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Chapter 1

ELEMENTS OF GROUP 1

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1.1 INTRODUCTION

The pattern adopted for reporting the chemistry of the elements of Groups I and II in the present review follows closely that of the 1979 Review.[1] Thus Chapters 1 and 2 are divided into sections covering topics, of current interest, in which the role of the metals is unique; the application of these metals as simple counter cations is not considered. For certain subjects (e.g. cation solvation, acyclic and cyclic polyether and cryptate complexes), the chemistry of the metals is closely linked; for these cases, the data abstracted are discussed once only in the appropriate section of this Chapter.

The organometallic chemistry of lithium[2] and that of the heavier alkali metals (Na-Cs)[3] has been the subject of separate annual surveys (for 1979); emphasis is directed to the synthesis, spectroscopic and structural properties, and reaction chemistry of the organo-alkali metal compounds.

1.2 THE ELEMENTS

1.2.1 General Properties

In a series of safety studies on Li-SO_2 batteries, equation (1),

$$2Li + 2SO_2 \longrightarrow Li_2S_2O_4 \qquad \ldots(1)$$

in which the electrolyte is acetonitrile plus a cosolvent containing SO_2 and LiBr, the thermal runaway process has been shown to arise from (i) the lithium-acetonitrile/cosolvent reaction (ii) the decomposition of $Li_2S_2O_4$ and (iii) the lithium-sulphur reaction (the sulphur originating from $Li_2S_2O_4$ decomposition).[4] The kinetics and mechanism of the room temperature lithium-acetonitrile/cosolvent reaction have been studied in detail;[5] film forming agents such as SO_2 and propylene carbonate retard the lithium-acetonitrile reaction whereas solvents such as methyl formate, dimethoxyethane and diglyme enhance it, probably due to a solubilising effect of the lithium film. The cosolvents themselves were found to be quite stable to lithium.[5] The compositions of several electrolytes, containing different cosolvents, consistent with maximum suppression of the lithium-acetonitrile reaction and maintenance of adequate conductivity have been assessed.[6]

The effect of methylation of tetrahydrofuran on its reactivity with lithium has also been considered.[7] The position of the methyl substituent is critical; whereas substitution at the 2-position leads to a product which is stable to lithium over a period of 10 months, substitution at the 3-position gave a product equally as reactive as tetrahydrofuran, decomposing over a period of 48 hours.[7]

The mechanism of the Li-$SOCl_2$ electrolyte cell, equation (2),

$$2SOCl_2 + 4Li \longrightarrow S + SO_2 + 4LiCl \qquad \ldots(2)$$

has been studied in organic solvents;[8] the formation of SOCl, SO, $(SO)_2$ and $(SO)_n$ as intermediates is proposed.

The potassium M_{23} soft X-ray emission and absorption edges have been measured at 100K.[9]

The structure and packing density of liquid metals (including Li-Cs: solid phase structure: body centred cubic, coordination number 8) has been discussed and the relative merits of the theories based on (i) the existence of microparacrystals in the melts and (ii) the Percus-Yevick hard sphere concept have been assessed.[10]

1.2.2 The Alkali Metals as Solvent Media

In contrast to the earlier reviews, surprisingly little data have been reported in this field during the period of this review; those which have been published are restricted to solutions of halides in liquid potassium[11,12] and in liquid caesium.[13,14] Neutron diffraction and viscosity data for solutions of KCl in liquid potassium ($0.05 \leqslant x_{KCl} \leqslant 0.25$) have been obtained.[11,12] Even in this (metallic) concentration range salient features of the salt structure are apparent and the melts may be regarded essentially as non-regular dense liquids.

Thermodynamic data for solutions of CsX(X=F, Cl, I) in liquid caesium ($0.00 < x_{CsX} \leqslant 1.00$) have been determined.[13] The enthalpy of mixing data are positive for all three systems over the entire composition range and indicate a tendency towards phase separation; furthermore the free energy data suggest a region of strong concentration fluctuations around $x_{CsX}=0.3$.[13]

The metal-non-metal transition in solutions of iodine in liquid caesium ($0.00 \leqslant x_I \leqslant 0.67$ at T=913K) has been investigated using ^{133}Cs and ^{127}I n.m.r. techniques.[14] Knight shift and spin lattice relaxation data reveal progressively more effective electron localisation as the iodine content of the solution is increased.

Marked inflections in the concentration dependence of both parameters occur at the point corresponding to the CsI salt composition.[14]

1.2.3 Metallic Solutions

Interest in liquid phase binary metallic solutions containing an alkali metal has been stimulated by the observation of chemical short range order (i.e. pseudo compound formation) at certain compositions (eg. $Cs_{0.5}Au_{0.5}$, $Na_{0.8}Pb_{0.2}$ and $Li_{0.75}Bi_{0.25}$) which, in some cases, may be correlated with the stoichiometries of stable intermetallic compounds (CsAu 'Na_4Pb' and Li_3Bi). Although it is generally thought that the origin of the short range order is ionic in nature, some authors are less specific involving the formation of 'finite lifetime complexes' which, although called molecules, may not be molecules in the standard chemical sense. Indeed, recently reported, preliminary UPS data for Li-Pb solutions ($0.00 \leqslant x_{Li} \leqslant 0.67$) are said not to agree with a simple ionic model which involves the complete filling of the Pb 6p shell as the $Li_{0.8}Pb_{0.2}$ stoichiometry is attained.[15]

The classical example of this phenomenon, also known as the metal-nonmetal transition, occurs for liquid $Cs_{0.5}Au_{0.5}$; evidence for the salt-like properties of this liquid have been reviewed by Hensel.[16] More recent ^{133}Cs n.m.r. data, confirming electron localisation on Au, the more electronegative component, have been reported.[17] Some physicochemical parameters (electrical conductivity, magnetic susceptibility and Knight shift) of liquid Cs-Au have been interpreted using a simple tight-binding solution model.[18,19] The success of the model originates from the fact that the metal-nonmetal transition is such a dominant phenomenon, i.e. the ionic character and the resulting strong short range order are the decisive factors governing the properties of the system, that details of the band structure are of secondary importance.[18,19]

Evidence for electron localisation and short range chemical order has also been obtained for liquid $Li_{0.5}Cd_{0.5}$,[20,21] $Li_{0.75}In_{0.25}$,[20] $Li_{0.8}Sn_{0.2}$,[20,22] $Li_{0.8}Pb_{0.2}$,[20,22-26] $Li_{0.75}Sb_{0.25}$,[26] $Li_{0.75}Bi_{0.25}$,[26] $Na_{0.75}Sb_{0.25}$[26] and $Na_{0.75}Bi_{0.25}$ using electrical resistivity[20,21] ^{7}Li Knight shift,[20-22] ^{8}Li nuclear spin lattice relaxation,[23] magnetic susceptibility[26] and diffraction methods.[24,25] Temperature normalised ^{8}Li nuclear spin lattice relaxation times $[(T_1.T)^{-\frac{1}{2}}]$ - concentration isotherms for liquid Li-Na, Li-Mg and

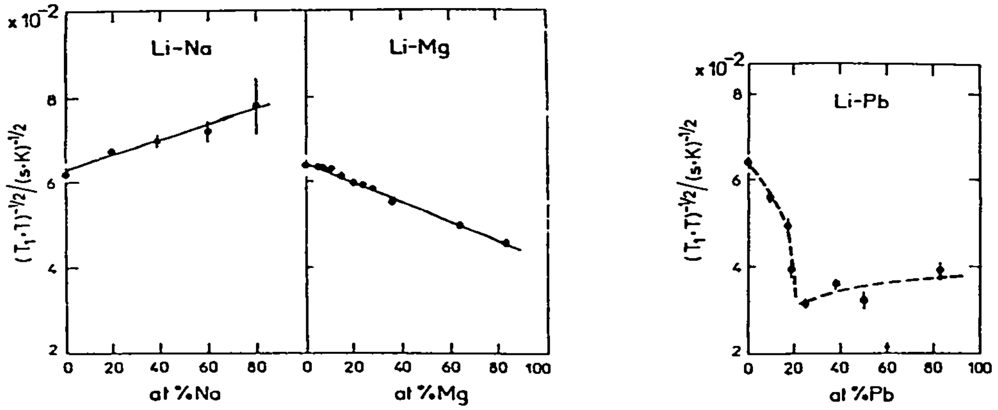
Li-Pb are compared in Figures 1(a)-1(c), respectively;[23] the anomalous behaviour of liquid $Li_{0.8}Pb_{0.2}$ is quite obvious. Similar anomalies, which have been attributed to the metal-nonmetal transition are evident in the isotherms of the magnetic susceptibility-concentration data for liquid Li-M(M=Sb,Bi) (at $Li_{0.75}M_{0.25}$),[26] of the ^{7}Li Knight shift-concentration data for liquid Li-Sn (at $Li_{0.8}Sn_{0.2}$)[20,22] and of the electrical resistivity-concentration data for liquid Li-In (at $Li_{0.75}In_{0.25}$)[20] collected in Figures 2(a)-2(c) respectively.

Lithium-rich electrical resistivity data for liquid Li-Si and Li-Ge solutions indicates that these systems also exhibit the metal-nonmetal transition, probably at $Li_{0.8}M_{0.2}$.[27]

The electrical transport properties of liquid Li-Pb have been independently interpreted using (i) a hard sphere model in which the formation of molecules (see before) is assumed[28,29] and (ii) a self consistent energy independent model pseudopotential theory.[30] The correlation between both sets of theoretical results and the experimental data is encouraging. Application of the latter theory to liquid Li-In and Li-Tl solutions indicates that the concentration dependence of the electrical resistivity of the binary solutions depends primarily on the fact that a significant fraction of the valence electrons are localised on the more electronegative component.[31] Similar calculations for liquid Li-Na, Li-Mg, Na-K, Na-Cs and K-Rb solutions can also be used to infer partial electron localisation on the more electronegative component.[31,32] Corroborative evidence for this conclusion for liquid Li-Mg solutions has been derived from neutron diffraction studies of liquid $Li_{0.7}Mg_{0.3}$ which indicate a slight preference for unlike nearest neighbours which diminishes with increasing temperature.[24,33]

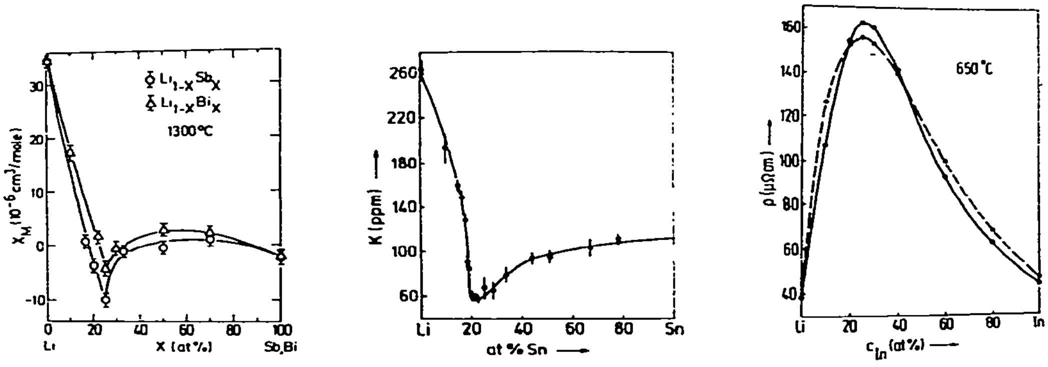
Small angle X-ray scattering data have been presented for liquid Na-K[34] and K-Cs[35] solutions ($0.00 \leq x_K \leq 1.00$ at T=373K). Comparison with corresponding results for liquid Na-Cs solutions shows that Na-K takes a position between Na-Cs, for which regular solution theory is not applicable because of the large atomic volume ratio, and K-Cs, which approaches the behaviour of ideal solutions quite closely. In the case of liquid Na-K solutions, there are distinct indications that concentration fluctuations occur in the liquid.[34]

The thermopower of liquid Li-Na solutions has been determined ($0.00 \leq x_{Li} \leq 1.00$ at T=673K);[36] for the consolute composition (x_{Li}=0.65) critical effects were observed in the temperature range



(a) (b) (c)

Figure 1. Temperature normalised ^{8}Li nuclear spin lattice relaxation times $[(T_1.T)^{-\frac{1}{2}}]$ - concentration isotherms for (a) liquid Li-Na (673K), (b) liquid Li-Mg (900K) and (c) liquid Li-Pb (1000K) (reproduced by permission from J. Physique 41 (1980) C8-409).



(a) (b) (c)

Figure 2. (a) Magnetic susceptibility-concentration isotherm for liquid Li-M(M=Sb,Bi) (1573K) (b) ^{7}Li-Knight shift-concentration data for liquid Li-Sn (at the liquidous temperature) and (c) electrical resistivity-concentration isotherm for liquid Li-In (923K) (reproduced by permission from (a) J.Physique 41(1980)C8-49, (b,c) J.Physique 41(1980) C8-516).

up to several degrees above the consolute temperature. The data are in reasonable agreement with calculations within the diffusion model.

Thermodynamic parameters for liquid Na-K,[37] Na-Cs,[37,38] K-Rb[37] and Na-Ga[39] solutions have been calculated using diverse theoretical models.

Density and compressibility data for liquid Li-Mg solutions have been derived from ultrasonic measurements;[33] specific heat data have also been obtained for these alloys.[33]

Several molten binary metallic solutions containing sodium or potassium M-In, M-Tl, M-Sn, M-Pb, M-Bi (M=Na,K) effectively catalyse the dehydrogenation of ethylbenzene to form styrene;[40] an approximate linear correlation appears to exist between the catalytic activity of the metallic solutions and its work function estimated using simple assumptions.[40]

1.2.4 Intermetallic Compounds

Four intermetallic compounds have been prepared in an investigation of the lithium rich section of the Li-Pt phase diagram ($0.6 \leqslant x_{Li} \leqslant 1.0$);[41] they are formed in peritectic reactions - Li_9Pt(444K), Li_5Pt(563K), $Li_{15}Pt_4$(586K) and Li_2Pt(1228K). Although structural data could not be evaluated for the phases, their magnetic susceptibilities and electrical resistivities have been determined.[41]

Successive formation of LiBi and Li_3Bi has been observed in the reaction of LiH with bismuth metal at temperatures upto 993K.[42]

Structural studies have been undertaken on K_2Cs,[43] K_3Ga_{13},[44] $Li_{12}Si_7$[45] and $Li_{12}Ge_7$[45] (formally described as $Li_{13}M_7$). A new phase transition has been found in K_2Cs at ca. 110K;[43] both X-ray scattering and electrical resistivity measurements suggest that an enormous volume change occurs during the transition which, it is thought, is electronic in nature.

Single crystal X-ray diffraction studies of K_3Ga_{13}[44] and of $Li_{12}Si_7$[45] have been effected; $Li_{12}Ge_7$ has been shown to be isostructural to $Li_{12}Si_7$.[45] The structure of K_3Ga_{13} is characterised by a relatively complex packing of two types of Ga_n (n=11,12) polyhedra with the potassium atoms occupying vacant holes in the structure.[44] The unit cell of $Li_{12}Si_7$ (Figure 3) contains two types of anionic Si_n cluster - planar Si_5 rings (r(Si...Si)= 235.6-238.1pm) of D_{5h} symmetry (analogues are known in $Li_{11}Ge_6$) and novel trigonal planar Si_4 clusters (r(Si...Si) = 236.5-239.3pm).[45]

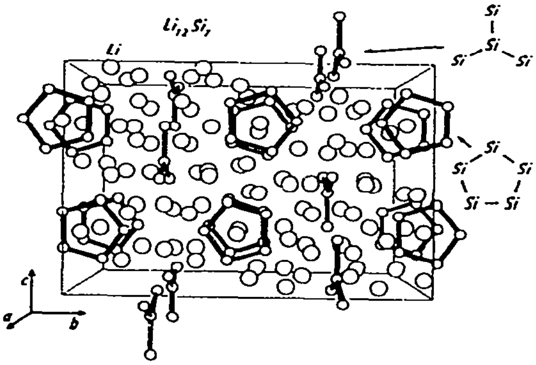


Figure 3. Crystal structure of $Li_{12}Si_7$; projection of the unit along [100] (reproduced by permission from Angew. Chem. Int. Ed. Engl., 19(1980)1033).

It has an almost negligible phase width ($1.69 \leqslant Li/Si \leqslant 1.71$), melts congruently (890K) and is extraordinarily sensitive to water and oxygen.[45]

1.3 CATIONIC SOLVATION

In contrast to the 1979 review, when several papers describing the chemistry of ion pairs in solution and in low temperature matrices were abstracted and discussed in this section (then entitled 'Ions and Ion Pairs'), only one correspondingly pertinent paper has been abstracted for this review. Consequently the format of this section has reverted to that of the 1978 review and the paper describing the matrix isolation study considered in section 1.5.1.

1.3.1 Solvation in the Gas Phase

Theoretical calculations on the solvation of alkali metal cations (Na^+-Cs^+) have been undertaken using one-layer and two-layer continuum models;[46] solvating species chosen include NH_3, H_2O, C_2H_5OH, and $(CH_3)_2CO$. The results obtained using the two-layer model are not significantly better than those derived using the one-layer model.[46]

1.3.2 Solvation in Solution

Hydration of the alkali metal cations has been the subject of structural,[47,48] spectroscopic,[49,50] and theoretical[51,52] studies. Neutron diffraction structural studies[47] of aqueous MCl(M=Li,Na,K, Cs) solutions have shown that the coordination numbers of the first hydration shell around the ions vary from 4 (for Li^+) through 6 (for Cl^-) to 8 (for Na^+, K^+ and Cs^+); average interatomic distances increase from r(Li...O)=190 through r(Na...O)=250, r(K...O)=270, and r(Cs...O)=295 to r(Cl...O)=310 pm. Complete determination of the orientational configuration around the ions was not achieved but the preliminary results indicate that the H_2O molecules in the first hydration shell adopt a linear configuration for Li^+ and Cs^+ but a bifurcated one for Cl^-.[47]

The experimental X-ray structure functions of aqueous MCl (M=Li – Cs) solutions have been satisfactorily reproduced by an independently modified first neighbour model(FNM2).[51] The original model (FNM1), used for the description of ionic hydration, has been modified by dropping the assumption that the structure of the "free solvent" is identical to that of the pure solvent. The refined structural parameters indicate the sensitivity of cationic hydration to the radius and concentration of the cations; on the other hand, chloride hydration is almost independent of both concentration and counter cation.[51]

Theoretically derived values for the H_2O binding energies in the first and second hydration spheres of a number of cations (including Li^+, Na^+, K^+, Ca^{2+} and Mg^{2+}) have been compared with experimentally observed hydration energies.[52] Furthermore the experimental values for the activation energy of water exchange in the first hydration layer have been shown to be related to these H_2O binding energies, giving strong support for an exchange mechanism which involves the second hydration shell and a higher coordinated transition state.[52]

X-ray diffraction structural data[48] for concentrated aqueous solutions of, inter alia, $CaCl_2$ (6.30M) cannot be interpreted in terms of a first neighbour model in which the hydrated ions have mean octahedral coordination geometry. They correlate much better with a model based on medium range order reminiscent of that of the corresponding hydrated crystal.[48]

Difference Raman spectroscopy of aqueous MOH (M=Li,Na,K) and NaOD versus H_2O has revealed two low frequency bands which are assigned to hydrated ion pairs of stoichiometry MOH,H_2O.[50] It is speculated that these ion pairs contain an almost symmetric O-M-O linkage with a bond angle of ca. 100°, which permits considerable fluxionality of the protons.

Vibrational spectroscopic studies of extremely concentrated aqueous LiCl solutions ($0 \leqslant x_{LiCl} \leqslant 0.4$) at high pressure and temperatures, indicate that a transition from 'water-like' to 'salt-like' behaviour occurs in the range : $0.12 \leqslant x_{LiCl} \leqslant 0.15$.[49]

Schmidt et al.[53-55] have described a comprehensive theoretical analysis of the vibrational spectra of solvated alkali metal cations. In an attempt to elucidate the structure of the primary solvation shell and to formulate a clearer picture of the vibrational states of these species, symmetrical[53] and distorted[54] solvation shells are considered, together with the interactions between the vibrations of the solvent shell and those of the trapped solvated ion.[55] For solutions in DMSO, Li^+, Na^+ and K^+ can be regarded as classical point charges; the spectra of Rb^+ and Cs^+, however, depend on dispersion forces. Li^+ and Na^+ may be regarded as atomic masses trapped inside an infinitely massive solvent cage; for K^+, Rb^+ and Cs^+, however, reduced mass effects are important in the determination of the vibrational frequency.[53]

1.4 MOLTEN SALTS

Interest in the field of molten salts has been maintained during the period of this review. A slight change of emphasis has occurred, however, vis-a-vis the earlier reviews; there has been a marked increase in the number of papers abstracted in which the solution chemistry of the molten salts is described, apparently at the expense of those in which their structural or thermodynamic properties are described.

1.4.1 Structural and Thermodynamic Properties

The formation of coordination complexes in molten salts has been considered in a review of the chemistry of these complexes in melts and in the vapour phase.[56]

Russian[57] and German[58] authors have independently determined density data for a number of halide systems. These include LiCl-$CaCl_2$,[57] RbCl-CsCl,[57] LiBr-MBr (M=Na,Rb),[57] LiBr-$CaBr_2$,[57,58] LiBr-$BaBr_2$,[57] NaBr-MBr_2 (M=Ca,Sr),[58] NaBr-$BaBr_2$,[57,58] KBr-CsBr,[57] KBr-MBr_2 (M=Ca,Sr),[58] RbBr-$CaBr_2$,[57] CsBr-MBr_2 (M=Ca[58],Ba[57]),

$CaBr_2$-$BaBr_2$,[57] NaI-TlI,[57] and RbCl-CdI_2;[57] the corresponding molar volumes have been calculated and appropriate isotherms constructed. With the exception of the LiCl-$CaCl_2$, LiBr-$CaBr_2$, NaBr-MBr_2 (M=Sr, Ba), KBr-CsBr, CsBr-$BaBr_2$ and RbCl-CdI_2 systems, which exhibit slight positive deviations from additivity, the isotherms vary linearly with concentration.

E.m.f. measurements on liquid KCl-$PbCl_2$ mixtures ($0.0 \leqslant x_{PbCl_2} \leqslant 1.0$; $873 \leqslant T/K \leqslant 1123$) have been used to derive appropriate thermodynamic properties of mixing;[59] the system exhibits negative deviations from ideality.

Equilibrium thermodynamic properties have been derived from liquidus data in the KNa||ClF, KNa||BrF, KNa||FI[60] and CsNa||ClF, CsNa||BrF, CsNa||FI[61] quaternary systems.

Internal cation mobilities in molten $LiNO_3$-KNO_3 and $NaNO_3$-$CsNO_3$ have been determined,[62] together with the diffusion coefficients of Rb^+ and Cs^+ in molten $LiNO_3$-MNO_3 (M=Na,K,Rb,Cs).[63] The diffusion coefficients decrease with increasing $LiNO_3$ content in the $LiNO_3$-$NaNO_3$ system but increase in the $LiNO_3$-MNO_3 (M=K,Rb,Cs) systems; these observations are rationalised by taking into consideration the free space in the solvent system and the ionic interactions between the diffusing and surrounding ions.[63]

1.4.2 Solution Properties

The behaviour of a large number of diverse molten salts, including halides, nitrates, nitrites and hydrogen sulphates, as non-aqueous solvents has been described during the period of this review.

The chemistry of Na_2O in molten NaCl has been the subject of two papers by Stern et al.[64,65] In an electrochemical study[64] of the oxidation of Na_2O by oxygen gas (< 10 Torr) at 1103K, they have shown that partial conversion of O^{2-} to O_2^{2-} occurs in the melt, equation (3),

$$2O^{2-} + O_2 \longrightarrow 2O_2^{2-} \qquad \text{...(3)}$$

resulting in two oxidisable species (O^{2-} and O_2^{2-}, equations (4)

$$2O^{2-} \rightleftharpoons O_2^{2-} + 2e \qquad \text{...(4)}$$

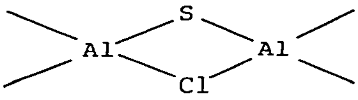
$$O_2^{2-} \rightleftharpoons O_2 + 2e \qquad \text{...(5)}$$

and (5). No evidence for the formation of O_2^- in these salts was obtained.[64] Stabilised zirconia electrolytes have been used to titrate O^{2-} into and out of molten NaCl;[65] the technique is thought to be applicable to the purification of melts and to the determination of oxide solubility products.

Thermodynamic parameters for the formation of $PaCl_4$ in LiCl-KCl molten eutectic have been reported;[66] the data were derived from e.m.f. measurements extrapolated to infinite dilution. The entropy of formation of $PaCl_4$ in the melt is so similar to that in the liquid state that Pa(IV) is thought to adopt similar configurations in the two environments.[66]

Raman studies of the redox reactions of titanium in molten LiCl-KCl-$BaCl_2$ eutectic provide evidence for the formation of K_2TiCl_6 and K_3TiCl_6.[67] Similar studies were effected in molten LiCl-CsCl eutectic but the results were inconclusive.[67]

Aspects of the chemistry of sulphur[68,69] and of uranium[70] in solution in molten chloroaluminates have been elucidated. Raman spectroscopic studies[68] of LiCl-CsCl-$AlCl_3$ and CsCl-$AlCl_3$ melts containing Li_2S indicate that a sulphur bridged chain species $[AlSCl_2]_n^{n-}$ is formed in basic solutions; these species are characterised by a strong polarised band near 325cm^{-1} which is assigned to the $-AlCl_2-S-AlCl_2-$ units. In neutral and acidic solutions, however, the ions dissociate forming soluble doubly bridged species such as $[Al_nS_{n-1}Cl_{2n+2-m}]^{(n-m)-}$ and solid AlSCl; the solutions exhibit a strong polarised band near 292 cm^{-1} which is assigned to the doubly bridged units (1) within the soluble anions.[68] Evidence for the presence of $S_3^{\cdot -}$ radical anions in basic CsCl-$AlCl_3$ melts has been obtained using similar Raman techniques.[69]



(1)

Electroreduction of U(IV) in acidic NaCl-$AlCl_3$ melts (448K) has been shown to occur via two reversible one-electron reactions, equations (6) and (7).[70] Thus U(IV) species in the solutions can be formulated

$$UCl_x^{(4-x)+} + e \rightleftharpoons U^{3+} + xCl^- \qquad (3 \geqslant x \geqslant 1) \qquad \ldots(6)$$

$$UCl_y^{(5-y)+} + e \rightleftharpoons UCl_x^{(4-x)+} + (y-x)Cl^- \quad (y-x=3) \qquad ...(7)$$

as UCl_3^+, UCl_2^{2+} and UCl^{3+} in contrast to U(V) species which are UCl_6^-, UCl_5 and UCl_4^+. However, since oxide impurities are almost inevitable in molten chloroaluminates, the existence of $UOCl_y^{(3-y)+}$ species cannot be totally excluded.[70]

Aluminium plating of iron and steel during electrolysis of molten NaCl-KCl mixtures containing $AlCl_3$ has been investigated;[71] the influence of codeposition of manganese, antimony or lead was studied and the effect of the addition of some surface active compounds determined.[71]

Several features of the chemistry of molten nitrate salts have been elucidated.[72-82] The electroreduction of molten alkali metal nitrates (at 623K) on a platinum electrode has been investigated.[72] The cation was found to play a major role in the reduction as well as in determining the ultimate fate of the oxide anion produced initially. Thus, NO_3^- reduction occurs most readily in $LiNO_3$ melt, the overvoltages required for reaction increasing with increasing cation size. Furthermore, the oxide anion became more prone to oxidation with increasing cation size, thus Li_2O was quite stable, but Na_2O and K_2O were readily oxidised to peroxides and superoxides. These observations can be rationalised by considering the thermodynamics of reaction (8); the free energy change ΔG^o_{623K} decreasing

$$M_2O(s) + MNO_3(\ell) \rightleftharpoons M_2O_2(s) + MNO_2(\ell) \qquad ...(8)$$

from +42.7 (for M=Li) through +7.5 (for M=Na) to −14.2 $kJ.mol^{-1}$ (for M=K).[72]

In a comprehensive series of papers, Holmberg et al.[73-76] have examined complex formation between Ag(I) and NO_2^-, PO_4^{3-}, IO_3^- and CrO_4^{2-} ions in molten equimolar $NaNO_3$-KNO_3 mixtures using e.m.f. (potentiometric), spectrophotometric and solubility methods ($523 \leqslant T/K \leqslant 623$). All the ions act as fairly weak ligands for Ag(I); the complexes formed are collated in Table 1. Stability constants have been derived for all the complexes and are quoted in the original papers.[73-76] Solid solutions were discovered in all four systems; these are also included in Table 1.[73-76] In conjunction with these studies Holmberg has elucidated the topology of the 553K isotherm in the quasi-ternary system Ag(K,Na)-I,NO_3.[77]

Holmberg et al.[78] have also followed the stepwise formation of

Table 1. Complex formation between Ag(I) and several anionic ligands in molten equimolar $NaNO_3$-KNO_3.

Ligand	Complexes			Solid Solution	Reference
NO_2^-	-	$Ag(NO_2)$	$Ag(NO_2)_2^-$	$(Ag,Na)NO_2$	73
PO_4^{3-}	$Ag_2(PO_4)^-$	$Ag(PO_4)^{2-}$	-	$(Ag,Na)_3PO_4$	74
IO_3^-	$Ag_2(IO_3)^+$	$Ag(IO_3)$	$Ag(IO_3)_2^-$	$(Ag,Na)IO_3$	75
CrO_4^{2-}	$Ag_2(CrO_4)$	$Ag(CrO_4)^-$	$Ag(CrO_4)_2^{3-}$	$(Ag,Na)_2CrO_4$	76

Co(II) halide complexes in molten $LiNO_3$-KNO_3 eutectic (433K) using a spectrophotometric technique. Stability constants for $CoCl_n^{2-n}$ and $CoBr_n^{2-n}$ ($0 \leq n \leq 4$) and the corresponding resolved species spectra for all complexes are reported. No definite conclusions on the coordination geometry of species intermediate between dodecahedral $Co(NO_3)_4^{2-}$ and tetrahedral CoX_4^{2-} can be obtained from the spectra. The order of decreasing complex stability is $Cl^- > Br^- \gg F^-$ (no fluoride complexes can be detected), which is in sharp contrast to the sequence $F^- > Cl^- > Br^-$ for aqueous solution. The shift in F^- position is attributed to the presence of high-field Li^+ cations in the solvent.[78]

The influence of H_2O on the reduction of Ni(II) in molten $LiNO_3$/KNO_3 eutectic (418K) has been ascertained;[79] the observed unusual electrochemical effects are attributed to the incorporation of aquo-ligands in the Ni(II) coordination sphere and the concomitant disruption of the bidentate NO_3^- groups.[79]

The extraction of Ni(II) from the molten $LiNO_3$-KNO_3 eutectic by tributylphosphate (TBP) has been studied spectrophotometrically.[80] The complex present in the melt, $M_2[Ni(NO_3)_4]$, (M=Li,K) passes into TBP during the extraction without modification of the Ni(II) coordination sphere or of the outer sphere environment of the Li^+ and/or K^+ ions. Thus the TBP does not enter the Ni(II) coordination sphere but is thought to solvate the entire complex during the extraction.[80]

The oxidation of zirconium and of zircaloy-2 samples in molten $NaNO_3$-KNO_3, $NaNO_3$-KNO_3-$NaNO_2$ and $NaNO_2$ has been studied at 573K; in particular, the mechanism of the oxide growth on the substrate surface has been elucidated.[81]

The effect of $Na_2P_2O_7$, an oxide ion acceptor which enhances the production of nitronium ions, equation (9), on the reaction of

$$NO_3^- \rightleftharpoons NO_2^+ + O^{2-} \qquad ...(9)$$

benzene with molten $NaNO_3$-KNO_3 mixtures has been assessed.[82] Its presence in the reaction mixture did have a positive effect on the production of nitrobenzene, although the overall yield was very poor.[82]

The claimed synthesis of Co(V) in molten $NaNO_2$ by oxidation of low oxidation state compounds using Na_2O_2[83] has been investigated further in a molten $NaNO_2$-KNO_2 eutectic;[84] experiments were also carried out using nickel and copper compounds.[84] No evidence was obtained for the formation of oxidation states higher than Co(II), Ni(II) and Cu(II); the quoted evidence for Co(V) has been rationalised in terms of Co(II) octahedrally coordinated by ligating oxygen atoms.[84]

A group of Australian workers[85,86] have investigated the reactions of a number of oxysalts, halides, and oxides (both binary and ternary) with molten $NaHSO_4$-$KHSO_4$ eutectic. Na_2CO_3, $NaNO_2$, KNO_3, Na_2SO_3 and $Na_2S_2O_3$ react to form H_2O and CO_2, NO and NO_2, NO_2 and O_2, SO_2, S_6 and SO_2, respectively.[85] NaCl, KBr and KI produce HCl, HBr and I_2, SO_2 and H_2O respectively.[85] K_2CrO_4 and $K_2Cr_2O_7$ are converted into the acids, H_2CrO_4 and $H_2Cr_2O_7$, which decompose subsequently to H_2O, O_2 and Cr_2O_3 which reacts further with the melt to produce H_2O and $Cr_2(SO_4)_3.H_2O$.[85] $K_2S_2O_8$ does not react with the melt but decomposes thermally to O_2 and $K_2S_2O_7$.[85] Ag_2O, MgO, ZnO, CoO, NiO, CuO, Al_2O_3, Fe_2O_3 and V_2O_5 react to produce soluble sulphates and H_2O, while CaO, BaO, Cr_2O_3 and SnO_2 react to form insoluble sulphates and H_2O.[86] Although redox processes are not involved in any of the above oxide reactions, MnO_2 is reduced by the molten salt to $Mn_2(SO_4)_3.H_2O$ and oxygen.[86]

1.5 SIMPLE COMPOUNDS OF THE ALKALI METALS

The remit adopted for this section is based on recent advances in the chemistry of the binary and ternary compounds of the alkali metals. To avoid unnecessary duplication with other Chapters of this review, the range of ternary compounds considered is restricted to those containing both an alkali metal and a transition metal.

Although a plethera of papers (mainly dealing with structural properties) have been abstracted for the ternary compounds, information for the binary compounds is much less extensive and somewhat fragmented.

1.5.1 Binary Compounds

Owing to the restricted number of papers describing the chemistry of binary compounds, the format adopted for this section is similar to that for the 1979 review where the data were considered en bloc rather than in a series of subsections.

The chemistry of the simple hydrides of the main group metals (including the alkali metals) has been reviewed.[87]

An STO-3G basis set has been proposed for the main group elements of the third row (including potassium).[88] Equilibrium geometries calculated for KH (and KOH, KCN) using this minimal representation are generally in close accord with available experimental data; the related smaller STO-2G basis set does not perform equally well in structural calculations.[88]

A novel catalytic method for the generation of non-solvated alkali metal-graphite intercalation compounds (MC_8, M=K-Cs) from graphite in an apolar medium, at room temperature and in short reaction times, has been described.[89] The catalysts used are monoolefintris(trialkylphosphane)cobalt(O) complexes which are reversibly reduced in an apolar medium (pentane). A reduced form of the catalyst $M[Co(olefin)(PR_3)_3]_2$ transports the alkali metal through the hydrocarbon solution to the graphite where the cobalt(O) complex is regenerated (Figure 4).[89]

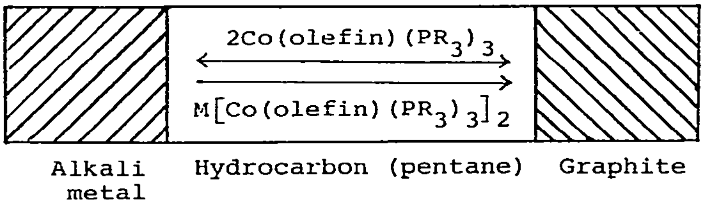


Figure 4. Catalytic intercalation of graphite (M=K-Cs)[89]

^{31}P n.m.r. studies of $^{6}Li_3P_7$ have shown that the P_7 skeleton possesses a triangularly monocapped trigonal prismatic structure which is noticeably compressed along the C_3-axis, thereby indicating predominant ionic character.[90]

The novel mixed suboxide Rb[$Cs_{11}O_3$] has been prepared;[91] it is formed in a peritectic reaction at 283K. Its structure (Figure 5)

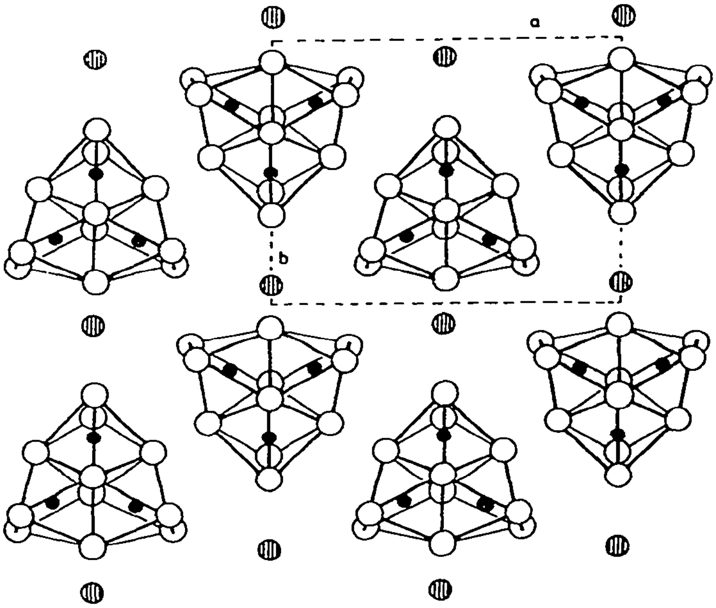


Figure 5. Crystal structure of Rb[$Cs_{11}O_3$]; projection of the unit cell along [001]. (Reproduced by permission from Z. Anorg. Allg. Chem., 463(1980)14).

consists of an idealised hexagonal close packed arrangement of [$Cs_{11}O_3$] groups with the Rb atoms occupying the quasi-tetrahedral holes; structural relationships with Cs[$Cs_{11}O_3$] and [$Cs_{11}O_3$] are discussed. Unit cell parameters are included in Table 2.

The kinetics of the reaction of M_2O_2 (M=Li,Na) with NO_2, equation (10), have been ascertained and the apparent activation energy and

$$M_2O_2 + 2NO_2 \longrightarrow 2MNO_3 \qquad \ldots(10)$$

order of the reactions with respect to NO_2 calculated.[92] The mechanism of the reaction of K_2O_2 with H_2O, equation (11), has

$$3K_2O_2 + 6H_2O \longrightarrow 2KO_2 + 4KOH,H_2O \qquad \ldots(11)$$

been established by continuous X-ray diffraction and thermal analysis; three possible mechanisms are proposed.[93]

I.r. spectra (4000–200 cm^{-1}) of several isotopic forms of solid $LiOH,H_2O$ ($^6LiOH,H_2O$, $^7LiOH,H_2O$, $^6LiOD,D_2O$, $^7LiOD,D_2O$) have been measured in an attempt to provide vibrational assignments of the lattice modes.[94]

Table 2. Unit cell parameters for $Rb[Cs_{11}O_3]$, Cs_2Se, Rb_2X_3 (X=S,Se,Te), Cs_2X_3 (X=S,Se,Te) and Na_2S_3,NH_3.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	β/°	Reference
$Rb[Cs_{11}O_3]$	orthorhombic	$Pmn2_1$	1648.4	1371.3	931	-	91
Cs_2Se	orthorhombic	Fdd2	1175	1649	677.5	-	98
Rb_2S_3	orthorhombic	$Cmc2_1$	751.3	1037.5	776.9	-	99
Rb_2Se_3	orthorhombic	$Cmc2_1$	785.6	1085.8	797.7	-	99
Rb_2Te_3	orthorhombic	Pnma	1610.9	1059.1	478.6	-	100
Cs_2S_3	orthorhombic	$Cmc2_1$	771.2	1093.9	811.1	-	99
Cs_2Se_3	orthorhombic	$Cmc2_1$	801.5	1140.6	828.2	-	99
Cs_2Te_3	orthorhombic	$Cmc2_1$	866.6	1206.5	868.0	-	100
Na_2S_3,NH_3	monoclinic	C2/m	925.7	705.6	891.9	102.71	101

Optimisation of geometrical parameters for LiOH using the approximation of overlapping atomic spheres has given calculated equilibrium internuclear distances for a linear molecule which are in satisfactory agreement with experimental data.[95] Potential energy surfaces and minimum energy paths for rearrangements (12) and (13) have been calculated using ab initio methods.[96] The

$$LiOH \longrightarrow HLiO \qquad ...(12)$$

$$LiOH^- \longrightarrow HLiO^- \qquad ...(13)$$

redistribution of electron density during rearrangement (11) has also been monitored.[97]

In a series of high temperature-high pressure synthetic reactions in liquid NH_3, Bottcher[98-101] has prepared a new modification of Cs_2Se[98] together with Rb_2X_3 (X=S,Se,Te),[99,100] Cs_2X_3 (X=S,Se,Te)[99,100] and Na_2S_3,NH_3.[101] Single crystal X-ray diffraction studies have been undertaken on all the products; unit cell parameters are included in Table 2. Na_2S_3,NH_3 has been shown to decompose at 783K to form β-Na_2S_2 and Na_2S_4.[101]

The soft sphere ionic radii for Group I and Group II metal halides recently proposed by Holbrook et al.[102] and reported in the 1978 review[103] have been criticised by Pauling[104] since they have little obvious physical significance; they are based on empirical observations having no theoretical basis. Pauling[104] also notes that a set of soft sphere radii formulated on a sound theoretical basis in 1928[105,106] gives better agreement with the experimental interionic distances in alkali metal halide crystals.

UPS (HeI and HeII) data for MF (M=Na-Cs) have been recorded in the vapour phase using a pseudo molecular beam technique.[107] The spectra are attributed mainly to monomers although evidence for dimers has been found in the spectra of NaF and possibly CsF.

Solomonik et al.[108] have undertaken a theoretical analysis of the Li_2F_2 molecule following their electron diffraction study discussed in the previous review;[109] equilibrium geometrical configurations, coefficients of general force fields and the normal vibrations were considered.[108]

Molecular chemiluminescence spectra for reaction (14) have been

$$M_2 + X_2 \longrightarrow MX^* + MX \quad (M=Na,K;\ X=Cl,Br,I) \qquad \ldots(14)$$

reported;[110] the MX* emitter is identified by comparison with previous absorption and emission data for these molecules. The Na_2/I_2 reaction as well as all reactions of Li_2 with the three halogens did not yield appreciable molecular emission.[110]

MI_3 species have been produced in an argon matrix by the salt-molecule reaction technique, equation (15);[111] the vibrational spectra of the matrix isolated species are in excellent agreement

$$MI + I_2 \xrightarrow[\text{matrix}]{\text{Ar}} MI_3 \qquad \ldots(15)$$

with previously obtained solution spectra.

A comprehensive thermodynamic study of disorder in $LiBr,H_2O$ has been completed by Staveley et al.[112] $LiBr,H_2O$ exists in two forms; the low temperature form, Figure 6(a), transforms into the high temperature β-modification, Figure 6(b), at 307K. The β-form is of particular interest from the point of view of disorder; from

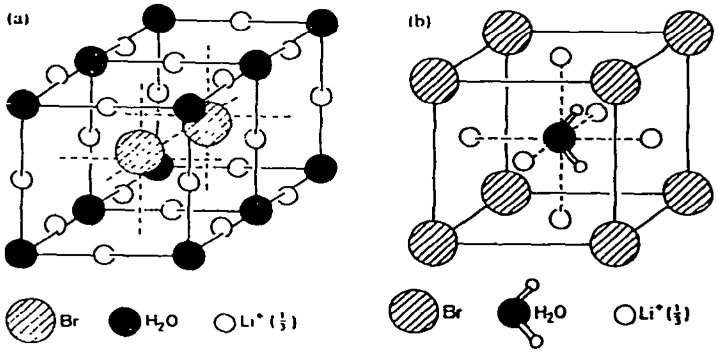


Figure 6. Crystal structures of (a) the low temperature, α-form and (b) high temperature, β-form of LiBr,H_2O (reproduced by permission from J. Chem. Soc. Faraday Trans. I, 76(1980)2362).

previous structural and n.m.r. studies it has been concluded that in this form the H_2O molecules are disordered among twelve possible orientations per molecule and the lithium ions positionally disordered among the face-centred sites of the cubic (perovskite) unit cell, Figure 6(b). The main conclusions from the thermodynamic study ((i) the α-form is uniquely ordered at OK, and (ii) the entropy gain at the α→β transition is only 6.87 $J.K^{-1}mol^{-1} \approx$ Rln2.3), however, imply that the β-form (at least just above the transition) is not nearly such a disordered structure as the previous studies had suggested.[112]

A number of lithium nitride halides, typically $Li_9N_2Cl_3$, Li_6NBr_3, Li_5NI_2, have been synthesised and shown to have a high Li^+ conductivity;[113] this property is attributed to cationic under-occupation of the adopted antifluorite lattice.

The standard enthalpy of formation of Cs_2CO_3, $\Delta H_f^o(Cs_2CO_3,c,298.15K) = -(1134.93 \pm 0.63) kJ.mol^{-1}$ has been determined from enthalpy of solution data for Cs_2CO_3 in aqueous CsOH.[114]

Electron diffraction studies of gaseous $CsNO_2$ show that it is a cyclic non-planar molecule of C_s symmetry with a dihedral angle of ca. 36(4)°.[115] Quoted internuclear distances and mean square amplitudes of vibration are r(Cs...O)=281.4, r(N...O)=138.0, r(Cs...N)=336.0, r(O...O)=212.3pm and ℓ(Cs...O)=19.1, ℓ(N...O)=4.3,

$\ell(\mathrm{Cs...N})=22.9$, $\ell(\mathrm{O...O})=5.4\mathrm{pm}$, respectively.[115]

1.5.2 Ternary Silicides, Arsenides, etc.

As explained earlier, the only ternary compounds considered in this and the two subsequent sections are those containing both an alkali metal and a transition metal. Schuster et al.[116-8] have prepared a series of ternary compounds containing a Group IV or Group V element. They have been characterised primarily by X-ray diffraction methods; the compounds and their unit cell parameters are listed in Table 3.

Table 3 Unit cell parameters for a number of ternary silicides, arsenides etc.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	Reference
$NaAu_3Si$	cubic	Pa3	891.6	-	-	116
$NaAu_3Ge$	cubic	Pa3	902.1	-	-	116
Na_2CdSn	hexagonal	$P6_3mmc$	499.0	-	1011.1	117
Na_2HgSn	cubic	$F\bar{4}3m$	722.7	-	-	117
Na_2CdPb	cubic	$F\bar{4}3m$	739.0	-	-	117
Na_2HgPb	cubic	$F\bar{4}3m$	736.2	-	-	117
Na_2AuAs	orthorhombic	Cmcm	887.1	712.9	576.0	118
Na_2AuSb	orthorhombic	Cmcm	927.9	756.2	584.1	118
K_2AuSb	orthorhombic	Cmcm	1045.9	786.1	650.0	118

1.5.3 Ternary Oxides and Chalcogenides

The synthesis of a large number of novel ternary oxides has been reported,[119-128] principally by Hoppe and his co-workers. The most pertinent features of these compounds are their structural properties; crystallographic data are summarised in Table 4. The majority of the data were obtained using X-ray diffraction methods; the high temperature structures of $NaTaO_3$, however, were determined using neutron diffraction techniques.[121] The ternary oxides were generally prepared by classical solid state reactions (e.g. high temperature reactions between alkali metal oxides, carbonates or nitrates with transition metal oxides). In an independent study, Fotiev et al.[129] have studied the mechanism of the formation of Na_2VO_3, $Na_2V_2O_5$ and $Na_4V_2O_7$ in the redox reaction between V_2O_3 and Na_2CO_3 under low oxygen partial pressures.

Vibrational spectroscopic properties of MVO_3 (M=K,Rb,Cs),[130] of $K_2Mo_2O_7$[131] and of mixed $K_2Mo_2O_7/K_2W_2O_7$[132] and $K_2Mo_2O_7/K_2Cr_2O_7$[132] phases have been examined and compared with theoretically derived data. The magnetic properties of $CsYbO_2$ have also been elucidated.[133]

The standard Gibbs free energy and enthalpy of formation of Cs_2CrO_4 have been derived[134] from high temperature enthalpy increment and associated heat capacity data : $\Delta G_f^o(Cs_2CrO_4,c,298.15K) = -1318.02$ kJ.mol^{-1}; $\Delta H_f^o(Cs_2CrO_4,c,298.15K) = -1430.01$ kJ.mol^{-1}. The enthalpy and entropy of the polymorphic transition (1031±3K) of Cs_2CrO_4 and of its fusion (1236±5K) have also been determined:[134] $\Delta H_{trans} = 2.9 \pm 0.6$, $\Delta H_{fus} = 35.2 \pm 0.7$ kJ.mol^{-1}; $\Delta S_{trans} = 2.8 \pm 0.6$, $\Delta S_{fus} = 28.6 \pm 0.5$ JK^{-1}mol^{-1}.

Thermodynamic parameters of mixed $KReO_4$-$CsReO_4$ phases have been determined (806K) using Knudsen cell mass-spectrometric techniques.[135]

A limited number of investigations of the physicochemical properties of the transition metal bronzes have been undertaken.[136-8] The electronic spectrum of the vanadium bronze, NaV_6O_{15}, has been calculated[136] on the basis of both a purely ionic approximation and a simple M.O.-L.C.A.O. approximation. Comparison of the theoretically derived spectra with the experimental data has given a more accurate estimate of the degree of ionic character in the bronze.[136]

Molybdenum bronzes of stoichiometry $A_xB_yMoO_3$ (A,B=Li,Na,K) have been obtained for the first time by electrolysis of ternary A_2MoO_4-B_2MoO_4-MoO_3 melts; the bronzes crystallise with a defective perovskite structure.[137]

The surface chemistry of sodium tungsten bronzes have been examined by cyclic voltammetry and Auger electron spectroscopy.[138] Electrochemical treatment leads to the formation of both semiconducting and metallic phases of hydrogen tungsten bronze.[138]

The Raman spectra of the polytungstate, K_2WO_4,nWO_3 ($5 \leq n \leq 7$) has been interpreted in terms of a structural model based on the hexagonal potassium tungsten bronze;[139] the analogous spectra of $K_2W_3O_{10}$ and of $K_2W_4O_{13}$ are also given and discussed.

Several authors in this field are now extending their studies to include quaternary oxides.[140-4] Such compounds may contain either two alkali metals and a single transition metal ($LiCsWO_4$[140]) or one alkali metal and two transition metals ($Na_5TbMo_4O_{16}$,[141] $K_2Ni_2Mo_3O_{12}$,[142] $Cs_8ZrMo_4O_{16}$,[143] $Cs_2HfMo_3O_{12}$[144]). Typical

Table 4 Crystallographic parameters for a number of ternary oxides

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	$\alpha/^{o}$	$\beta/^{o}$	$\gamma/^{o}$	Reference
$RbNbO_3$	triclinic	$P\bar{1}$	888.2	839.5	510.9	94.6	93.53	113.83	119
$RbTaO_3$	monoclinic	C2/m	958	850	813	-	94.8	-	120
$NaTaO_3$(298K)	orthorhombic	Pcmn	548.42	779.52	552.13	-	-	-	121
$NaTaO_3$(803K)	orthorhombic	Bmmb	784.53	785.41	786.33	-	-	-	121
$NaTaO_3$(893K)	tetragonal	C_4/mmb	555.52	-	393.38	-	-	-	121
$Na_4Mn_2O_5$	orthorhombic	Fddd	572	942	1967	-	-	-	122
Na_5CoO_4	orthorhombic	Pbca	1036	599	1805	-	-	-	123
$Na_{10}Co_4O_9$	triclinic	$P\bar{1}$	1218	852	832	119.9	87.8	116.7	124
Na_5NiO_4	orthorhombic	Pbca	1022	594	1798	-	-	-	125
Na_2NiO_2	orthorhombic	$Cmc2_1$	282	1014	828	-	-	-	126
$K_9Ni_2O_7$	cubic	$P2_13$	1091	-	-	-	-	-	127
$K_3Ni_2O_4$	orthorhombic	Cmcm	604	904	1056	-	-	-	128
$K_3Pt_2O_4$	orthorhombic	Cmcm	615	927	1151	-	-	-	128

examples, prepared during the period of this report, are listed in Table 5, together with pertinent crystallographic data.

The preparation of K_2MoO_3S, a pure monothiomolybdate has been reported;[145] it has been characterised by vibrational spectroscopic and X-ray diffraction techniques.

Several novel ternary sulphides have been synthesised and characterised.[146-9] ACu_4S_3 (A=K,Cs) and $CsCu_3S_2$ have been prepared by the high temperature (973-1073K) reaction of copper metal with A_2CO_3 and sulphur.[146,147] Schollhorn et al.[148,149] have described the synthesis of the ternary sulphides, $K_{0.3}TiS_4$,[148] $A_xMo_4S_6$ (A=K-Cs)[149] and $A_2Mo_{15}S_{20}$ (A=K,Rb)[149] by reduction of the binary transition metal sulphide (TiS_2) in an alkali metal halide (KCl) using the appropriate alkali metal (K) at 1300K. Single crystal X-ray diffraction analysis[148] of $K_{0.3}Ti_3S_4$ showed it to have a channel-type 3-D structure, built up by distorted TiS_6 octahedra joining common forces and edges. The channels, which are parallel to the hexagonal c axis, are incompletely occupied by potassium atoms (Figure 7). Crystallographic parameters for the ternary sulphides are collated in Table 6.

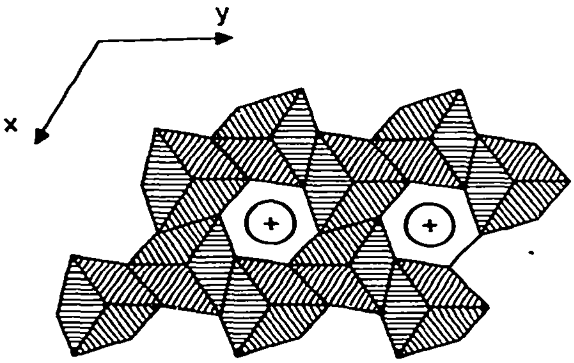


Figure 7. Structural scheme for $K_{0.3}TiS_4$; cross section perpendicular to the channel axis, circles indicate positions of K^+ cations (reproduced by permission from Angew. Chem. Int. Ed. Engl. 19(1980)492).

Table 5 Crystallographic parameters for a number of quaternary oxides

Compound	M*	Symmetry	Space Group	a/pm	b/pm	c/pm	β/°	Reference
$CsLiWO_4$	-	Cubic	$F\bar{4}3m$	835.0	-	-	-	140
$Na_5MMo_4O_{16}$	(M=Tb,Lu)*	Tetragonal	$I4_1/a$	1140.9	-	1145.3	-	141
$Na_5LuW_4O_{16}$	-	Tetragonal	$I4_1/a$	1138.7	-	1128.2	-	141
β-$K_2Mg_2Mo_3O_{12}$	-	Orthorhombic	$P2_12_12_1$	3177.5	1059.4	1060.3	-	142
α-$K_2Mg_2Mo_3O_{12}$	-	Monoclinic	$P2_1/c$	698	901	2000	108.53	142
$K_2M_2Mo_3O_{12}$	(M=Ni,Co,Zn)*	Monoclinic	$P2_1/c$	698	891	1974	107.92	142
$Cs_8MMo_4O_{16}$	(M=Hf,Zr)*	Monoclinic	C_2/m	1031	1935	831	109.07	143
$Cs_2MMo_3O_{12}$	(M=Hf,Zr)*	Monoclinic	C2/c	1934.1	695.0	1078.2	105.4	144

* The crystallographic data refer to the transition metal listed first.

Table 6 Crystallographic parameters for a number of ternary sulphides

Compound		Symmetry	Space Group	a/pm	c/pm	Reference
KCu_4S_3	-	Tetragonal	P4/mmm	389.9	926.2	146
$CsCu_4S_3$	-	Tetragonal	P4/mmm	397.5	968.9	147
$CsCu_3S_2$	-	Tetragonal	$P\bar{3}m1$	546.9	635.4	147
$K_{0.3}Ti_3S_4$	-	Hexagonal	$P6_3/m$	950.5	341.4	148
$A_xMo_4S_6$ (A=K,Rb,Cs)*		Hexagonal	-	873.8	441.3	149
$A_2Mo_{15}S_{20}$ (A=K,Rb)*		Hexagonal	-	922.7	1181.0	149

*The crystallographic data refer to the alkali metal listed first.

1.5.4 Ternary Halides

Interest in these compounds, particularly those containing lanthanide metals, has been maintained during the period of this report; research effort has been concentrated on phase equilibria between, structural chemistry of and spectroscopic properties of the ternary halides.

The pseudo-binary phase diagrams of the ACl-$EuCl_2$ (A=Na-Cs),[150] RbF-LaF_3,[151] KBr-$LnBr_3$ (Ln=Pr, Nd, Sm, Gd, Dy, Er, Yb),[152] RbBr-$LnBr_3$ (Ln=Nd, Sm, Gd, Dy, Er, Yb),[152] CsBr-$LnBr_3$ (Ln=Pr, Nd, Sm, Gd, Er, Yb),[152] NaI-LnI_3 (Ln=Ho, Sc),[153] AI-ScI_3 (A=K, Rb)[153] and CsI-LnI_3 (Ln=Ho, Tm)[153] have been studied using d.t.a and X-ray diffraction methods. As is typical of these systems, a plethora of compounds has been discovered. These include Eu(II) derivatives of stoichiometry A_2EuCl_4, $AEuCl_3$, and AEu_2Cl_5[150] and Ln(III) derivatives of stoichiometry A_3LnX_6, A_2LnX_5, $A_3Ln_2X_9$, $ALnX_4$ and ALn_2X_7;[151-3] structural data are quoted for all products in the original papers.[150-3]

A_2NpCl_5 (A=K,Rb) has been produced[154] by reduction of an acetonitrile/propionic acid (50/1) solution of ACl and $NpCl_4$ using zinc amalgam; it has been characterised by chemical analysis and Mössbauer spectroscopy. Furthermore, Mössbauer analysis of compounds analysing as $ANpCl_4.xCH_3CN$ (A=K,Rb; x=1,2) indicates that they are mixtures of A_2NpCl_5 and $ACl_3.4CH_3CN$ (A=K,Rb).[154]

Vapour pressure studies[155] of the NaF-ZrF_4 system have shown that the saturated vapour contains not only the pure components but also Na_2ZrF_6, $NaZrF_5$, $(NaZrF_5)_2$ and $NaZr_2F_9$.[155]

Numerous structural studies of the ternary halides have been undertaken;[156-69] crystallographic data are collected in Table 7. Although the majority of the data are derived from single crystal X-ray diffraction measurements, those for Cs_3CoCl_5 have been obtained as part of a temperature dependent single crystal neutron diffraction investigation (T=4.2K, 298K);[163,164] this ternary chloride is best formulated as $Cs_3^+[CoCl_4]^{2-}Cl^-$.

The structural and magnetic properties of the vanadium bronze K_xVF_3 have been elucidated as a function of composition $(0.45 \leqslant x \leqslant 0.56)$; the unit cell parameters vary linearly with composition according to $a/pm = 1219.0 + 81.5x$ and $c/pm = 373.5 + 41.1x$.[156] The thermal motion parameters of the cubic phase of $KMnF_3$ have been refined from precision single crystal X-ray diffraction data obtained at 198 and 293K.[169]

Polymorphic transitions have been studied in $KFeCl_4$[161] and KLn_2F_7 and KLn_3F_{10} (Ln=Tb-Lu,Y);[168] whereas $KFeCl_4$ exists in three modifications, equation (16),[161] the potassium lanthanide fluorides

$$KFeCl_4\text{-I} \xrightleftharpoons{297K} KFeCl_4\text{-II} \xrightleftharpoons{431K} KFeCl_4\text{-III} \qquad ...(16)$$

are dimorphic.[168]

The standard enthalpy of formation of $Cs_2Re_2Br_8$[170] and of $CsEuCl_3$[160] have been derived from enthalpy of oxidation (by aqueous bromate) and enthalpy of solution data, respectively : $\Delta H_f^o(Cs_2Re_2Br_8, c, 298K) = -(1171 \pm 35) kJ.mol^{-1}$; $\Delta H_f^o(CsEuCl_3, c, 298.15) = -(1265.0 \pm 5.6)$ $kJ.mol^{-1}$.

Evidence for the exchange of excitation energy between impurities (Cu(II), Mn(II)) in $KZnF_3$ has been established from an analysis of its emission spectra.[171]

The chemistry of the growth of a Cs_2CuCl_4 single crystal has been ascertained from a spectroscopic study (u.v., visible and i.r.) of Cs_2CuCl_4 single crystals and of the saturated solution from which they are grown.[172]

A series of quaternary halides containing two alkali metals, A_2BMX_6, have been prepared and characterised by X-ray diffraction techniques.[173-5] Several structural types are adopted including cubic K_2NaAlF_6, tetragonal $Rb_2NaTmCl_6$, hexagonal Cs_2LiGaF_6 and hexagonal-rhombohedral Cs_2NaCrF_6; typical crystallographic parameters are included in Table 7.

Table 7 Crystallographic parameters for a number of ternary halides

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	ß/°	Reference
$K_{0.5}VF_3$	Tetragonal	P4/mbm	1265.7	-	394.2	-	156
$CsScCl_3$	Hexagonal	$P6_3/mmc$	735.0	-	604.5	-	157
$RbMnBr_3$	Hexagonal	$P6_3/mmc$	756	-	635	-	158
$KNiCl_3$	Hexagonal	$P6_3cm$	1179.5	-	592.6	-	159
$CsEuCl_3$	Tetragonal	P4mm	558.8	-	561.9	-	160
$AFeCl_4$ (A=Li,Na,K(II))*	Monoclinic	$P2_1/c$	710.8	643.3	1296.2	93.62	161
$AFeCl_4$ (A=K(III),Rb,Cs)*	Orthorhombic	Pnma	1087.6	713.7	947.7	-	161
Cs_3CoCl_5	Tetragonal	I4/mcm	923.15	-	1455.35	-	162,163
Cs_2DyCl_5	Orthorhombic	Pbnm	1523.1	954.9	749.8	-	164
KSm_2X_5 (X=Cl,Br,I)*	Monoclinic	$P2_1/c$	888.9	784.6	1263	90.0	165
$RbSm_2X_5$ (X=Cl,Br)*	Monoclinic	$P2_1/c$	902.2	791.1	1268	90.0	165
LiV_2F_6	Tetragonal	$P4_2/mnm$	469.9	-	928.8	-	166
$Cs_3Sc_2Cl_9$	Rhombohedral	$R\bar{3}c$	1270.7	-	1811.7	-	157
AHg_5Cl_{11} (A=K,Rb,Cs)*	Monoclinic	C2/m	1171.8	1411.5	644.2	118.48	167
KHg_5Br_{11}	Monoclinic	C2/m	1229.3	1519.0	678.9	118.62	167
Rb_2LiFeF_6	Rhombohedral	$R\bar{3}m$	588.0	-	2879.0	-	173
Cs_2BPrF_6 (B=K,Rb)*	Cubic	-	962	-	-	-	174
Cs_2NaLnI_6 (Ln=Sc,Er)*	Cubic	-	1194.1	-	-	-	175
Cs_2NaLnI_6 (Ln=Lu,Tm,Er)*	Tetragonal	-	1204.9	-	1217.9	-	175
Cs_2LiLnI_6 (Ln=Sc,Lu,Tm,Ho)*	Hexagonal	-	819.1	-	700.3	-	175

* The crystallographic data refer to the metal listed first.

Mixed crystals of $Cs_2AgAuCl_6$ and $Cs_2Au^IAu^{III}Cl_6$ of general formula, $Cs_2Ag_{1-y}Au^I{}_yAu^{III}Cl_6$, (y=2x/(3-x)) have been prepared both by thermal decomposition ($523 \leq T/K \leq 623$) of $Cs_2Ag_{1-x}Au_{(1-x)/3}Cl_6$ ($0.00 \leq x \leq 0.63$) and by crystallisation from concentrated HCl solutions of $Cs_2AgAuCl_6$ and $CsAu^IAu^{III}Cl_6$ containing an excess of Cs^+ cations.[176] The mixed crystals are isostructural with $Cs_2Au^IAu^{III}Cl_6$ which is orthorhombic with a=1521, b=1516 and c=1032pm.[177]

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

The pattern adopted for this section of the review differs somewhat from that of the previous reviews. To accommodate the increasing awareness and interest in the role of the alkali metals in biological systems, the number of subdivisions devoted to specialised topics has been increased. These now cover alkali metal derivatives of carboxylic acids and of nucleotides and related compounds in addition to acyclic polyether complexes, crown complexes, cryptates, etc. As before, subdivisions relating to the individual alkali metals are included; for these, data pertinent to several alkali metals are discussed once only, in the subdivision relating to the lightest metal considered.

1.6.1 Acyclic Polyether Complexes

Several structural investigations[178-182] of complexes formed between acyclic polyethers and either alkali or alkaline earth metal cations have been undertaken. Reinhardt et al[178] have reported the crystal structure of tetraethylene glycol-$Ca(picrate)_2$-H_2O; a complex of a simple polyether. A perspective view of the complex is shown in Figure 8. The Ca^{2+} cation is coordinated by the five oxygen atoms of the glycol, r(Ca...O)=238.7 - 250.2pm, the phenoxide oxygen, r(Ca...O)=232.8, and a nitro oxygen, r(Ca...O)= 262.0pm of a chelating picrate ion and a water oxygen, r(Ca...O)= 238.1pm; the Ca^{2+} coordination geometry is highly distorted square anti-prismatic. In contrast to the position of the cation in complexes with other glycols, for example in heptaethylene glycol-$Sr(NCS)_2$ (see the 1979 review),[183] or in complexes involving polyethers with rigid end donor groups (see later) the Ca^{2+} cation in the present complex is displaced from the glycol donor ring in favour of the chelating picrate. This is attributed to the pronounced anion philicity of the Ca^{2+} cation.[178]

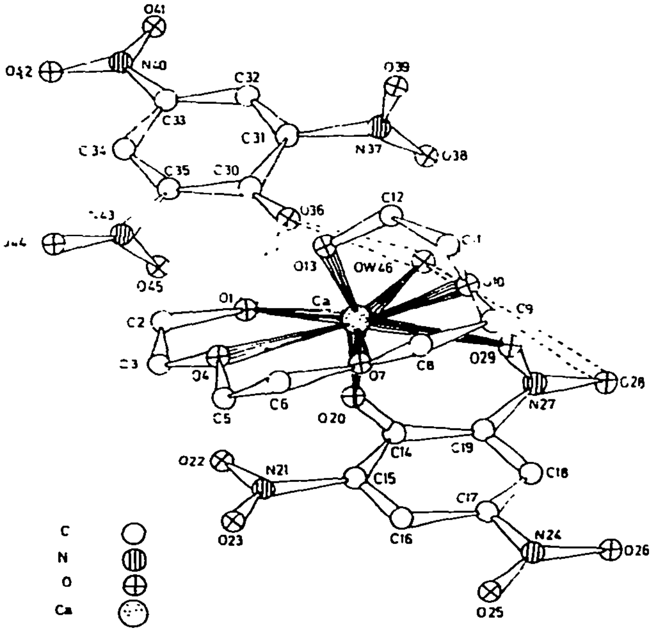
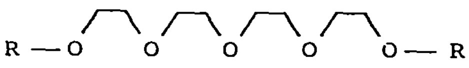


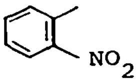
Figure 8. Molecular structure of tetraethylene glycol-Ca(picrate)$_2$-H_2O; projection along [001]. (Reproduced by permission from Inorg. Nucl. Chem. Letters, 16(1980)293).

Saenger et al. have extended their structural studies of alkali metal complexes of acyclic polyethers with rigid end donor groups to include, (2).KSCN,[179] [(3).KSCN]$_2$.H_2O[180] and (4).RbI;[181] they have also published a full paper on the structure of (5).[KSCN]$_2$.[182]

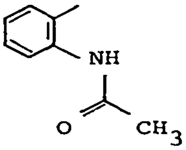


(2) - (4)

(2) R=



(3) R=



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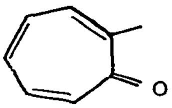
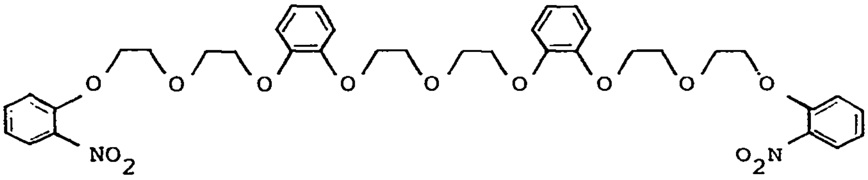




(5)

The preliminary paper was abstracted for the 1979 review;[183] hence the structure will not be considered here. The structures of (2).KSCN[179] and of (4).RbI[181] are relatively straightforward. In both complexes the polyether wraps around the cation, all five ether oxygen atoms ligating the alkali metal cation. Thus the 8-fold coordination of the K^+ cation comprises five ether oxygen atoms, r(K...O)= 278.5 - 321.7pm, one oxygen atom of each nitro group, r(K...O)= 279.6, 287.1pm and the nitrogen atom of the anion, r(K...N)= 271.8pm. Similarly, the 8-fold coordination of the Rb^+ cation comprises five ether oxygen atoms, r(Rb...O)= 294 - 318pm, the oxygen atoms of both tropolene rings, r(Rb...O)= 281,299pm and the iodide anion, r(Rb...I)=366.6pm.

Two complex molecules, (3).KSCN.H_2O and (3).KSCN exist in $[(3)\cdot KSCN]_2.H_2O$;[180] comparable projections of their structures are shown in Figures 9(a) and 9(b). The 7-fold coordination of the K^+ cations is very similar in the two molecules. Thus the ligands are wrapped circularly around the cation but are only coordinated by four of the five polyether oxygens, r(K...O)= 283.2-309.2pm (273.7 - 297.1pm). Two other coordination positions are occupied by acetylamino oxygen atoms of adjacent polyether molecules, r(K...O) = 276.5, 287.2pm (261.4, 270.5pm). The coordination sphere is completed either by a water oxygen (for (3).KSCN.H_2O), r(K...O) = 278.5pm or an anionic nitrogen atom (for (3). KSCN), r(K...N) = 284.3pm. The interaction of the cation with the acetylamino oxygen atoms of adjacent polyether molecules leads to polymeric structures (Figure 9(c)) not observed previously for similar complexes.[180]

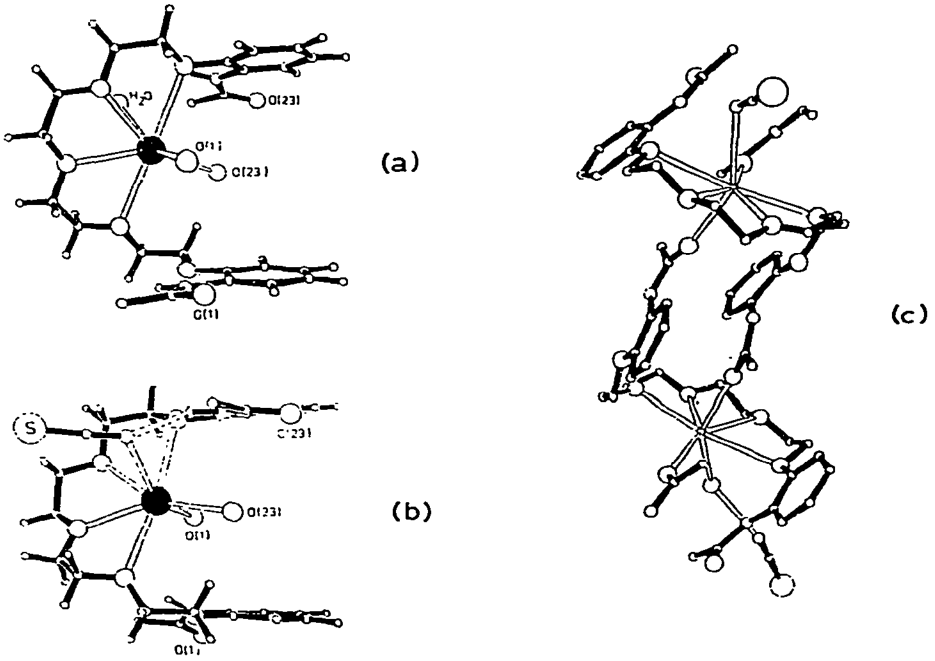
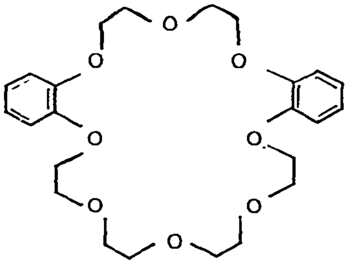


Figure 9. Comparable projections of the molecular structures of the complex fragments, (3).KSCN.H_2O (a) and (3).KSCN (b) in the linear polyether complex $[(3).KSCN]_2.H_2O$ together with a diagram showing the polymeric structure of the complex within the crystal lattice (c)(reproduced by permission from Z. Naturforsch., 35b(1980)352).

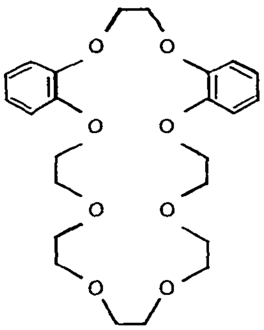
1.6.2 Crown Complexes

As for previous reviews a considerable number of papers pertinent to this section have been abstracted. There has been a slight change of emphasis in the topics studied, however, the number of solution studies (typically, determination of formation constants and extraction (distribution) coefficients) now predominating over the number of structural studies.

Novel crown complexes have been prepared using the asymmetric DB24C6 crown ethers (6) and (7),[184] the crown ether diesters (8) and (9),[185] and the phosphoryl containing macrocyclic ligand (10).[186-7] Formation constants of the 1:1 complexes of (6) and (7) with Na^+, K^+ and Rb^+ in methanol have been measured[184] together with those of the 1:1 complexes of (8) and (9) with M^+ (M=Li-Cs) and M^{2+} (M=Mg-Ba);[185] the data are compared with corresponding values for the parent crown ether ligands, DB24C8 and 18C6, respectively. Increase of the asymmetry of the position of the benzene rings in the 24C8 cyclic polyethers leads to more effective wrapping of the polyether around the metal cation.[184] Inclusion of ester carbonyl oxygens in the 18C6 macrocyclic ring leads to a marked reduction of the stability of the M^+ and M^{2+} cation complexes; complex stability is restored by inclusion of a pyridine moiety in the macrocyclic ring between the carbonyl oxygen atoms.[185] The complexing ability



(6)



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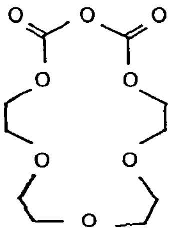

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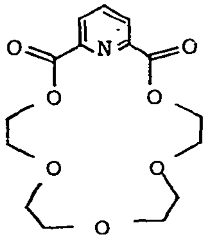
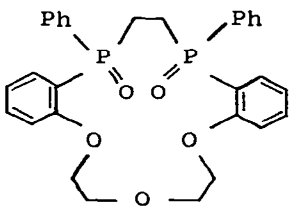
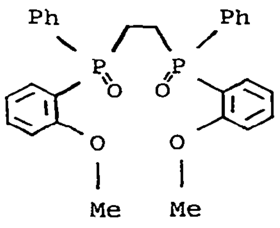


(9)



(10)



(11)

of (10) for M^{2+} (M=Mg,Ca) cations was compared with that of its acyclic analogue (11).[187]

The stabilities of complexes of the alkali metal cations with 12C4[188] 15C5[189] 18C6,[189] and DB24C6[189] in propylene carbonate have been elucidated. The alC4 complexes have been studied as part of an investigation of the electrochemical reduction of anhydrous $MClO_4$ (M=Li-Cs) and of their complexes with 12C4 by normal polarography and potentiometry using a dilute amalgam pool electrode.[188] Whereas the stable complex formed by Na^+ has 1:2 stoichiometry, the other alkali metal cations appear to form only 1:1 complexes; the stability constants of these latter complexes decrease with increasing ionic radius of the encapsulated ion.[188]

The formation constants of the 1:1 complexes of 15C5, 18C6 and DB24C8 with M^+ (M=Li-Cs) were derived from the results of conductometric studies;[188] they vary as follows:

15C5 : $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$

18C6 : $K^+ > Na^+ > Rb^+ >> Cs^+$

DB24C8 : $Na^+ > K^+ > Rb^+ >> Cs^+$

M^+ : 18C6 >> DB24C8 > 15C5

It is inferred from the observations that the complexation is not always primarily affected by the relative sizes of M^+ and the crown ether, but the competition between ligand coordination and solvation is an important parameter.[188] In an extension of the study,[189] thermodynamic parameters for the formation of the DB24C8 complexes in propylene carbonate and in methanol have been derived from a temperature dependent ($283 \leqslant T/K \leqslant 308$) conductometric study. The variation in these parameters with cation is very small; indeed the values are such that DB24C8 appears to show no selectivity for K^+, Rb^+ or Cs^+ in methanol.[189]

Complex formation between crown ethers and alkali metal salts of TCNE[191] and TCNQ[192] have been prepared and characterised by spectroscopic methods.

The extraction of alkali and alkaline earth metal cations from aqueous solution into organic solvents in the presence of crown ethers (typically 12C4, 15C5, DB18C6, DB24C6) has been assessed by a number of authors.[193-6] The overall extraction equilibrium constants for complexes of 12C4 with alkali metal picrates between H_2O and C_6H_6 vary as follows:[193]

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

This sequence is in qualitative agreement with the stability sequence discussed earlier.[188] The extraction of alkali metal cations by DB18C6 from H_2O into $CHCl_3$ in the presence of the triphenylmethane dye, bromophenol blue (BPB) has been shown to occur via formation of $[M(DB18C6)]^+BPB^-$ and $[M(DB18C6)]_2{}^+BPB^{2-}$.[194]

The rate of carrier facilitated transport of alkali metal cations (Li^+, Na^+, K^+) through a bulk $CHCl_3$ liquid membrane containing a neutral macrocyclic carrier (typically DB18C6) has been shown to be strongly dependent on the anion (F^-, Cl^-, I^-, SCN^-, $NO_3{}^-$, picrate$^-$).[195] Indeed the data for K^+ in the presence of DB18C6 ranged over 8 orders of magnitude according to anion; anions with smaller Gibbs free energies of hydration permitted faster cation transport.[195]

The coextraction of H_2O into $C_6H_5NO_2$ with alkali (Li^+-Cs^+) and alkaline earth metal (Ca^{2+}-Ba^{2+}) salts of 2,2',4,4',6,6'-hexanitrodiphenylamine (HND) in the absence or presence of a crown ether (typically 15C5, DB24C8) or a cryptate (typically C211, C222B) has been elucidated.[196] ^1H n.m.r. and near i.r. spectroscopic techniques show that coextraction is caused by cation hydration. Complexation causes an obvious decrease in hydration number: for example in the 1:1 crown ether-cation complexes more than 50% of the H_2O molecules are removed and in the 1:1 cryptand-cation complexes less than one H_2O molecule remains unmoved.[196]

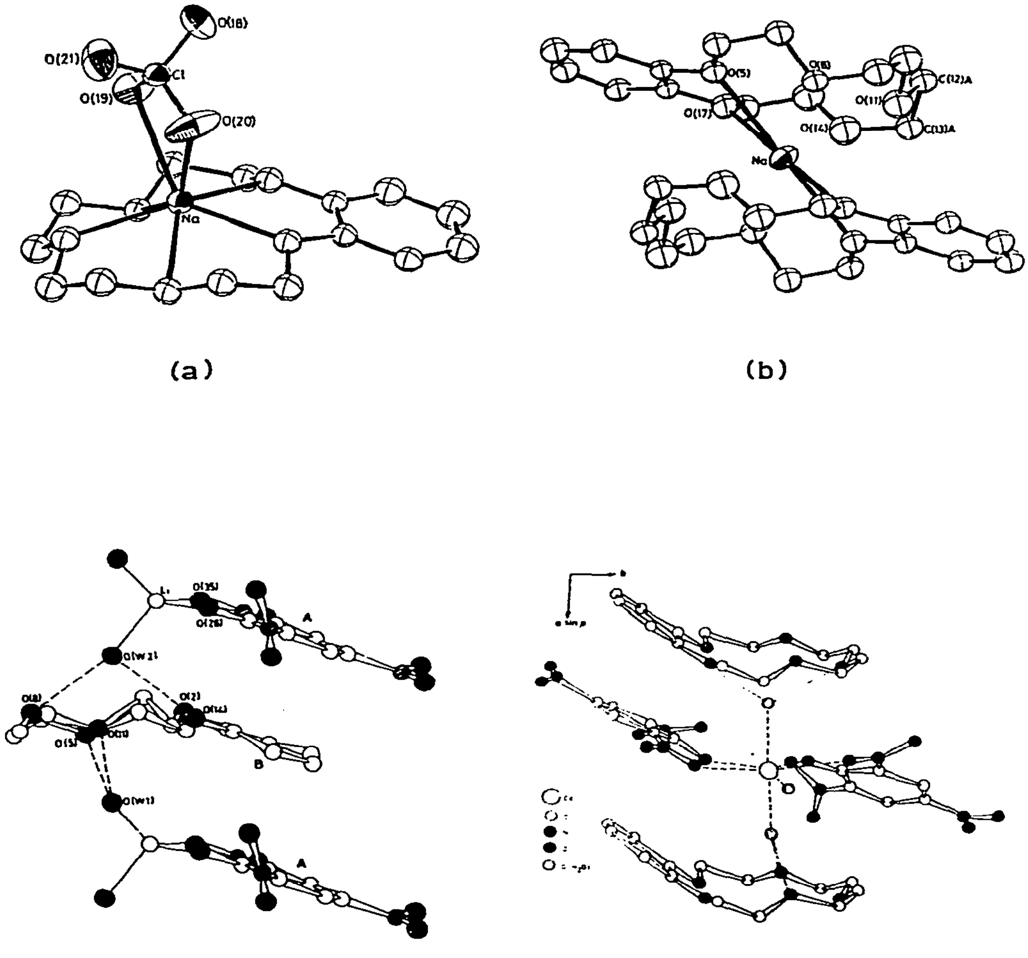
Single crystal X-ray diffraction structural analyses have been undertaken for several benzo-15-crown-5 complexes[197-200] (B15C5. $Na[ClO_4]$,[197] $(B15C5)_2.Na[ClO_4]$,[197] $(B15C5)_2.Na[BPh_4]$,[197] (B15C5).Li[picrate],$2H_2O$,[198] and (B15C5).Ca$[picrate]_2$,$3H_2O$[199]) as well as for DB30C10,K[SCN][200] and (9).K[SCN].[201]

The molecular structures of the Na^+ complexes of B15C5[197] differ quite markedly from those of the Li^+ [198] and Ca^{2+} [199] complexes. Whereas the Na^+ cation is coordinated primarily by oxygen atoms of the crown ether molecules (Figures 10(a), 10(b)), the Li^+ and Ca^{2+} cations are not bound to the crown ether molecules but are coordinated by oxygen atoms of the picrate anions and water molecules (Figures 10(c), 10(d)). Thus these latter compounds constitute unusual examples depicting total preference of the cations for anionic species in the presence of a potentially chelating crown ether.

In the 1:1 complex of B15C5 with $Na[ClO_4]$, Figure 10(a), Na^+ is irregularly coordinated to the five oxygen atoms of the crown ligand, r(Na...O)=237.3 - 246.4pm; and two from the perchlorate anion, r(Na...O) = 242.6, 263.4pm. The 2:1 complex with $Na[ClO_4]$ exhibits considerable disorder in the atomic positions; it has a centrosymmetric sandwich structure, Figure 10(b), and two conformers are present in the ratio 0.523:0.477. The coordination of the cation is not clear, owing to a wide spread of Na...O distances, r(Na...O) = 263.1 - 293.5pm. The 2:1 complex with $Na[BPh_4]$ also has a sandwich structure, but with no centre of symmetry, and again the coordination number of the cation is not clear, r(Na...O)= 248.2 - 330.4pm.

In the lithium picrate complex, Figure 10(c),[198] the cation is coordinated by two oxygen atoms from a chelating picrate anion, r(Li...O)=192, 204pm, and two water molecules, r(Li...O)=186,187pm, giving a tetrahedral coordination. In the calcium picrate complex, Figure 10(d),[199] the cation has a distorted pentagonal bipyramidal coordination sphere. The equitorial plane comprises four oxygen atoms from chelating picrate anions, r(Ca...O)=228 - 261pm, and a water molecule, r(Ca...O)=242pm; the apical positions are occupied by two water molecules, r(Ca...O)=223,227pm. In both complexes, the crown ether molecules are bound to the water molecules of the complex cationic system through weak hydrogen bonds, Figures 10(c), 10(d).[198,199]

The structure of DB30C10, K[SCN] has been determined and compared with those of DB30C10,KI and DB30C10,Rb[SCN],H_2O.[200] The ligand wraps around the K^+ cation coordinating it by all ten ring ether oxygen atoms, r(K...O)=283.5 - 294.0pm; the anion does not participate in the K^+ coordination sphere.[200] The K^+ coordination sphere in the K[SCN] complex of (9) is essentially



(a) (b)

(c) (d)

<u>Figure 10</u>. Molecular structures of selected B15C5 crown complexes (a) B15C5.Na$[ClO_4]$, (b) $(B15C5)_2$.Na$[ClO_4]$, (c)B15C5.-Li(picrate).$2H_2O$ and (d) (B15C5).Ca$(picrate)_2$.$3H_2O$ showing both chelation (a,b) and non-chelation (c,d) of the crown ether (reproduced by permission from (a,b) J. Chem. Soc. Dalton Trans., (1980)1066, (c) Inorg. Nucl. Chem. Letters, 16(1980)373 and (d) Inorg. Nucl. Chem. Letters, 16(1980)289).

a hexagonal bipyramid.[201] The cation is centred in the near regular hexagonal equatorial plane formed by the donor atoms of the ligand, r(K...O)=275.7 - 280.3, r(K...N)=282.6pm; the apical positions are occupied by the nitrogen and sulphur atoms of separate anions, r(K...N)=291.7pm, r(K...S)=339.5pm.[201]

1.6.3 Cryptates and Related Complexes

The classification and nomeclature of cryptands, coronands, podands and of their complexes has been discussed in detail by Weber and Vögtle.[202] Comprehensive ^{15}N n.m.r. spectroscopic studies of these ligands and of their complexes have been undertaken;[203] the complexation shifts tend to go downfield with increasing charge and increasing ionic nature of the N...M bond, but upfield with increasing polarisability of the ion.

Popov et al.[204-6] have reported the results of an extensive n.m.r. (^{7}Li, ^{13}C, ^{23}Na, ^{39}K, ^{133}Cs) study of the formation of alkali metal cryptates and related complexes in a series of non-aqueous solvents (typically CH_3NO_2, $(CH_3)_2CO$, CH_3CN, C_6H_5N). The formation constants of the complexes between Li^+, Na^+ and Cs^+ and C22 were shown to decrease in the order:[204]

$Li^+ > Na^+ > Cs^+$

This is markedly different from that observed for the analogous 18C6:

$Cs^+ > Na^+ > Li^+$

Popov et al.[205] have also shown that whereas K^+ forms an "inclusive" complex with C222 (ie. the cation is located within the ligand cavity), C221 and C211 have cavities which are too small to accommodate K^+ and hence the complexes have an "exclusive" configuration. Similarly, they have reported[206] that Cs^+ forms an "inclusive" complex with C322 but an "exclusive" complex with C222B; for C222, a ligand of intermediate size, temperature and solvent dependent "exclusive" $\rightleftharpoons$ "inclusive" equilibrium is observed.

Stability constants for the cryptates, $C22.M^+$ and $C222.M^+$ (M=Na-Cs) have been determined in CH_3CN by conductivity measurements, and compared with corresponding data in CH_3OH.[207] The stability constants are considerably higher, and the selectivity is different for C22 in CH_3CN than in CH_3OH; C222 forms much stronger complexes than C22. The data cannot be rationalised solely on the basis of the cryptand cavity geometry and the cation size; metal ion solvation must also be taken into account, especially for the smaller cations in strongly solvating solvents.[207] A similar conclusion has been reached from the results of a field desorption mass spectroscopic study of the cryptate complexes formed between C211, C221 and C222 with Li^+, Na^+ and K^+ in combination with the anions, Cl^-, Br^-, I^- and BPh_4^-.[208] The stability of the complexes was dependent not only on the fit of the cation in the cryptand but also on the counteranion; stability decreased in the order:

$BPh_4 > I > Br > Cl$.

Thermodynamic studies of cryptate formation between C222 and Li^+-Cs^+ in H_2O and CH_3OH, indicate that the cryptand does not isolate the complexed ion from the environment, since the thermodynamic parameters for the transfer of the complexed ions from H_2O to MeOH vary considerably with the concentration.[209] The kinetics of the uncatalysed and acid-catalysed dissociation of $C222.K^+$ in H_2O have been studied and the data compared with corresponding results for $C222.Tl^+$.[210]

The molecular structure of the complex between the tripod ether, tris-[(2-methyl-8-quinolyl-oxy)ethyl]amine and RbI, Figure (11), has been determined in a single crystal X-ray diffraction study.[211] The Rb^+ cation is coordinated by the iodide anion, r(Rb...I)=375.8 pm, and is also cradled by the three legs of the ligand so that all seven heteroatoms ligate the cation, r(Rb...N(amine))=299.9, r(Rb...N(quinolyl))=313.3 - 319.8, r(Rb...O)=302.9 - 305.9pm. Comparison of the coordination geometry with those of complexes with similar ligands indicates that the tripod wraps around the cation in the manner of an acyclic rather than cyclic polyether ligand.[211]

1.6.4 Salts of Carboxylic Acids

As mentioned earlier, this and the following section have been included in the review to cater for the increasing awareness and interest in the role of the alkali metals in biological systems. Without exception, the papers abstracted for this section describe aspects of the structural chemistry of these salts.[212-224]

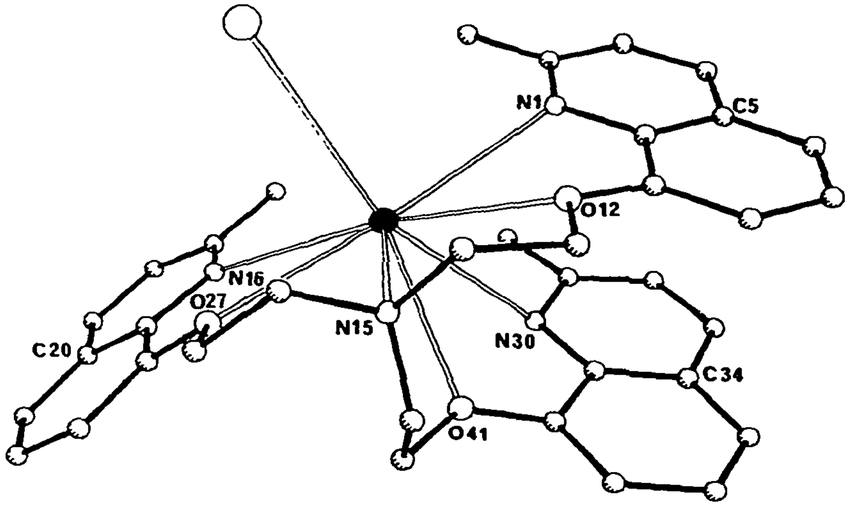


Figure 11. Molecular structure of the tripod complex, tris-[(2-methyl-8-quinolyl-oxy)ethyl]amine.RbI (reproduced by permission from Inorg. Chim. Acta, 45(1980)L35).

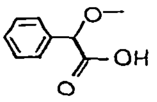
The electronic structure of lithium formate, monohydrate Li[HCOO],D_2O has been derived from diffraction data and compared with that calculated theoretically using a non-empirical Hartree Fock method with orthoganalised Slater orbitals for basis functions.[212] Comparison of the two sets of data shows that the experimental charge distribution differs from the theoretical one in its greater polarity; this is attributed to molecular interaction in the crystal.[212]

The structure of potassium formate, K[HCOO], has been elucidated in two independent laboratories;[213,214] the two determinations are effectively identical. The K^+ cation is 8-coordinate; its geometry can be described on the basis of a purely C_{2h} octahedral model with four monodentate formate anions, r(K...O)=281.9pm; and two bidentate formate anions r(K...O)=300.3pm.[213,214]

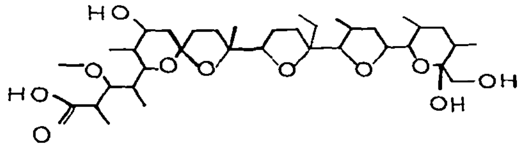
Neutron powder diffraction data (300K)[215] for the isostructural oxalate monoperhydrates, $M_2[C_2O_4],D_2O_2$ (M=K,Rb) have been refined on the basis of Pederson's structure[216] in an attempt to ascertain the positions of the deuterium atoms. The eight-fold coordination sphere of the cations is generated by six oxygen atoms from separate oxalato moieties, r(K...O)=269 - 303pm (r(Rb...O)=290.3 - 312.3pm), and two oxygen atoms from the peroxide link, r(K...O)=285, 298pm (r(Rb...O)=299.9, 303.8pm).

Single crystal X-ray diffraction studies of the hydrogen bis(dibromoacetates), $MH[Br_2HCCOO]_2$, (M=Rb,[217] Cs[218]) have shown that whereas the Rb^+ cation is surrounded by eight oxygen atoms, r(Rb...O)=294.4 - 375.9pm, and two bromine atoms, r(Rb...Br)=362.5 pm; the Cs^+ cation is surrounded by eight oxygen atoms, r(Cs...O)= 306.5 - 385.6pm, and three bromine atoms, r(Cs...Br)=385.6 - 395.2pm. In neither salt is the cation in a regular coordination sphere.[217,218]

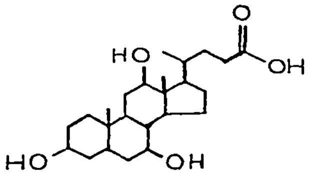
In the molecular structure of lithium hydrogen malate, $LiH[OOC.CH_2.CH(OH).COO]$, the Li^+ cation is tetrahedrally coordinated by oxygen atoms of four monodentate malate anions, r(Li...O)=191.7 - 199.7pm.[219]



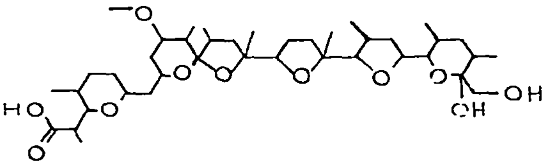
Methoxyphenylacetic acid



monensin



cholic acid



nigéricine

The cations in sodium and rubidium hydrogen bis(methoxyphenylacetate) (the molecular formula of the parent acid is shown above) have been shown to be six- and eight-coordinate, respectively.[220]

The NaO_6 polyhedra is a distorted square plane (composed of two carboxylate and two ketonic oxygen atoms) with an apposing bifurcated apex (composed of two carboxylate oxygen atoms, average r(Na...O)=237pm. The RbO_8 polyhedron can be derived from the NaO_6 one by extending out the bifurcated apices and inserting two extra oxygen atoms, average r(Rb...O)=299pm.[220]

The structures of sodium cholate monohydrate[221] and of rubidium deoxycholate monohydrate[222] (the molecular formula of cholic acid is shown above) have been ascertained. In the cholate, the Na^+ cation is in contact with five oxygen atoms; three from hydroxyl groups of different cholate anions, one from a carboxylic acid residue of a fourth anion and one from the disordered water molecule, average r(Na...O)=236.1pm.[221] In the deoxycholate, the Rb^+ cation is surrounded by six oxygen atoms : three from hydroxyl groups of different cholate anions, two from a bidentate and one from a monodentate carboxylic acid residue, average r(Rb...O)= 299.6pm. The water oxygen atom is located 331pm from the cation but is said not to be bonded to it since its lone pairs are not directed towards the cation.[222] In neither salt does the coordination sphere of the cation adopt a regular geometry.[221,222]

The complexation of sodium by ionophores (natural or synthetic compounds that facilitate transport of ions across membranes) has been investigated in structural studies of hydrated and anhydrous sodium monensin[223] and of anhydrous sodium nigéricine.[224] (The molecular formulae of these two ionophores are shown above). The conformations of the sodium-monensin complex (including the Na^+ coordination sphere) observed in the anhydrous and dihydrate crystal forms are nearly identical with each other and with that in a complex with NaBr. Thus, the Na^+ cation has a severely distorted octahedral coordination sphere, Figure 12(a), composed of both ether and hydroxyl oxygen atoms, r(Na...O)=233.6 - 254.3pm (hydrated),= 234.6 - 252.9pm (anhydrous), of a single monensin ligand which is bound around the cation by two hydrogen bonds.[223] The mechanism of the complexation process has been inferred from a comparison of the complexed structures with that of the free ionophore.[233]

A similar type of structure, Figure 12(b), occurs in the sodium-nigéricine complex;[224] in this case, however two hydrogen bonds bind the ligand around the cation forming a cavity within which the cation is in close association with five of the oxygen atoms situated within the cavity, r(Na...O)=225 - 252pm.[224]

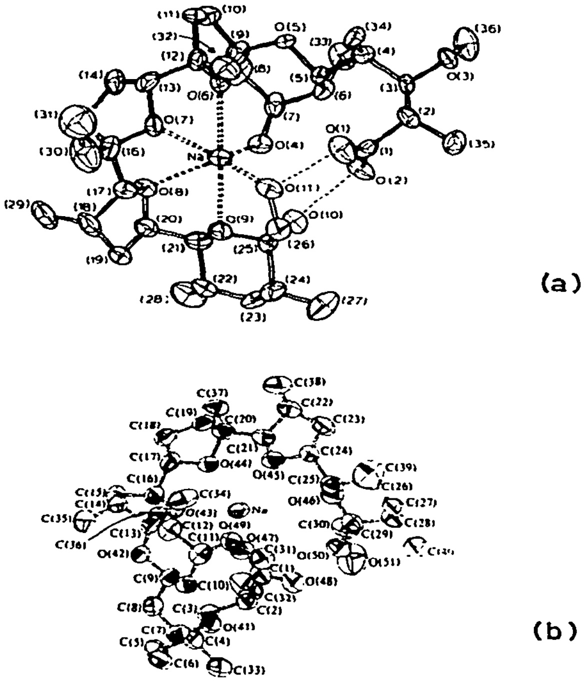
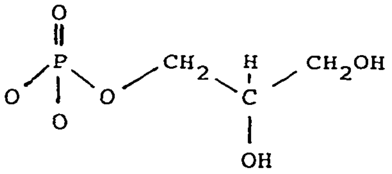


Figure 12. Molecular structures of the Na^+ complexes of the ionophores, monensin(a) and nigéricine (b)(reproduced by permission from (' J. Amer. Chem. Soc., 102(1980) 6725 and (b) Acta Cryst., B36(1980)936).

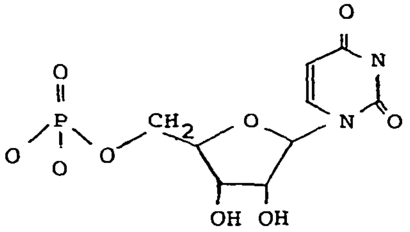
1.6.5 Salts of Nucleotides and Related Species

Several papers have been published[225-232] in which various aspects of complex formation between alkali metal cations and nucleotides or related species are discussed; in general, it is the structural properties of these systems, which are models for metal interactions with ribonucleic acid loops, that have been investigated. The complexing anions that have been studied include the DL α-glyceromonophosphate dianion,[225] the uridine 5'-monophosphate dianion,[226] the deoxyuridine 5'-monophosphate dianion,[227] the dihydrouridine 3'-monophosphate monoanion,[228] the adenosine 5'-diphosphate monoanion[229,230] and the guanosine 5'-monophosphate dianion;[231,232] the molecular formulae of these moieties are given below.

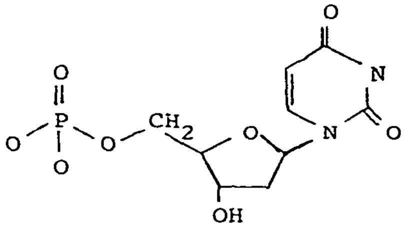
The structure of disodium DLα-glyceromonophosphate, hexahydrate has been redetermined.[225] It is complex, the two Na^+ cations being distributed over three crystallographically independent sites.



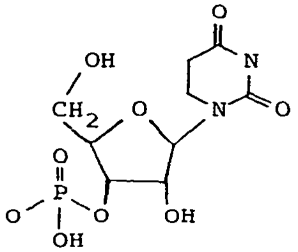
α-Glyceromonophosphate dianion



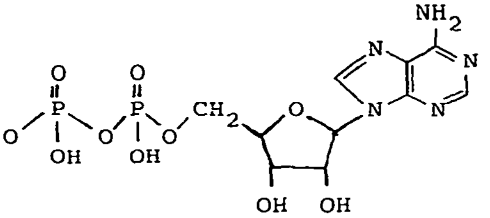
Uridine 5'-monophosphate dianion



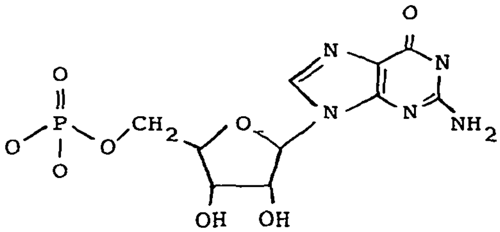
Deoxyuridine 5'-monophosphate dianion



Dihydrouridine 3'-monophosphate monoanion



Adenosine 5'-diphosphate monoanion



Guanosine 5'-monophosphate dianion

All three Na^+ cations are octahedrally coordinated by oxygen atoms from either water molecules, r(Na...O)=233.6 - 256.0pm, or the hydroxyl groups of the glyceromonophosphate moiety, r(Na...O)=235.3-249.8pm; surprisingly, the Na^+ cations are not linked directly to any phosphate oxygens.[225]

Single crystal X-ray diffraction studies of the uridine monophosphate (UMP) derivatives, $[5'\text{-UMP}]Na_2,7H_2O$,[226] $[5'\text{-deoxyUMP}]Na_2,5H_2O$[227] and $[3'\text{-dihydroUMP}]K,\frac{1}{2}H_2O$[228] have been undertaken. As for the glyceromonophosphate salt, the structures are exceedingly complex; for example there are four crystallographically independent Na^+ cations in $[5'\text{-deoxyUMP}]Na_2,5H_2O$.[227] The coordination spheres of both Na^+ (5- or 6-coordinate) and K^+ (8-coordinate) in these complexes comprise ligating oxygen atoms provided either by water molecules or the various constituent groups (ie. the uracil base, the ribose function, and the phosphate moiety) of the anion.[226-8]

The crystal and molecular structure of the monopotassium salt of adenosine 5'-diphosphate dihydrate, $[ADP]K,2H_2O$, has been determined independently by Saenger[229] and by Sundaralingam;[230] the two structures are, in a broad sense, identical, but differ in some minor details. The K^+ cation has seven neighbours within a

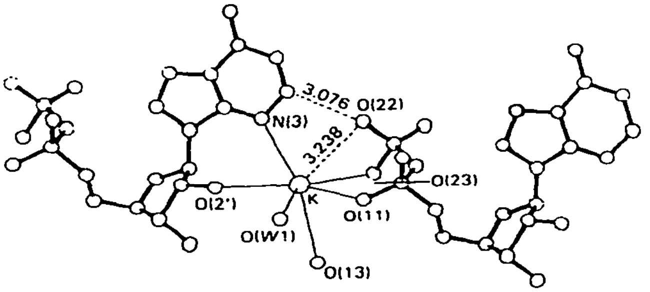


Figure 13. Coordination of the K^+ cation in the structure of $[ADP]K,2H_2O$ (reproduced by permission from Acta Cryst., B36(1980)2590).

sphere of radius 325pm., Figure 13. The cation is coordinated to three phosphate oxygen atoms O(11) O(12) and O(23) of one ADP anion, r(K...O)=276.7, 323.8 and 295.3pm, one phosphate oxygen atom O(13) of a second ADP anion, r(K...O)=314.7pm, a uracil nitrogen atom N(3) and ribose oxygen atom O(2') of a third ADP anion, r(K...N)= 316.2pm, r(K...O)=285.6pm, and the water molecule oxygen atom O(W1), r(K...O)=304.5pm. Of the seven ligating atoms only O(11) is close enough to the K^+ ion to satisfy the criterion for coordinative interaction; the other six must be considered to be more loosely coordinated.[229,230]

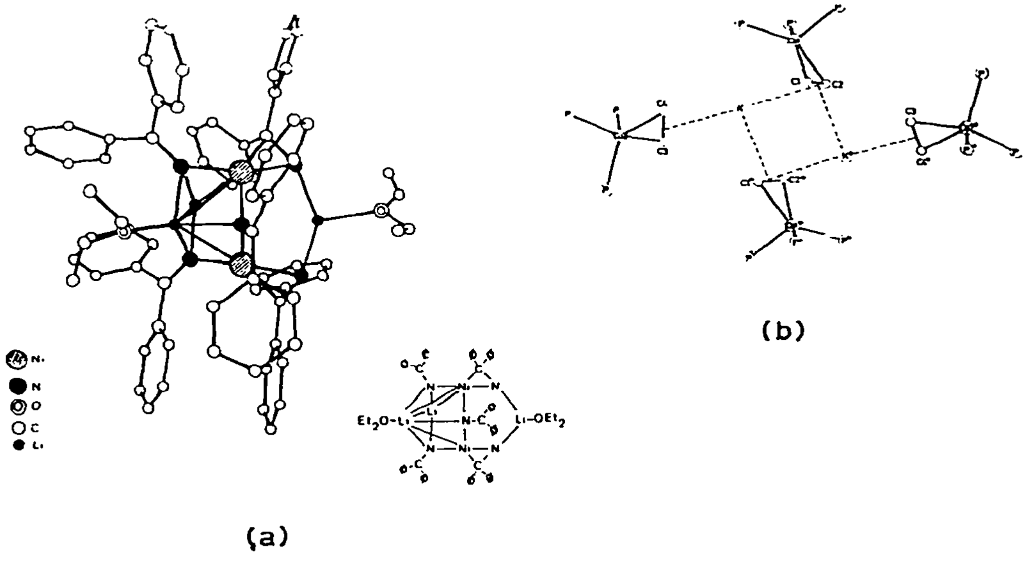
The role of alkali metal cations in the self assembly of the guanosine 5'-monophosphate dianion in aqueous solution has been studied by Laszlo et al. using ^{1}H, ^{23}Na, ^{31}P, ^{39}K, ^{87}Rb n.m.r.

techniques.[231,232] The self assembly process is critically dependent on the cation present. In the presence of Na^+, the hydrogen bonded planar tetrameric $(GMP)_4$ basic building blocks aggregate to form octamers and hexadecamers, the Na^+ being inserted in the central cavity of the $(GMP)_4$ tetramers. In the presence of both Na^+ and K^+, however, an organised structure $[(GMP)_4K^+(GMP)_44Na^+]^{11-}$ results. The K^+ ions bind selectively to the inner site, sandwiched between two $(GMP)_4$ tetramers; the Na^+ ions bind selectively to the outer sites, screening the electrostatic repulsion of the negatively charged phosphate groups.[231,232]

1.6.6 Alkali Metal-Transition Metal Multimetal Complexes

Following the recent serge of interest in the novel and attractive area of organometallic chemistry involving alkali metal-transition metal π-complexes, their syntheses, structural properties and reaction chemistry have been reviewed by Jonas and Kruger.[233]

Kruger et al.[234] have prepared a new multimetal complex by reaction of lithium benzophenoneimide with di-1,5-cyclooctadienenickel in diethyl ether; its structure, Figure 14(a), has been characterised



(a)

(b)

Figure 14. Structures of (a) $(Ph_2C{=}NH)_2(Ph_2C{=}NLi)_3Ni_2.(Et_2O)_2$ and (b) $K[Co(C_2H_4)(PMe_3)_3]_2$. (Reproduced by permission from (a) J. Organomet. Chem., 190(1980)315 and (b) Z. Naturforsch., 35b(1980)614).

by spectroscopic and X-ray methods. The salient structural features are (i) a Li-Li entity, r(Li...Li)=254.2pm, connected by two $Ph_2C=N$ units and (ii) two nickel atoms at a non-bonding distance, r(Ni...Ni)=301.3pm, bridged by another $Ph_2C=NLi$ moiety. In addition two $Ph_2C=NH$ molecules are π-bonded to the nickel atoms and also connected via a single lithium atom. Free coordination sites on all lithium atoms are occupied by ether molecules.[234]

$K[Co(C_2H_4)(PMe_3)_3]_2$ has been synthesised from potassium metal and $Co(C_2H_4)(PMe_3)_3$.[235] The single crystal X-ray structure determination of this compound shows that the unit cell, Figure 14(b), contains two K^+ cations in equal ionic contact with the C_2H_4 moieties of four $Co(C_2H_4)(PMe_3)_3$ complexes, two of which interact with both K^+ cations, r(K...C)=303 - 324pm. In hydrocarbon solvents, these compounds act as catalysts for alkali metal intercalation of graphite (Section 1.5.1). They are only stable in solution, however, under argon; under nitrogen or ethylene or in donor solvents, disproportionation occurs giving Co($\underline{O}$) and Co(-I) species.[235]

The reaction of $Li[Co(CO)_4]$ with $[Co_4(CO)_{12}]$ in di-isopropyl ether yields $Li[Co_3(CO)_{10}]$,i-PrO_2.[236] Its structure has been solved by single crystal X-ray methods. It consists of Li^+ cations and $[Co_3(CO)_{10}]^-$ anions; the former are tetrahedrally surrounded by one ether oxygen, r(Li...O)=191.0pm, and by three carbonyl oxygens, r(Li...O)=185.9-204.9pm., of three different anions.[236] Vibrational spectroscopic studies have been undertaken[237] on solutions of $Na[Co(CO)_4]$ dissolved in THF, 1,2-DME, THP and MTHF containing the cryptand C221. The results indicate that whereas the anion site has C_{2v} symmetry in THP and MTHF, it has T_d symmetry in THF and 1,2-DME; furthermore, the complexed Na^+ cation is isolated from the anion only in those cases with T_d symmetry.[237]

Treatment of a THF or CH_3CN solution of $Na[BPh_4]$ with N,N'-ethylenebis(salicylideniminato)oxovanadium(IV), VO(salen), affords $[(VO(salen))_2Na][BPh_4]$. X-ray analysis of this material shows that the Na^+ cation is trapped in a pseudooctahedral coordination cage provided by six oxygen atoms from four different VO(salen) units, r(Na...O)=236.1-243.8pm.[238] Complexation of K^+ cation by the CO(salen) ligand occurs only in the presence of a catalytic amount of Na^+ cation.[238]

The unusual dimeric species $\{Li[ReO(OPr^i)_5].LiCl(THF)_2\}_2$ has been obtained from the reaction of $LiOPr^i$ with $ReOCl_4$ in THF.[239] The structure of this centrosymmetric dimer is illustrated in Figure 15.

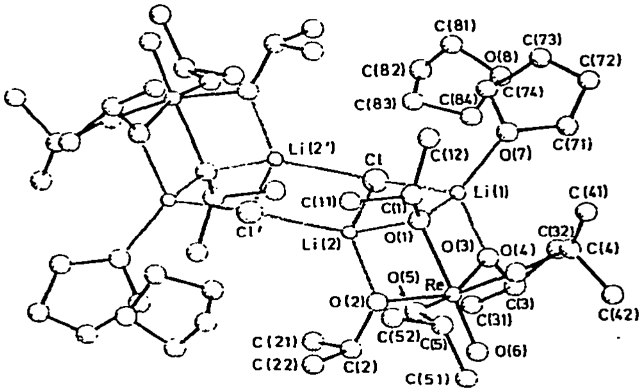


Figure 15. Molecular structure of $\{Li[ReO(OPr^i)_5].LiCl.(THF)_2\}_2$ (reproduced by permission from J. Chem. Soc., Dalton Trans., (1980) 2467).

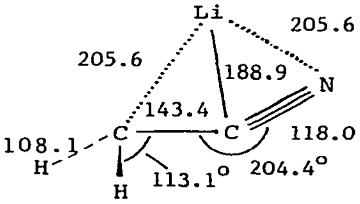
Each half of the dimer contains an octahedral $[ReO(OPr^i)_5]^-$ ion in which three alkoxo-oxygen atoms [O(1) O(2) and O(3)] form bridges with two Li^+ cations to produce $\overline{Re-O-Li-O}$ heterocycles. The Li^+ cations are also involved with a OPr^i group in a $\overline{Li-O-Li-Cl}$ ring. Pertinent interatomic distances vary as follows: r(Li...O)=185.5-199.5, r(Li...Cl)=237.9-242.2pm.[239]

1.6.7 Lithium Derivatives

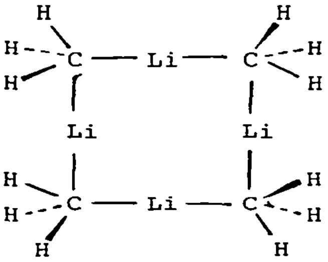
Although there are a vast number of publications dealing with lithium chemistry, those abstracted for this review are relatively few in number, emphasis being placed on the inorganic chemistry of lithium; the organometallic chemistry of lithium, which accounts for the majority of these papers, is ignored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

Molecular orbital calculations have been completed for methyl lithium, CH_3Li,[240-2] and its derivatives CH_2FLi[243] and CH_2CNLi,[244] for ethyl lithium, C_2H_5Li[242] and for the alkyl lithium clusters, $(CH_3Li)_4$ $(2 \leqslant n \leqslant 6)$[241,242] and $(C_2H_5Li)_2$.[242] Basis set and configuration interaction studies of the electronic and geometric structures of CH_3Li indicate that the charge separation along the C-Li bond can be set between 0.45 and 0.75e with a value of ca. 0.55-0.60e being the most reasonable estimate.[240] IMDO-M.O. calculations, however, suggest that the $^7Li-^{13}C$ n.m.r. coupling constant should be very large, consistent with a C-Li bond which is predominantly covalent in character. Complete geometry optimisation of a number of structures for CH_2CNLi, showed the most stable structure to be of a peculiar 'umbrella-shaped' configuration (12), in which the Li atom apparently acts as a bridge to compress the C-C bond;[244] this structure corresponds approximately to that found previously for CH_2FLi[245] and discussed in the 1979 review.[246]

Theoretical calculations[241] for the methyllithium clusters, $(CH_3Li)_n$ $(1 \leqslant n \leqslant 6)$ using the approximate M.O. method, PRDDO, show that there exist stable planar arrangements of Li and C atoms for each oligomer $2 \leqslant n \leqslant 6$ (typically (13)) and that a condensed tetramer and condensed hexamer (14) are also stable. The bonding in these clusters is multicentred involving closed three centre Li-C-Li and closed four centre Li_3C bonds. The ethyllithium compounds are found to be very similar to their methyl counterparts.[242] IMDO M.O.



(12)
distances/pm.; angles/°



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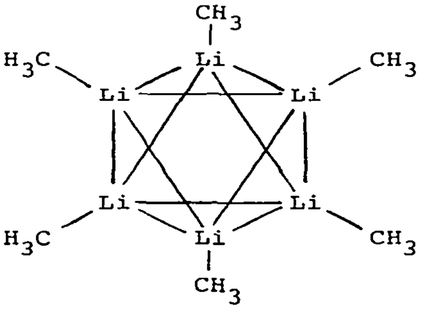

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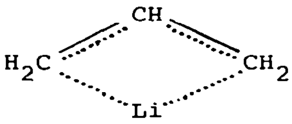


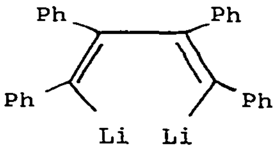
(15)

calculations suggest that a marked decrease in the ^7Li-^{13}C n.m.r. coupling constant should occur on going from CH_3Li to $(CH_3Li)_4$;[241] this decrease is attributed to (i) the decrease in C-Li overlap in going from two-centre bonding and (ii) the large decrease in s-character on the Li atom on oligomerisation.

Temperature dependent $(180 \leq T/K \leq 304)$ ^6Li and ^{13}C n.m.r. studies of propyllithium in cyclopentane show the existence of several $(C_3H_7Li)_n$ oligomers with n=6,8 or 9.[247] The distribution of the oligomers varies with temperature (above 250K, the hexamer is almost exclusively present) and they all undergo fast intra-aggregate C-Li bond exchange.[247]

The THF solution structure of allyllithium has been studied independently by three groups of workers[248-250] using ^1H- and ^{13}C-n.m.r. techniques. The results are somewhat inconclusive; whereas it is concluded from the results of the two ^{13}C-n.m.r. studies[248,249] that the compound has a bridged structure with C_s symmetry (15), the ^1H-n.m.r. spectra support the contention that the allyl-alkali metal compounds (M=Li-Cs) are ionic in solution but exist as intimate ion pairs or clusters.

Von Schleyer et al.[251] have proposed that combined Möbius-Hückel aromaticity stabilises doubly lithium bridged $R_4C_4Li_2$ systems and they suggest that molecules such as 1,4-dilithiated-1,2,3,4-tetraphenylbuta-1,3-diene traditionally written in the all-cis form (16), in reality adopts the doubly lithium bridged configuration (17). Their conclusions are based on a series of full geometry optimisation calculations for a series of $C_4H_4Li_2$ trial structures; the Möbius-Hückel aromatic candidate was found to be remarkably stable relative to all the other structures considered.[251]



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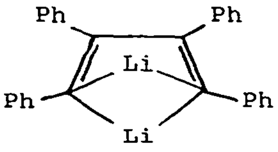
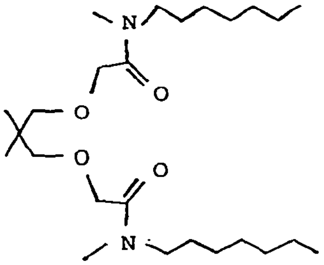


(17)

Complexation of the alkali metals by simple amides,[252] complex polydentate amido ethers (18,19),[253] glycine[254] and urea[255] has been investigated. ^{13}C-n.m.r. techniques indicate that Li^+ binds to the amide carbonyl group both in neat amide solutions and in concentrated aqueous salt solutions.[252] ^{1}H- and ^{7}Li-n.m.r. spectroscopic studies have shown that the tetradentate ligand (18) is a much more effective complexing agent for Li^+ than its bidentate analogue (19).[253] Thermodynamic studies of the interaction of glycine with MCl (M=Li-K,Cs) provide evidence for what may be termed a hydrophilic-hydrophilic interaction between the amino acid and M^+.[254] The geometry of urea-cation bonding in crystalline urea adducts has been surveyed;[255] in complexes with M^+ (M=Li-Cs) the urea coordinates to two cations.



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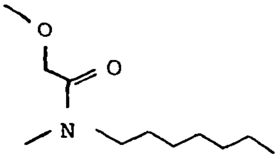
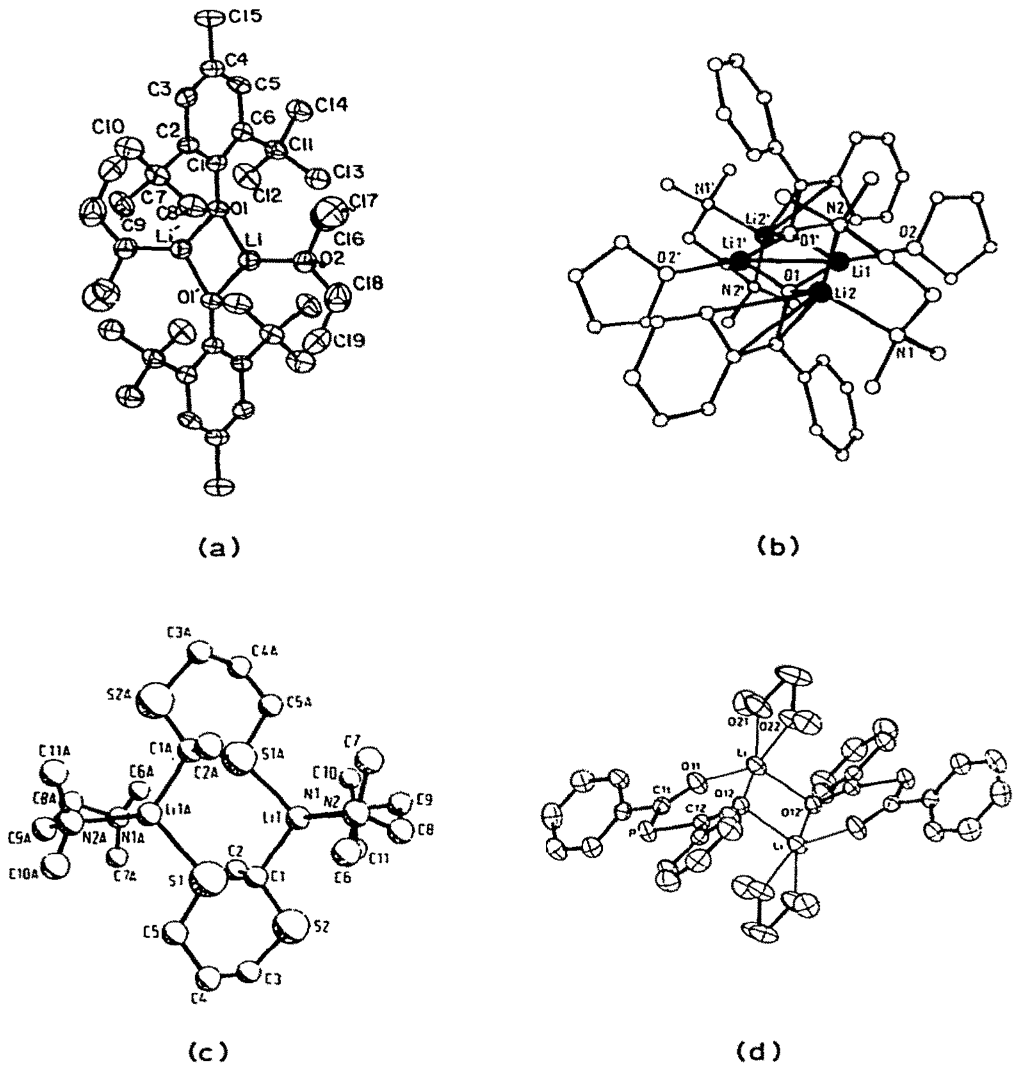


(19)

The remaining papers abstracted for this section[256-64] pertain to single crystal X-ray diffraction studies for a series of diverse and apparently unrelated lithium derivatives. Some features, however, are common to a number of the structures. Thus the lithium 2,6-di-tert-butylphenoxide, Figure 16(a),[256] the complex of benzophenonedilithium with THF and TMEDA, Figure 16(b),[257] the adduct of 2-lithio-2-methyl-1,3-dithiane with TMEDA, Figure 16(c),[258] and the complex of lithium dibenzoylphosphide with 1,2-dimethoxyethane, Figure 16(d),[259] all have dimeric structures. The figures are generally self explanatory; a particularly interesting feature is the fact that the 2,6-di-tert-butylphenoxide contains 3-coordinate Li^+ atoms, presumably because of the bulky phenoxide ligand.[256]

The crystal and molecular structures of $[LiSiMe_3]_6$,[260] $Li_2Hg(SiMe_3)_4$[261] and $Li_2Hg(SiMe_2Ph)_4$[261] have been reported by Oliver et al. The molecular structure of $[LiSiMe_3]_6$[260] consists of discrete centrosymmetric hexameric units with a core of Li atoms surrounded by $SiMe_3$ moieties. The geometry of the lithium core can be described either as a six-membered ring in a highly folded



(a)

(b)

(c)

(d)

Figure 16. Dimeric structures of (a) lithium 2,6-di-tert-butylphenoxide, (b) the complex of benzophenonedilithium with THF and TMEDA, (c) the adduct of 2-lithio-2-methyl-1,3-dithiane with TMEDA and (d) the complex of lithium dibenzoylphosphide with 1,2-dimethoxyethane (reproduced by permission from (a) J. Amer. Chem. Soc., 102(1980)2086, (b) Angew. Chem. Int. Ed. Engl., 19(1980)817, (c) Angew. Chem. Int. Ed. Engl., 19(1980)53, and (d) Angew. Chem. Int. Ed. Engl., 19(1980)741).

chair conformation with an acute seat-to-back angle or as a distorted octahedron severely compressed along a 3-fold axis so as to form a shortened trigonal antiprism (cf. the structure of the Li_6 core in the structure of $[LiN{=}Ct\text{-}Bu_2]_6$ discussed in the 1979 review).[262] The six triangular faces of the antiprism each have one long, r(Li...Li)=325pm., and two short, r(Li...Li)=272pm. distances. The $SiMe_3$ moieties lie above these faces and are more closely associated with the two Li atoms related by the longer Li...Li distance, r(Li...Si)=265,277pm. The bonding is described in terms of four-centered electron deficient Si-Li bonds with minimal Li-Li or Li-H interactions.[260] The crystal structure of $Li_2Hg(SiMe_3)_4$ consists of tetrahedral $Hg(SiMe_3)_4$ moieties with the Li atoms embedded in two of the faces.[261] The Li atoms serve as bridges between the $Hg(SiMe_3)_4$ moieties which join along an edge of the tetrahedron giving a zigzag chain. The environment around each Li atom consists of three carbon atoms, r(Li...C)=232-263pm., two silicon atoms, r(Li...Si)=269,287pm., and one mercury atom, r(Li...Hg)=257pm.[261] The structure of $Li_2Hg(SiMe_2Ph)_4$ consists of discrete formula units with the Hg on a twofold axis of symmetry and the Li^+ atoms enclosed in a cage of five carbon atoms, r(Li...C)=242-261pm., three silicon atoms, r(Li...Si)=290-304pm., and one mercury atom, r(Li...Hg)=258pm. The Li-C, -Si,-Hg and -H interactions are considered and their implications with regard to the bonding in these systems discussed.[261] Oliver et al.[263] have also reported that $[LiSiMe_3]_6$ reacts with TMEDA to yield $[LiSiMe_3]_2$,3TMEDA; the reactions of the two reagents with simple organic substrates have been examined.[263]

Saenger et al.[264] have described the molecular structure of $(\alpha\text{-cyclodextrin})_2,LiI_3,I_2,8H_2O$. The structure is complex, the Li^+ cation serving to hold the cyclodextrin molecules together by interaction with surrounding hydroxyl groups.[264]

1.6.8 Sodium Derivatives

The alkali metals Na, K, Rb and Cs dissolve in 12C4 to give blue solutions containing the metal anions, M^-, equation (17);[265] the

$$2M(s) \rightleftharpoons M^+(solv) + M^-(solv) \qquad ...(17)$$

stability of the solutions decreases with increasing size of the alkali metal. Addition of LiCl to a sodium metal solution resulted in a marked increase in Na^- concentration; this is consistent with the 12C4 complexing Li^+, precipitating NaCl and hence shifting equilibrium (17) to the right hand side. The solution reacts readily with H_2O and with NH_3, equations (18) and (19), with rapid bleaching of the solution. The solution also reacted with Ph_3CH

$$Na^+Na^- + 2H_2O \longrightarrow H_2 + 2NaOH \qquad \text{...(18)}$$

$$Na^+Na^- + 2NH_3 \longrightarrow H_2 + 2NaNH_2 \qquad \text{...(19)}$$

to give a red solution containing Ph_3C^-, equation (20).[265]

$$Na^+Na^- + 2Ph_3CH \longrightarrow 2Ph_3C^- + 2Na^+ + H_2 \qquad \text{...(20)}$$

E.s.r. studies have shown that photolysis of rapidly quenched alkali metal hexamethylphosphoramide solutions produces high concentrations of paramagnetic solvated alkali metal atoms.[266] It is argued that the precursor metal anion M^- species in these vitreous solids is quite noticeably solvated and is best viewed as a distinct centrosymmetric species, the paired valence electrons residing on an expanded outer s-orbital on the metal.[266]

Solvent extraction of Na^+ from 1 mol dm^{-3} sodium salt solutions with trioctylphosphine oxide (TOPO) in hexane improves with anion as follows:[267]

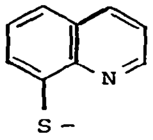
$$ClO_4^- > SCN^- > I^- > NO_3^-$$

This gradation is explained in terms of the hydrophilic and hydrophobic tendencies of the anions. The extracted species was always $[Na(TOPO)_3]^+X^-$. Similar experiments for a series of alkali metal perchlorates indicate that solvent extraction improves as follows:[268]

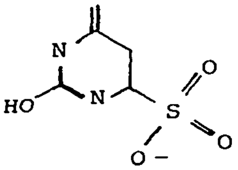
$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$

presumably because of the more efficacious solvation of the smaller cations by TOPO. The extracted species was either $[M(TOPO)_3]^+ClO_4^-$ (M=Li-Cs) or $[M(TOPO)_4]^+ClO_4^-$ (M=Rb,Cs).[268]

Structural studies have been undertaken on sodium quinolate-8-thiolate dihydrate,[269] sodium 5,6-dihydrouracil-6-sulphonate monohydrate,[270] and dehydrated zeolite A.[271] The geometry of the



quinoline-8-thiolate



5,6-dihydrouracil-6-sulphonate

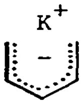
Na$^+$ coordination sphere in the two salts is distorted octahedral. In the case of the thiolate, the Na$^+$ cations are surrounded by the sulphur, r(Na...S)=280.9pm and nitrogen, r(Na...N)=249.0, atoms of a bidentate thiol residue and four water oxygen atoms, r(Na...O)= 238.6-242.1pm.[269] For the sulphonate, however, the Na$^+$ cations are coordinated by an unsymmetrical bidentate sulphonate group, r(Na...O)=237.8, 244.8pm, a monodentate sulphonate group, r(Na...O)= 239.1, a ketonic oxygen r(Na...O)=241.8pm, and a hydroxyl oxygen, r(Na...O)=239.4pm, from four separate uracil residues; the sixth position is occupied by a water oxygen atom, r(Na...O)=242.3pm.[270]

Pluth and Smith[271] have extended their accurate single crystal X-ray diffraction study of zeolite structures to include dehydrated zeolite A. In contrast to the conclusions of Seff et al.[272] and in support of their conclusions vis-a-vis dehydrated K$^+$-exchanged zeolite A[273] (reported in the 1979 review)[274] they found no evidence for near zero coordination of sodium cations. Instead Na(1), which occur near the centre of most 6-rings, has three nearest neighbours at 232pm and three more at 290pm; Na(2), which is off-centre for most 8-rings, has one sided coordination to O(2) at 238pm and two O(1) at 256 and 267pm; Na(3), which projects into the large cavity opposite a 4-ring, also has one sided coordination to two O(3) at 259pm and two O(1) at 261pm; because of low fractional occupancy of Na(3), the latter two distances are subject to an unknown error which should decrease the observed values.[271]

1.6.9 Potassium, Rubidium and Caesium Derivatives

The crystal and molecular structures of the potassium salt of dipicrylamine, $K^+[C_{12}H_4N_7O_{12}]^-$,[275] the acetone·solvate of the potassium salt of p-chloranil, $K^+[C_6Cl_4O_2]^-$,$(CH_3)_2CO$,[276] and of the 1:1 adduct of KF with succinic acid, $KF(CH_2COOH)_2$[277] have been determined. The K^+ cations of the dipicrylamine derivative are 8-coordinate in a distorted square antiprismatic arrangement; they are linked to four different dipicrylamine moieties, r(K...O)=276-326pm.[275] In the p-chloranil derivative the K^+ cations lie close to the centre of a triangle of oxygen atoms provided by two anions and one solvate molecule r(K...O)=268-285pm; this coordination is quite unusual and differs markedly from that in the solvent-free salt.[276] The feature of major interest in the structure of the 1:1 KF:succinic acid adduct is an unexpectedly short O...H...F hydrogen bond, r(O...F)=244.0pm.[277]

^1H n.m.r. studies and trimethylsilylation reactions on pentadienylpotassium and its deuterated derivatives in THF and in the solid state indicate that the structure of the anion is U-shaped in solution (20), but W-shaped in the solid phase (21).[278]



(20)

(21)

It is suggested that the solid state geometry is controlled by the packing modes in the crystal lattice although X-ray analysis of single crystals of the salt give insufficient data to warrant a definite conclusion.[278]

Finally, the Raman spectra of the crystalline solvate $K_2[COT]$,nTHF (COT = cyclooctatetraene) and of its solution in THF have been recorded and assigned.[279] A rather strong line has been assigned to the symmetric stretching vibrations of the K^+ cations relative to the 8-membered ring.[279]

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