solid NaI.

Standard thermodynamic data for the formation of K_2S have been derived[99] from the results of bomb calorimetry studies of the combustion of K_2S in fluorine gas; the data are compiled in Table 3.

Single crystals of KHS have been prepared[100] by reaction of KNH_2 with H_2S in liquid NH_3. The structure of KHS (Figure 2) has been solved by X-ray diffraction methods. Although it crystallises with rhombohedral symmetry, it is best considered in the alternative hexagonal setting (Figure 2a); the interatomic distances within the octahedral coordination polyhedra of both ions are $r(K...S) = 331$ or $r(K...H) = 287$ pm.[100]
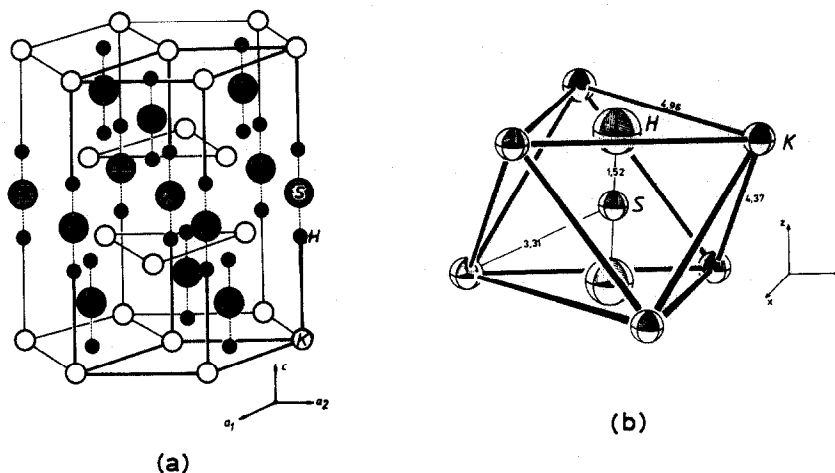

(a)

(b)

Figure 2. Aspects of the crystal structure of KHS; (a) the hexagonal unit cell and (b) the coordination polyhedron of the SH⁻ anion (reproduced by permission from Z. Anorg. Allg. Chem., 473(1981)125).

<u>Table 3.</u>   Standard thermodynamic data for the formation of K_2S,[99] $CsNO_3$,[105] $Na_2CO_3.3NaHCO_3$ [Wegscheider's salt][106] and of $Na_2CO_3.NaHCO_3.2H_2O$ [Trona].[106]

Compound	$-\Delta H_f^O(X,c,298.15)$ kJ mol^{-1}	$-\Delta S_f^O(X,c,298.15)$ J K^{-1} mol^{-1}	$-\Delta G_f^O(X,c,298.15)$ kJ mol^{-1}
K_2S	406.2±2.9	46.3±16.7	392.4±5.8
$CsNO_3$	505.8±0.5	334.6±0.5	406.0±0.5
$Na_2CO_3.3NaHCO_3$	3984.03±0.80	-	-
$Na_2CO_3.NaHCO_3.2H_2O$	2682.11±0.44	-	-

Anhydrous CsOH has been synthesised by reaction of $CsOH.H_2O$ with $CsNH_2$ in supercritical NH_3.[101]   Temperature dependent structural studies have shown that the orthorhombic modification (a = 435.0, b = 1199, c = 451.6 pm; anti-NaOH type structure) is converted into a cubic midification (a = 642.7; NaCl structure) at 497.5K.[101]

^{2}H-double resonance studies of various anhydrous and hydrated alkali metal (Li,Na,K) hydroxides have been undertaken;[102] the ^{2}H-quadrupole coupling constants of the OH$^-$ anion are correlated with its stretching force constants. ^{23}Na-quadrupole resonance has also been detected in both NaOH and $NaOH.H_2O$.[102]

The existence of orientational disorder in the CN$^-$ anions of $NaCN.2H_2O$ suggested by van Rij and Britton[103] on the basis of a refinement of X-ray diffraction data has been confirmed spectroscopically by Falk.[104]   Doubling of CN$^-$ stretching fundamentals occurs.   The ratios of doublet band areas are consistent with the energy of the NC...Na orientation being higher than that of the CN...Na orientation by 0.8±0.3 kJ mol^{-1}.   The fraction of reversed CN$^-$ groups at 295K is estimated by Falk[104] to be 0.33±0.06, somewhat greater than the previous estimate of 0.20 by van Rij and Britton.[103]

Standard thermodynamic parameters for the formation of $CsNO_3$, according to equation (31), have been recommended[105] from an analysis of heat capacity data (5 ≤ T/K ≤ 350).   Standard enthalpy of formation data for $Na_2CO_3.3NaHCO_3$ and of $Na_2CO_3.NaHCO_3.2H_2O$ have been

$$Cs(c) \; + \; \tfrac{1}{2}N_2(g) \; + \; \tfrac{3}{2}O_2(g) \rightleftharpoons CsNO_3(c) \hspace{2cm} \dots(31)$$

calculated[106] from enthalpy of solution data in excess aqueous NaOH. Data for the three salts are included in Table 3.

Weppner et al have published the results of a comprehensive study of phase equilibria in the quasi-binary systems Li_3N-LiX (X = Cl,Br, I)[107] and LiOH-LiX (X = Br,I);[108] they have also reported free energy of formation for the ternary lithium nitride halides $Li_xN_yX_z$.[107] Salient properties of $Li_xN_yX_z$ are collected in Table 4.[107] With the exception of $Li_9N_2Br_3$, they have all been obtained previously and characterised crystallographically; $Li_9N_2Br_3$ crystallises in a body-centred tetragonal structure with a = 1176.1 and c = 599.3 pm.[107] Each of the LiOH-LiX (X = Br,I) systems contains two intermediate ternary compounds, $Li_2(OH)I$, $Li_5(OH)_4I$, $Li_2(OH)Br$ and $Li_4(OH)_3Br$, all of which decompose in

Table 4. Salient properties (melting points, T_m, peritectic decomposition temperatures, T_d, free energies of formation from the elements, $\Delta G_f^O(X,c,T)$, and free energies of formation from Li_3N and LiX (X = Cl,Br,I), $\Delta G_r^O(X,c,T)$) of the compounds formed in the quasi-binary Li_3N-LiX (X = Cl,Br,I) systems.

Compound	T_m/K	T_d/K	T/K	$-\Delta G_f^O(X,c,T)$ kJ (g. atom)$^{-1}$	$-\Delta G_r^O(X,c,T)$ kJ (g. atom)$^{-1}$
$Li_9N_2Cl_3$	983	-	595	169±1	81
$Li_{11}N_3Cl_2$	978	-	595	154±2	95
Li_6NBr_3	-	873	573	135±2	30
$Li_9N_2Br_3$	-	783	573	118±2	37
$Li_{13}N_4Br$	-	757	573	66±3	29
Li_5NI_2	846	-	560	124±2	48
$Li_{6.67}N_{1.89}I$	1048	-	586	90±2	47

peritectic reactions at 452, 575, 518 and 564K, respectively.[108] With the exception of $Li_2(OH)Br$, the X-ray powder diffraction patterns obtained are complex and could not be indexed unambiguously.

$Li_2(OH)Br$ crystallises in a primitive cubic (a = 405.6 pm, Pn3m space group) antiperovskite type structure with statistical occupation of 2/3 of the available Li^+ positions.[108]

1.4.3 Ternary Pnictides

As in previous Reports, the range of ternary compounds considered in this and the subsequent sections is limited to those containing both an alkali and a transition metal; this restriction prevents unnecessary duplication with other Chapters of this review.

Schuster et al[109-111] have prepared a series of ternary pnictides. They have been characterised primarily by X-ray diffraction methods; the compounds and their unit parameters are listed in Table 5. Schuster et al[112] have also measured (80 ⩽ T/K ⩽ 290) the magnetic susceptibilities of the ternary compounds Li_2LnX_2 (Ln = Ce,Pr,Nd, Tb; X = P,As,Sb,Bi); the data support the existence of the Ln^{3+} cation in the materials.

1.4.4 Ternary Oxides and Chalcogenides

Recent progress in the chemistry of ternary oxides[113] and of ternary sulphides[114] has been comprehensively reviewed; chemical, structural, magnetic and spectroscopic properties are considered in detail. The magnetic properties of the ternary oxides adopting

Table 5. Unit cell parameters for a number of ternary pnictides

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	Ref.
LiMnX (X = P,As,Sb)*	tetragonal	P4/nmm	413.3	–	595.7	109
NaMnX (X = P,As,Sb,Bi)*	tetragonal	P4/nmm	408.6	–	688.4	109
K_2PdP_2	orthorhombic	Cmcm	635.5	1389.8	590.0	110
K_2PtAs_2	orthorhombic	Cmcm	646.5	1410.6	609.6	110
KRh_2P_2	tetragonal	I4/mmm	388.4	–	1298.6	111
KM_2As_2 (M = Fe,Co,Rh)*	tetragonal	I4/mmm	384.2	–	1386.1	111

* The crystallographic data refer to the element listed first.

either the K_2NiF_4 or α-$NaFeO_2$ structural types have also been reviewed;[115] the relationship between structure and magnetic behaviour is stressed.

There has been a remarkable decrease in the number of papers published in which the synthesis and structural characterisation of ternary oxides is described. Those materials which have been prepared[116-120] are listed in Table 6 together with pertinent structural data. Although most of these data were obtained using X-ray diffraction methods,[116-119] the structure of Na_2CrO_4(II) was determined using neutron diffraction techniques;[120] the results obtained confirm the earlier X-ray diffraction strcuture. The ternary oxides were generally prepared by classical solid state methods (i.e., high temperature reactions between alkali metal oxides, carbonates or nitrates with transition metal oxides). The high pressure modification of $LiVO_2$ was obtained[116] by treating the ambient pressure modification to 6.0-6.5 GPa at 1300K; it is metastable and has retained its structure for the past ten years.

As part of an extensive study of the processes occuring in solid state reactions in both inert and oxidising atmospheres, Fotiev et al have investigated the interaction of Na_2CO_3 with V_2O_3,[121] FeO,[122] Fe_3O_4[122] and FeV_2O_4.[122] In an inert atmosphere, interaction takes place as a direct redox process between the reagents; in an atmosphere of air, the Fe^{2+} and V^{3+} are initially oxidised to Fe^{3+} and V^{5+} and then there is successive interaction of the oxidation products with Na_2CO_3. Fotiev et al[123] have also determined the formation conditions for the quaternary oxides $NaFe_3V_4O_{15}$ and $NaFeV_2O_7$.

A small number of quaternary oxides have been prepared and characterised, primarily by structural methods.[124-6] The majority of these materials are molybdates; they are listed together with pertinent unit cell parameters in Table 6. In another investigation of the chemistry of quaternary molybdates, Dion and Noel[127-9] have defined basic phase relationships in the pseudo-ternary Na_2O-UO_3-MoO_3 system and have studied the hydrogen reduction of a number of ternary and quaternary oxides formed in this sytem.

I.r. spectroscopic studies ($650 \leqslant \bar{\nu}/cm^{-1} \leqslant 1200$) have been undertaken for $Cs_xV_2O_5$ ($0 \leqslant x \leqslant 0.664$);[130] the data suggest, in agreement with earlier X-ray diffraction results, that the CsV_3O_8 phase appears at about $x = 0.008$.

Table 6. Crystallographic parameters for a number of ternary oxides, quaternary oxides and ternary selenides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	α/°	β/°	γ/°	Ref.
$LiVO_2$ (H.P.)	cubic	Fd3m	822.7	-	-	-	-	-	116
$NaCeO_2$	tetragonal	(α-$LiFeO_2$)	478	-	1099	-	-	-	117
$NaLnO_2$ ($Ln=Nd,Sm,Eu,Gd$)*	cubic		493	-	-	-	-	-	117
Na_4RuO_4	tetragonal	$I4_1/amd$	562.3	-	866	-	-	-	118
Na_2RuO_3	orthorhombic	-	545.4	937.7	3146	-	-	-	118
$Na_4Ru_3O_8$	cubic	Pm3	889.0	-	-	-	-	-	118
$Na_2Ru_4O_9$	monoclinic	C2/m	2318	283.0	1100	-	104.5	-	118
$NaRu_4O_8$	tetragonal	I4/m	987.2	-	311.5	-	-	-	118
$Na_2Ru_9O_{19}$	orthorhombic	-	1245	380.8	765.0	-	-	-	118
Na_3RuO_4	monoclinic	-	1099.0	1275.4	568.1	-	109.9	-	118
$Na_6Au_2O_6$	tetragonal	$P4_2/mnm$	946.5	-	450.6	-	-	-	119
Na_2CrO_4(II) 296K	orthorhombic	Cmcm	586.2	925.1	714.5	-	-	-	120
$NaLiV_2O_6$	monoclinic	C2/c	1018.7	907.4	584.0	-	108.95	-	124
$Na_2M_5Mo_6O_{24}$ ($M=Mg,Co,Zn$)*	triclinic	P1̄	1057.5	861.7	695.1	103.42	102.67	112.37	125
α-K_5YMoO_4 (H.T)	hexagonal	P3̄1m	1045.3	-	410.4	-	-	-	126
Na_3FeSe_3	monoclinic	$P2_1/n$	745.2	717.6	1308.1	-	90.5	-	137
KAgSe	tetragonal	P4/nmm	452	-	759	-	-	-	138

* The crystallographic data refer to the element listed first.

Thermodynamic parameters have been reported for several ternary oxides;[20] interest in these data has been stimulated by the roles played by the oxides (Cs_3CrO_4,[131] Cs_4CrO_4,[132] MUO_3 (M = Li,Na,K, Rb),[133] Na_3UO_4,[20] β-$Cs_2U_2O_7$[134]) in nuclear reactor technology. Whereas the thermodynamic data for Cs_3CrO_4, Cs_4CrO_4 and MUO_3 (M = Li,Na,K,Rb) were determined from solution calorimetry studies (using either XeO_3 or $Ce(SO_4)_2$ as oxidant), those for Na_3UO_4 were derived from measurements of oxygen activities in equilibrium with UO_2 and Na_3UO_4 in the presence of liquid sodium. In the case of β-$Cs_2U_2O_7$, earlier data[135] have been revised in the light of the recent critical re-evaluation of thermochemical quantities for UO_2Cl_2. The results for Cs_3CrO_4 and Cs_4CrO_4 have been used to derive thermochemical quantities for the reduction of caesium chromates.[132] All the thermodynamic data are collected in Table 7.

The equilibrium phase diagram for the Na_2S-CdS system has been constructed from d.t.a and X-ray diffraction data.[136] Three ternary sulphides exist; two decompose in peritectic reactions, Na_6CdS_4 (1123±5K) and Na_2CdS_2 (1173±5K), the third melts congruently Na_4CdS_3 (1113±5K).

The ternary selenide Na_3FeSe_3 has been prepared by reaction of Na_2CO_3 with iron sponge at 1000K under a stream of hydrogen saturated with selenium.[137] An alternative chemical transport method, in which NaH-iron sponge-selenium mixtures were heated in a glass ampoule subjected to a 700-800K temperature gradient, has also been devised.[137] Structural parameters for Na_3FeSe_3[137] are included in Table 6 together with those for KAgSe.[138]

1.4.5 Ternary Halides

Discussion in this section is restricted to the chemistry of anhydrous ternary halides; solvated halides are not considered. Recent progress in the chemistry of ternary fluorides has been comprehensively reviewed;[113] chemical, structural, magnetic and spectroscopic properties are considered in detail.

Phase relationships in the RbBr-$TmBr_3$[139] and KI-ZrI_4[140] systems have been elucidated using d.t.a, X-ray diffraction and chemical analyses. Two compounds, Rb_3TmBr_6 and $Rb_3Tm_2Br_9$ are formed in the former system;[139] they undergo peritectic decomposition reactions to form $Rb_3Tm_2Br_9$ and RbBr (at 583K) and RbBr and $TmBr_3$ (at 733K), respectively. $Rb_3Tm_2Br_9$ undergoes a polymorphic transition at 613K. Only one compound, K_2ZrI_6, was observed in

Table 7. Standard thermodynamic parameters for the formation of a number of caesium chromates and alkali metal uranates and for the reduction of caesium chromates.

Compound	$-\Delta H_f^o(X,c,298)$ kJ mol^{-1}	$-\Delta S_f^o(X,c,298)$ J K^{-1} mol^{-1}	$-\Delta G_f^o(X,c,298)$ kJ mol^{-1}	Reference
Cs_3CrO_4	1543.13±2.7	393.4	1425.91±4.0	131
Cs_4CrO_4	1588.5±3.2	-	-	132
$LiUO_3$	1522.1±1.7	-	-	133
$NaUO_3$	1494.6±1.6	-	-	133
KUO_3	1522.9±1.6	-	-	133
$RbUO_3$	1520.9±1.7	-	-	133
Na_3UO_4	2050	448.0	1916	20
$\beta-Cs_2U_2O_7$	3220.2±1.8	-	-	134

Reduction	$-\Delta H_r^o(298)$ kJ mol^{-1}	$-\Delta S_r^o(298)$ J K^{-1} mol^{-1}	$-\Delta G_r^o(298)$ kJ mol^{-1}	
$Cs_2CrO_4(c) + Cs(c) \rightleftharpoons Cs_3CrO_4(c)$	113.1±3.3	17.6±1.6	107.8±3.3	132
$Cs_3CrO_4(c) + Cs(c) \rightleftharpoons Cs_4CrO_4(c)$	45.4±4.2	19.4±5.2	39.6±4.5	132

30

Table 8. Crystallographic parameters for a number of ternary halides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	β/°	Reference
$A_x VF_3$	orthorhombic		~1300	~740	~750	-	143
$KCoF_3$	cubic	Pm3m	406.88	-	-	-	144
$\alpha\text{-}CsCrCl_3$ (295K)	hexagonal	$P6_3/mmc$	725.7	-	623.8	-	145
$\alpha\text{-}CsCrI_3$ (295K)	hexagonal	$P6_3/mmc$	810.7	-	691.7	-	145
$\alpha\text{-}CsCuCl_3$ (430K)	hexagonal	$P6_3/mmc$	721.2	-	614.1	-	146
$NaFeF_4$	monoclinic	$P2_1/c$	790.8	535.1	753.1	101.92	147
Li_2MnBr_4 (298K)	tetragonal	-	777.6	-	1109.1	-	148
Li_2MnBr_4 (673K)	cubic	-	1123	-	-	-	148
Li_2MnBr_4 (773K)	cubic	-	563	-	-	-	148
Li_2CdBr_4 (623K)	cubic	-	1134	-	-	-	148
Li_2CdBr_4 (723K)	cubic	-	569	-	-	-	148
K_2CuF_4	tetragonal	(K_2NiF_4)	414.7	-	1273	-	149
Cs_3CoCl_5	tetragonal	I4/mcm	923.15	-	1455.35	-	150
Cs_3CoBr_5 (4.2K)	tetragonal	I4/mcm	946	-	1504	-	151
K_3UF_9	orthorhombic	-	697.4	753.4	976.8	-	152
Rb_3UF_9	orthorhombic	-	712.1	761.2	961.4	-	152
$K_3Cu_2F_7$	tetragonal	I4/mmm	415.6	-	2052	-	149
$Rb_3Cu_2Cl_7$	orthorhombic	Ccca	2484.3	721.6	721.6	-	153
$Cs_3Y_2I_9$	hexagonal	$P6_3/mmc$	840.6	-	2128.0	-	154
Cs_3ZrI_9	hexagonal	$P6_3/mmc$	826.9	-	1990.8	-	154

the latter system;[140] it melts congruently at 1220K and undergoes two polymorphic transitions at 843 and 912K.

Na$_2$MnF$_5$ has been prepared in quantitative yield by reduction of KMnO$_4$ with acetylacetone in the presence of NaHF$_2$;[141] it was characterised by i.r., magnetic susceptibility and chemical analytical methods. Conditions for the preparation of single crystals of Cs$_2$CuCl$_4$ and of CsCuCl$_3$ from aqueous solution have been quoted in detail.[142]

Numerous structural studies of ternary halides have been undertaken;[143-154] crystallographic data are collected in Table 8. Although the majority of the data are derived from single crystal X-ray diffraction measurements, those for Cs$_3$CoBr$_5$ were obtained in a low temperature (4.2K) single crystal neutron diffraction study.[151] Detailed analysis of the electron density distribution (derived from single crystal X-ray diffraction intensity data) in KCoF$_3$ showed that the high spin $(t_{2g})^5(e_g)^2$ electronic configuration is a good approximation for the Co^{2+} ion in this material.[144] Similarly the high spin $(t_{2g})^3(e_g)^1$ electronic configuration of Cr^{2+} in α-CsCrX$_3$ (X = Cl,I)[145] and the $(t_{2g})^6(e_g)^3$ electronic configuration of Cu^{2+} in α-CsCuCl$_3$[146] are held responsible for the Jahn-Teller distortion of the BaNiO$_3$ structure adopted by these materials.

Polymorphic transitions in Li$_2$MBr$_4$ (M = Mn,Cd) have been investigated in detail. Salient features are given in Table 8 and Scheme 4. At room temperature, Li$_2$MnBr$_4$ is tetragonal whereas Li$_2$CdBr$_4$ forms a mixture of CdBr$_2$ and cubic Li$_{1-x}$Cd$_{x/2}$Br$_2$ mixed

Li$_2$MnBr$_4$: tetragonal $\xrightleftharpoons{543K}$ cubic-I $\xrightleftharpoons{733K}$ cubic-II

Li$_2$CdBr$_4$: CdBr$_2$/Li$_{1-x}$Cd$_{x/2}$Br$_2$ $\xrightleftharpoons{513K}$ cubic-I $\xrightleftharpoons{633K}$ cubic-II
mixed crystals

crystals. Both halides form two high temperature cubic phases - a spinel phase (cubic-I) and a defect NaCl phase (cubic-II).

Boo et al[143] have undertaken extensive studies of the structural and magnetic properties of the pseudo hexagonal M$_x$VF$_3$ (M = K,Rb,Cs) compounds. These materials, which are analogues of the hexagonal tungsten bronzes, M$_x$WO$_3$ (space group P6$_3$/mcm) undergo distortions

which lower their symmetry from hexagonal to orthorhombic in two
unique ways.   The distinction between the two is defined by the
ratio of orthohexagonal dimensions, $|a|/\sqrt{3}|b|$, which is either
greater than unity, M_xVF_3-I, or less than unity, M_xVF_3-II.   In the
K_xVF_3 and Rb_xVF_3 systems a transition occurs from M_xVF_3-I to
M_xVF_3-II at $x = 0.26$ and 0.24; the Cs_xVF_3 system adopts the
M_xVF_3-II structure over its entire composition range.   Evidence
of atomic ordering has also been obtained; four stoichiometric
phases were observed for compositions $x = 0.167, 0.222, 0.250$ and
0.333.   Although all four phases which are designated $\alpha(x)$ and
have unique modulated structures were found in the Rb_xVF_3 system,
only three phases, $\alpha(0.167)$, $\alpha(0.222)$ and $\alpha(0.333)$, were found in
the K_xVF_3 system; in the Cs_xVF_3 system the Cs^+ ions appear to be
mostly random.[143]

Single crystal spectroscopic studies have been effected on
NaMnF$_3$,[155] NaCoF$_3$,[155] CsCuCl$_3$,[156] Cs$_2$CeCl$_6$[157] and Cs$_3$Ti$_2$Cl$_9$;[158]
aspects of the structural chemistry of these halides are inferred
from the interpretation of the spectra.[155-7]

Vapour pressure studies of MF-ZrF$_4$,[159] NaCl-ZrCl$_4$[160] and
NaCl-HfCl$_4$[160] systems have been undertaken and thermodynamic data
derived for the associated equilibria.   Vapour pressure
measurements of the exchange reactions, equation (32), have also
been effected.[160]   They indicate that the efficiency of the alkali

$$HfCl_4(g) + M_2ZrCl_6(s.s) \rightleftharpoons M_2HfCl_6(s.s) + ZrCl_4(g) \qquad \ldots(32)$$

(M = Li,Na,K; s.s = solid solution)

metal halides in the separation of hafnium from zirconium (by a
recently developed process based on the selective reactivity of
$ZrCl_4$ and of $HfCl_4$ with alkali metal chlorides) increases in the
sequence

LiCl < NaCl < KCl

The thermal stabilities of K$_2$TcI$_6$[161] and Cs$_2$CeCl$_6$[162] have been
ascertained by d.t.a. and t.g.a. techniques.   Whereas K$_2$TcI$_6$
decomposes via K$_2$TcI$_3$ to metallic technetium and KI,[161] Cs$_2$CeCl$_6$
decomposes directly to CsCl, CeCl$_3$ and chlorine gas.[162]   The
thermal analysis data for Cs$_2$CeCl$_6$ were used to calculate the
enthalpy of the decomposition reaction ($\Delta H_r^o(298) = 29.9\pm3.5$ kJ
mol^{-1}) and to estimate the enthalpy of formation of Cs$_2$CeCl$_6$

$(\Delta H_f^{\circ}(Cs_2CeCl_6,c,298K) = -1974.09 \pm 8.37 \text{ kJ mol}^{-1})$.   The enthalpies of fusion of $KMCl_3$ (M = Mg,Ca), K_2MCl_4 (M=Mg,Sr,Ba), K_2LaCl_5, K_3LnCl_6 (Ln=Pr,Nd) and KLn_3Cl_{10} (Ln=Gd,Dy) have been determined.[163]

1.5   COMPOUNDS OF THE ALKALI METALS CONTAINING ORGANIC MOLECULES OR COMPLEX IONS.

The format adopted for this section is similar to that used for the 1980 Review.[164]   Thus the text is simplified by incorporation of subdivisions for specialised topics currently of interest in bioinorganic chemistry.   These include acyclic polyether, crown and cryptate complexes, together with derivatives of carboxylic acids, nucleotides, etc.   Subdivisions for the individual alkali metals are also included; for these, data pertinent to several alkali metals are discussed once only, in the subdivision for the lightest element considered.

1.5.1   Acyclic Polyether Complexes

Complex formation between alkali and alkaline earth metal cations and acyclic polyethers, especially those with terminal groups containing donor atoms has been the subject of a small number of papers.[165-8]   A comparative study of the complexing ability of (6), its conjugate base and its crown analogue, B18C6, for alkali (Li,Na,K,Rb,Cs) and alkaline earth metal (Ca,Sr,Ba) cations has been undertaken using spectroscopic methods.[165]   The derived equilibrium constants indicate that B18C6 binds the cations more strongly than does its open chain sexadentate analogues, of which the conjugate base is the more effective.   Complexation of the alkali (Na,K,Rb) and alkaline earth metal (Ca) cations by a series of acyclic polyethers with various end groups (7; $1 \leqslant n \leqslant 3$; R = R' = OH, $OCH_2C_6H_5$, OCH_2CH_2OH, $OCH_2CO_2C_2H_5$, OCH_2COOH) has been elucidated

(6)

(7)

by thermodynamic methods.[166]   Stability constants increase as n is
increased and as R and R' are varied through the series OH,
$OCH_2C_6H_5$, OCH_2CH_2OH, $OCH_2CO_2C_6H_5$, OCH_2CO_2H.   There is no evidence
that internal hydrogen bonding contributes to the stability of
these complexes.[166]   Complex formation between Na^+ and a similar
series of acyclic polyethers ($\underline{7}$; $5 \leqslant n \leqslant 8$; R = $NHCOCH_3$, $CONHCH_3$) has
been studied by multinuclear (^1H-, ^{13}C- and ^{23}Na-) nmr techniques.
Derived thermodynamic data emphasise the significant role sometimes
played by solvent participation during complex formation.[167]

   The molecular structure of ($\underline{8}$).$NaClO_4$; a complex containing a
linear polyether with terminal amino and carboxyl functions, has
been determined from single crystal X-ray diffraction data.[168]
There are two molecules per asymmetric unit (Figure 3) which are
related to each other by an approximate non-crystallographic centre
of symmetry.   Both polyether ligands exist in the Zwitterion
configuration with ion pair attraction between the amino (NH_3^+) and
carboxyl (COO^-) end groups.   The Na^+ coordination sphere (Figure 3)

($\underline{8}$)

comprises four polyether oxygen atoms in a equatorial plane (the
fifth polyether oxygen atom - the aminophenoxy end group oxygen
atom - does not coordinate the Na^+ cation), together with a
perchlorate oxygen atom and a translated carboxyl oxygen atom in
the axial positions.   Pertinent interatomic distances are
included in Figure 3.

   The complexing ability of a series of oligoethylene glycols,
$HO(CH_2CH_2O)_nH$ ($1 \leqslant n \leqslant 4$), for alkali (Li,Na,K,Cs) and alkaline
earth metal (Mg,Ca,Sr,Ba) cations has been assessed in a study of
the lipophilization in toluene of the otherwise insoluble
2-nitrophenolate salts.[169]

Figure 3. Molecular geometry of the asymmetric unit of (<u>8</u>).NaClO$_4$; giving pertinent interatomic distances/Å (reproduced by permission from Z. Naturforsch., 36b(1981)102).

1.5.2   Crown Complexes

Compared to previous Reports there has been a marked increase in the number of papers on alkali and alkaline earth metal complexes of crown and related macrocyclic ligands.   Consequently this topic has been divided into two subsections in which complexes formed by 'classical' crown compounds and by novel macrocyclic ligands of unusual design are considered.

The template effect of alkali and alkaline earth metal cations in the synthesis of 12C4,[170] 15C5,[170] 18C6[170] and of B18C6[171] has been studied quantitatively.   The different catalytic abilities of the various cations was noted - optimum yields of 12C4, 15C5 and 18C6 were obtained with Li$^+$, Na$^+$ and K$^+$, respectively[170] - and discussed[171] in terms of the structural and electronic effects of the metal cations.

Structural studies have been undertaken on 15C5.NaSCN.½H$_2$O[172]

(B15C5)$_2$.K[picrate],[173] (18C6)$_2$.K$_2$[phthalocyanine],[174] and
DB18C6.KI.(NH$_2$)$_2$CS.[175] The sodium derivative contains two
crystallographically distinct Na$^+$ cations.[172] Each cation is
situated at the centre of a 15C5 crown ether cavity, r(Na(1)...O) =
233-251 pm, r(Na(2)...O) = 235-250 pm, the coordination sphere
being completed in axial positions either by an N-bonded SCN$^-$
anion, r(Na(1)...N) = 226 pm and a water oxygen atom, r(Na(1)...O) =
246 pm or by a single N-bonded SCN$^-$ anion, r(Na(2)...N) = 248 pm.
The difference in the two Na$^+$ cations arises from the adoption by
the 15C5 ligands of one of two disordered positions generated from
the presence in the structure of statistical mirror planes.[172]

   The three potassium derivatives contain three different types of
K$^+$ coordination sphere; they are shown in Figure 4.   In
(B15C5)$_2$.K[picrate], (Figure 4a),[173] the cation is sandwiched between
two B15C5 crown ether ligands, r(K...O) = 281-296 pm and has no
interaction with the picrate ion.   In (18C6)$_2$.K$_2$[phthalocyanine],
(Figure 4b),[174] the K$^+$ coordination sphere is atypical, the
potassium being external to the 18C6 cavity; it is raised 160 pm
from the mean plane of oxygen atoms.   In fact two K$^+$ ions are
sandwiched separately between crown ether rings, r(K...O)$_{av}$ = 339 pm,
and a phthalocyanine macrocycle, r(K...N)$_{av}$ = 291 pm in the
trimacrocyclic sandwich complex illustrated in Figure 4b.   In
DB18C6.KI.(NH$_2$)$_2$CS, (Figure 4c),[175] the K$^+$ ion is situated at the
centre of the crown ether cavity and is in contact with all six
ether oxygen atoms, r(K...O) = 271-280 pm; the sevenfold hexagonal
pyramidal coordination is completed by the iodide anion, r(K...I) =
357 pm.   The thiourea molecule neither participates in the
complexation of K$^+$ nor has it any contact with the polyether ligand;
instead it forms polymeric chains by hydrogen bonding to sulphur atoms
of adjacent thiourea molecules and to iodide anions (Figure 4c).[175]

   Field desorption mass spectrometry studies have been shown to be
useful in the structural characterisation of crown ether complexes
of alkali metal cations.[176] Strong peaks for the [crown ether.M]$^+$
cationic moiety are invariably detected at low emitter currents
for neutral or ionic complexes despite the general weakness of
alkali metal-oxygen bonds.   Analysis of the field desorption mass
spectra of B15C5.NaI.H$_2$O (which is known to exist as
[B15C5.Na.H$_2$O]$^+$ I$^-$), diMe-B15C5.NaBr ([diMe-B15C5.Na.Br])
DB30C10.KI ([DB30C10.K]$^+$ I$^-$) and (9).NaBr.xH$_2$O (which is of unknown
structure), has led to the assignment of the ionic structure

Figure 4. Perspective views of the K^+ coordination sphere in
(a) $(B15C5)_2 \cdot K[\text{picrate}]$, (b) $(18C6)_2 \cdot K_2[\text{phthalocyanine}]$
and (c) $DB18C6 \cdot KI \cdot (NH_2)_2CS$ (reproduced by permission
from (a) Inorg. Nucl. Chem. Letters, 17(1981)207,
(b) J. Am. Chem. Soc., 103(1981)4629 and (c) Angew.
Chem. Int. Ed. Engl., 20(1981)1045).

$[(\underline{9}) \cdot Na]^+ Br^- \cdot xH_2O$ for the latter complex.[176]

(<u>9</u>)

Field desorption mass spectrometry studies have also been used to derive stability data for DB18C6 complexes of alkali metal cations (Li-Cs) in the gas phase.[177] The ratio of the ion intensities $I_{[L.M]}{}^+/I_M{}^+$ decreases sharply in the series

$$Na^+ > K^+ > Rb^+$$

for the $[DB18C6.M^+].I^-$ complexes, indicating the greater stability of the sodium complex. This sequence is somewhat unexpected since the greatest stability in aqueous solutions is found for the $[DB18C6.K^+].I^-$ complex. It is important to recall, however, that desolvation of the cation always occurs on formation of the $[L.M]^+$ complex.[177]

The stabilities of sodium cation complexes with 15C5, B15C5 and 18C6 (as well as with C211, C221, C222 and C222B),[178] and of alkali metal cation (Na-Cs) complexes with 18C6[179] have been determined in both aqueous and non-aqueous solvents using multinuclear (^{13}C-, ^{23}Na-) n.m.r.[178] and conductivity[179] techniques. The stabilities of the sodium ion complexes[178] varied in the order

$$[18C6.Na]^+ > [15C5.Na]^+ > [B15C5.Na]^+$$

and those of the 18C6 complexes[179] varied in the order

$$[18C6.K]^+ > [18C6.Rb]^+ > [18C6.Cs]^+ > [18C6.Na]^+$$

The selectivity of several small crown ethers (B12C4, B13C4, DB14C4, B15C5 and DB18C6) for a series of lithium salts has been assessed by solubility measurements.[180] B13C4 was found to be the most effective complexing agent for Li^+. Indeed, both benzene and dichloromethane solutions of B13C4 selectively extract lithium salts from aqueous solutions.

Solvent extraction processes involving alkali metal salts in the presence of crown ethers have been investigated by four independent groups of authors.[181-5] The distribution of alkali metal picrates (MX, M = Li-Cs) between water and benzene has been studied[181,182] in the presence of tributylphosphate (TBPO), 12C4, 15C5, B15C5 and mixtures thereof. Extraction constants for rubidium and caesium picrates are determined in the presence of all four ligands; they increase in the sequence

TBPO < 12C4 < 15C5 < B15C5

reflecting the increase in the number of donor oxygen atoms on the ligand.   Extraction processes for all the alkali metal picrates in the presence of B15C5 have been elucidated.[182]   B15C5 extracted the salts as either $[B15C5.M]^+X^-$ or $[(B15C5)_2.M]^+X^-$ complexes; in the presence of TBPO, B15C5 extracted rubidium and caesium picrates as $[B15C5.M.TBPO]^+X^-$ complexes.   The sequence of extraction constants of these complexes are

$$[B15C5.Na]^+ > [B15C5.K]^+ > [B15C5.Rb]^+ > [B15C5.Li]^+ > [B15C5.Cs]^+$$

$$[(B15C5)_2.K]^+ > [(B15C5)_2Rb]^+ > [(B15C5)_2.Cs]^+$$

$$[B15C5.Rb.TBPO]^+ > [B15C5.Cs.TBPO]^+$$

The distribution of alkali metal picrates (MX; M = Li-Cs) between water and polyurethane foam has been studied[183] in the presence of DCH18C6.   The sequence of extraction constants for the $[DCH18C6.M]^+X^-$ complexes is

$$[DCH18C6.K]^+ > [DCH18C6.Rb]^+ > [DCH18C6.Cs]^+ > [DCH18C6.Na]^+$$

   The effect of anions on the extraction of alkali metal salts from water into dichloroethane has been investigated in the presence of DCH18C6 and DCH24C8.[184]   A significant effect is observed for DCH18C6, the extraction constants increasing in the sequence

$$ClO_4^- > I^- > NO_3^- > Br^- > OH^- \gg Cl^- > F^-$$

This sequence is independent of the alkali metal, the extraction constants of the $[DCH18C6.M]^+X^-$ and $[DCH24C8.M]^+X^-$ complexes increasing in the same sequence as for the distribution of $[DCH18C6.M]^+X^-$ between water and polyurethane foam.[183]   The effect of ionic strength on the extraction of potassium picrate into dichloromethane as $[18C6.K]^+X^-$ has also been assessed.[185]
   Several unusual anions have been stabilised by alkali metal-crown ether cations; compounds which have been isolated include $[DB18C6.K]^+[Al_2(CH_3)_6O_2]^-$,[186] $[18C6.Na]^+[M(CO)_5SH]^-$ and

$[18C6.Na]^+[M_2(CO)_{10}(\mu\text{-SH})]^-$ (M = Cr,Mo,W)[187,188] and
$[(18C6)_{14}Cs_9]^{9+}[Rh_{22}(CO)_{35}H_x]^{5-}[Rh_{22}(CO)_{35}H_{x+1}]^{4-}$;[189] single crystal
X-ray structural analysis of these salts has elucidated the molecular
geometries of both the cations and the anions. The preliminary
communication[186] in which the preparation and structural
characterisation of $[DB18C6.K]^+[Al_2(CH_3)_6O_2]^-$ is reported gives
details of the structure of the anion but not of the cation.

Structural analysis of $[18C6.Na]^+[W(CO)_5SH]^-$ and of
$[18C6.Na]^+[W_2(CO)_{10}(\mu\text{-SH})]^-$ has shown that both complexes are chain
polymeric with sodium-carbonyl linkages between alternating cations
and anions (Figure 5).[187,188] The Na^+ cations are situated in a
hexagonal bipyramidal coordination sphere in both complexes. In
the former complex (Figure 5a), the Na^+ coordination geometry is
slightly distorted with the six oxygen atoms of the 18C6 molecule
occupying the equatorial plane, r(Na...O) = 262-291 pm, and the
oxygen bonded carbonyl of one anion, r(Na...O) = 241 pm, and the
thiolato sulphur atom of a second anion, r(Na...S) = 301.4 pm,
occupying the two axial sites. In the latter complex (Figure 5b),
however, the Na^+ coordination geometry is very distorted. As
before, the equatorial plane comprises the six oxygen atoms of the
18C6 molecule, r(Na...O) = 257.5-272.7 pm, and the 8-fold
coordination is completed by oxygen atoms on adjacent dinuclear
anions, r(Na...O) = 245.8, 247.1 pm.

$[(18C6)_{14}Cs_9]^{9+}[Rh_{22}Co_{35}H_x]^{5-}[Rh_{22}Co_{35}H_{x+1}]^{4-}$ has been isolated
from the reaction of $Rh(CO)_2acac$ with $PhCO_2Cs$ in 18C6 after 15-17
hours at 423-428K.[189] The complex, the largest discrete aggregate
of metal atoms reported to date, has been characterised by low
temperature (163K) single crystal X-ray diffraction studies. The
overall composition of the cationic complex can be broken down into
the three complexes: $[(18C6)Cs]^+$, $[(18C6)_2.Cs]^+$, $[(18C6)_3.Cs_2]^{2+}$;
the asymmetric unit contains three 1:1, two 2:1 and two 3:2
complexes. Whereas the 1:1 complex is well known, the 2:1 and
3:2 complexes are novel, the 3:2 complex being an unprecedented
species. The molecular geometries of the three complexes are
shown in Figure 6. In the 1:1 complex (Figure 6a), the Cs^+ cation
is external to the 18C6 cavity, r(Cs...O) = 309-369 pm, its
coordination sphere being completed by two symmetry related
bridging carbonyl ligands of the nearest cluster anion, r(Cs...O) =
351 pm. The Cs^+ cation in the 2:1 complex (Figure 6b) is
sandwiched between two 18C6 moieties with r(Cs...O)$_{av}$ = 335 and

(a)

(b)

Figure 5. Molecular structures of (a) $[18C6.Na]^+[W(CO)_5SH]^-$ and
(b) $[18C6.Na]^+[W_2(CO)_{10}(\mu-SH)]^-$ (reproduced by permission
from J. Organomet. Chem., 212(1981)C10).

343 pm for the six oxygen atoms of crown(1) and crown(2),
respectively (Figure 6b).   The 3:2 complex, a so-called "club
sandwich" complex, contains two Cs^+ cations sandwiched between three
18C6 moieties (Figure 6c).   Average caesium-oxygen contacts are:
359 and 379 pm between Cs(3) and the six oxygen atoms of crown(3)
and crown(4), respectively and 369 and 403 pm between Cs(4) and the
six oxygen atoms of crown (4) and crown(5), respectively.[189]
  The complexation of $^{24}Na^+$ and $^{22}Na^+$ by crown ethers (and
cryptands) has been investigated in chloroform-water systems in
view of possible equilibrium isotope shifts.[190]   With crown ethers
$^{24}Na^+$ enhancement varied from insignificant values (for large
crown ethers) up to 3.1±0.4% (for 18C6).   In the case of cryptands,
$^{24}Na^+$ enrichment of 5.2±1.8% (for C221) and $^{22}Na^+$ enrichment of
5.4±0.5% (for C222) was achieved.[190]
  The formation of complexes of DB18C6 with RMgX (R = Me,Et; X =
Br,I) and RCaX (R = Me,Et,Ph; X = Br,I) has been studied

Figure 6. Ortep diagrams of the fragments of the $[(18C6)_{14}Cs_9]^{9+}$ cationic complex of $[(18C6)_{14}Cs_9]^{9+}[Rh_{22}(CO)_{35}H_x]^{5-}$ $[R_{22}(CO)_{35}H_{x+1}]^{4-}$: (a) $[(18C6)Cs]^+$, (b) $[(18C6)_2Cs]^+$, (c) $[(18C6)_3Cs_2]^{2+}$ (reproduced by permission from Inorg. Chem., 20(1981)227).

spectrophotometrically.[191] Their reactions with aldehydes result in the formation of the corresponding alcohol with practically 100% specificity.[191]

The facile transfer of $K_2S_2O_8$ into a variety of solvents (including hydrocarbons) in the presence of various crown ethers has been reported.[192] The utilisation of these solutions for the initiation of the rapid polymerisation of acrylic and methacrylic monomers at temperatures close to ambient has also been described.[192]

1.5.3   Complexes of Macrocyclic Polyethers of Novel Design

The desire to design and prepare macromolecular moieties, containing 3-D cavities of controlled geometry, capable of selectively binding specific substrates has led to a proliferation of macrocyclic polyethers. A large number of these materials

(10-27) have been shown to form complexes with either alkali
or alkaline earth metal cations;[193-201] the complexes have
been identified in either solution[193-8] or solid state[199-201]
structural studies.   Complex formation between (10), (11), (12)
and alkali and alkaline earth metal cations has been studied
spectrophotometrically.   Though 1:1 (11): M^{n+} (M = Na,K, Ca)
moieties are formed in the presence of the DB18C6 derivatives (11),
2:1 (10):K^+ and 1:1 (10):M^{n+} (M = Na,Ca) moieties are the major
species present with the DB15C5 derivatives, (10).[193]   Complexes
with 1:1 (12):M^{n+} (M = Li,Na,Mg-Ba) molar ratios are formed with
the phosphoryl containing macrocyclic ligand (12).[194]

(10)

(11)

(12)

(13)

(14)

(15)

(16)

(17)

(18)   (19)   (20)

(21)   (22)

(24)   (23)

ArNHCO ... CONHAr   ArNHCO ... COO⁻

⁻OOC ... COO⁻   ⁻OOC ... CONHAr

(25)   (26)

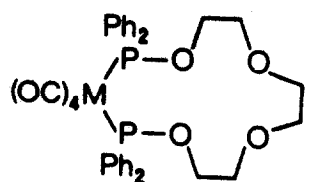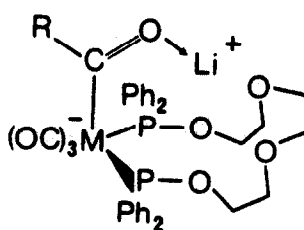$(OC)_4M$ ... Ph_2 ... $\xrightarrow[C_6H_6]{RLi}$ ... $(OC)_3\bar{M}$ ... Ph_2

(27)   (28)

Formation constants for the 1:1 complexes between the macrocyclic polyether-diester ligands (13-17) and Na$^+$, K$^+$, Cs$^+$ and Sr^{2+} ions[195] and between the isomeric macrobicyclic polyethers (18-20) and Na$^+$, K$^+$, Rb$^+$ and Cs$^+$ ions[196] have been determined in methanol by thermodynamic methods. The values for the latter complexes show very significant differences between the isomeric ligands increasing from (20) through (18) to (19); the highest values occur for K$^+$ cations. This behaviour is consistent with the hypothesis that hydrogen atoms on cyclohexane junctions are somewhat electropositive, so that the cavity is most electronegative in (19), least electronegative in (20) and intermediate in (18).[196]

Extraction constants[197] for a number of alkali metal (Li-Cs) and alkaline earth metal (Mg-Ba) picrates by macrocyclic polyether-ester ligands (21) have been determined; the selectivity of the macrocycles for the different cations is discussed in detail.[197] Ion selectivity studies[198] for alkali metal cations (Li-Cs) have been undertaken using macrocyclic polyether ligands containing the bicyclohexyl moiety (22,23); the selectivities of the ligands were similar to those of the analogous binaphthyl derivatives of 18C6.[198]

Preliminary communications have been reported in which the structures of (24).2LiI.4H$_2$O,[199] the Ca^{2+} and Sr^{2+} complexes of (25) and (26),[200] and the complex formed (28) on reaction of (27) with PhLi in benzene,[201] are described. The structure of the double loop complex[199] is unusual in that both of the rings bind one of the water molecules of solvation and a Li$^+$ cation in the same cavity (Figure 7). The metal cation is at the centre of a distorted trigonal bipyramid formed by three polyether oxygen atoms, the coordinated water oxygen atom and an oxygen atom from a solvating water molecule. In accord with the VSEPR theorem three shorter Li$^+$...O contacts lie in the equatorial plane, r((Li...O) = 193-198 pm, while the two apical distances are somewhat longer, r(Li...O) = 212, 223 pm.[199]

The complexing properties of the anti-(side discriminated) and syn-(face discriminated) tetrafunctional macrocycles (25) and (26), respectively, have been compared[200] in their complexes with Ca^{2+} and Sr^{2+}, respectively. Although the syn-isomer wraps itself tightly around the cation, the anti-isomer adopts a more open structure. Thus, the carboxylate groups of the syn-isomer coordinate on the same side of the macrocycle, whereas those of
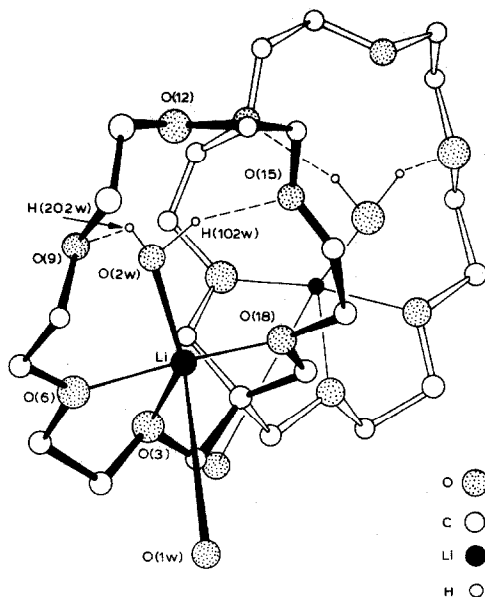
Figure 7. Perspective diagram of the molecular structure of the cation in (24).2LiI.4H$_2$O (reproduced by permission from J. Chem. Soc. Chem. Commun., (1981)472).
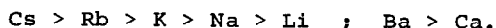
the anti-isomer coordinate on opposite sides of the macrocycle. The cations are nine-coordinate in both complexes. Although the coordination sphere of the syn-complex is completed by a chloride anion, the ninth position of the anti-complex is occupied by a water molecule.[200]

The structure of (28) contains a cavity with a radius of 200 pm in which the Li$^+$ cation resides. The cavity is defined by the benzoylate oxygen and the four oxygen atoms of the diphosphinite-polyether ring; unfortunately details (bond distances and angles) of the Li$^+$ coordination sphere are not quoted in the preliminary publication.[201]
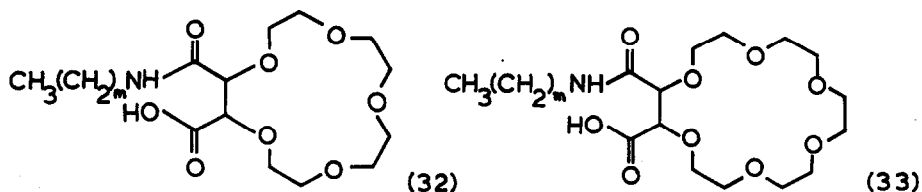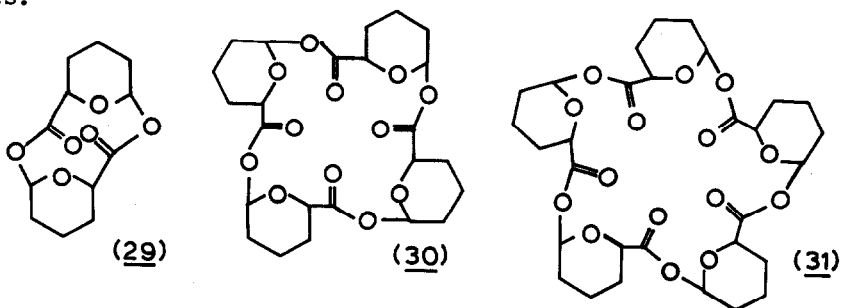
Ion transport mechanisms involving alkali metal cation complexes of macrocyclic polyether ligands have been studied in several laboratories.[195,202-6] A correlation between the toxicity of crown ethers and their capability of transporting K$^+$ ion has been noted;[202] it is based on the results of a study of the antibacterial activity of and ion (Li-Cs) transport efficiency and selectivity of 15C5, 18C6, B18C6 and DCH19C6.

The capacity of several macrolides, consisting of alternating

tetrahydropyran and ester moieties (29-31), for transporting and binding alkali (Li-Cs) and alkaline earth metal (Ca,Ba) picrates has been assessed.[203] Whereas (29) was totally ineffective, (30) and (31) were found to be quite effective with ion selectivity sequences:

Cs > Rb > K > Na > Li ; Ba > Ca.

The observed properties are discussed in comparison with those of some natural and synthetic ionophores.[203] The polyether-diester macrocycles (15) have also been found to be effective carriers of Cs^+ across a $CHCl_3$ liquid membrane separating aqueous phases.[195]

Transport of alkali metal ions against their concentration gradients has been achieved using an artificial membrane system based on a series of 15C5 and 18C6 monoamides bearing long chain alkyl groups (32,33).[204,205] Under the influence of a proton gradient the carriers move alkali metal cations from basic to acidic solution through a chloroform membrane as depicted in Figure 8a; transport occurs against the concentration gradient as a result of a coupled counterflow of protons. Carriers derived from 18C6 transport K^+ selectively and all ions more rapidly than 15C5 derivatives which are, however, selective for Na^+.[205]

LEFT | MEMBRANE | RIGHT

(a)

(b)
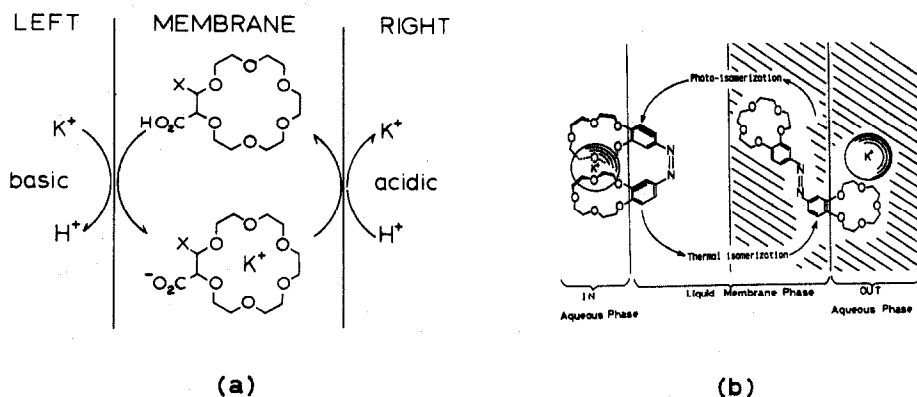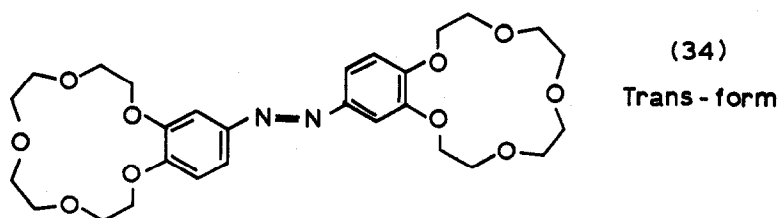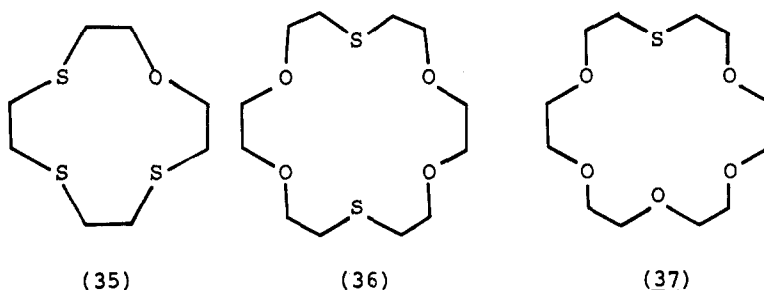
Figure 8.   Schematic mechanisms for (a) carrier mediated
             counter-transport of a metal ion and a proton and
             (b) light driven ion transport (reproduced by permission
             from (a) Canad. J. Chem., 59(1981)1734 and (b) J. Am.
             Chem. Soc., 103(1981)111).

A photoresponsive bis(crown ether) with an azo-linkage (34),
capable of transporting alkali metal cations across a liquid
o-dichlorobenzene membrane has been synthesised.[206]   The trans-cis
isomerism of (34) is photosensitive, whereas the cis-trans isomerism
is thermally sensitive; the interconversion is reversible such as

(34)

Trans-form

the motion of a butterfly.   Ion transport studies showed that the
transport phenomenon was light sensitive, the transport velocity
of the cation being accelerated when the liquid membrane in
contact with the 1N aqueous phase was partially photoirradiated.
This was thought to imply that ion transport can be facilitated by
the interconversion between cis-(34) and trans-(34) occurring in
the membrane phase as depicted in Figure 8b.[206]

Complexes of polyether sulphides with alkali metal cations have been investigated by two independent groups of authors.[207-211] Complex formation between (35) and (36) and Li^+, Na^+ and Cs^+ has

(35)   (36)   (37)

been studied by multinuclear ($^7Li-$, $^{23}Na-$, $^{137}Cs-$) n.m.r. techniques.[207]   The stabilities of the complexes have been compared with those of the corresponding polyethers 12C4 and 18C6; in all cases, substitution of the oxygen atoms by sulphur atoms results in a substantial decrease in complex stability.[207]

   The results of a comprehensive series of crystal structure analyses of the polyether sulphide (37)[208] and its complexes with NaSCN,[209] KSCN,[210] and RbSCN[211] have been reported by Dalley et al.   In all three complexes the cation coordinates to all five oxygen atoms of the polyether sulphide.   The sulphur-cation interaction, however, depends on the cation; although there is no interaction for the Na^+ cation, there is a weak interaction for K^+ and Rb^+ cations.[208]   The Na^+ cation sits in a cavity formed by the five oxygen atoms to which it is coordinated.   The nitrogen atom of the NCS$^-$ anion completes the sixfold coordination of the Na^+ cation; the sulphur atom of the NCS$^-$ anion translated a unit cell in the c direction interacts weakly with the Na^+ cation on the other side of the macrocycle.[209]   The K^+ cation sits in the cavity formed by the six heteroatoms of the macrocyclic ligand and is coordinated to all six atoms.   The SCN$^-$ ions interact but weakly wit the K^+ ion in axial positions and link adjacent molecules.[210]   The Rb^+ cation is located above the mean plane of, and coordinates to, all the heteroatoms of the macrocycle.   It also coordinates in axial positions to the SCN$^-$ anion (which exhibit an 80% preference for coordination through the nitrogen atom) and a sulphur atom from

an adjacent ligand.[211]   With the exception of this latter interatomic distance, r(Rb...S) = 347.0 pm, all salient structural data are summarised in Table 9.

Table 9.   Salient interatomic distances/pm in the structures of (37).NaNCS,[209] (37).KCNS[210] and (37).RbNCS.[211]

Compound	M^+...S	M^+...O	M^+...N(CS)	M^+...S(CN)	Distance of M^+ from mean plane of heteroatoms
(37).NaNCS	448.6	247.9–257.6	239.6	320.7	23*
(37).KCNS	328.4	276.8–287.4	304.3	336.6	20
(37).RbNCS	337.4	286.0–304.3	317.1	343.1	120

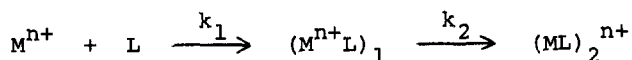* This distance is that from the mean plane of the five oxygen atoms.

1.5.4   Cryptates and Related Complexes

Surprisingly few papers describing the chemistry of cryptates and related complexes have been published during the period of the Review.   A combination ambient temperature X-ray and low temperature (20K) neutron diffraction study of $[K-C222]^+[Cr_2(CO)_{10}(\mu-H)]^-$ has been undertaken to determine the influence of the lattice environment and the K^+ ion on the anion's metal carbonyl framework and the ordered Cr-H-Cr bond.[212]   The K^+ ion is within the cryptate moiety and is coordinated to six oxygen, r(K...O) = 278-289, and two nitrogen, r(K...N) = 298,302, donor atoms.   Comparison of these distances with corresponding data for $[K-C222]^+I^-$ indicates that interaction with the $[Cr_2(CO)_{10}(\mu-H)]^-$ anion leads to an elongation of the cryptate moiety (r(N...N) increases by $\sim$27 pm and r(K...N) increases by $\sim$15 pm).[212]

Several studies of the solution chemistry of cryptate complexes have been undertaken.[213-7]   Volumes of complexation of C211, C221 and C222 with Li^+-Cs^+ in methanol and of C222 with, inter alia Ca^{2+}-Ba^{2+} in water have been determined at 298K using a flow digital densitometer.[213]   The interactions show a discontinuity when the radius of the cation is equal to the radius of the cavity of the undistorted cryptate.
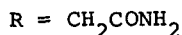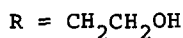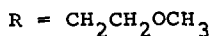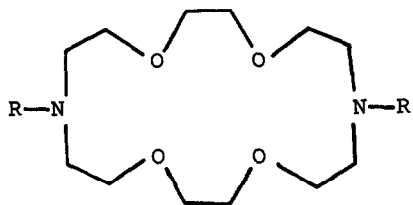
The kinetics of complexation of Li^+ and Ca^{2+} by C211 have been

measured in water at 298K using a stopped flow calorimeter.[214]
The complexation reaction exhibited a minimum of two relaxations;
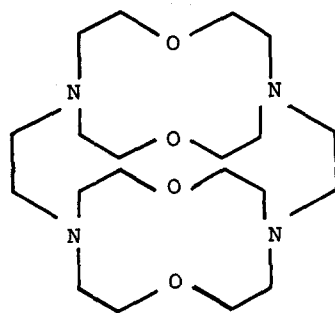the following reaction mechanism was proposed:

$$M^{n+} + L \xrightarrow{k_1} (M^{n+}L)_1 \xrightarrow{k_2} (ML)_2^{n+}$$

Cox, Schneider et al have undertaken a kinetic and thermodynamic
study of the complexation of Li^+-Cs^+ and of Ca^{2+} by C211, C221 and
C222 in various solvents (aqueous and non-aqueous)[215,216] and of
Li^+-Cs^+ by $C2_D22$ and $C2_B2_B2$.[217] The stability constants of the
$[M-C2_D22]^+$ and $[M-C2_B2_B2]^+$ moieties were compared with previous results
for $[M-C222]^+$ and $[M-C2_B22]^+$ complexes; the substituents cause a
reduction in the stability of the cryptates and an increase in the
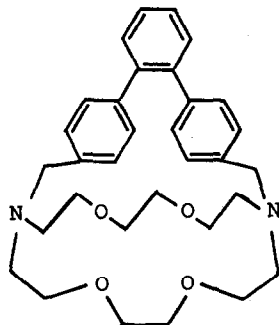dissociation rates.[217]

The stability constants of N,N'-disubstituted diaza-crown ether
complexes (38) with Na^+, K^+, Mg^{2+}, Ca^{2+} have been obtained in
aqueous solution at 298K.[218] They are discussed in terms of metal
ion hydration, metal ion/cavity size, type of donor atom and the

R = $CH_2CH_2OCH_3$

R = CH_2CH_2OH

R = CH_2CONH_2

(38)

(40)

(39)

topology of the ligand; comparisons are made with C22, C21, C222
and C221.[218]

   The molecular structures of the diaza-crown ether complexes,
(<u>39</u>).NaNCS.CH$_3$OH,[219] and of (<u>40</u>).NaBF$_4$,[220] have been elucidated.
The pseudo crown section of the ligand in the former complex adopts
the 'boat' configuration, thereby allowing all six heteroatoms to
coordinate the Na$^+$ ion in a biapical square pyramidal arrangement,
r(Na...O) = 240.7-247.6 pm, r(Na...N) = 268.5, 269.8 pm, whilst the
terphenyl residue folds away (Figure 9a).   There is no direct
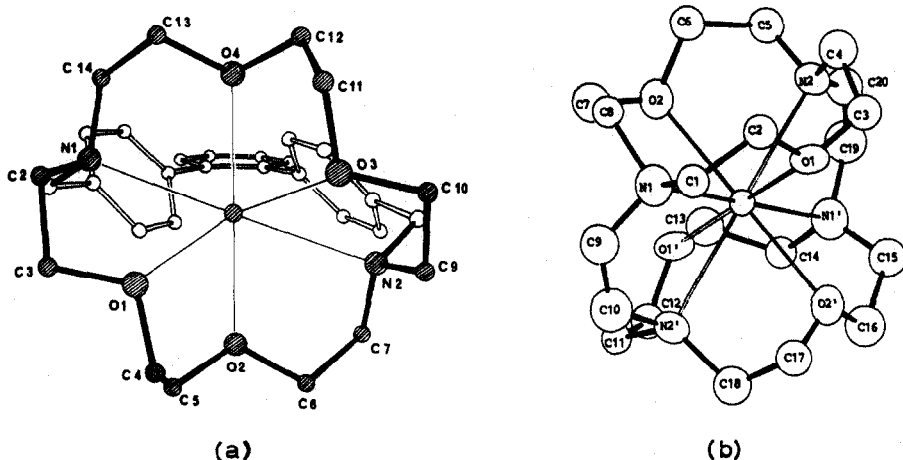contact between Na$^+$ and NCS$^-$; the anion is hydrogen bonded to a

(a)   (b)

<u>Figure 9</u>. Perspective views of the cationic structure in
          (a) (<u>39</u>).NaNCS.CH$_3$OH and (b) (<u>40</u>).NaBF$_4$ (reproduced
          by permission from (a) Acta Crystallogr., B37(1981)1832
          (b) Acta Chem. Scand., A35(1981)717).

methanol molecule.[219]   In the latter complex, the Na$^+$ ion is
enveloped by the tricyclic ligand, (<u>40</u>) such that it is coordinated
by all eight heteroatoms, r(Na...O) = 247, 250 pm, r(Na...N) = 264,
265 pm (Figure 9b); there is no interaction between Na$^+$ and BF$_4^-$.[220]

1.5.5   <u>Salts of Carboxylic Acids</u>
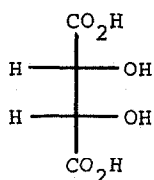
   As in the 1980 Review, interest in these salts has centred on
their structural chemistry.   The crystal and molecular structures
of lithium hydrogen acetylenedicarboxylate monohydrate[221] and of
lithium hydrogen phthalate monomethanol solvate[222] have been
determined by X-ray and neutron diffraction methods respectively;
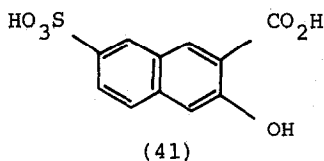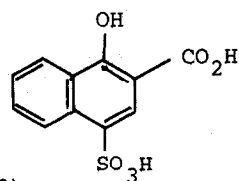although the Li$^+$ cations are effectively four-coordinate in both

molecules, one of the two crystallographically distinct Li^+ ions in the latter has two more distant neighbours. The Li^+ cation in the acetylene dicarboxylate salt is approximately tetrahedrally surrounded by four oxygen atoms from three anions, $r(Li...O) = 192.6-197.9$ pm and from the water molecule, $r(Li...O) = 187.1$ pm.[221] One of the Li^+ cations in the phthalate salt, is sited in a fairly regular tetrahedral coordination sphere comprised of four oxygen atoms from four anions, $r(Li...O) = 192.1-194.1$ pm; the other Li^+ ion is sited in a grossly distorted tetrahedral coordination sphere comprised of four oxygen atoms from two phthalate anions, $r(Li...O) = 205.2,205.6$ pm, and two solvate molecules, $r(Li...O) = 192.2,194.4$ pm, with two more distant phthalate oxygen atoms, $r(Li...O) = 268.2, 282.3$ pm.[222] The elctron distribution in the D_2O solvate of lithium formate has been studied[223] by difference methods using experimental X-ray structural data and theoretical quantum-mechanical calculations.

The structures of seven sodium salts, viz, sodium oxalate,[224] sodium dihydrogen triacetate,[225] sodium 1,1-dihydroxyacetate,[226] dextrarotatory (+) sodium ammonium tartrate tetrahydrate and racemic (±) sodium ammonium tartrate monohydrate,[227] sodium 3-hydroxy-7-sulphonato-2-naphthoic acid trihydrate[228] and sodium 1-hydroxy-4-sulphonato-2-naphthoic acid dihydrate,[228] have been either refined[224] or elucidated[225-8] during the period of this Review. The refined structure of sodium oxalate[224] is substantially the same as that determined earlier[229] with some minor modifications to bond lengths. The Na^+ ion is in a distorted octahedral environment; this is also the case in the other six salts.[225-8] In the acetate,[225] the Na^+ ion is surrounded by oxygen atoms from two acetate anions, $r(Na...O) = 231.6,232.6$ pm, and four acetic acid molecules, $r(Na...O) = 244.8-258.0$ pm; $r(Na...O)$ are shorter for the acetate anions owing to the greater electrostatic attraction between these moieties and the Na^+ ion.[225] The six oxygen atoms surrounding the Na^+ ion in the dihydroxyacetate[226] come from two monodentate and two bidentate anions, $r(Na...O) = 232.9-245.8$ pm. The Na^+ coordination sphere in the dextrarotatory tartrate tetrahydrate is composed of six oxygens from three anions, $r(Na...O) = 239.6-250.6$ pm, and three water molecules, $r(Na...O) = 235.3-237.3$ pm; that in the racemic tartrate monohydrate, however, is composed of six oxygen atoms from two monodentate and one bidentate anion, $r(Na...O) = 229.0-248.9$ pm, and two water molecules, $r(Na...O) = 244.3, 263.9$ pm.[227]

Tartaric acid

CO_2H
H —— OH
H —— OH
CO_2H

(41)

3-hydroxy-7-sulphonato-
2-naphthoic acid.

HO_3S ⸺ CO_2H / OH

(42)

1-hydroxy-4-sulphonato-
2-naphthoic acid.

OH ⸺ CO_2H / SO_3H

The major difference in the structures of the two naphthoic acid derivatives is in the extent of the distortion of the octahedral Na^+ coordination sphere.[228] For (41), the distortion is only slight, the six oxygen atoms coming from a bidentate sulphonato group, r(Na...O) = 235.3,245.0 pm, and a carboxyl group, r(Na...O) = 237.6 pm of separate anions and three water molecules, r(Na...O) = 245.2-249.3 pm. For (42), however, gross distortion occurs, the six oxygen atoms coming from two monodentate sulphonato groups, r(Na...O) = 230.4,262.0 pm, a hydroxyl group, r(Na...O) = 262.7 pm, and a carboxyl group, r(Na...O) = 247.1 of four separate anions and two water molecules, r(Na...O) = 234.6, 239.6 pm.[228]

The structure of KHC_2O_4, $H_2C_2O_4$,$2H_2O$ has been redetermined in space group $P1$ as opposed to the earlier $P\bar{1}$;[230] the refinement was undertaken to analyse the hydrogen bonding in the structure.
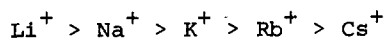
Single crystal X-ray diffraction studies of the methyloxoxanthates $M[SOCOCH_3]$ (M = K,[231] Rb[232]) have shown that whereas the K^+ ion is surrounded by four oxygen, r(K...O) = 276.4-307.5 pm, and four sulphur atoms, r(K...S) = 331.7-367.4 pm from five anions, the Rb^+ ion is surrounded by five oxygen, r(Rb...O) = 286.5-353.3 pm, and three sulphur atoms, r(Rb...S) = 340.9-353.4 pm, from six anions. In neither salt is the cation in a regular coordination sphere; that of the K^+ ion consists of two interpenetrating distorted O_4 and S_4 tetrahedra,[231] whereas that of the Rb^+ ion is a distorted bicapped trigonal prism.[232]

In the structure of the α-cyclodextrin (α-CD) inclusion complex with the potassium salt of γ-aminobutyric acid (GABA), α-CD.$GABA^-K^+$.$10H_2O$, the anions are inserted in the cavities of the α-CD molecules and do not coordinate the K^+ ion.[233] The K^+ ion is coordinated to six oxygen atoms in a distorted octahedral arrangement; four atoms, two from water molecules, r(K...O) = 273, 300 pm, and two from glucose moieties, r(K...O) = 296,304 pm, form

a rough plane and the other two atoms, one from a water molecule, $r(K...O) = 277$ pm, and one from a glucose moiety, $r(K...O) = 277$ pm, occupy the apices.[233]

Field desorption mass spectra of sodium acetate, sodium propionate, labelled analogues and mixtures have been measured.[234] In particular, hydrogen and alkyl group exchange accompanying the desorption process was investigated. Unfortunately a simple mechanistic scheme cannot be formulated owing to the complexity of the intermolecular reactions.[234] ^{39}K quadrupole resonance signals have been detected in a number of potassium salts at room temperature;[235] these include potassium hydrogen oxalate, potassium hydrogen maleate, dipotassium maleate, potassium hydrogen chloro-maleate and potassium hydrogen phthalate.

Aqueous solution behaviour of alkali metal (Li-Cs) citrates[236] and sodium cholate[237] has been investigated using n.m.r. techniques. The formation constants of the alkali metal citrate complexes decrease in the sequence

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

Although the cholate anion is monomeric at low concentrations (< 0.01 mol dm^{-3}), tetramer formation occurs at higher concentrations; it is complete at very high concentrations (>0.11 mol dm^{-3}).[237]

A group of Russian authors have reported the results of a comprehensive study of the thermal decomposition of the phthalates, $M_2X.2H_2O$,[238,239] MHX,[238,239] $RbH_3X_2.2H_2O$[240] and CsH_3X_2[241] (M=Rb,Cs; X=phthalate). The normal phthalate dihydrates $M_2X.2H_2O$ initially undergo total dehydration, the rubidium salt via the monohydrate, $Rb_2X.H_2O$, the caesium salt via the hemihydrate, $Cs_2X.\frac{1}{2}H_2O$. Subsequently the anhydrous salts decompose to M_2CO_3, CO_2 and carbon. At very high temperatures combustion of carbon and decomposition of M_2CO_3 occurs. The anhydrous hydrogen phthalates, MHX, decompose directly to the normal phthalate and phthalic acid; subsequent decomposition is as for the anhydrous normal phthalate. Thermal decomposition of $RbH_3X_2.2H_2O$ and of CsH_3X_2 proceeds in a series of distinct steps. The initial step in both cases leads to formation of the anhydrous hydrogen phthalate, MHX and phthalic acid; subsequent decomposition is as for the anhydrous hydrogen phthalate.

1.5.6 Salts of Nucleotides and Moieties of Biological Significance

Several papers have been published[242-6] in which various aspects of complex formation between alkali metal cations and nucleotides or related species are discussed. Although the majority of the papers are structurally based, complex formation between Na^+ or K^+ and adenosine-5'-triphosphate(ATP) has been studied in solution using potentiometric and calorimetric methods.[242] The formation constants of $[M(ATP)]^{3-}$ complexes agree with those previously reported and indicate a high stability. No evidence for the formation of $[MH(ATP)]^{2-}$ or $[M_2(ATP)]^{2-}$ complexes was obtained under the conditions of the experiment ($C_M+ \leqslant 0.1$ mol dm^{-3}).[242]

Structural data have been obtained for the disodium salt of guanosine-5'-monophosphate (GMP) hydrate,[243] the monosodium salt of cytidine-5'-diphosphoethanolamine (CDPE) hydrate,[244] and the lithium salt of the coenzyme nicotinamide adenine dinucleotide (NAD^+) dihydrate.[245]

There are four crystallographically independent Na^+ ions, each of which is six-coordinate, in the structure of the GMP derivative (Figure 10a). Na(1) has four water oxygen atoms, r(Na(1)...O) =

NAD^+

pseudo-diad

nicotinamide-5'-ribonucleotide   adenylic acid

236.5-249.5pm, and two N(7) atoms of separate guanosine bases, r(Na(1)...N) = 241.9, 261.1 pm, as neighbours. Na(2) and Na(3) are completely surrounded by water oxygen atoms, r(Na(2)...O) = 239.6-275.8 pm and r(Na(3)...O) = 233.8-261.8 pm, Na(4) coordinates to four water oxygen atoms, r(Na(4)...O) = 227.1-282.8 pm and the two hydroxyl oxygen atoms of a ribose moiety, r(Na(4)...O) = 231.4, 247.1 pm.[243] The Na^+ coordination sphere in the CPDE derivative is complex.[244] The ion is surrounded by four oxygen atoms, two

from the ribose moiety, r(Na...O) = 238.7, 238.9 pm, one phosphate oxygen, r(Na...O) = 222.0 pm and one water oxygen, r(Na...O) = 229.3 pm, and a single nitrogen atom from the cytosine base, r(Na...N) = 245.5 pm; a sixth coordination position is occupied by a more remote cytosine oxygen atom, r(Na...O) = 297.0 pm.[244]

Figure 10. Coordination polyhedra of (a) Na$^+$ in [GMP]Na$_2$.H$_2$O and (b) Li$^+$ in Li$^+$.NAD$^+$.2H$_2$O. Schematic diagram (c) of the stacking in Li$^+$.NAD$^+$.2H$_2$O (reproduced by permission from (a) Acta Crystallogr., B37(1981)1825 and (b,c) J. Am. Chem. Soc., 103(1981)907).

As might be expected the structure of Li$^+$.NAD$^+$.2H$_2$O is very complex.[245] The role played by the Li$^+$ ion in the molecular stacking in the unit cell is shown in Figure 10c; it links the NAD$^+$ molecular units, which adopt an extended form with nicotinamide and adenine nearly perpendicular to each other at 1200 pm separation, in an antiparallel fashion with alternating adenine and nicotinamide residues on adjacent molecules. The coordination geometry of the Li$^+$ ion (Figure 10b) is approximately tetrahedral and comprises N(7) of the adenine moiety, r(Li...N) = 213 pm, the nicotinamide phosphate oxygen, r(Li...O) = 186 pm, and the pyrophosphate free oxygens, r(Li...O) = 188, 192 pm.[245]

Structural studies have been undertaken for the sodium salt of phosphoenolpyruvate (HO$_2$C.CH(CH$_3$).O.PO$_3$H$_2$)[246] and for the monosodium

and disodium salts of N-formyl, N-hydroxyglycine (hadacidin -
$HO_2C.CH_2.N(OH).CHO$).[247]   Two crystallographically independent Na^+
ions exist in the phosphoenolpyruvate salt.[246]   Na(1) has six
oxygen nearest neighbours, four contributed by phosphate residues
of different anions, r(Na...O) = 236.3-265.8 pm, and two by water
molecules, r(Na...O) = 240.9, 249.0 pm.   Na(2) is coordinated
to five oxygen atoms, three from independent anions, r(Na...O) =
230.9-255.8 pm, and two from water molecules, r(Na...O) = 233.5,
241.8 pm.   In the monosodium salt of hadacidin,[247] which is an
L-aspartate antagonist for the enzyme adenylosuccinate synthetase,
the Na^+ ion resides in a distorted octahedral environment of
oxygen atoms, four of which are provided by three anions,
r(Na...O) = 233.5-258.6 pm, and two by water molecules, r(Na...O) =
228.3, 238.1 pm.   The Na^+ ion coordination is much more complex
in the disodium salt of hadacidin, there being three
crystallographically independent cations.[247]   Na(1) is in a
distorted trigonal bipyramidal coordination sphere of oxygen atoms,
four of which come from three anions, r(Na...O) = 231.8-236.1 pm, and
one from a water molecule, r(Na...O) = 233.6 pm.   Na(2) is
octahedrally coordinated by two oxygen atoms from symmetry related
anions, r(Na...O) = 245.4 pm, and four oxygen atoms from symmetry
related water molecules, r(Na...O) = 239.2, 254.0 pm.   Na(3) is
octahedrally coordinated by four oxygen atoms from symmetry related
anions, r(Na...O) = 233.0, 267.9 pm and by two oxygen atoms from
symmetry related water molecules, r(Na...O) = 244.1 pm.   The
distortion of the coordination octahedra around Na(2) and Na(3) of
the disodium salt is much less than that around the cation in the
monosodium salt of hadacidin.[247]

   Structural features of the hydrated forms of sodium[248] and
potassium[249] sucrose octasulphate, $C_{12}H_{14}O_{11}.(SO_3M)_8.nH_2O$ (M = Na,
K), have been elucidated.   Although the potassium salt[249] is
crystalline, the sodium salt[248] is amorphous.   Thus, whereas the
structure of the potassium salt has been determined by conventional
methods, that of the sodium salt has been elucidated from X-ray
scattering intensity data using the radial distribution function
together with the correlation method.   Each of the eight K^+ ions
is surrounded by five to seven oxygen atoms forming irregular
coordination polyhedra.   On average each K^+ ion (except for K(7))
is surrounded by 4.7 oxygen atoms from sulphato groups and 1.7
oxygen atoms from water molecules, r(K...O)$_{av}$ = 283.2 pm.   K(7) is

surrounded by seven oxygen atoms from sulphato groups, $r(K...O)_{av}$ = 281.4 pm.[249] The model which best fitted the scattering intensity data for the amorphous sodium salt was based on the structure of the potassium salt. Each sulphur atom is tetrahedrally surrounded by oxygen atoms, $r(S...O)_{av}$ = 150 pm, while each Na^+ ion is octahedrally surrounded by oxygen atoms, $r(Na...O)_{av}$ = 242 pm.[248]

The crystal structure of a complex of valinomycin (a cyclic dodecadepsipeptide containing D-valine, D-α- hydroxyvaleric acid, L-valine and L-lactic acid in the sequence cyclo(L-Val-D-Hyv-D-Val-L-Lac)$_3$) with potassium picrate has been determined by single crystal methods.[250] The K^+ ion resides inside the valinomycin cavity, $r(K...O)$ = 267-281 pm, and has a weak but definite interaction with an oxygen atom of the para-nitro group of the picrate anion, $r(K...O)$ = 386 pm.[250]

1.5.7 Multimetal Complexes Containing Alkali Metals

Structural studies have been undertaken on a small number of multimetal complexes including lithium; both methyl(-Li(μ-Me)$_2$M-) and chloro(-Li(μ-Cl)$_2$M-) bridging units have been studied. Three compounds containing methyl bridging units have been structurally characterised.[151,152] $[Li(tmen)(\mu-Me)_2Mg(\mu-Me)_2Li(tmen)]$ and $[Li(tmen)(\mu-Me)_2Mg(\mu-Me)_2Mg(\mu-Me)_2Li(tmen)]$ have been prepared by reaction of (MeLi)$_4$ with (Me$_2$Mg) in dry ether containing tmen.[251] The structure of the former has been elucidated by single crystal methods. The Mg atom is tetrahedrally surrounded by methyl groups, $r(Mg...C)$ = 223.1-229.5 pm, which form bridges to the crystallographically distinct Li atoms, $r(Li(1)...C)$ = 227.5, 229.5pm, $r(Li(2)...C)$ = 226.1, 230.4 pm, which are chelated by tmen ligands $r(Li(1)...N)$ = 209.4, 210.0 pm, $r(Li(2)...N)$ = 209.3, 211.5 pm. The Li^+ coordination polyhedra is distorted tetrahedral. The structure of the latter complex is assumed by inference.[251] $[Li_3(tmen)_3ErMe_6]$ has been crystallised from a solution of ErCl$_3$ and (MeLi)$_4$ in dry ether containing tmen.[252] Structural analysis has shown that the Er atom is surrounded in a distorted octahedral configuration by six methyl groups, $r(Er...C)$ = 257 pm, which form three bridges to lithium atoms, $r(Li...C)$ = 222 pm, chelated by tmen molecules, $r(Li...N)$ = 221 pm. Once again the Li^+ coordination polyhedron is distorted tetrahedral.[252]
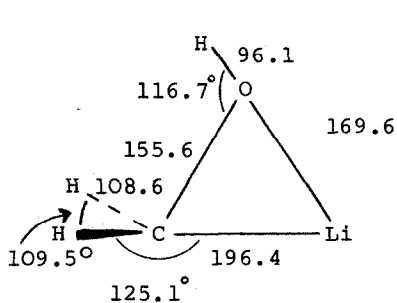
A plethera of complexes containing chloro bridging units have been prepared and characterised.[253] They include

(a) $\left[\text{Ln}\{h^5-[C_5H_3(\text{SiMe}_3)_2]\}_2(\mu\text{-Cl})_2\text{LiL}_2\right]$ (Ln = Sc,Y,La,Ce,Pr,Nd or Yb; L = thf or Ln = Y,La; L_2 = tmen or Ln = Y,Nd; L_2 = dme),

(b) $\left[\text{LnCl}_{2-n}(\text{OAr}^{Me})_n(\mu\text{-Cl})_2\text{Li}(\text{thf})_2\right]$ ($\text{OAr}^{Me} = \text{OC}_6H_2\text{Bu}^t_2\text{-}2,6\text{-Me-}4$; Ln = Y,La,Er,Yb; n = 1 or Ln = Y, n = 2) and (c) $\left[\text{ErCl}\{N(\text{SiMe}_3)_2\}(\mu\text{-Cl})_2\text{Li}(\text{thf})_2\right]$. Structural analysis of the compound $\left[\text{Nd}\{h^5-[C_5H_3(\text{SiMe}_3)_2]\}_2(\mu\text{-Cl})_2\text{Li}(\text{thf})_2\right]$ has shown that both metal atoms are in distorted tetrahedral environments; detailed structural parameters are not quoted in this preliminary communication.[253]

1.5.8   Lithium Derivatives

Although there are a vast number of publications dealing with lithium chemistry, the majority have been ignored since they deal with organolithium chemistry which is reviewed elsewhere. The only papers which have been abstracted for this Review are those involving either theoretical studies of small molecules or experimental studies of inorganic derivatives.

The results of several ab initio MO calculations on small organolithium moieties have been presented.[254-8]   Of the many isomeric forms considered for LiCH_2OH and LiCH_2NH_2, the most stable structures are the bridged species, (43) and (44), respectively;[254] they correspond to the most stable isomer of LiCH_2F discussed in the 1979 review.[259]   Similarly the most stable structure of $\text{LiCH}_2\text{CH}_2\text{Li}$ was found to be the C_{2h} molecule (45) with a trans conformation (dihedral angle $\emptyset\text{LiCCLi} = 180°$) but an unusual partially bridged geometry ($\angle\text{LiCC} = 73.2°$).[255]   However, the D_{2h} symmetrically

(43)   (44)

distances / pm.

H   Li   Li   H   H
H   \   /
 \ :   /\   O....Li....O
  C———C   / \ | · |
 /   \\   H--C————C--H | Li |
Li   H H   / \   /   ·   \
        H   H   H   O....   ....O
                        Li   H   H

(45)   (46)   (47)

trans doubly bridged structure (46), a transition state for dyotropic
rearrangement is only 7.9 kJ mol^{-1} higher in energy.[255]

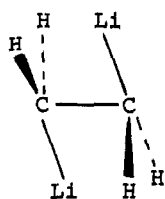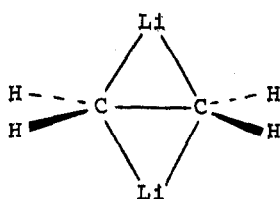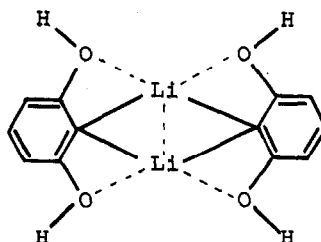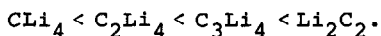Theoretical studies[256] of 2,6-substituted phenyl lithium dimers
(planar tetraco-ordinate carbon candidates) have shown that
although the dimer of phenyl-lithium has an intrinsic preference
for a planar geometry at the carbon atom (ΔH_f^O(calc) = -141.0 kJ
mol^{-1}) vis-a-vis a tetrahedral geometry at the carbon atom (-116.3
kJ mol^{-1}), the introduction of two water molecules is sufficient
to reverse the stability order of planar (-669.4 kJ mol^{-1}) and
tetrahedral (-725.4 kJ mol^{-1}) isomers.[256]   For the dimer of
2,6-dihydroxyphenyl-lithium, however, the intrinsic preference for
the phenyl-lithium dimer unit to adopt a planar geometry (47) is
reinforced through 'intramolecular solvation'.   It is thought
that the large difference in stability between the planar isomer
(-942.1 kJ mol^{-1}) and the tetrahedral isomer (-820.0 kJ mol^{-1})
may be sufficient to stabilise the planar isomer vis-a-vis a
solvated tetrahedral isomer.[256]

Ab initio calculations of the relationship between the energies
of carbanions, R$^-$ and their lithiated counterparts, RLi[257] and of
hydride abstraction from ethyl, n-butyl and s-butyl lithium[258]
have also been undertaken.

Studies[260] of the thermal rearrangements of the lithiated
compounds CLi_4, CH_2Li_2 and C_3Li_4 have produced the following
thermal stability sequence
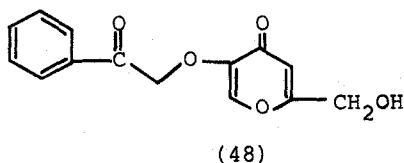
$CLi_4 < C_2Li_4 < C_3Li_4 < Li_2C_2$.

It has also been shown that flash vacuum heating of these compounds
results in vapour transport with no more than 10% decomposition
(normal heating results in 100% decomposition to Li_2C_2); this
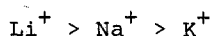observation illustrates that it may be possible to structurally

characterise gas phase polylithium organic moieties.[260]

Earlier assignments of the structures of $CH_2=CH-CH_2X$ (X = Li,K,Cs, MgBr) have been confirmed in a high resolution ^{13}C-n.m.r. study of terminally monodeuterated derivatives in thf.[261] Thus, allyl lithium forms a distorted π-complex, allyl potassium and allyl caesium are perfectly symmetrical or slightly asymmetrical π-complexes and allyl magnesium bromide exists in a σ-covalent structure which rapidly and reversibly converts into its 'metallomeric' mirror image.[261]

Complexation of alkali metal cations by 1,2-dimethoxyethane[262] by the dicarbonyl ligands, $CH_3CO(CH_2)_nCOCH_3$ ($0 \leqslant n \leqslant 2$),[263] by phenacyl kojate (48)[264] and by 2.2'-bipyridine[265] has been

(48)

investigated in a variety of aqueous and non-aqueous solvents. Dielectric relaxation studies[262] of solutions of $MClO_4$ (M = Li,Na) in dme indicate that solvation of Li^+ and Na^+ by dme cannot be described as for thf or ethylacetate for which the assumption of rigidly bound solvating molecules is acceptable, but must allow for some freedom in the orientation of the solvating dme molecules. Multinuclear ([7]Li, [23]Na, [39]K) n.m.r. studies[263] of the interaction of alkali metal cations with $CH_3CO(CH_2)_nCOCH_3$ have shown that the chemical shifts can be regarded as a semi-quantitative measure of the strength of the ion-ligand interaction, at least within a series of homologous ligands. Conductometric studies[264] have been applied in an attempt to ascertain synthesis conditions for a series of complexes of alkali metal cations with phenacyl kojate. Complex formation between alkali metal cations (Li,Na,K,Cs) and 2,2'-bipyridine has been investigated[265] by multinuclear ([7]Li-, [13]C-, [23]Na-, [39]K-, [133]Cs-) n.m.r. techniques. The stabilities of the complexes fall in the sequence

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

and vary inversely with the solvating abilities of the solvents; no complexes were detected in solutions containing Cs^+.[265]

Complexation of secondary butyl lithium by tmen has been examined[266] by n.m.r. spectroscopic techniques at low temperatures (203 ≤ T/K ≤ 253); evidence for an endothermic disproportionation of the 1:1 sec-BuLi:tmen complex to the 1:2 complex is reported.

^{7}Li n.m.r. spectra[267] of the (Li$^+$, Li$^+$ triple ion) couple ($\underline{49}$) in CH$_2$Cl$_2$ and Me$_2$SO exhibits two sharp signals; the

$$[C211Li]^+ \left[\left(\underset{Me}{\overset{O}{\underset{\underset{H}{C}}{\overset{\|}{C}}}} \cdots \overset{-}{\cdots} \cdots \underset{OEt}{\overset{O}{\overset{\|}{C}}} \right)_2 Li^+ \right]^-$$

($\underline{49}$)

$$[C211K]^+ \left[\left(\underset{Me}{\overset{O}{\overset{\|}{C}}} \cdots \underset{CH}{\cdots} \cdots \underset{OEt}{\overset{O}{\overset{\|}{C}}} \right)_2 Li^+ \right]^-$$

($\underline{50}$)

corresponding spectra of the (K$^+$, Li$^+$ triple ion) couple ($\underline{50}$) shows only one absorption with the same shift as the lower field signal of ($\underline{49}$). It is concluded that the lower field signal belongs to the triple ion and the high field signal to the cryptate cation. Although the chemical shift of the high field signal is independent of solvent that of the low field signal is strongly affected by solvent; it is assumed that the structure of the triple ion can be distorted to permit solvation by a basic solvent.[267]

^{7}Li and ^{13}C n.m.r studies[268] of thf solutions of lithium salts of picolyl (pyridylmethyl)-type delocalised anions suggest that they form tight ion pairs in which the cation-anion interaction occurs primarily at the ring nitrogen atom.

The molecular structures of lithium pentakis(methoxycarbonyl)cyclo-pentadiene monohydrate[269] and of the 1:1:1 adduct of 2-lithio-2-phenyl-1,3-dithiane with thf and tmen[270] have been determined from single crystal X-ray diffraction studies. The Li$^+$ ion is tetrahedrally coordinated in both complexes. In the former complex it is surrounded by four oxygen atoms, two from one anion, one from a second anion and the fourth from a water molecule.[269] In the latter complex, however, it is surrounded by the two nitrogen atoms of the tmen molecule, r(Li...N) = 211.0, 214.8 pm, the oxygen atom of the thf molecule, r(Li...O) = 197.0 pm and the

and the carbon atom of the dithiane derivative, r(Li...C) = 228.0 pm.[270]

Treatment of $Co_2(CO)_8$ with LiBr in dry ether yields mixtures of $Li^+[Co(CO)_4]^-$ and $Li^+[Co_3(CO)_{10}]^-$.[271] Similar mixtures were also obtained by reaction of lithium metal with $Co_2(CO)_8$ in wet ether. I.r. studies have shown that $[Co(CO)_4]^-$ is strongly distorted by Li^+ and to a lesser extent by Na^+ in dry ether.[271]

1.5.9   Sodium Derivatives

The ^{23}Na-n.m.r. spectrum of Na^- in solutions of sodium in hexamethylphosphoric triamide has been reported;[272] it gives the first indication of a genuine sodium anion formed in a metal solution in the absence of cation-complexing agents.

A solvate of molecular composition NaI.(51).C_2H_5OH has been obtained from alcoholic solutions containing stoichiometric quantities of salt and chelating agent;[273] it has been characterised by i.r.,electronic and ^{31}P-n.m.r. spectroscopy.

$$\begin{array}{ccc} & \overset{\displaystyle Ph}{\underset{\displaystyle |}{}} & \\ Ph_2PCH_2PCH_2PPh_2 \\ \overset{\|}{O} \quad \overset{\|}{O} \quad \overset{\|}{O} \end{array}$$

(51)

Sodium chelates of methylen-bis(iminodiphenylphosphorane) (52) have been synthesised[274] by reaction of excess NaH with the corresponding methanido-bis(aminophosphonium) salts (53); the latter are produced by reaction of bis(diphenylphosphino)methane with amines in CCl_4 (Scheme 5).

$Ph_2PCH_2PPh_2$ + 2PhNH$_2$ $\xrightarrow{\quad Et_3N + CCl_4 \quad}$

or

$Ph_2PCH_2PPh_2$ + 2RNH$_2$ $\xrightarrow{\quad CCl_4 \quad}$

$\left[\begin{array}{c} Ph_2P - CH - PPh_2 \\ | \qquad\quad | \\ HNR \quad\; HNR \end{array} \right]^+ Cl^-$ (53)

+2NaH $\downarrow$ -NaCl -2H$_2$

$$\begin{array}{c} H \\ C \\ Ph_2P \diagup \quad \diagdown PPh_2 \\ | \qquad\qquad | \\ RN \qquad\quad NR \\ \diagdown \quad\; Na \quad\; \diagup \end{array}$$ (52)
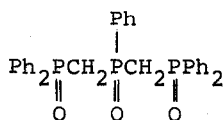
R = Me,Et,n-Pr or Ph
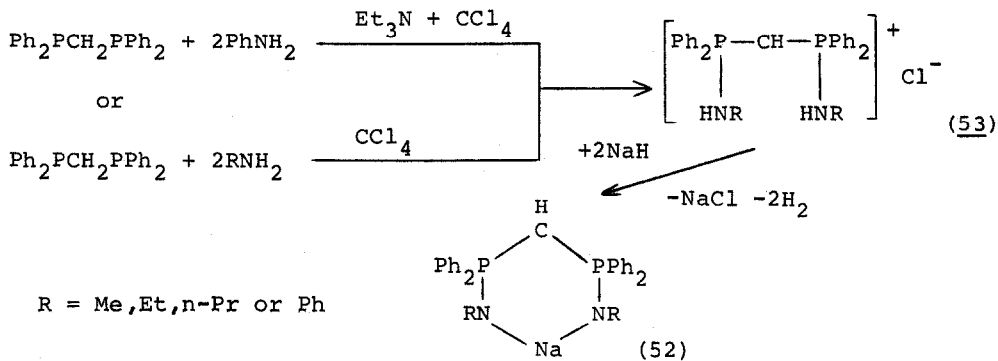
Scheme 5

The remaining papers[275-7] abstracted for this section pertain
to single crystal X-ray diffraction studies of four diverse sodium
derivatives. The structures of two p-terphenyl(tp) ion pairs have
been determined;[275] whereas that of the complex $[Na_2tp(thf)_6]$ is
a contact ion pair structure, that of $[Na_2tp_3(dme)_6]$ is a solvent
separated ion pair structure. The structure of $[Na_2tp(thf)_6]$ is
built up of $[Na(thf)_3]^+$ cations and of p-terphenyl anions; the Na^+
ions are located above and below the centre of the central ring of
the anion, r(Na...C) = 278-286 pm, the other side of the Na^+
coordination sphere being filled by three thf molecules, r(Na...O) =
229-231 pm. The oxygen atoms of the three thf molecules lie at
the corners of an equilateral triangle which is almost parallel to
the plane of the anion. The structure of $[Na_2tp_3(dme)_6]$ consists
of $[Na(dme)_3]^+$ cations, p-terphenyl anions and p-terphenyl
molecules. The Na^+ coordination sphere is disordered.
Unfortunately a suitable disorder model for the $[Na(dme)_3]^+$ cations
could not be developed; the quoted coordinates of the dme molecules
represent small peaks in a dense electron density cloud about the
Na^+ ion with a chemically acceptable geometry.[275]

The structure of sodium methanesulphonate[276] contains three
crystallographically independent Na^+ ions. Two Na^+ ions are each
surrounded by six oxygen atoms from six different anions forming
distorted octahedral configurations with r(Na...O) = 227.6-266.9 pm.
The third Na^+ ion is surrounded by eight oxygen atoms from two
unidentate, r(Na...O) = 231.8-246.9 pm and three bidentate,
r(Na...O) = 241.8-309.9 pm, anions.[276] In the structure of
sodium scylloinositol diborate decahydrate[277] each Na^+ ion is
octahedrally coordinated by the oxygen atoms of six water molecules,
r(Na...O) = 236-244 pm; the Na^+ ions are situated in parallel
columns close to the screw axes with r(Na...Na) = 342 pm.

1.5.10   Potassium, Rubidium and Caesium Derivatives

The papers abstracted for this section deal almost exclusively
with crystal-chemical studies; in all, the crystal and molecular
structures of five potassium[278-282] and of two rubidium[283,284]
derivatives have been elucidated. A variety of K^+ coordination
numbers and geometries occur in the 1:1 adduct of KF with
deuterated succinic acid, $KF(CH_2COOD)_2$,[278] the monopotassium salts
of quinoline-8-thiol-5-sulphonic acid (54)[279] and nitromalonamide
(55)[280] and the tetra-thf solvate of the dipotassium salt of

phthalocyanine.[281]   The K^+ ion is six coordinate in the 1:1 KF :
succinic acid adduct, the irregular coordination polyhedra being
composed of two fluorine atoms, r(K...F) = 268.5,287.4 pm and four
carboxyl oxygen atoms, r(K...O) = 281.8-285.2 pm.   Seven
coordinate K^+ ions are found in the two monopotassium salts.   In
the quinoline derivative,[279] the K^+ ion is surrounded by seven
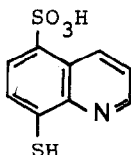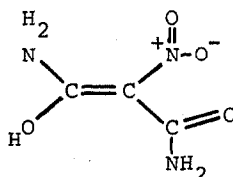
(54)   (55)

oxygen atoms from four different anions, r(K...O) = 273-289 pm;
in the nitromalonamide derivative,[280] however, it is surrounded by
seven oxygen atoms from five different anions, r(K...O) = 272-306
pm.   The coordination of the K^+ ion in the phthalocyanine derivative
is quite unusual.[281]   The K^+ ions are effectively sandwiched
between a 4N-isoindole plane, provided by the phthalocyanine
dianion, r(K...N)$_{av}$ = 278.3 pm and a 4O-plane, generated by four
dmf molecules, r(K...O)$_{av}$ = 284.7 pm.   The overall coordination
polyhedron is a distorted cubic arrangement.

     The ylides, $R_2P(CH_2C_6H_5)=CHC_6H_5$, react with lithium alkyls,
sodium amide and potassium hydride in thf to yield the corresponding
alkali metal complexes, $K^+[(C_6H_5CH)_2P(CH_3)_2]^-$.   The products have
been characterised by chemical and spectroscopic methods and in the
case of the potassium complex by single crystal X-ray diffraction
studies.   The structure (Figure 11a) is complex; the K^+ ion resides
in the space between three anions, there being one carbon atom
within 300 pm, 10 within 350 pm and 17 within 400 pm.

     The crystal structure of Rb.tcnq.(II) has been redetermined.[283]
The Rb^+ cation is surrounded by eight nitrogen atoms, r(Rb...N) =
305-327 pm, in a distorted coordination geometry.   The interplanar
spacing between the neighbouring tcnq anions is 325 pm, which is
markedly lower than that reported earlier.[285]

     Ten coordinate Rb^+ occurs in the structure of NNN'N'-tetrakis-
[2-(8-quinolyloxy)ethyl]ethylene diamine, rubidium iodide.[284]   The
wrapping of the decadentate tetrapod ligand around the Rb^+ ion is

shown in Figure 11b; it is best described as spherical with r(Rb...O)=
280.6,323.1 and r(Rb...N) = 302.6-319.1 pm.
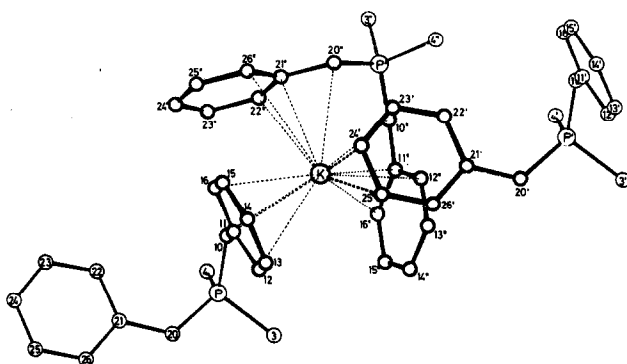
(a)
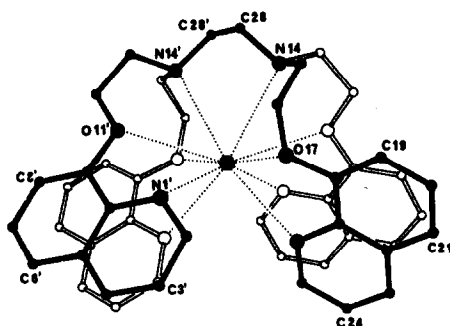
(b)

Figure 11.   Coordination of the cations in (a) potassium
phosphonium bis(benzylide) and (b) the
NNN'N'-tetrakis[2-(8-quinolyloxy)ethyl]ethylene
diamine-rubidium iodide complex (reproduced by
permission from (a) Chem. Ber., 114(1981)608,
and (b) Inorg. Chim. Acta, 54(1981)L185).

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