Coordination Chemistry Reviews, 56 (1984) 1–77
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

Chapter 1

ELEMENTS OF GROUP 1

Peter Hubberstey

0010-8545/84/$23.10

1.1 INTRODUCTION

As for the 1981 review,[1] the papers abstracted for Chapters 1 and 2 of the present review have been restricted to those containing some facet of alkali or alkaline earth metal chemistry in which the role of the metal is unique. Consequently, the format of these two Chapters has been devised so that the chemistry of both sets of elements is considered collectively in sections which reflect topics of current interest and importance. For certain subjects, (e.g., molten salts, polyether and cryptate complexes) the chemistry of the two groups of metals is closely interwoven; in these cases, the data abstracted are discussed once only in the appropriate section of this Chapter.

The organometallic chemistry of lithium[2] and that of the heavier alkali metals (Na-Cs)[3] has been the subject of separate annual surveys for the year 1980; structural and spectroscopic studies, theoretical calculations, synthetic aspects and chemical properties are discussed in detail.

The feasibility of obtaining high resolution solid state ^{23}Na F.T. *n.m.r.* spectra of sodium salts, using magic angle sample spinning techniques, has been demonstrated;[4] the necessity of operating at the highest field strengths possible ($\geq$12T) with ultra high speed variable angle spinner assemblies to obtain suitably resolved spectra is emphasised.

1.2 THE ELEMENTS

The application of the lighter alkali metals (Li, Na) in energy production and storage continues to stimulate interest in their chemistry. Chemical aspects of the role of liquid lithium as a candidate for use as coolant/tritium breeder in the thermonuclear reactor were considered at an international conference on 'Material Behaviour and Physical Chemistry in Liquid Metal Systems' (March 1981, Karlsruhe FRG). Subjects covered corrosion and interstitial element transfer, materials behaviour and compatibility, impurity analysis and control together with basic physical inorganic chemistry. Similar topics, but on this occasion restricted to liquid lithium chemistry, were discussed at the second topical meeting on 'Fusion Reactor Materials' (August 1981, Seattle, Wa., U.S.A.). Since the majority of the papers published in the proceedings of these two conferences[5,6] are technological in origin they are of but peripheral interest to the average inorganic chemist and hence will not be considered in detail. Those few papers which are of more general interest have been abstracted, however, and are reviewed, as appropriate, in the following subsections.

The use of lithium and sodium based electrodes in battery systems has led to a large number of papers, primarily in the Journal of the Electrochemical Society, in which various aspects of the chemistry of these metals and of their intermetallic compounds are described. Although most effort has been concentrated on low temperature lithium-sulphur dioxide and lithium-thionyl chloride cells, some work on moderate temperature lithium or sodium-transition metal oxide or chalcogenide cells has been reported. Once again the majority of papers published in this field are technologically oriented and hence are of only limited interest to the average inorganic chemist. Although these papers are not considered in detail, and hence the specialist reader is referred to the appropriate volume of the Journal of the Electrochemical Society[7], a small number of papers of more general interest have been abstracted and are included, as appropriate, in the following subsections.

1.2.1 General Properties

The results of a thermodynamic study[8] of the combustion of sodium at constant volume indicate that Na_2O_2 is formed preferentially at low $Na:O_2$ ratios and low temperatures. As the $Na:O_2$ ratio and/or temperature is increased, increasing amounts of Na_2O are formed until at sufficiently high ratios and/or temperatures Na_2O is the exclusive product.

Kinetic investigations ($724 \leqslant T/K \leqslant 844$) of the third order recombination of atomic sodium[9] and of atomic potassium[10] with molecular oxygen (equation 1) have been undertaken using time

$$X + O_2 + M \rightarrow XO_2 + M \qquad X = Na;\ K;\ \ M = He, Ne, CO_2 \ \ldots(1)$$

resolved atomic resonance absorption spectroscopy. The derived rate constants, although of similar magnitude to those for other recombinations of this type, were approximately three orders of magnitude greater than those reported previously from flame measurements. In the light of these results, early experimental data on alkali metals in premixed oxygen-rich $H_2/O_2/N_2$ flames have been re-examined.[11,12] It is suggested that the flame data may be satisfactorily interpreted in terms of free atoms and hydroxides alone (equation 2), without recourse to postulating the presence of

$$X + OH + M \rightarrow XOH + M \quad X = Na,K; \quad M = H_2O,\ H_2 \text{ or } N_2 \quad \ldots(2)$$

superoxides. Both the flame results and those of the recent independent experiments on superoxide formation are consistent with bond energies for $Na-O_2$ and $K-O_2$ of 170±25 and 170±30 $kJ.mol^{-1}$, respectively.[11]

The kinetics of the reaction of hydrogen gas with liquid caesium (to form CsH) have been determined ($373 \leqslant T/K \leqslant 576$).[13] The reaction obeys first order kinetics with an apparent activation energy of 42.4 $kJ.mol^{-1}$. The results are compared with data for the lighter alkali metals. The reaction rates, which decrease in the order

$$Li > Cs > K > Na$$

are tentatively rationalised in terms of the differing strengths of the M-H (M = Li, Na, K, Cs) bonds.[13]

Lithium dithionite, $Li_2S_2O_4$, has been reported as the discharge product of the $Li-SO_2$ battery by three independent groups.[14-16] Auger electron spectroscopy studies[14] of ultra-pure lithium surfaces subjected to solution phase (CH_3CN; 0.5 $mol.dm^{-3}$) and gas phase SO_2 have shown that $Li_2S_2O_4$ is formed (equation 3) in the solution reactions and for high doses of gas phase SO_2 but that Li_2O/Li_2S mixtures are formed (equation 4) for low doses of gas phase SO_2. The $Li_2S_2O_4$ has been characterised by i.r. and X-ray

$$2Li + 2SO_2 \rightarrow Li_2S_2O_4 \quad \ldots(3)$$

$$6Li + SO_2 \rightarrow 2Li_2O + Li_2S \quad \ldots(4)$$

photoelectron spectroscopy and X-ray pwder diffraction analysis;[15] differential scanning calorimetry studies of $Li_2S_2O_4$ and of the reaction between lithium and $Li_2S_2O_4$ have also been undertaken.[16]

The generation of gases in $Li-SOCl_2$ batteries has been investigated.[17,18] The principal gases evolved under normal working conditions are hydrogen (from reaction of lithium metal with protic species in the liquid electrolyte), sulphur dioxide (product of the electrochemical discharge) and nitrogen (present in lithium as Li_3N and released on discharge).[17] During reversal of the cells, the formation of Cl_2O has been demonstrated;[18] it is thought to occur in the process:

$$SOCl_2 - e \rightarrow SOCl^+ + \frac{1}{2}Cl_2$$

$$SO_2 - 2e \rightarrow SO^{2+} + O \quad \text{or} \quad SO_2 + Cl_2 \rightarrow SO^{2+} + 2Cl^- + O$$

$$Cl_2 + O \rightarrow Cl_2O$$

It is suggested that its presence may account for the reported explosions of these cells.[18]

X-ray and neutron diffraction, magnetic and thermochemical data have been used by Sienko et al.[19] to re-evaluate the structural chemistry of the expanded metal compounds $Li(NH_3)_4$ and $Li(ND_3)_4$. Whereas $Li(NH_3)_4$ exists in three b.c.c. modifications, $Li(ND_3)_4$ only adopts two, no evidence being found for the highest temperature modification; the data are summarised in Table 1.

Table 1. Structural data for $Li(NH_3)_4$ and $Li(ND_3)_4$.[19]

Phase	a/pm $Li(NH_3)_4$	a/pm $Li(ND_3)_4$	Comments
I ($82 < T/K < 89$)	1498.0(T/K=85)	-	bcc; probably not I$\bar{4}$3d
II ($25 < T/K < 82$)	1493.0(T/K=60)	1493.0(T/K=60)	bcc; probably I$\bar{4}$3d
III ($T/K < 25$)	No data	1480.0(T/K=20)	bcc; superstructure with period 2a

1.2.2 The Alkali Metals as Solvent Media

The solution chemistry of the liquid alkali metals, particularly lithium and sodium, has been extensively studied during the past year. Two critical reviews of solubility data for non-metals in

Table 2. Solubility data for solutes in liquid alkali metals; coefficients of the $\ln x_M = A - B(T/K)^{-1}$ expressions.

Solvent	Solute	A	B	Temperature range (K)	ref.
Lithium	Hydrogen	3.507	5314	523-775	20
Lithium	Deuterium	3.101	5082	472-771	20
Lithium	Carbon	-1.100	5750	477-908	20
Lithium	Silicon	5.548	6775	500-700	20
Lithium	Germanium	5.459	6630	530-715	20
Lithium	Tin	4.742	6794	579-745	23
Lithium	Lead	5.717	6722	513-670	23
Lithium	Nitrogen	2.976	4832	468-723	20
Lithium	Oxygen	1.428	6659	530-715	20
Sodium	Hydrogen	4.375	7118	*	21
Sodium	Carbon	2.99	12991	*	21
Sodium	Oxygen	0.960	5631	*	21

* Not quoted.

liquid lithium have been published independently by Hubberstey et al.[20] and by Casteels et al.[21] The solutes considered, LiH, Li_2C_2, Li_3N, Li_2O, are those of significance to the corrosion chemistry of liquid lithium. With the exception of the Li_2C_2 data, the recommended solubilities are very similar; the discrepancy in the carbon data is due to the omission by Casteels et al.[21] of recently published high quality results reported in the 1979 Review.[22] The solubilities recommended by Hubberstey et al.[20] are summarised in Table 2. Novel solubility data for $Li_{22}Sn_5$ and $Li_{22}Pb_5$ in liquid lithium have been published[23] and compared with corresponding results for Li_2C_2, $Li_{22}Si_5$ and $Li_{22}Ge_5$; they are included in Table 2. The sensitivity of the solubilities of the Group IV elements to the overall phase relationships is noted, that for carbon being much smaller than those for the heavier elements, which vary according to the trend:

$Sn \ll Si < Ge < Pb$

The anomalously low solubility of tin is correlated with the correspondingly high melting point and exothermic enthalpy of formation of $Li_{22}Sn_5$.[23]

Casteels et al[21] have also collated solubility data for NaH, Na_2C_2 and Na_2O in liquid sodium; their recommended data are included in Table 2. They have used their data for both solvents to calculate activity-composition relationships for the various solutes. These relationships are of particular value for interpretation of activity data derived from the electrochemical and thermodynamic meters developed recently for monitoring NaH, Na_2C_2 and Na_2O in liquid sodium, the application of which has been reviewed by Hobdell and Smith.[24]

Thermodynamic quantities, such as partial molar enthalpies and entropies of solution, have been deduced from the solubility data by Casteels et al;[21] they indicate a similar solvation pattern for these non-metals in both solvents. Hubberstey and Dadd[25] have also shown that an empirical correlation exists between solvation enthalpies of the neutral gaseous solute species and the corresponding resistivity coefficients for both liquid lithium and liquid sodium solutions; limited results for liquid potassium solutions suggest that they follow a similar pattern.[25]

Comparative studies of the solution chemistry of liquid lithium and sodium have shown marked differences in the behaviour of certain solutes.[26,27] Surface studies[26] of stainless steels and refractory transition metals after immersion in the two solvents at 873K have shown that whereas the principal corrosive species in lithium is Li_3N, that in sodium is Na_2O; the corrosion products are Li_9CrN_5 and $NaCrO_2$, respectively. A series of gas (nitrogen) absorption, X-ray diffraction and electrical resistivity studies[27] of carbon chemistry in these two solvents indicate that whereas Li_2C_2 reacts with Li_3N in liquid lithium at 750K to form Li_2NCN, in liquid sodium at 973K the corresponding product is NaCN. In sodium-barium solutions at 673K, however, the reaction product is BaNCN. The formation of the different products is rationalised by thermochemical arguments.[27]

Interaction between Li_3N and $Li_{22}Si_5$ when dissolved in liquid lithium at 750K leads to the insoluble product, Li_5SiN_3.[28] The kinetics of the various dissolution and precipitation processes are such that addition of gaseous nitrogen to $Li\text{-}Li_{22}Si_5$ solutions leads to a homogeneous solution reaction, whereas addition of solid silicon to $Li\text{-}Li_3N$ solutions leads to a heterogeneous reaction mechanism at the solid-liquid interface. In an independent investigation,[29] the compatibility of Si_3N_4 to liquid lithium at 873K has been determined; the product of the reaction was thought to be Li_2SiN_2. The difference in products may be due to the reaction conditions; whereas in the former experiment[28] lithium is in vast excess ($x_{Li} \geqslant 0.97$) and the reactions occur in solution, in the latter experiment[29] near equimolar quantities were used, the reactions occurring at the liquid metal-ceramic interface. Similar compatibility studies involving MgO, BN and ZrO_2 (CaO or Y_2O_3 stabilised) and liquid lithium at 873K or 1123K have been undertaken.[29] Although there was no evidence for reaction in the Li-MgO system, ternary products such as Li_3BN_2 and Li_2ZrO_3 were thought to form in the Li-BN and Li-ZrO_2 systems. Thermodynamic analysis ($500 \leqslant T/K \leqslant 1000$) of the systems Li-Be-O-C, Li-Be-O-N and Li-Be-C-N have shown that, of the various compounds considered BeO, Be_2C, Be_3N_2, $BeCO_3$, $Be(NO_3)_2$ and $Li_2Be_2O_3$), only Be_2N_2 is stable in liquid lithium.[30]

Kinetic studies[31] of the removal of hydrogen (tritium) from liquid lithium at 573K have shown that the rate determining step is mass transfer in the yttrium solid phase. Physical and chemical characteristics of different yttrium samples were measured to identify those properties which have the greatest effect on hydrogen recovery rate.[31]

Solute interaction investigations in liquid sodium have included the Na-C-H,[32] Na-C-O,[33,34] and Na-C-N[33] systems. High CH_4 partial pressures have been measured over liquid sodium containing NaH after addition of Na_2C_2(723K), Na_2CO_3(798K) or NaCN(863K);[32] it is suggested that the CH_4 arises from monatomic dissolved carbon atoms formed by the dissociation of the metastable C_2^{2-} anion. Theoretically based thermodynamic analyses of the Na-C-O system ($700 \leqslant T/K \leqslant 1000$) have been effected by two independent groups.[33,34] Migge[33] has shown that Na_2CO_3 can only co-exist with liquid sodium at temperatures above 923K (Figure 1a); at lower temperatures Na_2O and carbon are formed (Figure 1b). Similar conclusions were derived by Johnson et al[34] who have presented an amendment to an earlier paper on this system[35] which was in error because of the omission of O_2 as a gas phase species. Migge[33] has also considered the addition of aluminium to this system; depending on the carbon and oxygen activities, sodium-aluminium solutions are in equilibrium with either Al_4C_3 or $NaAlO_2$ (Figure 1c). In a theoretical treatment ($800 \leqslant T/K \leqslant 1000$) of thermochemistry in the Na-C-N system Migge[33] has predicted that, depending on the carbon and nitrogen activities liquid sodium can be in equilibrium with carbon, NaCN, Na_2NCN or Na_3N (Figure 1d).

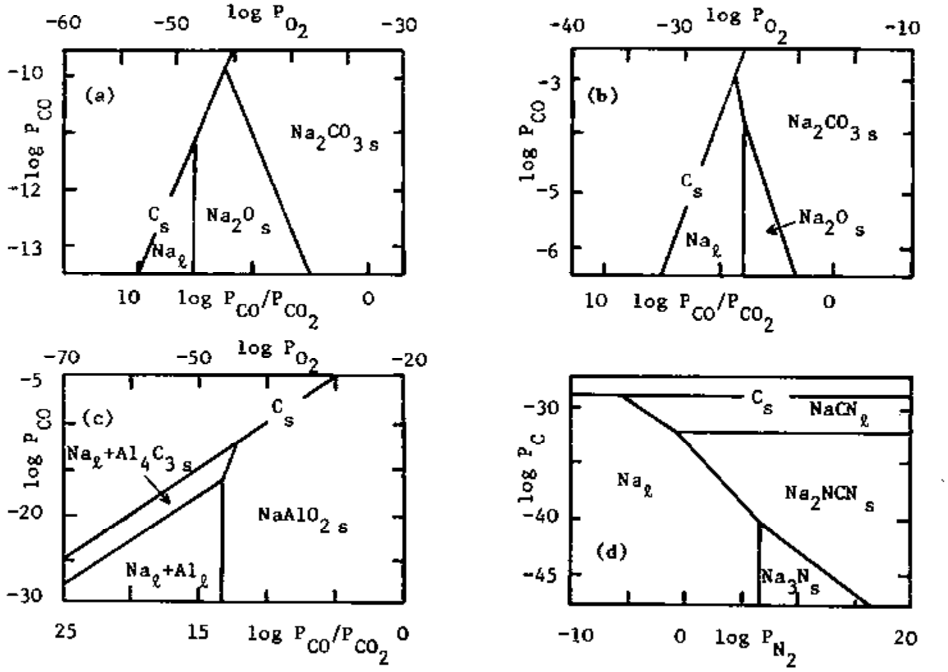


Figure 1. Metallurgical phase diagrams for the Na-C-O system at 700K(a) and 1100K(b), for the Na-Al-C-O system at 1000K(c) and for the Na-C-N system at 1000K(d).

The NaH-Na_2O-NaOH equilibrium in liquid sodium is of continuing interest and significance; four papers[36-39] have been presented on this topic during the period of the Report. Ullmann[36] has undertaken a critical survey of the reactions of hydrogen and oxygen with liquid sodium. He has also considered the chemical equilibrium between hydride, oxide and hydroxide in liquid sodium (equation 5) as have Smith and Whittingham.[37] The two sets of

$$\mathrm{H(soln.)} + \mathrm{O(soln.)} \rightleftharpoons \mathrm{OH(soln.)} \qquad \ldots(5)$$

results are in excellent agreement. The temperature dependence of the equilibrium constant, K_{eq} (equation 6) is best represented by Ullmann's relationship (equation 7) for temperatures between 623

$K_{eq} = [OH]/[O][H]$ ...(6)

$\log(K_{eq}/at.fr^{-1}) = 1.53 + 1340(T/K)^{-1}$ ...(7)

and 773K. The magnitude of K_{eq} indicates that 5-15%(0.5-1.4%) of the oxygen in solution is present as OH at a hydrogen concentration of 1 wppm (0.1 wppm). Consequently hydroxide formation is unlikely to be of significance in sodium systems unless there are high hydrogen and oxygen impurity concentrations. The temperature dependence of the free energy of formation of OH in sodium (equation 8), calculated from the equilibrium constant data agrees

$\Delta G^{o}_{OH}/J.mole^{-1} = -25660 - 29.30(T/K)$ ...(8)

well with that (-25.7 kJ.mol^{-1}) derived from a Born-Haber cycle.

Experimental results for the decomposition of NaOH in liquid sodium ($703<T/K<823$) have been used[38] to construct a series of isotherms showing the change which occurs in the hydrogen equilibrium pressure over Na-NaOH solutions of differing initial OH content as the reaction proceeds to completion (i.e. as hydrogen is successively removed from the system). The curves were interpreted within the framework of scheme 1.

$Na(l) + NaOH(s) \rightarrow Na(l;satd. with NaOH) + NaOH(l;satd. with Na) \rightarrow$

$\rightarrow Na(l;satd. with NaOH) + NaOH(l;satd. with Na) + Na_2O(s)$

$\rightarrow Na(l;satd. with NaOH) + Na_2O(s)$

Scheme 1.

The hydrogen equilibrium pressure-temperature diagram for the liquid Na-H-O system has been constructed[39] using published data supplemented by experimental measurements of hydrogen equilibrium pressures over condensed phases ($Na_2O(s)$, NaH(s), NaOH(s,l)) which occur in this system. The four condensed phases Na(l), NaOH(l), $Na_2O(s)$ and NaH(s) constitute an invariant equilibrium reaction which occurs at 685K and 24 kPa hydrogen pressure. Potential applications of the diagram, which is a simplification of the composition-temperature phase diagram for the Na-H-O system, are outlined.[39]

The solubility of manganese in liquid sodium has been determined by two independent groups using atomic absorption spectroscopic methods.[40,41] The results are of a similar order; those quoted by Stanaway and Thompson[40] for sodium containing 15-20 wppm oxygen are given by equation (9) whereas those quoted by Mathews et al[41] for 'low oxygen' sodium (no oxygen analysis data are quoted; the metal was, however, pregettered using magnesium) are given by equation (10). Stanaway and Thompson[40] also reported preliminary

$$\log(S/\text{wppm Mn}) = 2.325 - 2017(T/K)^{-1} \quad 623 \leq T/K \leq 973 \text{ corr. coefft.} = 0.96 \qquad \ldots(9)$$

$$\log(S/\text{wppm Mn}) = 3.64 - 2601(T/K)^{-1} \quad 549 \leq T/K \leq 811 \text{ corr. coefft.} = 0.83 \qquad \ldots(10)$$

data for cobalt in liquid sodium ($673 \leq T/K \leq 973$); unfortunately no firm conclusions can be derived since the solubility values differ with the analytical technique (radiochemistry and atomic absorption spectroscopy). Similarly, Mathews et al[41] also reported preliminary data for iron in liquid sodium ($718 \leq T/K \leq 846$); the data are quite scattered and do not exhibit any pattern. For all three solutes, the solubility values were found to increase with the oxygen content of the sodium, presumably because of the formation of more soluble oxygenated species.

1.2.3 Metallic Solutions

The intriguing question of the existence of chemical short range order in metallic solutions has continued to arouse interest.[42-55] Van der Lugt et al[42] have collated physicochemical data (electrical resistivity, thermopower, Knight shift, density and neutron diffraction) for the series of liquid metallic solutions:

Li-Na; Li-Mg; Li-Cd; Li-In; Li-Pb; Li-Sn

The properties of these solutions change systematically in the order given above, as (it is argued) the extent of chemical short range order increases. Thus whereas the Li-Na system exhibits a large miscibility gap accompanied by strong critical fluctuations at the consolute point, the Li-Sn system exhibits a strong tendency to compound formation at $Li_{80}Sn_{20}$ as electron transfer from Li to Sn occurs giving rise to strong Coulombic interactions.[42]

During 1981, chemical short range order has been experimentally investigated in the Li-Ge,[43] Li-Sn,[44] Li-Pb,[45] Na-Cs,[46,47] Na-Hg,[48,49] Na-In,[50] Na-Sn,[44,50,51] Na-Pb,[44] Na-Bi[46] and Cs-Tl[52] systems using ^{7}Li-Knight shift,[43] electrical resistivity,[44,50] neutron diffraction,[45] e.m.f.,[46-48,50,51] magnetic susceptibility,[49] and reflectance[52] methods. Evidence is provided for strong chemical interactions in the Li-Ge,[43] Li-Sn[44] and Li-Pb[45] systems. In all three cases, the effect is centered on the composition $Li_{80}M_{20}$ (M = Ge-Pb) corresponding to the intermetallic compound $Li_{22}M_{5}$ (M = Ge-Pb). Similarly the existence of strong chemical interactions has been inferred from experimental data available for the Na-Sn,[44,51] Na-Pb[44] and Na-Bi[46] systems. The effect is centered on the compositions $Na_{80}M_{20}$ (M = Sn,Pb) and $Na_{75}Bi_{25}$ corresponding to the intermetallic compounds $Na_{15}M_{4}$ (M = Sn,Pb) and $Na_{3}Bi$. The Na-Sn system is unusual in that two independent studies of the system also provide some evidence, based on electrical resistivity and e.m.f. data, for a second effect centered on the composition $Na_{57}Sn_{43}$ which corresponds to the intermetallic compound $Na_{4}Sn_{3}$. A theory, based on the hard sphere model, for liquid binary solutions in which two types of compound are formed has been developed and applied to the Na-Sn system.[53] The theoretical results are in good agreement with the experimental data predicting the formation of compounds at approximately $Na_{75}Sn_{25}$ and $Na_{50}Sn_{50}$. Not all authors accept the necessity for the introduction of the concept of chemical short range order. The contrary viewpoint is put forward by Cusack et al[50] who claim that the results of their combined (simultaneous) electrical resistivity and e.m.f. studies on the Na-Sn and Na-In systems are such that the solutions are nothing other than metallic; they believe that the nearly free electron theory can account for all the observations.[50]

Reflectance data for the Cs-Tl system[52] are interpreted in terms of charge transfer from Cs to Tl which gives rise to a highly ordered non-metallic structure at $Cs_{50}Tl_{50}$; the system is thus analogous to the classical Cs-Au system which exhibits chemical short range order at $Cs_{50}Au_{50}$.

Although compound formation is not invoked to interpret the data for the liquid Na-Hg solutions[48,49] it is concluded that a kind of substitutional order occurs in the Hg-rich liquid (upto $Na_{33}Hg_{67}$ - the composition of the intermetallic compound $NaHg_2$) while relatively disordered states are observed for the Na-rich liquid.

Comprehensive e.m.f. studies of Na-Cs solutions ($0.05 \leq x_{Na} \leq 0.92$; $378 \leq T/K \leq 443$; $10^5 \leq P/Pa \leq 3 \times 10^7$) have been undertaken by Cusack et al;[47] no evidence for the existence of Na_2Cs clusters in the liquid was obtained. Much more limited studies on this system ($0.2 \leq x_{Na} \leq 0.3$; liquidus $\leq T/K \leq 423$) by Thompson et al[46] indicate that its behaviour is close to ideality throughout the range studied.

Theoretical studies of the M-Au (M = Li-Cs),[54] M-Sb (M = Na, Cs),[55] and Li-Pb[55] systems have also been undertaken using a model which incorporates chemical short range order and charge transfer in a self-consistent way. Calculations for the M-Au systems[54] indicate that a metal-non-metal transition (due to chemical short range ordering) will occur at compositions close to $M_{50}Au_{50}$ for M-Au (M = Rb,Cs) solutions but not for M-Au (M = Li-K) solutions in agreement with the experimental observations.[54] The M-Sb (M = Na,Cs) solutions[55] have a large degree of local chemical order and a charge transfer of approximately 2.5 electrons/atom close to $M_{75}Sb_{25}$ where the metal - non-metal transitions occur. At other compositions the solutions are random and the charge transfer drops to approximately 0.25 electrons/atom. For the Li-Pb system,[55] an intermediate degree of local order and charge transfer of approximately 1.5 electrons/atom are consistent with the experimental results close to $Li_{80}Pb_{20}$.

1.2.4 Intermetallic Compounds

The structural properties of a wide range of alkali metal-containing intermetallic compounds have been elucidated during the period of the Report;[56-61] those materials which have been subjected to single crystal X-ray diffraction studies[57-61] are listed in Table 3 together with pertinent crystallographic data.

A theoretical MO analysis[56] of $Li_{12}Si_7$ has led to the suggested formulation: $Li_{24}Si_{14} \equiv (Li^+)_9(Li_3{}^+)_5(Si_4{}^{2-})(Si_5{}^{6-})_2$. The planar Si_4 star-shaped clusters and the planar Si_5 rings are formulated as $Si_4{}^{2-}$ and $Si_5{}^{6-}$ by analogy with the π-isoelectronic carbonate $CO_3{}^{2-}$ and cyclopentadienide $C_5{}^{6-}$ ions, respectively.

Schafer et al[58,59] and Ling and Belin[60] have independently

Table 3. Crystallographic parameters for a number of intermetallic compounds.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	Ref.
Li_7Ge_{12}	orthorhombic	$Pmn2_1$	1154.1	807.3	1535.9	57
$Na_{22}Ga_{39}$	orthorhombic	Pnma	1558.5	1494.8	2163.2	60
Na_7Ga_{13}-I	rhombohedral	R3m	1496.5	-	3893	58
Na_7Ga_{13}-II	orthorhombic	Pnma	1562.5	1497.9	2167.8	59
$NaGa_4$	tetragonal	I4/mmm	423.0	-	1127.2	58
Cs_2In_3	orthorhombic	-	680.5	696.5	1640.0	61
$CsIn_4$	tetragonal	-	708.9	-	669.3	61

reported the existence of a second Na-Ga intermetallic compound of composition close to $Na_{36}Ga_{64}$; the former authors designate it Na_7Ga_{13}-II, whereas the latter authors designate it $Na_{22}Ga_{39}$. Schafer et al[58,59] note that Na_7Ga_{13}-II is isolated from a 3% sodium deficient solution whereas Na_7Ga_{13}-I is isolated from a 1% gallium deficient solution. Both structures are built up from Ga_{12} and Ga_{15} clusters connected to form a 3-D network; the sodium cations are inserted into the structure ensuring electrical neutrality.

^{133}Cs *n.m.r.* spectroscopic data for Cs_3Sb are not compatible with a purely ionic model.[62] They are, however, consistent with a partially covalent tight binding band structure model in which the charge on the Cs sites is assumed to be 0.57 electrons/atom.

Experimental methods for the determination of thermodynamic properties of alkali metal containing intermetallic compounds have been critically assessed.[63] Enthalpy of formation data for a number of lithium derivatives have been derived both from solution enthalpies (in liquid tin at 800K),[64] and from vapour pressure measurements (above LiH + Si mixtures);[65] the data are collected in Table 4.

Differential scanning calorimetry studies[66] of the formation of LiB_3 and Li_7B_6, according to equations (11) and (12), have also been undertaken; the effect of boron particle size and of surface boron oxides is discussed.

$$xLi + 6B \rightarrow 2LiB_3 + (x-2)Li \qquad ...(11)$$

$$2LiB_3 + (x-2)Li \rightarrow Li_7B_6 + (x-7)Li \qquad ...(12)$$

Table 4. Formation Enthalpies, $\Delta H_f(X,c,800K)/kJ.mol^{-1}$, for a number of lithium intermetallics.

Intermetallic Compound	$-\Delta H_f(X,c,800K)$ / $kJ.mole^{-1}$	Ref	Intermetallic Compound	$-\Delta H_f(X,c,800K)$ / $kJ.mol^{-1}$	Ref
LiIn	49.0	64	Li_2Si	82.4	65
LiTl	39.8	64	LiSn	49.6	64
Li_5Tl_2	177.1	64	Li_5Sn_2	219.8	64
Li_3Tl	95.6	64	Li_7Sn_2	276.3	64
			$Li_{22}Sn_5$	845.1	64
LiBi	71.0	64			
Li_3Bi	191.6	64	LiPb	48.6	64
			Li_7Pb_2	282.6	64

1.3 MOLTEN SALTS

Recent developments in molten salt chemistry have followed the trends noted in previous Reports. As before the abstracted papers relate to a wide range of salt systems. Two common themes emerge, however, the papers being collated in two subsections devoted to structural and thermodynamic properties and to chemical properties.

1.3.1 Structural and Thermodynamic Properties

The structures of molten LiBr (843K),[67] $NaBeF_3$ (743K)[68] and Na_2BeF_4 (923K)[68] have been investigated by X-ray diffraction methods. The nearest neighbour internuclear distance (265 pm) and coordination number of the first nearest neighbours (3.80) derived from the experimental data for molten LiBr are in good agreement with those (240 pm; 4.27) obtained from computer simulation experiments.[67] The fundamental structural unit in both

$NaBeF_3$ and Na_2BeF_4 is the BeF_4 tetrahedron.[68] Whereas molten $NaBeF_3$ contains dimeric $Be_2F_7^{3-}$ and/or trimeric $Be_3F_{10}^{4-}$ moieties, molten Na_2BeF_4 contains mainly monomeric BeF_4^{2-} moieties. Mean r(Be...F) distances in the tetrahedra are slightly larger in the melt ($NaBeF_3$, 160pm; Na_2BeF_4, 165pm) than those found in the solid (Na_2BeF_4, 154-156 pm). In the molten state, a configuration of four Na^+ cations around a BeF_4^{2-} unit is suggested; the four cations occupy two corner sites and two edge sites. Mean r(Na..F) distances in the melt ($NaBeF_3$, 235pm; Na_2BeF_4, 222pm) are close to those in the solid (Na_2BeF_4, 227-254pm) and to the sum of the radii of Na^+ and F^- (231pm).

Raman spectra of the molten KCl-$ZnCl_2$ system ($613 \leqslant T/K \leqslant 923$; $0.17 \leqslant x_{ZnCl_2} \leqslant 1.0$)[69] suggest the presence of both $ZnCl_4^{2-}$ tetrahedra and network structure $(ZnCl_2)_n$ polymers.

Theoretical calculations[70] of the liquidus temperatures of binary salt mixtures containing common anions (LiF-KF, LiF-NaF, NaF-KF, LiCl-KCl, NaCl-CsCl, $LiNO_3$-$NaNO_3$, LiF-CaF_2, NaF-CaF_2, NaCl-$SrCl_2$) have been undertaken using a simple theory which is dependent on three physicochemical parameters (lattice energy, latent enthalpy of melting and sum of ionic radii) for each salt. There is generally very good agreement between the calculated and experimental values.

Potentiometric and vapour pressure data derived from the NaCl-$AlCl_3$ system ($448 \leqslant T/K \leqslant 573$; $x_{AlCl_3} \leqslant 0.5357$)[71] are best explained by a combination of the three acid-base equilibria (13)-(15); identical equilibria have been described for the analogous

$$2AlCl_4^- \rightleftharpoons Al_2Cl_7^- + Cl^- \qquad ...(13)$$

$$3Al_2Cl_7^- \rightleftharpoons 2Al_3Cl_{10}^- + Cl^- \qquad ...(14)$$

$$2Al_3Cl_{10}^- \rightleftharpoons 3Al_2Cl_6 + 2Cl^- \qquad ...(15)$$

KCl-$AlCl_3$ system in the 1979 Report.[72] The solubility of NaCl in $NaAlCl_4$ melts has also been investigated ($448 \leqslant T/K \leqslant 573$).[71] The potential use of Pb^{2+} as a basicity indicator in NaCl-$AlCl_3$ and KCl-$AlCl_3$ melts has been justified.[73] The energy of the outer shell ${}^3P_1 \leftarrow {}^1S_0$ transition of Pb^{2+} doped into these solutions is very sensitive to basicity, sudden shifts in the maximum (upto 3000 cm^{-1}) occuring at the $AlCl_4^-$ stoichiometry (i.e., at the equivalence point when there is a rapid change of Cl^- activity).

1.3.2 Solution Properties

The application of diverse molten salts, including halides[74-84] nitrates,[85-90] carbonates,[91,92] sulphates,[74,75,92-94] dichromates[86] and tungstates[95] as non-aqueous solvent media has been been described during the period of this Report.

Dissolution of Mn_2O_3[74] and of Y_2O_3[75] in molten NaCl at 1100K has been studied using both coulometric and potentiometric methods. The solution of Mn_2O_3[74] (equation 16) involves reduction of

$$Mn_2O_3(s) + 4NaCl(l) \rightarrow 2MnCl_2(soln.) + 2Na_2O(soln.) + \tfrac{1}{2}O_2(g) \qquad \ldots(16)$$

$$Mn_3O_4(s) + 3Na_2SO_4(l) \rightarrow 3MnSO_4(soln.) + 3Na_2O(soln.) + \tfrac{1}{2}O_2(g) \qquad \ldots(17)$$

$$Y_2O_3 \rightleftharpoons 2Y^{3+} + 3O^{2-} \qquad \ldots(18)$$

$$O^{2-} + Y_2O_3 \rightleftharpoons 2YO_2^- \qquad \ldots(19)$$

manganese(III) to manganese(II). A similar reduction (equation 17) occurs during solution of Mn_3O_4 in molten Na_2SO_4 at 1200K. In both cases the solubility depends on the oxygen overpressure. (N.B. different oxides were studied since Mn_2O_3 loses oxygen at 1150K to form Mn_3O_4).[74] On the other hand, solution of Y_2O_3 in neither molten NaCl (1100K) nor molten Na_2SO_4 (1200K) involves redox processes.[75] The equilibrium constants of the acidic (equation 18) and basic (equation 19) dissolution mechanisms of Y_2O_3 have been determined.[75] The dissolution processes for Sm_2O_3 in molten LiF (equation 20) and in molten LiF-SmF_3 mixtures (equation 21) have been determined polarographically.

$$2LiF + Sm_2O_3 \rightarrow 2SmOF + Li_2O \qquad \ldots(20)$$

$$SmF_3 + Sm_2O_3 \rightarrow 3SmOF \qquad \ldots(21)$$

The chemistry of $AlCl_3$ in molten LiCl-KCl eutectic containing sulphides has been elucidated by potentiometric methods at 723K.[77] The principal solution species is the AlS^+ moiety; its formation in these solutions effectively solubilises Al_2S_3. Potentiometric studies of iron oxides in molten LiCl-KCl eutectic at 743K have also been effected together with complementary cyclic voltammetry, X-ray diffraction and i.r. studies.[78] In the absence of O^{2-}, iron(III) oxidises the solvent to Cl_2 with concomitant formation of $FeCl_2$. In the presence of O^{2-}, however, iron(III) is precipitated as Fe_2O_3; this product is quite stable and does not decompose to form oxygen and Fe_3O_4. In sufficiently basic solutions (i.e. solutions of high O^{2-} activity), Fe_2O_3 redissolves to form FeO_2^- ions (equation 22). In basic medium, iron(II) is

$$Fe_2O_3(s) + O^{2-}(soln.) \rightarrow 2FeO_2^-(soln.) \qquad ...(22)$$

$$3FeO(s) + O^{2-}(soln.) \rightarrow 2FeO_2^-(soln.) + Fe(s) \qquad ...(23)$$

$$Fe_3O_4(s) + O^{2-}(soln.) \rightarrow 2FeO_2^-(soln.) + FeO(s) \qquad ...(24)$$

$$3Fe_3O_4(s) + 4O^{2-}(soln.) \rightarrow 8FeO_2^-(soln.) + Fe(s) \qquad ...(25)$$

precipitated as FeO. In highly basic medium it disproportionates to form Fe and FeO_2^- (equation 23). The simultaneous presence of iron(II) and iron(III) can lead to formation of Fe_3O_4. This oxide disproportionates into FeO and FeO_2^- in basic media (equation 24) and even into Fe and FeO_2^- (equation 25) when the basicity is sufficiently high to promote disproportionation of FeO.[78]

Thermodynamic properties (chemical potentials) of infinitely dilute solutions of UCl_3 and of UCl_4 in molten KCl-NaCl-$MgCl_2$ (30:20:50) ternary eutectic mixtures have been determined.[79] A comparison of these data with corresponding results for LiCl-KCl and NaCl-KCl eutectic mixtures has shown that the relative complexing power of the three solvents increases in the order:

LiCl-KCl < KCl-NaCl-$MgCl_2$ < NaCl-KCl

A number of aspects of the chemistry of chloroaluminate melts have been elucidated.[80-83] Electrochemical separation of zirconium from hafnium in slightly acidic NaCl-$AlCl_3$ melts (x_{AlCl_3} ~0.505; T = 448K) has been effected;[80] the process is based on the differing kinetics of the electro-reduction of M(IV) in these melts. The separation factors achieved are better than those obtained by chemical reduction.[80]

The chemistry of sulphur in chloroaluminate melts is still of considerable interest to molten salt chemists.[81-83] Bjerrum et al[81] have identified S_4^+ and S_8^+ radicals as two of the three products formed either by anodic oxidation of sulphur or by reaction between chlorine and sulphur in highly acidic NaCl-$AlCl_3$ (37:63; T = 423K) melts; the third product is tentatively assigned as the S_{12}^{2+} ion. Tanemoto et al[82] have shown that the oxidation of sulphur in NaCl-$AlCl_3$ melts differs quite markedly from acidic (47:53; p_{Cl^-} = 5.4; T=448K) to basic (50.1:49.9; p_{Cl^-} = 1.5;T=448K) media. The main oxidation product, S_2Cl_2, is stable over the entire p_{Cl^-} range studied. Of the minor products, however, low oxidation state moieties, such as S_8^+ and S_8^{2+}, are only found in acidic melts, whereas SCl_3^+ is only stable in basic melts. Bjerrum et al[83] have also confirmed the formation of an S_3^- moiety in basic CsCl-$AlCl_3$ ($653 \leq T/K \leq 743$). Reaction between sulphur and aluminium in this solvent leads to an equilibrium between S_3^-, $[AlSCl_2]_n^{n-}$, and molecular sulphur. The S_3^- species has also been observed in molten LiCl-CsCl eutectic (T = 648K) as the product of the reaction between sulphur and Li_2S.[83]

The reaction of SnO_2 with molten NaX-$NaPO_3$ (X = F,Cl) has been investigated ($1123 \leq T/K \leq 1173$);[84] the products include mixed sodium tin phosphates as well as sodium pyrophosphate and sodium orthophosphate.

Several features of the solution chemistry of molten nitrates have been elucidated; solvents considered include $NaNO_3$,[85] KNO_3,[85,86] $LiNO_3$-KNO_3 eutectic,[87] equimolar $NaNO_3$-KNO_3[88,89] and KNO_3-$Ba(NO_3)_2$ eutectic.[90] A synthetic method for $MMoO_4$ and MWO_4 (M = Ca-Ba) using $NaNO_3$ or KNO_3 as solvents at 723K has been perfected.[85] The method is based on the metathetical reaction of $M(NO_3)_2$ (M = Ca-Ba) with Na_2MoO_4 or K_2WO_4; the product is separated from the fused salt, when cold, by repeated washing with water. Cryoscopic studies[86] of the solution of various alkali metal isopolymolybdates (M_2MoO_4, $M_2Mo_3O_{10}$, $M_2Mo_4O_{13}$, $M_2Mo_5O_{16}$; M = Rb,Cs) and of some related molybdenum(VI) compounds ($Na_2CrO_4.MoO_3$, $K_2CrO_4.2MoO_3$, $Cr_2Mo_3O_{12}$ and V_2MoO_8) in molten KNO_3 have shown that, with the exception of V_2MoO_8, the solutes undergo either simple dissociation (equation 26) or rearrange after dissociation to form heteropolyions of the type $[CrMo_2O_{10}]^{2-}$ (equation 27). The solute

V_2MoO_8 dissolves without any apparent dissociation (equation 28). Similar studies have been undertaken for these solutes in molten

$$KNO_3 + M_2Mo_xO_y \rightarrow K^+ + NO_3^- + 2M^+ + Mo_xO_y^{2-} \qquad ...(26)$$

$$KNO_3 + 2Na_2CrO_4.MoO_3 \rightarrow K^+ + NO_3^- + 4Na^+ + CrMo_2O_{10}^{2-} + CrO_4^{2-} \qquad ...(27)$$

$$KNO_3 + V_2MoO_8 \rightarrow K^+ + NO_3^- + V_2MoO_8 \qquad ...(28)$$

$K_2Cr_2O_7$; effectively identical observations were made.[86]

Chromium(II) chloride reacts rapidly with molten $LiNO_3$-KNO_3 eutectic at temperatures just above its melting point to form gaseous NO_2 and a dark brown black solution which probably contains Cr(III) and Cr(VI).[87] At higher temperatures (>473K) a green precipitate of Cr_2O_3 and an orange solution of $Cr_2O_7^{2-}$ is formed. Above 723K, both compounds are slowly converted into a yellow solution of chromate(VI) containing NO_2^-; the latter is formed by partial decomposition of the solvent.[87]

The principal products of the reaction of MSO_4 (M = Co,Ni,Cu) with molten $NaNO_3$-KNO_3 mixtures are Co_3O_4, NiO and CuO, together with Na_2SO_4 and K_2SO_4;[88] the formation of NO_2 and O_2 has also been detected. The proposed reaction mechanism[88] is summarised in Scheme 2:

$$MSO_4(s) + 2NO_3^-(soln) \rightarrow M(NO_3)_2(soln) + SO_4^{2-}(soln) \quad (M=Co,Ni,Cu)$$

$$2M(NO_3)_2(soln) \rightarrow 2MO(s) + 4NO_2(g) + O_2(g) \qquad (M = Ni,Cu)$$

$$3Co(NO_3)_2(l) \rightarrow Co_3O_4(s) + 6NO_2(g) + O_2(g)$$

Scheme 2

The behaviour of NH_3 in anhydrous molten $NaNO_3$-KNO_3 mixtures has been ascertained at 518K and compared with that in melts containing added H_2O, NO_2^- and NH_2^-.[89] The chemistry of the NH_2^- ions, which are involved in the ammonia electro-reduction pathway, is described.

Thermodynamic parameters for the formation of PbX^+, PbX_2 (X = Cl-I) in dilute solutions of $Pb(NO_3)_2$ and KX (X = Cl-I) in molten

KNO_3-$Ba(NO_3)_2$ (87.6:12.4; $568.2 \leq T/K \leq 628.2$) have been measured using an e.m.f. method;[90] no evidence was found for the formation of dinuclear species.

The solubility of oxygen in molten Li_2CO_3-K_2CO_3 (62:38) has been determined at 923K.[91] Chemical analysis of the system showed the principal dissolved species to be the O_2^{2-} ion; small concentrations of the O_2^- ion were also observed, together with negligible quantities of molecular oxygen.[91] The oxidation of graphite in Na_2CO_3-Na_2SO_4 melts ($0 < x_{Na_2SO_4} \leq 1$; $1173 < T/K \leq 1273$) has been studied in both oxidising and inert atmospheres.[92] Reaction sequences are proposed for the observed oxidation processes in pure Na_2CO_3, pure Na_2SO_4 and the mixed melts.

The solution chemistry of Mn_3O_4 (equation 17)[74] and of Y_2O_3 (equations 18,19)[75] in molten Na_2SO_4 at 1200K have been described earlier in this subsection. Other examples of molten sulphate chemistry published during 1982 have involved either $K_2S_2O_7$-K_2SO_4[93] or $K_2S_2O_7$[94] as solvents. Physicochemical data obtained on addition of V_2O_5 to $K_2S_2O_7$-K_2SO_4 melts (saturated with K_2SO_4; $683 \leq T/K \leq 723$)[93] could best be explained assuming the formation of oxosulphato complexes such as $[VO_{(5-n/2}(SO_4)_n]^{n-}$ (e.g. $[VO(SO_4)_3]^{3-}$) and $[VO_2(SO_4)_2]^{3-}$. The solubility of K_2SO_4 in $K_2S_2O_7$-K_2SO_4 melts ($693 \leq T/K \leq 723$) has also been determined by potentiometric methods.[93] The stoichiometries of the reactions of the first row transition metals (Ti-Zn) with molten $K_2S_2O_7$ have been established.[94] The metals were oxidised to M(IV), M(III) or M(II) as appropriate with concomitant reduction of the melt to SO_2 and SO_4^{2-}; the reactions are summarised in equations (29)-(31).

$$M(s) + 3S_2O_7^{2-}(soln) \rightarrow MO^{2+}(soln) + 4SO_4^{2-}(soln) + 2SO_2(g) \quad (M = Ti,V) \qquad ...(29)$$

$$2M(s) + 6S_2O_7^{2-}(soln) \rightarrow 2M^{3+}(soln) + 9SO_4^{2-}(soln) + 3SO_2(g) \quad (M = Cr,Fe) \qquad ...(30)$$

$$M(s) + 2S_2O_7^{2-}(soln) \rightarrow M^{2+}(soln) + 3SO_4^{2-}(soln) + SO_2(g) \quad (M = Mn,Co,Ni,Cu,Zn) \qquad ...(31)$$

The kinetics and mechanism of the growth of crystalline $BaWO_4$ from Na_2WO_4 melts have been elucidated as a function of temperature

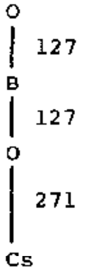
$(1073 \leq T/K \leq 1273)$ and cooling rate $(0.67 \leq R_T/K.min^{-1} \leq 3.37)$.[95]

1.4 SIMPLE COMPOUNDS OF THE ALKALI METALS

The primary remit adopted for selection of abstracts for this section is that they must describe significant advances in the chemistry of the binary and ternary compounds of the alkali metals; several subsections are included to cover these topics. Following the precedent set in the 1981 Review,[96] a subsection devoted to the recent chemistry of ion pairs is also included. A further addition is a novel subsection dealing with theoretical calculations on small molecules containing alkali metals (normally lithium); previously these moieties have been considered in the section entitled 'lithium derivatives'.

1.4.1 Ion Pairs

Ion pairs have been studied in both the gas phase[97-99] and in low temperature matrices. Gas phase structures of $Cs[BO_2]$,[97] $Cs[NO_2]$,[98] $Rb[NO_2]$[98] and $Cs[SO_4]$[99] have been determined by a group of Russian authors using electron diffraction methods. Interpretation of electron diffraction data is complex, most structural parameters being determined with a comparatively large error. Indeed for $Cs[BO_2]$[97] it is impossible to make an unambiguous statement of the structure; the most realistic analysis of the results indicate that the $[BO_2]^-$ anion is linear with a Cs^+ cation attached at one end (1). The structure of the $M[NO_2]$ (M = Rb,Cs) ion pairs (2,3) are quite different from that suggested for $Cs[BO_2]$; they correspond to a planar MONO (M = Rb,Cs) ring of C_{2v} symmetry.[98] The equilibrium configuration of the $Cs_2[SO_4]$ ion pair (4) has D_{2d} symmetry with the Cs^+ cations lying on a C_2 axis



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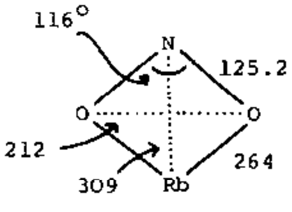

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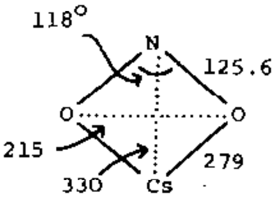

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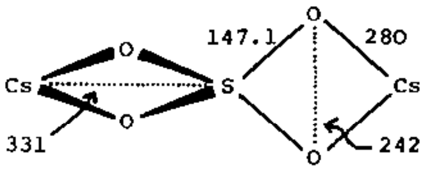
distances/pm

of the regular $[SO_4]^{2-}$ tetrahedron.[99] Where available, structural data are included on diagrams (1) to (4).



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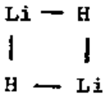
(4)

I.r. studies of $M[XO_2]$ ($Na[PO_2]$, $Cs[AsO_2]$ and $K[SbO_2]$)[100] and of $K_2[MO_4]$ (M = Cr,Mo,W),[101] isolated in various cryogenic matrices, have been used for structural characterisation. All three $M[XO_2]$ moieties have C_{2v} ring structures (c.f. (2) and (3)) with estimated OPO, OAsO and OSbO bond angles of 114(3), 115(5) and 106(5)$^\circ$, respectively.[100] On the other hand, the three $K_2[MO_4]$ moieties have D_{2d} structures (c.f. (4)) with estimated OCrO, OMoO and OWO bond angles of 96(5), 98(5) and 108(4)$^\circ$, respectively.

1.4.2 Theoretical Treatment of Small Moieties

A series of ab initio SCF LCAO MO calculations has been effected by Solomonik et al[102-105] to determine the geometric structures, potential surfaces, force fields and vibrational frequencies of Li_2H_2,[102] Li_2F_2,[103] $[Li_2H]^+$,[104] $[LiBeH_2]^+$,[104] $[LiBH_3]^+$,[104] and $LiBeF_3$.[105] The equilibrium geometry of Li_2H_2[102] and of Li_2F_2[103] is a planar ring of D_{2h} symmetry (5). The instability of the alternative $C_{\infty v}$ linear dimer (6) vis à vis the planar ring has been established; this alternative configuration (6) represents a saddle point on the potential surface of the appropriate molecule.



(5)

Li-H-Li-H

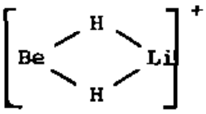
(6)

$[Li\text{-}H\text{-}Li]^+$

(7)

$[Li\text{-}H\text{-}Be\text{-}H]^+$

(8)



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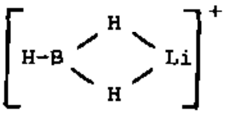

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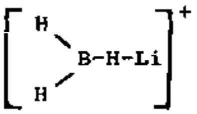

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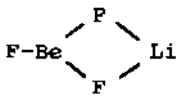


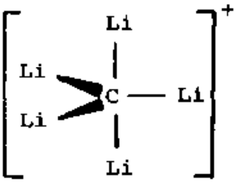
(12)

The cations, $[Li_2H]^+$ and $[LiBeH_2]^+$ have linear equilibrium configurations with $D_{\infty h}$ (7) and $C_{\infty v}$ (8) symmetry, respectively;[104] the ion $[LiBH_3]^+$ has a planar cyclic (bidentate) C_{2v} symmetry (10).[104] The cyclic C_{2v} structure of $[LiBeH_2]^+$ (9) and the unidentate structure of $[LiBH_3]^+$ (11) correspond to saddle points on the potential surfaces of the appropriate ion.[104] The formation energy of these complex ions (according to equation (32)) decreases regularly from 252 kJ mol^{-1} (for $[Li_2H]^+$) through

$$Li^+ + MH_n \rightarrow [LiMH_n]^+ \quad (M = Li,\ n = 0;\ M = Be,\ n = 1;\ M = B,\ n = 2) \qquad \ldots(32)$$

71 kJ mol^{-1} (for $[LiBeH_2]^+$) to 51 kJ mol^{-1} (for $[LiBH_3]^+$).[104] The calculated vibrational frequencies of $LiBeF_3$ based on the planar cyclic (bidentate) C_{2v} structure (12) have been compared[105] with experimental data for matrix isolated $LiBeF_3$.

Theoretical analyses (ab initio SCF LCAO MO calculations) of the electronic structures and spectroscopic properties of the diatomic LiC[106] and LiN[107] moieties have been undertaken; similar studies have also been completed for the carbene, Li_2C.[106] Pople and Schleyer have embarked on an extensive theoretical study of the geometries, stabilities and electronic states of lithium-substituted carbenium ions, $[CLi_{3-n}H_n]^+$ (n = 0-3),[108] and lithiated carbocations $[CLi_{4+n}]^{n+}$ (n = 1,2).[109] They conclude[108] that lithium is a remarkably effective stabilising substituent for carbenium ions, the thermodynamic stability of $[CLi_3]^+$ being extraordinary. The calculated geometry and electronic structure of this ion is unusual. It prefers a C_{2v} Jahn-Teller distorted geometry and a triplet ground state; $[CHLi_2]^+$ is similar but $[CH_2Li]^+$ and $[CH_3]^+$ are indicated to have singlet ground states.[108] Calculations for various geometries (C_s, C_{3v}, D_{3h}) of the carbocation $[CLi_5]^+$ invariably collapsed to the D_{3h} structure (13) on geometry optimisation.[109] By imposition of C_{4v} symmetry, however, the energy of an additional isomer (14) was shown to be only marginally greater (by ca. 4.0 kJ mol^{-1}) than that of the D_{3h} isomer inferring that the potential energy surface of $[CLi_5]^+$ should be extremely flat with almost no activation required for pseudo-rotational scrambling.[109] Preliminary studies of the $[CLi_6]^{2+}$ ion, assuming an octahedral geometry (15), indicate that it has an essentially neutral central atom bonded to a "sphere" of



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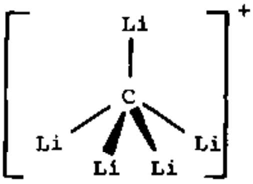

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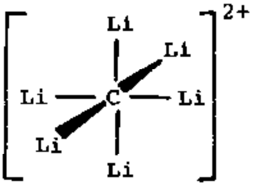
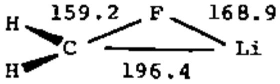


(15)

partially positively charged lithium atoms. The $[CLi_3]^+$ and $[CLi_5]^+$ species have been observed by Lagow et al[109] in a flash vapourisation study of $(CLi_4)_n$, prepared by reaction of lithium vapour with CCl_4. The mass spectroscopic studies also established the formation of the ions, $[C_2Li_7]^+$ and $[(C_2Li_2)_n]^+$ (n = 1-3) together with the CLi_4, C_2Li_8 and C_3Li_{12} moieties.[109] Lagow et al,[110,111] in related studies, have synthesised CH_2Li_2,[110] (by the Ziegler pyrolysis of methyllithium between 503 and 513K) and $CHLi_3$[111] (by cocondensing lithium vapour and $CHCl_3$ on a cryogenic surface) and subjected them to flash vapourisation mass spectrometry. The ionic species obtained from CH_2Li_2 included those derived not only from the monomer through tetramer clusters but also from those species plus and minus a lithium atom.[110] The corresponding products obtained from $CHLi_3$ included $[CH_3Li]^+$, $[CH_2Li_2]^+$, $[CHLi_3]^+$, $[CLi_4]^+$, $[C_2Li_2]^+$ and $[C_2Li_4]^+$.[111]

Using ab initio SCF LCAO MO methods, Schleyer et al[112] predict that the non-tetrahedral structural features of CH_2LiF (16), reported in the 1979 Review,[113] are retained in its C_{2h} symmetry dimer (17). The CH_2LiF units in the dimer have essentially the same geometries as in the monomer. The C-Li bonds remain relatively strong but r(Li(1)...F(1)) is lengthened; r(Li(1)...F(2)) is close to that calculated for Li_2F_2 (18). The structure of $CH_2LiF.LiF$ (19) is also of interest. In effect a CH_2 unit has been inserted into a Li-F bond of Li_2F_2. The C-Li bond is longer and the C-F bond shorter than in (16) or (17); the geometry around the carbon aton in (19) is, however, closer to tetrahedral.[112]



(16)

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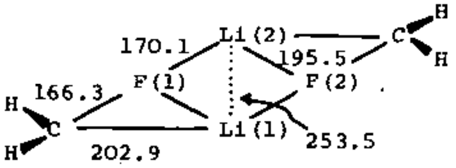

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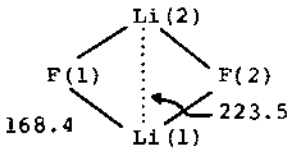

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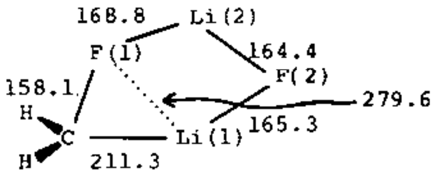

(19)

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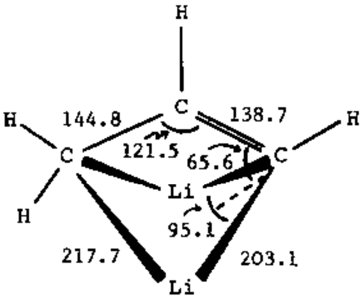
Schleyer et al[114] have calculated on the basis of ab initio (3-21G//3-21G) calculations that two symmetrically bridged structures for dilithiated propene, $CH_2CHCHLi_2$ (20) and (21) are comparably stable.



(20)

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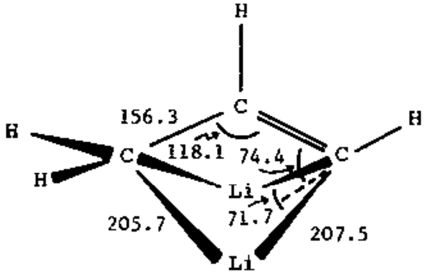
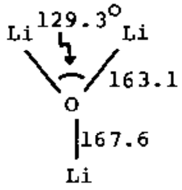
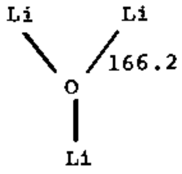


(21)

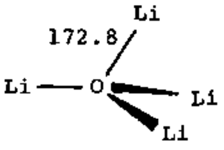
Schleyer and Pople[115] have reported the results of calculations on OLi_3 and OLi_4, two of a large number of molecules whose unusual stoichiometries suggest violations of the octet rule; the equilibrium geometries of these species involve polyco-ordinated central atoms which therefore appear to have some hypervalent character. Thus, although the hypervalent species OH_3 and OH_4 are only weak van der Waals complexes between H_2O and H or H_2, the calculations indicate that both OLi_3 and OLi_4 are thermodynamically stable towards dissociation or loss of an electron. A large number of OLi_3 and OLi_4 structures were examined. The only minimum found for OLi_3 was for (22) with C_{2v} symmetry. The closely related D_{3h} structure (23) is only 2 kJ mol^{-1} higher in energy but is a transition structure on the potential energy surface. Two minima were found on the OLi_4 potential energy surface; the most stable form (by ca. 75 kJ mol^{-1}) has tetrahedral geometry (24). The



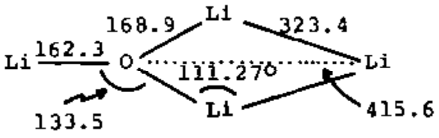
(22) C_{2v}



(23) D_{3h}



(24) Td



(25) C_{2v}

distances/pm; angles/°

other metastable form (25) is best regarded as a OLi_3^+, Li^- ion pair. The nature of the hypervalent bonding in these moieties is discussed in detail.[115]

1.4.3 Binary Compounds

As for previous Reviews, the number of papers abstracted for this section is relatively small; hence the data are considered en bloc rather than in a series of subsections. There is a possibility, however, that increased attention may be directed to lithium containing binary compounds in the future since they and similar ternary compounds are being actively considered for use as tritium breeding materials in fusion reactors;[116] they are particularly attractive owing to their apparent safety advantages vis-à-vis liquid lithium, the primary alternative.

Electrochemical studies[27] of the interaction of lithium with carbon in liquid sodium have lead to a new value for the free energy of formation of Li_2C_2 ($\Delta G_f^O(Li_2C_2,c,873K) = -89$ kJ mol^{-1}).

A small number of papers in which diverse properties of alkali metal halides are reported have been abstracted.[117-121] Pyrohydrolysis of NaF has been studied[117] as a function of temperature ($1173 \leqslant T/K \leqslant 1268$) and water partial pressure ($3 \times 10^3 \leqslant p_{H_2O}/Pa \leqslant 45 \times 10^3$). The products of the reaction are the gaseous species NaOH and HF. A detailed kinetic analysis of the reaction is undertaken.[117] The curious anomalous behaviour of KF in both X-ray (attenuation of high energy satellite intensity) and Auger (peak splitting) spectroscopy has been advanced[118] as evidence for transitory covalency. Mass spectroscopic studies[119] of the vapour above alkali metal iodides MI(M = Na-Cs) have led to sublimation and dimerisation enthalpies; the data are collected in Table 5. Thermodynamic quantities for the mixed dimer formation reaction (equation 33) have also been derived using mass spectroscopic techniques (793 < T/K < 1083).[120] The data ($\Delta H_r^o = -1.67$ kJ mol^{-1}; $\Delta S_r^o = 5.69$ J.K^{-1}.mol^{-1}) are indicative of nearly 100% ionic bonding in all three dimers and that mixing of Na^+ and K^+ ions does not enhance the bond strength.[120] Analysis of ultra-high mass spectral data (>m/z = 18000 and n = 1-70) of $[Cs(CsI)_n]^+$ clusters induced by xenon ion bombardment of CsI and analysed by a high performance secondary ion mass spectrometer indicates that the clusters adopt 'cubic-like' atomic configurations, reminiscent of those in the bulk crystal.[121] Comparison with data for MI (M = Na-Rb) cluster ions suggests that they too adopt 'cubic-like' structures.[121]

$$Na_2Cl_2 + K_2Cl_2 \rightleftharpoons 2NaKCl_2 \qquad \ldots(33)$$

Table 5. Enthalpies of sublimation, ΔH_{sub}, and of dimerisation, ΔH_{dim}, for alkali metal iodides.[119]

	ΔH_{sub}(800K)/kJ.mol^{-1}	$-\Delta H_{dim}$(800K)/kJ.mol^{-1}
NaI	170.8	126.5
KI	168.7	129.7
RbI	169.6	129.2
CsI	165.0	118.1

The mixed oxides, KNaO and RbNaO have been prepared by thermal treatment (630K; 60 minutes) of equimolar mixtures of Na_2O and M_2O (M = Rb,K); single crystals of KNaO were obtained by extension of the thermal treatment (740K; 60 days).[122] Pertinent unit cell parameters are included in Table 6.

Thermodynamic parameters for a number of gaseous potassium-containing species have been determined in a comprehensive series of effusion mass spectroscopic studies;[123] recommended data are quoted in Table 7.

Table 6. Unit cell parameters for MNaO (M = K,Rb) and Li_2LnSb_2 (Ln = Ce,Pr,Nd).

	Symmetry	Space Group	a/pm	c/pm	Ref.
KNaO	Tetragonal	anti-PbClF	400.2	621.4	122
RbNaO	Tetragonal	anti-PbClF	409.3	653.1	122
Li_2CeSb_2	Tetragonal	P4/nmm	433.5	1096.0	128
Li_2PrSb_2	Tetragonal	P4/nmm	432.9	1099.9	128
Li_2NdSb_2	Tetragonal	P4/nmm	428.0	1091.0	128

Table 7. Enthalpy of formation (ΔH_f^o(X,g,298.15K)) and bond dissociation enthalpy (D^o(K-X)) data for several potassium containing species.[123]

Compound	$-\Delta H_f^o$(X,g,298.15K) / kJ.mol^{-1}	Bond	D^o(K-X) / kJ.mol^{-1}
K_2O	155.5±12.0	K-O	261.9±4.0
KH	110.0±16.0	K-H	193.3±16.0
KOH	228±2.0	K-OH	352.3±2.0

E.s.r. spectra[124] of γ-irradiated RbOH aqueous glasses at 77K contain a novel feature not previously observed for the corresponding MOH (M = Li-K) glasses. It is assigned to the aquated Rb atom; this is thought to be the first report of the e.s.r. detection of solvated alkali metal atoms in high dielectric media such as H_2O or NH_3.[124]

Independent structural studies of LiOH, H_2O[125,126] and of CsOH, H_2O[127] have been undertaken. Theoretical electron density maps[125] for LiOH,H_2O have been computed and compared with experimental maps[126] obtained from combined X-ray and neutron diffraction data (298K) in an attempt to analyse the hydrogen bonding in this material. High temperature (355K, 400K) X-ray studies of $CsOH,H_2O$[127] show that it contains layered $[H_3O_2^-]$ polyanions separated by layers of Cs^+ cations. At lower temperatures (293K), however, the X-ray data, when combined with i.r. spectral data, show that it is possible to distinguish between OH^- anions and H_2O molecules.[127]

1.4.4 Ternary Pnictides

To avoid unnecessary duplication with other Chapters of this Review, the ternary compounds considered are 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 oxides, chalcogenides and halides, only one solitary paper dealing with ternary pnictides has been discovered. Schuster et al[128] have prepared a series of antimonides, Li_2LnSb_2 (Ln = Ce,Pr,Nd) and characterised them by X-ray diffraction methods; pertinent unit cell parameters are collated in Table 6.

1.4.5 Ternary Oxides and Chalcogenides

Several novel oxides[129-137] and selenides[138,139] have been synthesised; whereas the former were obtained primarily by Hoppe and his coworkers,[129,132-137] using classical solid state methods the latter were prepared by Bronger and Schils[138,139] by reaction of alkali metal carbonates with the appropriate transition metal in the presence of selenium. These products are listed in Table 8 together with pertinent structural data.

Fotiev et al[140,141] have continued their extensive studies of the mechanisms of solid state syntheses especially those in which ternary alkali metal vanadium oxides are formed. Thermodynamic and experimental studies of the VO_2-Na_2CO_3,[140] V_2O_3-Na_2CO_3,[140] V_3O_5-Na_2CO_3[141] and V_3O_5-Na_2SO_4[141] systems suggest that as well as simple addition type reactions involving loss of CO_2, a significant part is played by redox reactions.

Neutron powder diffraction studies have been completed for the mixed valence compounds $Li_xPt_3O_4$,[142] $Na_xPt_3O_4$,[143] and the non-stoichiometric solid solution, $9LiTaO_3,Ta_2O_5$.[144] The mixed valence compounds $Na_xPt_3O_4$ crystallise with cubic symmetry in the

Table 8. Crystallographic parameters for diverse ternary oxides and selenides.

Compound	Symmetry	Space Group	a/pm	b/pm	c/pm	β/°	Ref
$Li_{16}Nb_4O_{18}$	triclinic	$P\bar{1}$	1521	881	585	-	129
			(109.8°)	(101.4°)	(87.0°)		
Na_5NbO_5	monoclinic	C2/c	624	1020	1016	109.3	130
KNb_3O_8	orthorhombic	Amam	890.3	2116.0	379.9	-	131
Na_5TaO_5	monoclinic	C2/c	633	1026	1017	109.1	130
$CsTa_5O_{14}$	orthorhombic	Pbam	2623.5	742.9	738.8	-	132
$KMnO_2$	monoclinic	$P2_1/m$	1014.2	1130.9	626.9	95.0	133
K_2FeO_4	orthorhombic	Pnam	769.0	1032.8	585.5	-	134
$Rb_3Cu_5O_4$	monoclinic	$P2_1/c$	988.6	750.8	1440.1	106.9	135
Na_3AgO_2	orthorhombic	Ibam	546	1092	592	-	136
$K_4Ag_4O_4$*	tetragonal	$I\bar{4}m2$	989.3	-	544.5	-	137
$Cs_2Cu_5Se_4$	orthorhombic	Cmcm	399.2	1941.7	1321.9	-	138
$K_2Ag_4Se_3$	Monoclinic	C2/m	1777.0	444.7	1185.6	108.4	139

* Several isostructural compounds of formulae M_4CuO_4 (M = Li-Rb) and $M_4Ag_4O_4$ (M = Li-Cs) were prepared.

space group Pm3n; the unit cell parameter a_o varies linearly with composition from 568.68pm for $Na_{1.0}Pt_3O_4$ to 567.5pm for $Na_{0.73}Pt_3O_4$.[143] The structure of the analogous $Li_{0.64}Pt_3O_4$ is different in that it crystallises with cubic symmetry in the space group $P\bar{4}3n$ whereas the Na^+ cations occupy 8-coordinate cubic sites in the Pt_3O_4 framework, the coordination geometry of the Li^+ cations is built up of four short (222pm) and four long (265pm) Li-O bonds in the configuration of two interpenetrating tetrahedra.[142] A similar distortion of the $Na_xPt_3O_4$ structure was observed for $Na_{0.14}Co_{0.37}Pt_3O_4$ in which there was ordering of Na^+ Co^{2+} and vacancies in the cubic coordination sites.[142] The powder neutron diffraction data for $9LiTaO_3,Ta_2O_5$ have been used to refine several structural models with the Rietveld method.[144] The best fit to the experimental observations is obtained with the defective structure model, proposed by Nassau and Lines,[145] which is based on the formulation $[Li^+_{1-5x}\square_{4x}]M^{5+}_{1+x}O_3$; in this case, x = 1/32.

The high temperature phase transformation in the vanadium oxide bronze, β-$Li_{0.27}V_2O_{4.95}$ is accompanied by a redistribution of Li^+

cations among the possible positions in the crystal lattice.[146] The concomitant changes in physicochemical properties are assumed to be the consequence of the structural changes.

High resolution solid state n.m.r. spectra of $NaVO_3$ (^{51}V; $I = 7/2$)[147] and of $KMnO_4$ (^{55}Mn; $I = 5/2$)[148] have been measured using rapid magic angle rotation techniques. The results indicate the general feasibility of obtaining such spectra from quadrupolar nuclei with large chemical shifts and quadrupole interactions.

Magnetic properties of α- and β-$Li_2Eu_5O_8$ have been determined ($1.2 \leq T/K \leq 50$);[149] susceptibility data ($4.2 \leq T/K \leq 50$) can be analysed in terms of a linear-chain Heisenberg ferromagnetic model for both compounds. At lower temperatures, both phases undergo three dimensional antiferromagnetic ordering.[149]

Free energy data for the formation of the vanadium oxide bronzes, β-$M_{0.27}V_2O_5$ (M = Li,Na,K), from MVO_3 and V_2O_5 (equation 34) have

$$0.27MVO_3 \; + \; 0.865V_2O_5 \rightleftharpoons Li_{0.27}V_2O_5 \; + \; 0.0675O_2 \qquad \ldots(34)$$

been acquired; the ΔG^{o}_{298} values for this reaction decrease from lithium (10.16 $kJ.mol^{-1}$) through potassium (5.33 $kJ.mol^{-1}$) to sodium (1.31 $kJ.mol^{-1}$). Enthalpy of formation ($\Delta H^{o}_{f}(X,s,298.15K)/kJ.mol^{-1}$) data for δ-Li_4MoO_5 (-2184.5±104) and Li_2MoO_4 (-1498.6±68) have been determined from a high temperature mass spectroscopic study of the vapour above the evaporated solids;[151] similar data were obtained for α-Na_2UO_4 (-1897.3±1.1) and α-$Na_2U_2O_7$ (-3194.8±1.8) from enthalpy of solution results for these materials in 1.505 $mol.dm^{-3}$ H_2SO_4.[152] Enthalpies of melting and melting temperatures of $MReO_4$ (M = Li-Cs) have been measured by differential enthalpic analysis using a high-temperature Calvet microcalorimeter.[153] A mass spectroscopic study of the vaporisation of Li_2TiO_3 has also been undertaken.[154]

Electrical conductivity measurements ($15 \leq T/K \leq 300$)[155] have demonstrated that the mixed valence compound $Na_3Cu_4S_4$ is metallic; the conductivity is anisotropic with enhanced conductivity parallel to the crystal needle axis corresponding to pseudo one-dimensional $[Cu_4S_4]^{3-}_{\infty}$ columns in the structure.[155]

1.4.6 Ternary Halides

Compounds covered in this subsection are restricted to anhydrous ternary alkali metal-transition metal halides; solvated species are not considered. The majority of the studies effected are directed towards structural elucidation of novel ternary halides; those compounds which have been characterised are listed in Table 9 together with salient crystallographic data.[156-172] Diverse synthetic methods have been used to procure these materials. In general the chlorides, bromides and iodides have been prepared by classical solid state methods although MDy_2Cl_7 (M = K,Rb) were synthesised[163] by heating equimolar mixtures of MCl and Dy_2O_3 dissolved in concentrated HCl, firstly to dryness and then to 773K for 48 hours in a stream of dry HCl. The fluorides, on the other hand, were obtained either by high pressure fluorination of, for example, $CsFeBr_4,2H_2O$ ($\rightarrow\beta$-$CsFeF_4$),[159] $CsCuCl_3$ ($\rightarrow CsCuF_4$),[160] M_2CO_3 (M = K,Rb,Cs)/$[Co(NH_3)_6]Cl_3$ mixtures ($\rightarrow MCoF_4$),[159] $Li_2[Ni(CN)_4],3H_2O$ ($\rightarrow Li_2NiF_5$)[167] or by crystallisation from 40% aqueous HF solution ($\rightarrow M_2PtF_6$).[169]

The synthesis of K_2IrCl_5 by thermal decomposition of $K_2[Ir(H_2O)Cl_5]$ in air at ca. 558K has also been reported.[173] Although extensively characterised by various physicochemical methods it is not included in Table 9 since the X-ray diffraction data are inconclusive; the powder pattern is quoted but no structural parameters are proposed.

Phase relationships in the MBr-$TmBr_3$ (M = Li,[174] Na, K, Cs[175]) systems have been established by d.t.a., X-ray diffraction and crystal optical methods. Two compounds, Li_5TmBr_8 and Li_3TmBr_6, are formed in the $LiBr$-$TmBr_3$ system;[174] whereas the former undergoes peritectoid decomposition at 673K, the latter decomposes in a peritectic reaction at 831K. Only one compound was observed in each of the $NaBr$-$TmBr_3$ and KBr-$TmBr_3$ systems.[175] Whereas $NaTmBr_4$ decomposes in a peritectic reaction at 781K, K_3TmBr_6 melts congruently at 979K; both bromides undergo polymorphic transformations at 723K and 701K, respectively.[175] The $CsBr$-$TmBr_3$ system contains two compounds, Cs_3TmBr_6 and $Cs_3Tm_2Br_9$.[175] The former melts congruently at 1083K, after a polymorphic transformation at 727K; the latter decomposes in a peritectic reaction at 941K. X-ray diffraction studies were undertaken on all six compounds; unfortunately the results were inconclusive [174,175]

Boo et al[156] have extended their detailed studies of the structural chemistry of M_xVF_3 (M = alkali metal) species. They

Table 9. Crystallographic parameters for a number of ternary halides.

Compound	Symmetry	Space Group (Structure Type)	a/pm	b/pm	c/pm	$\beta/^{o}$	Ref.
$Cs_{0.5}VF_3$	cubic		1049.1	-	-	-	156
$Cs_{0.5}VF_3$	orthorhombic		747.2	744.1	1043.5	-	156
$KFeBr_3$	orthorhombic	Pnma	922.0	402.6	1489.9	-	157
$RbMnBr_3$	hexagonal	$P6_3cm$	1292.4	-	654.7	-	158
$LiCoF_4$	monoclinic	$P2_1/m$	554.0	466.5	544.7	114.25	159
$NaCoF_4$	orthorhombic	α-$NaTiF_4$	496.5	551.6	1080.0	-	159
$KCoF_4$	orthorhombic	β-$RbFeF_4$	752.6	758.4	579.2	-	159
$MCoF_4$ (M=Rb,Cs)*	tetragonal	β-$RbAlF_4$	1222.2	-	1235.6	-	159
β-$CsFeF_4$	tetragonal	β-$RbAlF_4$	1249.1	-	1327.2	-	159
$CsCuF_4$	tetragonal	$KBrF_4$	584.9	-	1204.3	-	160
$MNbCl_6$ (M=Rb,Cs) (298K)†	monoclinic	$CsWCl_6$	1198.5	623.3	1518.0	128.7^{o}	161
$MNbCl_6$ (M=Rb,Cs) (588K)†	cubic	-	1019.9	-	-	-	161
KHo_2F_7	monoclinic	α-$KErF_7$	1428.7	800.4	1195.0	125.33^{o}	162
KDy_2Cl_7	monoclinic	$P2_1/a$	1273.9	688.1	1262.1	89.4(γ)	163
$RbDy_2Cl_7$	orthorhombic	Pnma	1288.1	693.5	1267.2	-	163
$NaNp_2F_9$	orthorhombic	Pnma	861.7	1127.4	695.5	-	164
β-$RbLu_3F_{10}$	orthorhombic	Acam	1601.3	1318.2	843.5	-	165

K_2MF_4 (M=Mn,Co,Ni)*	tetragonal	K_2NiF_4	417.4	-	1327.2	-	166
Li_2NiF_5	monoclinic		978.8	488.6	996.6	135.6	167
Na_2NiF_5	monoclinic		756.4	568.6	537.8	92.3	167
K_2ErF_5	orthorhombic	$Pna2_1$	659.2	722.1	1076.4	-	168
M_2PtF_6 (M=Rb,Cs)*	tetragonal	-	596.3	-	480.4	-	169
Cs_2MI_6 (M=Ti,Zr,Hf,Pd,Pt)*	cubic	K_2PtCl_6	1147.3	-	-	-	170
Cs_2UCl_7	monoclinic	K_2NbF_7	756	1595	1017	90°	171
K_3UCl_8	cubic	-	1112	-	-	-	171
Cs_3UCl_8	tetragonal	-	1127	-	1180	-	171
$K_3M_2F_7$ (M=Mn,Co,Ni)*	tetragonal	$Sr_3Ti_2O_7$	418.7	-	2158.6	-	166
$Rb_2Mn_2F_7$	tetragonal	$Sr_3Ti_2O_7$	537	-	2780	-	172

* The crystallographic data refer to the element listed first.

† Isomorphous tantalum compounds have also been synthesised.

have shown that, over the composition range $0.45 \leqslant x \leqslant 0.52$, M_xVF_3 (M = Rb,Cs) adopt the modified pyrochlore structure. Although optical and magnetic analyses provide evidence for two distinct structures (cubic and orthorhombic) in each system, X-ray studies have only confirmed the existence of orthorhombic Rb_xVF_3 and both Cs_xVF_3 structures. The orthorhombic phase is thought to be an ionically (electronically) ordered structure composed of linear chains of V^{2+} ions orthogonal to linear chains of V^{3+} ions. The arrangement of the cations in this structure is shown in Figure 2 together with those in the disordered (random) modified pyrochlore, pyrochlore and fluorite structures from which it is derived; the anions are located in all the tetrahedral holes of the fluorite cationic structure.[156]

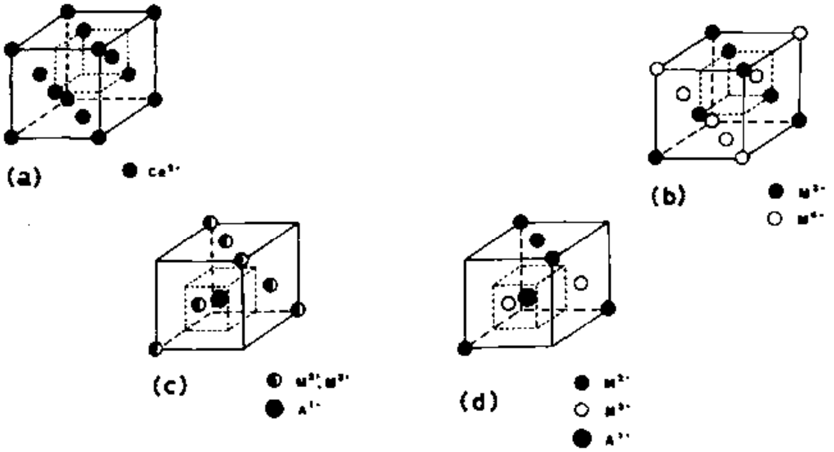


Figure 2. Cationic arrangements in (a) fluorite, CaF_2 (entire unit cell), (b) pyrochlore, $M_2^{III}M_2^{IV}O_7$, showing ionic ordering of M^{3+} and M^{4+} (1/8 unit cell), (c) modified pyrochlore, $AM^{II}M^{III}F_6$, showing random locations of M^{2+} and M^{3+} (1/8 unit cell) and (d) modified pyrochlore, $A_xM^{II}M^{III}F_6$, showing ionic ordering of M^{2+} and M^{3+} (1/8 unit cell) (reproduced by permission from Inorg. Chem., 21(1982) 3898).

The anharmonic vibration of Cu^{2+} ions in Jahn-Teller distorted $KCuF_3$ crystals and its effect on electron density distribution has been described;[176] the X-ray diffraction intensity data on which the analysis was based were published earlier.[177]

The magnetic and structural properties of $KFeBr_3$ have been determined as a function of temperature ($4.2 \leqslant T/K \leqslant 298$).[157] Although paramagnetic at 298K it becomes magnetically ordered at $T_N \sim 9.5$K. At 4.2K the magnetic structure consists of antiferromagnetically coupled ferromagnetic chains parallel to the b axis.

Chemical interaction with the formation of M_2UCl_6 (M = K,Rb,Cs) has been observed in the corresponding MCl-$MUCl_6$ systems;[171] thermally unstable M_2UCl_7 (M = Cs) and M_3UCl_8 (M = K,Cs) have also been observed as intermediate products. Similar behaviour is not observed in the analogous sodium system.[171] Structural[171] and thermochemical[178] data for K_3UCl_8, Cs_3UCl_8 and Cs_2UCl_7 are included in Tables 9 and 10, respectively.

Thermodynamic functions for the formation of Na_2CdCl_4, $Na_{0.77}CdCl_{2.77}$ (which only exists for $T > 609$K) and Na_6CdCl_8 from the constituent binary chlorides have been derived from e.m.f. studies of the appropriate solid state reactions;[179] pertinent data are collected in Table 10.

Table 10. Thermodynamic functions for the formation of a number of ternary chlorides from the binary chlorides.

Compound	T/K	$\Delta G^{o}(X,c,T/K)$ / kJ mol^{-1}	$\Delta H^{o}(X,c,T/K)$ / kJ mol^{-1}	$\Delta S^{o}(X,c,T/K)$ / J.K^{-1}.mol^{-1}	Ref.
K_3UCl_8	298	-	-36.4	-	178
Cs_3UCl_8	298	-	-180.7	-	178
Cs_2UCl_7	298	-	-99.2	-	178
Na_2CdCl_4	578	-5.9±0.2	-1.7±0.2	7.3±0.4	179
$Na_{0.77}CdCl_{2.77}$	623	-3.7±0.6	4.8±0.5	-11.8±0.8	179
Na_6CdCl_8	623	-0.23±0.12	0	0	179

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

As for the 1981 Review,[180] this section is simplified by incorporation of subdivisions for specialised topics (eg., acyclic polyether, crown and cryptate complexes, salts of nucleotides and carboxylic acids) currently of interest in bioinorganic chemistry.

Subdivisions for the individual alkali metals are also included; for these, data pertinent to several alkali metals are discussed once only, in the subdivision for the lightest element concerned.

1.5.1 Acyclic Polyether Complexes

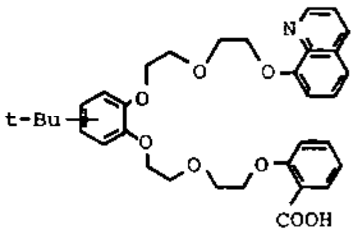
The evolution of acyclic and cyclic multifunctional ligands has been traced.[181] The formation of metal complexes and their application as bioinorganic models is noted; minor reference to alkali metal and alkaline earth metal complexes is given.

The solubilisation of $KMnO_4$ by various acyclic and cyclic polyethers in organic solvents has been investigated.[182] In general acyclic polyethers are less effective than cyclic polyethers of comparable molecular weight; each mole of 18C6 is capable of solubilising one mole of $KMnO_4$ in most solvents, whereas dimethylpentaethylene glycol (the corresponding linear polymer) is much less effective, particularly in solvents of low polarity.[182]

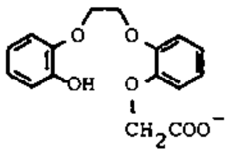
The transport of alkali metal cations, using the pentaethylene glycol derivative (26), across a chloroform liquid membrane system from an aqueous alkaline solution to an aqueous acidic solution has been investigated;[183] the cation selectivity of (26) varies in the sequence:

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

Single crystal X-ray diffraction studies have been undertaken on a small number of novel materials containing acyclic polyether derivatives.[184-186] The Sr^{2+} cation in the 1:1 complex between hexaethylene glycol and $Sr(NCS)_2$ is coordinated by the seven oxygen atoms of the acyclic polyether, $r(Sr...O) = 260.3\text{-}275.0pm$, and by two nitrogen atoms of SCN^- anions, $r(Sr...N) = 262.8, 263.4$ pm in an ill-defined geometry.[184]



(26)



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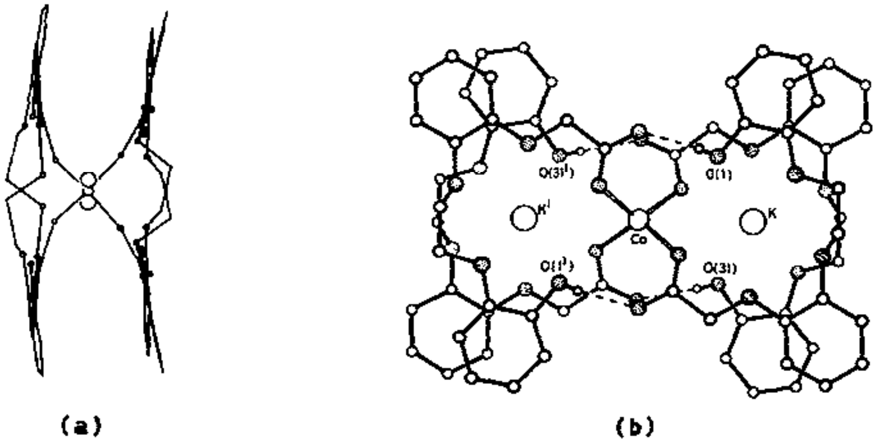
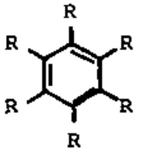
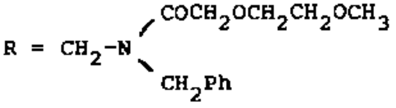


Figure 3. The molecular structure of $[Co[(\underline{27})_2K]_2]$ viewed down the a and b axes (reproduced by permission from J. Chem. Soc., Dalton Trans., (1982)1239).

The structure of a novel neutral trinuclear K-Co-K complex, $[Co[(\underline{27})_2K]_2]$ in which the K^+ cations are each coordinated by two acyclic polyether ligands ($\underline{27}$) has been described.[185] Views of the molecular structure down the a and b axes are shown in Figure 3. Each of the four ligands in the complex is bound to the central Co atom through the carboxylate group, r(Co...O) = 195.5 pm. The K^+ ions lie sandwiched between two ligands, interacting with five oxygen atoms from each ligand, r(K...O) = 270.5-293.1pm, in an approximately pentagonal antiprismatic arrangement.[185]

Two crystallographically distinct K^+ ions occur in the $3KSCN.H_2O$ complex of hexakis-[N-benzyl-(2-methoxyethoxy)acetamidomethyl]-benzene ($\underline{28}$).[186] The first, located in a general position in the unit cell is coordinated to four ether oxygens, r(K...O) = 270-308 pm, and two carbonyl oxygens, r(K...O) = 276, 284 pm, belonging





$$R = CH_2{-}N\begin{cases} COCH_2OCH_2CH_2OCH_3 \\ CH_2Ph \end{cases}$$

($\underline{28}$)

to non-equivalent 'legs' of adjacent host molecules as well as the nitrogen atom of a SCN^- anion, r(K...N) = 303pm. The second located on a two-fold rotation axis, is situated between two equivalent host molecules. Unfortunately, severe disorder of the two equivalent 2-methoxyethoxy units involved in coordination does not permit a critical assessment of the coordination geometry.[186]

1.5.2 Crown Complexes

Since interest in alkali and alkaline earth metal complexes of crown and related macrocyclic ligands has been maintained at the level of the 1981 Review, this topic has again been divided into two subsections in which complexes formed by 'classical' crown compounds and by novel macrocyclic ligands of unusual design are considered.

Dye[187] has reported the synthesis of a compound of stoichiometry, 18C6.Cs, by reaction of equimolar amounts of Cs, Li and 18C6 in methylamine in a fused silica apparatus; crystallisation was effected from an equimolar mixture of isopropylamine and diethyl ether after evaporation of the original solution to near dryness. The dark blue crystals are stable in vacuo for days at room temperature and below; they melt at ~338K to yield an unstable deep blue liquid. Their optical, magnetic and electrical properties suggest that it is an electride, $[18C6.Cs^+].e^-$, although the ceside, $[(18C6)_2.Cs^+].Cs^-$, cannot be ruled out.[187]

Single crystal X-ray diffraction studies have been completed on $[(12C4)_2.Na]^+.ClO_4^-$,[188] $[15C5.Na]^+.(CH_3COCHCOOC_2H_5)^-$,[189] $[18C6.Li.(H_2O)_2]^+.ClO_4^-$,[190] and $[18C6.Li_2.(H_2O)_2]^{2+}$,$2SCN^-$.[190] The coordination geometry of the cation is different in all four compounds. In $[(12C4)_2.Na]^+.ClO_4$, the Na^+ cation is sandwiched between the two 12C4 rings; its 8-fold coordination geometry can be described as slightly distorted square antiprismatic with r(Na...O) = 247.4-254.3pm.[188] The Na^+ cation in $[15C5.Na]^+.(CH_3COCHCOOC_2H_5)^-$, is similarly located between the 15C5 ring and the enolate anion; it lies 105pm above the mean plane of the heteroatoms of the 15C5 ring. The irregular 7-fold coordination geometry is provided by the five ether oxygens of the ring, r(Na...O) = 242-256pm, and the two carbonyl oxygens of the enolate anion, r(Na...O) = 230, 232pm.[189] In $[18C6.Li.(H_2O)_2]^+.ClO_4^-$ and $[18C6.Li_2.(H_2O)_2]^{2+}.2SCN^-$ the 18C6 ring, which is too large for the small Li^+ ion is effectively narrowed by encapsulated water molecules thereby creating the approximately tetrahedral coordination geometries preferred by the Li^+ ion. The Li^+ cation in the perchlorate complex is surrounded by two ether oxygens, r(Li...O) = 207.0, 212.4pm and two water oxygens, r(Li...O) = 190.6, 192.2pm. The two Li^+ cations in the thiocyanate complex are crystallographically distinct; one is similarly coordinated to that in the perchlorate complex by two ether oxygens r(Li...O) = 199.5, 207.3pm and two water oxygens 189.9, 196.6pm, whereas the other is coordinated by one ether oxygen, r(Li...O) = 199.1pm, one water oxygen, r(Li...O) = 199.6pm and two nitrogen atoms from thiocyanate anions, r(Li...N) = 199.8, 201.1pm.[190]

A series of alkali metal cation-TCNQ complexes with crown ethers, cryptands and polyethylene glycol derivatives have been isolated.[191] Similar alkline earth metal cation-TCNQ complexes with crown ethers have been isolated.[192] They are classified into various groups depending on their electrical resistivities and electronic reflection spectroscopic properties.[191,192]

Field desorption mass spectroscopic studies[193] of a series of three macrocyclic and two macrobicyclic polyether complexes of K^+ cations have been undertaken. Whereas the B15C5 ligand gave the $[(B15C5)_2K]^+$ sandwich ion and the DB24C8 gave the $[DB24C8.K]^+$ ion, the 18C6 ligand seemed to yield spectra corresponding to KCNS alone. The two macrobicyclic ligands gave spectra consistent with 1:1 complexes (cf. the $[DB24C8.K]^+$ ion). Chemical ionisation desorption mass spectra with NH_3 as carrier gave $[L.NH_4]^+$ as the most abundant ion for all five ligands (L); B15C5 also gave some $[(B15C5)_2.NH_4]^+$. Similar spectra with CH_4 as carrier gave more extensive fragmentation although the parent $[L.H]^+$ ion was in fair abundance.[193]

The complex $[DB18C6.K]^+{}_3[Co(CN)_5]$ has been prepared and its electronic, i.r. and e.p.r. spectra determined.[194]

A molecular mechanics study of different conformations of alkali metal complexes of 18C6 has been effected;[195] a simple model based on a primarily electrostatic M^+...crown interaction was employed. The lowest energy conformations calculated for $[18C6.Na]^+$ and $[18C6.K]^+$ had C_1 and D_{3d} symmetry, respectively, as observed in the solid state. Calculations on solution conformations show that although $[18C6.K]^+$ is intrinsically less stable than $[18C6.Na]^+$, it has a more negative formation energy in aqueous solution due to the much greater hydration energy of Na^+ vis-à-vis that of K^+.[195]

Solvent extraction processes involving alkali metal salts in the presence of crown ethers have been investigated by four independent groups of authors.[196-199] The distribution of potassium picrate between aqueous KCl solutions and 57 organic solvents has been studied[196] in the presence and absence of 18C6. Although 18C6 markedly enhances (upto a factor of $x10^3$) extraction into halogenated hydrocarbon solvents it has little effect for oxygenated solvents.[196]

Extraction of alkali metal cations from aqueous solutions into $CHCl_3$ containing both DB18C6 and an anionic azo dye (Tropeoline OO or Methyl Orange) occurs via formation of $[DB18C6.M]^+X^-$ (X = anionic azo dye);[197] for Cs^+, $[(DB18C6)_2.Cs]^+X^-$ is also formed. Similar $[DB18C6.K]^+X^-$ complexes have been prepared in the presence of the anionic sulphonephthalein dyes (Bromothymol Blue and Bromocresol Green).[200]

The effect of salting out agents on the extraction of alkali metal cations from aqueous solutions into 25% benzene/75% 2-ethylhexanol containing DCH18C6 has been ascertained;[198] salts containing a common counteranion tend to increase the distribution coefficient (eg. KCl extraction in the presence of $MgCl_2$). The effect of different anions on the extraction of alkali metal cations from aqueous solutions into m-cresol containing DCH18C6 has also been studied;[198] for potassium halides the distribution coefficient decreases in the sequence:

$$F > I > Br \sim Cl$$

The selectivity of DCH18C6 for extraction of alkali metal salts from aqueous solutions containing mineral acids (HNO_3, HCl, $HClO_4$) into 1,2-dichloroethane is independent of both the identity of the acid and the pH of the solution;[199] indeed, it is the same as that which is characteristic of neutral and alkaline solutions, viz:

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

The stabilities of diverse crown complexes have been established by a variety of techniques.[201-204] 1:1 Complexes of $LiBPh_4$ with DB18C6 (or triphenylphosphine oxide, TPPO) have been prepared in 1,2-dichloroethane solutions containing stoichiometric amounts of reactants. Similar 1:1 complexes were formed[201] from stoichiometric amounts of lithium picrate and TPPO, glyme-4 or glyme-5; sodium picrate, however, requires at least a 10-fold excess of TPPO or glyme-5 to form 1:1 complexes in 1.2-dichloroethane.[201] Conductance and spectrophotometric studies show that the 1:1 complexes dissociate to a very small extent and react with additional ligand to form 2:1 and 3:1 complexes.[201]

Formation constants[202] for 1:1 complexes of Na^+, K^+ or Ba^{2+} with 18C6 in methanol and methanol/water mixtures are approximately 3 or 4 orders of magnitude greater than those of the corresponding complexes formed by the acyclic analogue glyme-5. Formation constants[203] for 1:1 complexes of alkali metal cations with B15C5 in propylene carbonate decrease in the order:

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

Although this sequence is consistent with the 'size-fit concept', B15C5 shows poor selectivity.[203]

The validity of the 'size-fit concept' has been questioned by Michaux and Reisse[204] using thermodynamic parameters derived for the 1:1 and 1:2 complexation reactions of Na^+ and K^+ with 12C4, 15C5 and 18C6 in water and in methanol at 298K. The authors claim that these parameters are such that crown ring and cation sizes must be abandoned as predictors of the selectivity of crown ethers towards alkali metal cations in solution. For 18C6, an alternative quantitative interpretation in which the crown ether develops interactions that are stronger with Na^+ than with K^+ is proposed.[204]

The kinetics of the complexation of Sr^{2+} by DB18C6 in methanol at 258K have been elucidated using a stopped flow technique.[205] Normally, such a reaction is too fast to be studied by conventional stopped flow methods but the use of alkaline earth metal cations slows down the reaction as does use of the less flexible DB18C6.

Multinuclear n.m.r. (^{19}F and ^{39}K) studies[206] of solutions of $[18C6.K]^+F^-$ in various organic solvents belie the suggestion of the formation of 'naked' fluoride anions in the solvent. The fact that the ^{19}F n.m.r. line widths are essentially indistinguishable from those of solid KF suggests that the $[18C6.K]^+$ and F^- ions interact strongly forming tight ion pairs or possibly higher aggregates.[206]

Polymeric crown ethers, synthesised by condensation of polymer bound catechol and polyglycol dihalides, exhibit completely reversible, temperature dependent cation complexation;[207] it is suggested that these materials may be of use in, inter alia, water desalination processes and thermoregulated polymeric delivery systems for Na^+ and K^+. The selectivity of DB14C4, when incorporated in solvent polymeric membrane electrodes, for Li^+ cations (in the presence of M^+(M = Na-Cs) and M^{2+}(M = Mg-Sr)) has been assessed.[208] The crucial importance of the counteranion is noted; bulky, spherical, polarisable, monovalent anions enable the cation to interact more effectively with the ligand binding sites, generating a more selective and specific system.[208]

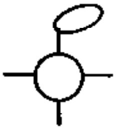
1.5.3 Complexes of Macrocyclic Polyethers of Novel Design

A large number of macrocyclic polyethers of novel design have been prepared and their complexation reactions with alkali and alkaline earth metal cations studied as part of the continuing quest for synthetic materials capable of selectively complexing these cations and transporting them across organic membranes and through concentration gradients. Complex formation has been identified both in solution[209-219] and in solid state structural studies.[220-226]

The complexing ability of a series of macrocycles based on porphyrins appended with between one and four B15C5 moieties at the methine positions ((29)-(33)) has been investigated using spectroscopic methods.[209] The larger cations (K^+, Ba^{2+}) which require two B15C5 cavities for complexation promote dimerisation of the porphyrins; the dimers exhibit axial symmetry with the planes separated by ~420pm. The smaller cations (Na^+, Mg^{2+}, Ca^{2+}) form simple 1:1 complexes with each of the appended B15C5 moieties.[209]

The interaction between alkali metal cations and three homologous series of bis(crown) schiff bases (34-36) has been studied using spectroscopic techniques.[210] 1:1 Pocket complexes of the type (37) were formed by bis(B15C5) ligands (35) with cations larger than Na^+, while similar complexes were formed by bis(B18C6) ligands (36) with cations larger than K^+; the bis(B12C4) ligands (34) did not complex strongly with any cation.[210]

Complexation of M^{2+}(M = Mg-Ba) by a series of crown ethers (12C4, (38), (39) DB30C10) in anhydrous propylene carbonate has been investigated by a competitive potentiometric method.[211] Whereas 12C4 forms 1:2 complexes with all M^{2+} ions, (38) forms 1:1 complexes with all M^{2+} ions and 1:2 complexes with Sr^{2+} and Ba^{2+}; the other two ligands (39) and DB30C10 only form 1:1 complexes.



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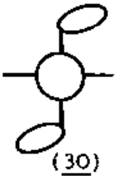

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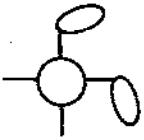

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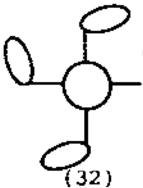

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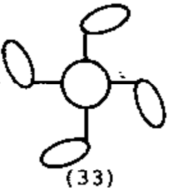

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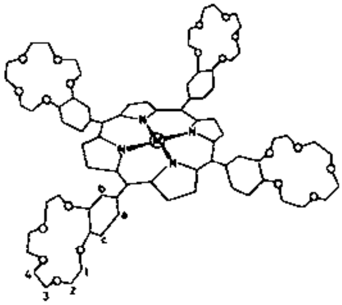

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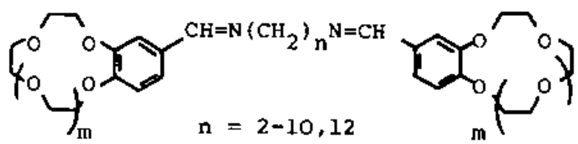
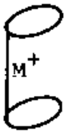


n = 2-10,12

(34) m=1

(35) m=2

(36) m=3



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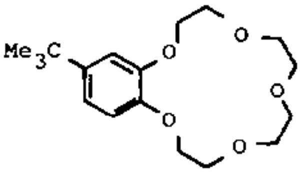

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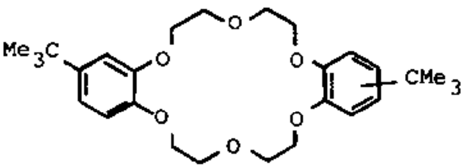

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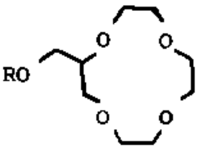
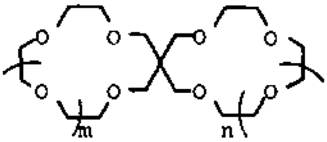


R = H-; $C_6H_5CH_2$-; C_8H_{17}-

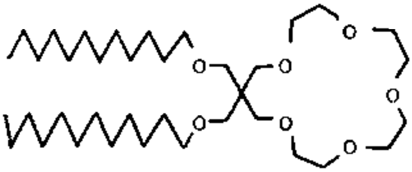
(40)



(41) m=4, n=6

(42) m=5, n=5

(43) m=6, n=6



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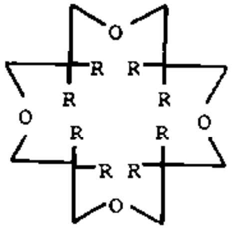
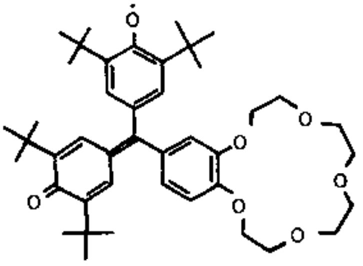


(45) R = H

(46) R = Me



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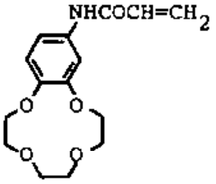

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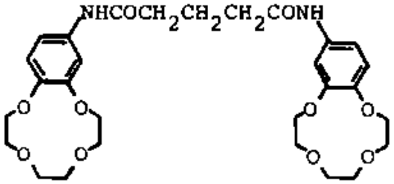

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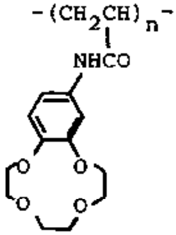

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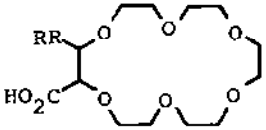
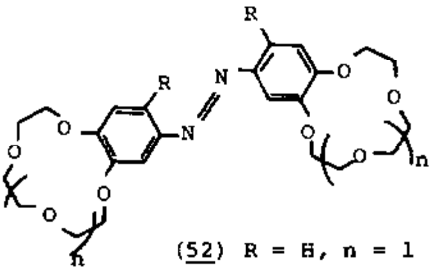


R = $CH_3(CH_2)_mNHCO$-

m = 1,3,7

(51)



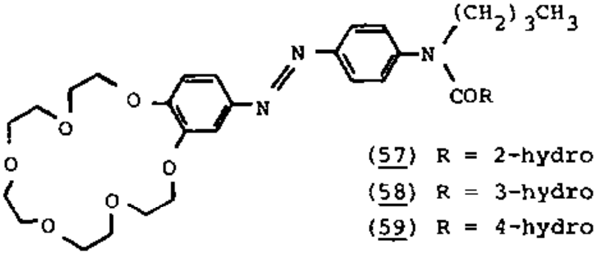
(52) R = H, n = 1

(53) R = H, n = 2

(54) R = H, n = 3

(55) R = t-Bu, n = 2

(56) R = t-Bu, n = 3



(57) R = 2-hydroxy-5-nitrophenyl
(58) R = 3-hydroxyphenyl
(59) R = 4-hydroxyphenyl

The relative stabilities of the various complexes are discussed in detail.[211] The stabilities of the 1:2 complexes formed by Na^+ with 12C4 and with various hydroxymethyl 12C4 derivatives (40) have also been ascertained;[212] they are compared with those of the corresponding 15C5 and hydroxymethyl 15C5 derivatives.

Complex formation between $NaClO_4$ and the spiro-bis-crown ethers (41-43) in pyridine solution has been studied by ^{23}Na n.m.r. spectroscopy.[213] With (42) and (43), both 1:1 and 2:1 complexes are formed corresponding to single and double occupation of the two equivalent binding sites offered by these dicoronands. With (41), however, only 1:1 complexes form since the 12C4 ring interacts but weakly with Na^+. Similar ^{23}Na n.m.r. studies[213] suggest the formation of a 1:1 complex between $NaClO_4$ and the surfactant-type crown ether (44). Single crystal X-ray diffraction studies[220] of the analogous $[(44)K]^+SCN^-$ complex have been undertaken. Analysis of the data indicates that the molecular geometry within the crown ether moiety closely resembles that in $[15C5.Na]^+SCN^-$; the Na^+ ion is coordinated by the five heteroatoms of the 16C5 ring, $r(Na...O)_{av}$ = 243pm, and by the nitrogen atom of the SCN^- anion, r(Na...N) = 233.4pm in a pseudo pentagonal pyramidal geometry.

Complexation of Li^+ by 16C4, (45) and its octamethyl derivative (46) has been investigated by multinuclear (^1H, ^{13}C, ^7Li) n.m.r. techniques;[214] the stoichiometry of the products is both solvent and counteranion dependent. Complex formation between alkali metal cations (Na^+, K^+, Rb^+) and the spin labelled crown ether (47) has been studied by e.s.r. techniques in solid ethanol matrices at 77K.[215] The existence of 2:1 complexes with K^+ and Rb^+ and of a 1:1 complex with Na^+ was confirmed; the spectra of the 2:1 complexes indicated a similar conformation of the ligand in both complexes. None of the counteranions used (Br^-, I^-, SCN^-) had any appreciable effect on the e.s.r. spectra of any of the complexes.[215]

Solvent extraction processes involving alkali metal complexes of novel macrocyclic ligands have been investigated by three groups of authors.[216-219] A comparative study of the ability of 12C4, (48), (49) and (50) to extract alkali metal picrates from aqueous solution into $CHCl_3$ has been undertaken.[216] The distribution coefficients for (49) decrease in the sequence:

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

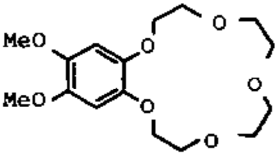
Similarly for (50) they decrease in the order:

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

The improved Na^+ selectivity of (50) over (49) is due to the easy formation of 2:1 complexes by the cooperative action of two adjacent crown ether units.[216] The extraction of K^+ from aqueous alkaline solutions into $CHCl_3$ in the presence of a crown ether with a carboxylic acid functional group (51) has been investigated as a function of a number of variables.[217] A mechanism involving rate limiting adsorption of carrier or desorption of complex at the water-chloroform interface, depending on experimental conditions, is shown to be consistent with available data.

Shinkai, Manabe et al[218,219] have extended their studies of alkali and alkaline earth metal extraction processes using photoresponsive crown ethers. They have assessed[218] the efficacy of the five photoresponsive azobis(benzocrown ether)s, (52-56) in promoting the extraction of Rb^+ and Cs^+ from aqueous solution into 1,2-dichlorobenzene. The results suggest that the cavity size of the cis conformation of the non-substituted derivatives decreases from (54) through (53) to (52) and that these cavities are much larger than those of (55) and (56), the tert-butyl substituted derivatives, probably owing to the steric repulsion of the tert-butyl groups. The most effective extractants for Rb^+ and Cs^+ were (53) and (54), respectively. They also noted that Rb^+ and Cs^+ maximise the concentration of the cis isomers and minimise the rate of thermal cis-trans isomerisation for (53) and (54), respectively.[218] These authors[219] have also synthesised three photoresponsive ionophores (57)-(59) and studied their effect on the extraction of M^+(M = Na-Cs) and M^{2+}(M = Ca-Ba) cations from water into 1,2-dichlorobenzene. In general, the extraction process was enhanced by U.V. irradiation; in particular, the cis conformation of (57) exhibited markedly improved extractabilities for Na^+ and Ca^{2+}. The results suggest that the enhanced extractability is due to the formation of an intramolecular $PhO^-...M^+...$crown sandwich type complex.[219] The effect of U.V. irradiation on Na^+ and Ca^{2+} transport through a liquid membrane (1,2-dichloromethane/n-butanol; 90/10) in the presence of (57) to (59) has also been elucidated by these authors;[219] distinct rate enhancement was observed.

Structural studies have been undertaken on several complexes containing novel macrocyclic polyether ligands; these include $[(60).Na]^+.Br^-$,[221] $[(61).K]^+.NCS^-$,[222] $[(62).K]^+.NCS^-$,[223] $[(63).K]^+ClO_4^-$,[224] $[(64)_2K]^+.NCS^-$,[225] and $[(68).Sr]^{2+}.2ClO_4^-$.[226]



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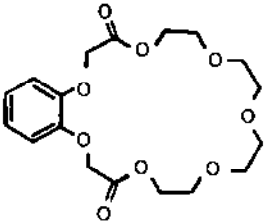

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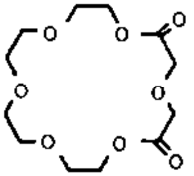

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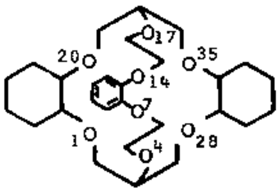

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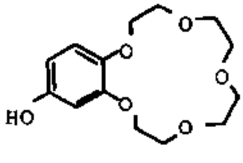

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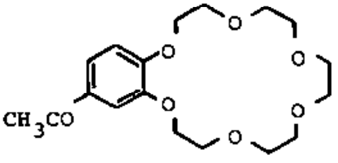


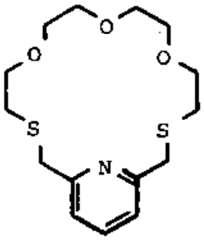
(65)

The coordination sphere of the Na^+ ion in $[(60).Na]^+.Br^-$ is composed of the five heteroatoms of the B15C5 ring, r(Na...O) = 236.5-245.2pm, and the bromide anion, r(Na...Br) = 276.3pm in a pseudo pentagonal based pyramidal geometry; the Na^+ ion is located 86pm above the plane of the heteratoms of the ring.[221]

The four potassium complexes[222-225] contain widely differing K^+ coordination spheres. The K^+ ion in $[(61).K]^+NCS^-$ is situated at the centre of the heteroatoms of the 18C6 ring, $r(K...O)_{av}$ = 275pm, and is also coordinated to two thiocyanate anions, one on either side of the ring. Disorder in the anion is such that there are two sets of positions with population factors of ~75% (Set A) and ~25% (Set B), with r(K...N(A)) = 287.3, r(K...N(B')) = 293.9, r(K...S(A')) = 335.5, r(K...S(B)) = 312.4pm. In $[(62).K]^+NCS^-$, the K^+ ion lies at the centre of the plane of the heteratoms of the B21C7 ring, r(K...O) = 276.9-307.1pm; its coordination sphere is completed by the nitrogen atom of the NCS^- anion, r(K...N) = 279.5pm. The wide range of K-O distances is thought to reflect a relatively weak host-guest interaction.[223] The environment of the K^+ ion in $[(63).K]^+ClO_4^-$ is complex; it constitutes nine oxygen atoms. The cation is approximately coplanar with O(1), O(4), O(7), O(14), O(17) and O(20) of the macrobicyclic polyether, r(K...O) = 267.0-285.3pm; its coordination geometry is completed on one side by a perchlorate oxygen, r(K...O) = 292.2pm, and on the other side by two oxygen atoms on a cyclohexane ring (O(28) and O(35)), r(K...O) = 281.6, 314.5pm.[224] Two crystallographically distinct K^+ ions occur in $[(64)_2K]^+NCS^-$. They are both located between pairs of B15C5 rings, r(K(1)...O) = 282-299 pm, r(K(2)...O) = 276-309 pm; the SCN^- anions do not feature in the K^+ coordination sphere.[225]

A detailed discussion of the structure of $[(65)Sr]^{2+}2ClO_4$ is precluded by a combination of poor crystal quality and crystallographic problems.[226] Several features may be noted, however. Two crystallographically distinct Sr^{2+} cations occur in the structure; their 8-fold geometry is similar and is composed of the six heteroatoms of the B18C6 ring, r(Sr...O) = 261-278 pm and two perchlorate oxygens, r(Sr...O) = 255-272pm, on either side of the ring.[226]

The crystal and molecular structure of $[(66).Ba]^{2+}.2SCN^-$ and of $[(66)Cu]^{2+}2Cl^-$ have been derived from single crystal X-ray diffraction data.[227] The Ba^{2+} ion fits ideally into the centre



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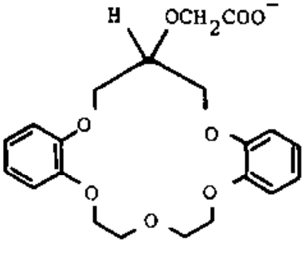
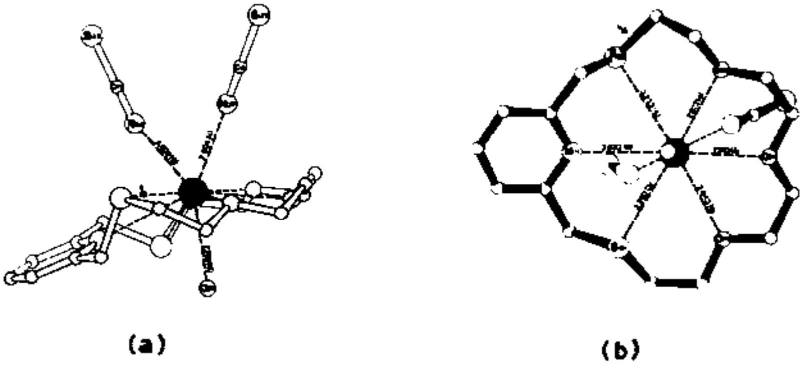


(67)

of the cavity of the macrocyclic ring (Figure 4) and is 9-fold coordinated to all six heteroatoms of the ligand, one water oxygen and two thiocyanate nitrogens; pertinent interatomic distances are shown in Figure 4. In the corresponding copper(II) complex $[(\underline{66})Cu]^{2+}2Cl^-$, however, the ligand adopts a puckered geometry in which only the three adjacent S N S heteroatoms of the ligand coordinate the cation. The square pyramidal coordination geometry of the Cu^{2+} ion is completed by the two chlorine anions; the oxygen atoms of the ligand are not involved in transition metal



(a) (b)

Figure 4. Perspective view of $[(\underline{66})Ba]^{2+}.2SCN^-$ (reproduced by permission from Inorg. Chim. Acta, 58(1982)27).

coordination.[227]

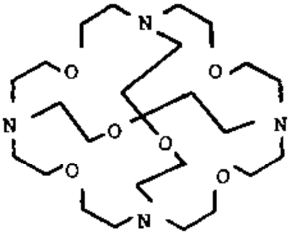
A mixed complex of cobalt(III) and sodium with (<u>67</u>) as a ligand, $[(NH_3)_5Co(\underline{67})Na]^{3+}.3ClO_4^-.2H_2O$, has been prepared by reaction of $[(\underline{67})Na]$ with $[(NH_3)_5Co(DMSO)](ClO_4)_3.2H_2O$ in acetone.[228] After partial removal of solvent, chloroform was added and the resultant solution saturated with $NaClO_4,H_2O$. The product was isolated by filtration after overnight storage at 258K; it is thought to have the formulation:

$$\left[(NH_3)_5Co^{III}O\cdot CO\cdot CH_2O\text{–}\enclose{circle}{Na^+}\right]^{3-}\ 3ClO_4^-.2H_2O$$

1.5.4 Cryptates and Related Complexes

The fascinating observations of the formation of naked anionic clusters by reaction of Zintl-type phases with C222 in dry ethylenediamine at room temperature, first reported in the 1981 Review, has been pursued further.[229-231] Reaction of KTlSn[229] leads to $[C222K]_3^+.(TlSn_9^{3-},TlSn_8^{3-})_{\frac{1}{2}}en$, a compound which contains thallium nonastannide and thallium octastannide in a novel 50:50 occupational structural disorder of a single anionic site. The conformation of the $[C222.K]^+$ cations is similar to those in the $[C222.K]^+$ salts of $(Tl_2Te_2)^{2-}$, $(HgTe_2)^{2-}$ and $(Te_3)^{2-}$ and as such is unremarkable.[229] Reaction of barium metal/selenium powder mixtures[230] or dissolution of $Ba_4Sb_4Se_{11}$[231] affords the complexes $[Ba(en)_4]^{2+},Se_4^{2-},en$ and $[Ba(en)_4]^{2+}(SbSe_2)_2^-$, respectively. The structures of the complexes are characterised by $[Ba(en)_4]^{2+}$ cationic moieties, Se_4^{2-} or $(SbSe_2)^-$ chain anions and in the case of the former product, ethylenediamine solvate molecules. The Ba^{2+} coordination polyhedron in the former complex is a loosely packed tetragonal prismatic arrangement, r(Ba...N) = 279.0-281.6 pm;[230] that in the latter complex is composed of a similar arrangement of four ethylenediamine molecules, r(Ba...N) = 287.9-299.7 pm with an additional coordination position occupied by a selenium atom, r(Ba...Se) = 356.9 pm.[231]

Spectroscopic studies of solutions formed by addition of alkali metals, (Na-Cs) to thf, dioxane and toluene containing the cryptands C221, C222 and (<u>68</u>) have been undertaken.[232] Although the formation of M^- and e^-_{solv} has been confirmed for all alkali metals in thf solutions, in dioxane solutions only the M^- absorption is observed; in toluene solutions, only sodium gives rise to the M^- anion.[232]



(68)

Cryptand exchange kinetics involving calcium cryptates have been ascertained using a stopped flow apparatus with optical detection.[233] The observed rate constants for replacement of either C222 or $C2_B22$ by C221 in water or aqueous methanol correspond to that of the dissolution of the original cryptate.[233]

1.5.5 Salts of Carboxylic Acids

The majority of the papers abstracted for this subsection report the results of structural studies.[234-241] The structure of sodium formate has been the subject of yet another investigation[234] and that of sodium phthalate hydrate (1/3.5) has been determined for the first time.[235] Electron density difference maps have been derived[234] from low temperature (120K) neutron and X-ray diffraction studies on sodium formate crystals and compared with theoretical deformation density maps based on 4-31G + BP SCF calculations. The agreement between the experimental and theoretical results is reasonable. The Na^+ cation in NaHCOO is approximately octahedrally coordinated by six oxygen atoms from one bidentate and four monodentate formate anions with r(Na...O) = 238.6-249.2 pm.[234] Sodium phthalate hydrate (1/3.5) contains four crystallographically distinct Na^+ polyhedra.[235] They are all six coordinate with distorted octahedral geometry. The nearest neighbour environment of the Na^+ ions includes from two to four anion oxygen atoms and is made up to six by water oxygen atoms; r(Na...O) values vary from 232 to 276 pm.

The crystal and molecular structures of three potassium salts have been reported; whereas that of potassium trihydrogen dioxolate dihydrate (potassium tetraoxalate)[236] is a redetermination, those of potassium hydrogen bis(p-fluorobenzoate)[237] and potassium hydrogen furan-2,5-dicarboxylic acid[238] are novel. The triclinic structure of potassium trihydrogen dioxalate dihydrate has been redetermined[236] to resolve the dichotomy between the early structure published by Haas[242] (refined in $P\bar{1}$) and the recent structure reported by Emsley et al[243] (refined in $P1$); the present results confirm and amplify Haas's work showing his centrosymmetric $P\bar{1}$ structure to be essentially correct. The K^+ coordination sphere in potassium hydrogen bis(p-fluorobenzoate)[237] is effectively a highly distorted octahedron, the six oxygen atoms being provided by six anions with $r(K...O)_{av}$ = 278 pm. That in the furan derivative,[238] however, is a seven coordinate distorted monocapped octahedal structure, the seven oxygen atoms being provided by six different anions with $r(K...O)_{av}$ = 282.7 pm.

Structural analysis of the KF adducts of succinic acid[239] and malonic acid[240] has been carried out as part of a study of hydrogen bonding in fluorine containing species. Both compounds contain polymeric chains composed of alternate acid molecules and fluoride anions joined by very short bonds, $r(O...F) \approx 244$ pm; although there is only one chain type in the succinic acid adduct, five chains can be distinguished in the malonic acid adduct. The K^+ ion in the former is six-coordinate (two fluorine atoms, $r(K...F)$ = 268.4, 287.4 pm, and four carbonyl oxygen atoms, $r(K...O)$ = 281.8, 284.3 pm), whereas those in the latter (there are five crystallographically distinct K^+ ions) are eight-coordinate (two fluorine atoms and six carbonyl oxygen atoms all within 310 pm).

Spectroscopic studies (i.r., ^1H and ^{13}C n.m.r.)[241] of a series of mono potassium salts of cycloalkane 1:1 dicarboxylic acids have shown that whereas a strong almost symmetrical intramolecular hydrogen bond occurs in the cyclopropane 1:1 dicarboxylic acid salt, an asymmetrical hydrogen bond occurs in the corresponding cyclobutane and cyclopentane salts.

The synthesis of potassium phthalates has been studied in diverse solvents.[244] Crystallisation from aqueous solutions of phthalic acid ($H_2\Phi$) containing excess KOH yields $KH\Phi$ (equations (35) and (36)); crystallisation from ethanol under similar conditions gives $K_2\Phi$, $KH\Phi$ (equations (35),(36) and (37)). A reaction mechanism based on a tetrameric structure for phthalic acid is proposed.

$$\tfrac{1}{2}(H_2\Phi)_4 \; + \; KOH \xrightarrow{H_2O} KH\Phi.H_2\Phi \; + \; H_2O \qquad ...(35)$$

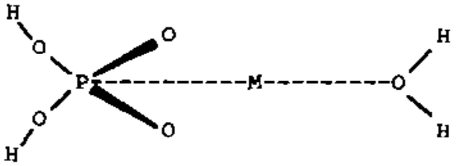
$$KH\Phi.H_2\Phi \; + \; KOH \xrightarrow{H_2O} (KH\Phi)_2 \; + \; 2H_2O \qquad ...(36)$$

$$(KH\Phi)_2 \; + \; KOH \xrightarrow{EtOH} K_2\Phi.KH\Phi \; + \; H_2O \qquad ...(37)$$

Thermal decomposition of $Li_2\Phi,1.5H_2O$, and $LiH\Phi,2H_2O$, when heated in air to 1275K has been studied by t.g.a. X-ray diffraction and chemical analysis.[245] $Li_2\Phi,1.5H_2O$ is thermally stable upto 333K; it then completely dehydrates in two stages via $Li_2\Phi,0.75H_2O$, with exothermic effects at 348 and 393K. The anhydrous normal phthalate is stable upto 613K; it then undergoes decomposition in four mass loss steps with exothermic effects at 698, 833, 953 and 1088K following the usual thermal decomposition scheme for alkali metal normal phthalates. $LiH\Phi,2H_2O$ is stable upto 338K; it then completely dehydrates in two stages, via $LiH\Phi,H_2O$ with exothermic effects at 358 and 393K. The anhydrous acid phthalate is thermally unstable and decomposes immediately after formation in two mass loss steps ($408 \leqslant T/K \leqslant 488$) to form the anhydrous normal phthalate. Subsequent decomposition is as described above.[245]

1.5.6 Salts of Nucleotides and Moieties of Biological Significance

Structural aspects of complex formation between alkali or alkaline earth metal cations and diverse nucleotides or related species have formed the subject matter of a number of recent publications.[246-253] Ab initio SCF studies[246] of interactions between Li^+, Na^+, Be^{2+} and Mg^{2+} with $H_2PO_4^-$ indicate that the most stable binding site for all cations is a symmetric C_{2v} complex with the metal cation interacting equally with two phosphate oxygen atoms (69). Significant electron transfer was found for all complexes except that for Na^+, inferring that Li^+, Be^{2+} and Mg^{2+} interactions with $H_2PO_4^-$ are not totally electrostatic. Hydration



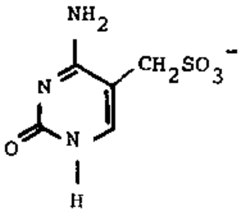
(69)

of neither Li^+ nor Be^{2+} significantly alters the covalency of the metal phosphate bond. The significance of these results to complex formation by nucleotides and related species is stressed.[246]

Single crystal X-ray diffraction studies of the monosodium salt of cyclic adenosine-3',5'-monophosphate (cAMP) tetrahydrate[247] and of the disodium salt of guanosine-5'-monophosphate (GMP) heptahydrate[248] have been undertaken. Both Na^+ ions in the asymmetric unit of the cAMP derivative exhibit six-fold coordination as do the four crystallographically distinct Na^+ ions in the structure of the GMP derivative; the coordination geometries vary from fairly regular to somewhat distorted octahedra as the extent of coordination by the nucleotide ligand increases. In the cAMP derivative,[247] Na(1) is coordinated to five water molecules and one cAMP oxygen atom, r(Na(1)...O) = 237.7-245.4 pm, whereas Na(2) is coordinated to three water molecules and three oxygen atoms of the cAMP molecule, r(Na(2)...O) = 235.4-273.4 pm. Two of the Na^+ ions in the GMP derivative[248] are completely hydrated, r(Na(2)...O) = 238.2-274.6 pm, r(Na(3)...O) = 232.8-261.1 pm, while the other two Na^+ ions are coordinated either by the N(7) atoms of independent GMP molecules, r(Na(1)...N(7)) = 241.5, 261.3 pm, or by the O(2') and O(3') atoms of the same GMP molecule, r(Na(4)...O(2')) = 249.2 pm, r(Na(4)...O(3')) = 230.5 pm; the other four coordination sites of both Na(1) and Na(3) are occupied by water molecules r(Na(1)...O) = 234.6-249.1 pm, r(Na(4)...O) = 228.1-280.3 pm.[248] Multinuclear (^1H, ^{13}C and ^{31}P) n.m.r. solution data[249] for the disodium salt of GMP are incompatible with previously proposed self association models of GMP which consist of stacks of planar hydrogen bonded tetramers or continuously hydrogen-bonded helices. Instead, at higher temperatures ($T > 303K$), the results are consistent with stacking of monomers, whereas at lower temperatures ($T < 303K$), they suggest the formation of asymmetric hydrogen bonded dimers. At even lower temperatures, a second incompletely characterised complex, possibly a stacked symmetric dimer, forms.[249]

Sodium complexes of three cytosine derivatives (70)-(72) and of one thymine derivative (73) have been the subject of structural studies. The sodium ions in Na(70),$3H_2O$,[250] Na(72),H_2O[251] and $2CH_3Hg$(73),$NaNO_3$[252] adopt distorted octahedral six-fold coordination geometries; that in Na(71),H_2O,[250] however, is located in a distorted square pyramidal five-fold coordination polyhedron.

The Na^+ coordination sphere in Na(70),$3H_2O$ is composed of one ketonic oxygen, r(Na...O) = 247.1 pm and two sulphonate oxygens,



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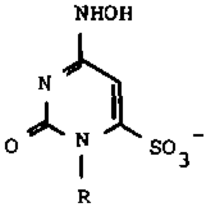
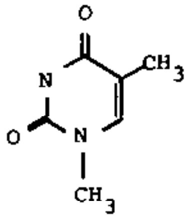


(71) R = H

(72) R = Me



(73)

r(Na...O) = 232.3, 239.1 pm from three separate anions and three water molecules, r(Na...O) = 234.4-265.2 pm.[250] In Na(71),H_2O, the Na^+ is surrounded by one ketonic oxygen, r(Na...O) = 238.2 pm and three sulphonate oxygens, r(Na...O) = 228.9-235.3 pm from four different anions and one water molecule, r(Na...O) = 245.1 pm;[251] in the corresponding methyl derivative, Na(72),H_2O, it is surrounded by one ketonic oxygen r(Na...O) = 244.0 pm, one sulphonate oxygen, r(Na...O) = 233.2 pm and one hydroxyl oxygen, r(Na...O) = 249.4 pm, from three different anions and three water molecules, r(Na...O) = 239.6-243.7 pm.[251] The Na^+ cation in $2CH_3Hg$(73),$NaNO_3$ occupies a centre of inversion; it is coordinated by four carbonyl oxygens, r(Na...O) = 232.4, 243.6 pm from two pairs of symmetry related thymine molecules and by two nitrate oxygens, r(Na...O) = 240.6 pm, from a pair of symmetry related anions.[252]

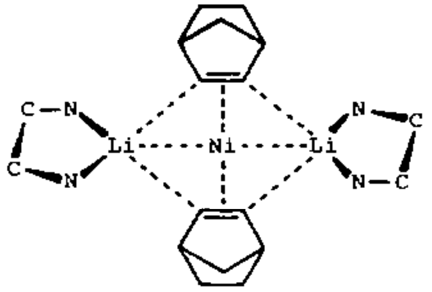
Crystal and molecular structures have been reported for diverse sodium complexes of the antibiotic representatives, monensin B,[253] carfecillin,[254] valinomycin[255] and enniatin B;[256] in all cases, the authors concentrate on the conformation of the organic moiety. In the sodium salt of monensin B monohydrate,[253] the anion totally encapsulates the Na^+ cation providing a six-fold coordination sphere of oxygen atoms, r(Na...O) = 233-247 pm. In the other three complexes, the Na^+ cation is external to the organic moiety; that in the sodium salt of carfecillin is coordinated by carboxylate oxygens with r(Na...O) lying in the range 233.4-241.0 pm. In the valinomycin-sodium picrate-monohydrate complex,[255] the Na^+ ion is bonded to three carbonyl oxygen atoms of a single valinomycin molecule, r(Na...O) = 233-254 pm, to two oxygen atoms of a picrate anion, r(Na...O) = 237, 264 pm and to a water molecule r(Na...O) = 233 pm. By comparison with the corresponding valinomycin-potassium picrate complex, the Na^+ ion is more weakly bound to valinomycin and more strongly bound to picrate. The structure of the enniatin B sodium nitrate, nickel nitrate, sesquimethanol solvate, trihydrate complex contains two crystallographically independent Na^+ ions one of which is octahedrally surrounded by six solvate molecules, $r(Na(1)...O)_{av}$ = 250 pm, the other of which has a trigonal prismatic coordination sphere comprising six oxygen atoms from three solvate molecules, $r(Na(2)...O)_{av}$ = 291 pm and three carbonyl oxygen atoms from a single enniatin B molecule, $r(Na(2)...O)_{av}$ = 308 pm. The large discrepancy in bond distances between the two Na^+ coordination spheres is attributed to the overall geometry of the surrounding solvate molecules.

Multinuclear n.m.r. techniques have been used to study complexation in aqueous solution between Li^+ and D,L-noradrenaline[257] and between Li^+, Na^+ or K^+ and the cyclic pentapeptide, cyclo(Pro-Phe-Gly-Phe-Gly) (74) or the corresponding cyclic decapeptide with dimer sequence (75).[258] Although complex formation between Li^+ and D,L-noradrenaline was not detected,[257] selective complexation of Li^+ by (74) and of K^+ by (75) was observed;[258] the conformational changes occuring during complex formation are discussed.[258]

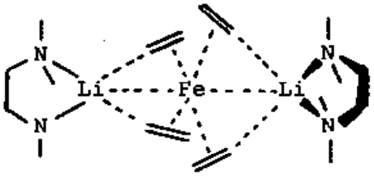
1.5.7 Lithium Derivatives

Although there are a vast number of publications dealing with lithium chemistry, those abstracted for this review are relatively few in number, the majority of the papers being ignored since they consider some aspect of the organometallic chemistry of lithium which is reviewed in detail elsewhere.[2]

The structural chemistry of lithium-containing moieties such as $[Li(tmeda)]^+$ and $[Li(pmdeta)]^+$ (tmeda = tetramethylethylenediamine; pmdeta = pentamethyldiethylenetriamine) has been elucidated both theoretically[259] and experimentally.[260-263] The electronic structures of transition metal-olefin complexes with lithium containing moieties have been investigated using semi-empirical MO calculations of the INDO-type.[259] Various bonding interactions derived in detail for structure fragments are extended to the more complex organometallics such as (76) and (77). Each lithium centre exhibits a roughly tetrahedral (76) or five-fold (77)



(<u>76</u>)



(<u>77</u>)

coordination; strong covalent bonding between Li and N on one side and between Li and C on the other is caused by transfer of electron density from the diamine ligand via Li to the π-acceptor orbital of the olefinic ligand.[259]

Structural studies have been effected for three complexes containing the $\{Li(tmeda)\}^+$ moiety, $[\{C_6H_4C_6H_4\}\{Li(tmeda)\}]$ (<u>78</u>),[260] $[\{C_3H_5\}\{Li(tmeda)\}]$ (<u>79</u>),[261] and $[\{o\text{-}C_6H_4(CHSiMe_3)_2\}\{Li(tmeda)\}_2]$-(<u>80</u>),[262] and for one complex containing the $\{Li(pmdeta)\}^+$ moiety, $[\{CH(SiMe_3)_2\}\{Li(pmdeta)\}]$ (<u>81</u>).[263] The molecular structures of (<u>78</u>), (<u>80</u>) and of (<u>81</u>) are shown in Figure 5. The lithium atoms in the two former $\{Li(tmeda)\}^+$ derivatives have similar distorted tetrahedral coordination polyhedra. That in (<u>78</u>)[260] is generated by the two nitrogen atoms of the ethylenediamine, r(Li...N) = 211, 213 pm and the two C(2) carbon atoms of the biphenyl ligand, r(Li...C) = 212, 215 pm (Figure 5(a)), whereas that in (<u>79</u>)[261] is composed of the two nitrogen atoms of the ethylenediamine, r(Li...N) = 219 pm and the two terminal carbon atoms of adjacent allyl anions, r(Li...C) = 222, 230 pm, which form part of a polymeric $...C_3H_5[LiC_3H_5]_nLi...$ chain.[261] The structure of (<u>80</u>)[262] (Figure 5(b)) comprises two $\{Li(tmeda)\}^+$ moieties one each side of a planar o-xylidene moiety; each lithium atom is associated with four carbon atoms, the two α-carbon atoms, r(Li...C) = 234, 241 pm, and their adjacent aromatic carbon atoms, r(Li...C) = 232, 242 pm as well as the two nitrogen atoms of the ethylenediamine ligand, r(Li...N) = 210 pm. The coordination environment of the lithium atom in (<u>81</u>)[263] (Figure 5(c)) is essentially a distorted tetrahedron comprising the three nitrogen atoms of the diethylenetriamine moiety, r(Li...N) = 220-230 pm, and the α-carbon atom of the anion, r(Li...C) = 213 pm.

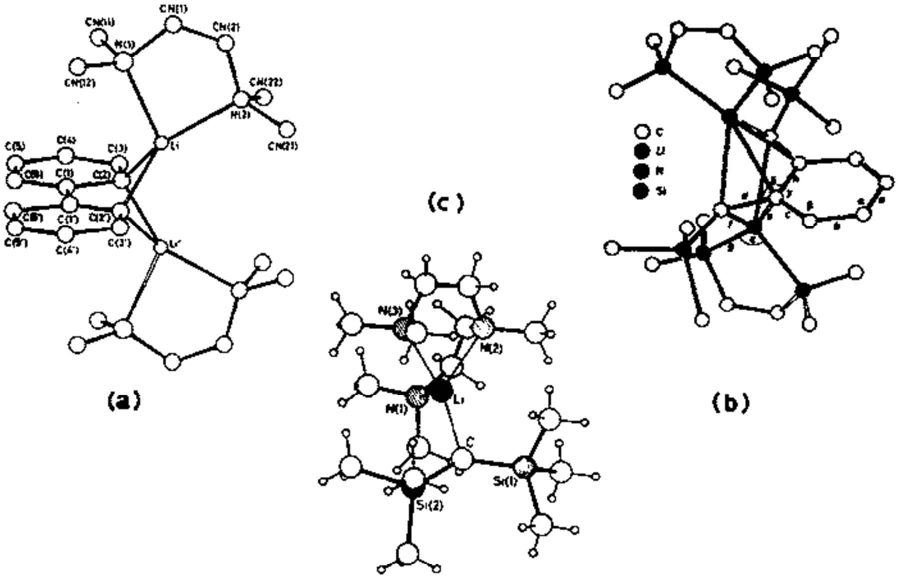
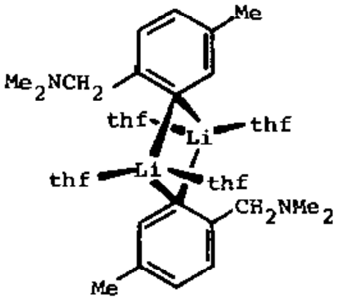
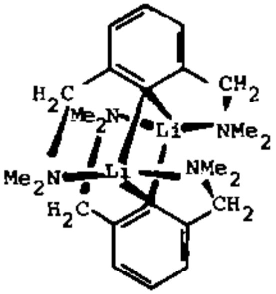


Figure 5. Molecular structures of (a) $[\{C_6H_4C_6H_4\}\{Li(tmeda)\}_2]$, (b) $[\{o\text{-}C_6H_4(CHSiMe_3)_2\}\{Li(tmeda)\}_2]$ and (c) $[\{CH(SiMe_3)_2\}\{Li(pmdeta)\}]$ showing the coordination of the $\{Li(tmeda)\}^+$ and $\{Li(pmdeta)\}^+$ moieties to the organic anions (reproduced by permission from J. Chem. Soc. Chem. Commun., (a) (1982)1184, (b) (1982)14, (c) (1982)1323).

A novel tetranuclear aryllithium cluster $Li_4[C_6H_4\text{-}2\text{-}(CH_2NMe_2)]_4$ has been isolated[264] from an ether-hexane solution containing an exact equimolar mixture of n-butyllithium and N,N-dimethylbenzylamine. Structural analysis shows that the four Li atoms form an approximately regular tetrahedron with r(Li...Li) = 248.9, 257.7pm; each of the $2\text{-}(Me_2NCH_2)C_6H_4$ ligands is bonded to the Li_4 tetramer via the ortho-carbon atom of the benzene ring to a face of three Li atoms, r(Li...C) = 225-230 pm and via the lone pair of the nitrogen atom to one of these three Li atoms, r(Li...N) = 201.1 pm. Multinuclear n.m.r. studies of $Li_4[C_6H_3\text{-}2\text{-}(CH_2NMe_2)\text{-}5\text{-}Me]_4$ when dissolved in toluene showed that the tetranuclear structure is retained in solution upto 363K. Similar studies in the presence of ether and thf indicate that whereas the Li_4 aggregate is also stable in weakly coordinating solvents (eg., ether), strongly coordinating solvents (eg., thf) effectively break it down into the dinuclear species, $Li_2[C_6H_3\text{-}2\text{-}(CH_2NMe_2)\text{-}5\text{-}Me]_2$,4thf. The solution structure (82) of this species is predicted by comparison with that of (83) of $Li_2[C_6H_3\text{-}2,6\text{-}(CH_2NMe_2)_2]$.[264]



(82)



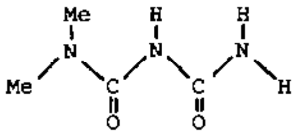
(83)

The alkali metal (Li-Cs) derivatives of $HC_5(CO_2Me)_5$ have been synthesised and characterised spectroscopically.[265] The structures of $Li[C_5(CO_2Me)_5].H_2O$ and of $K[C_5(CO_2Me)_5].MeOH$ have been elucidated by single crystal X-ray diffraction methods. The Li^+ ion adopts an approximately tetrahedral coordination geometry comprising three carbonyl oxygens from two anions, r(Li...O) = 190.0-191.4 pm and the water molecule, r(Li...O) = 188.1 pm; the K^+ ion, on the other hand, is surrounded by five carbonyl oxygens from three anions, r(K...O) = 264.5-286.2 pm and the methanol molecule, r(K...O) = 288.4 pm; in a distorted octahedral arrangement.[265]

Complex formation between alkali metal cations and various ligands has been studied both theoretically[266] and experimentally.[267-270] The 1:1 complexes of Li^+-K^+ with N,N-dimethylbiuret (84) have been studied by ab initio SCF MO calculations with minimal GLO basis sets;[266] the simple planar chelate geometry is shown to be the most stable form for all species.

Spectroscopic (i.r., ^1H n.m.r.) studies[267] of the molecular interaction between Li^+ and propan-1-ol have shown that, contrary to expectation, the strongest interaction occurs between the Li^+ ion and the two methylene groups; the anticipated strong interaction with the hydroxyl group is but weak and is comparable with that of the methyl group.[267]

The interaction of Li^+-Rb^+ with the complexing agents (85)-(87) has been studied in aqueous solutions and in mixed solvents of



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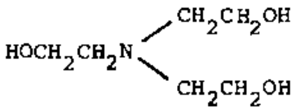

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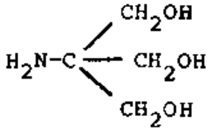

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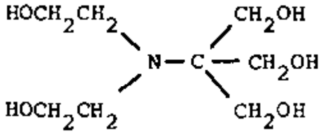
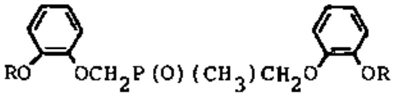


(87)

(88) ROR

(89) $ROCH_2P(O)(C_6H_5)_2$



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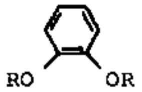


(90)

(92) $(CH_3)_{3-n}P(O)[(CH_2O)R]_n$

(n = 1,2,3)

$R = -CH_2P(O)(CH_3)_2$

water with dioxane, methanol or dmso using pH-potentiometric methods;[268] the stabilities of the complexes increase with decreasing cation radii in all solvents.

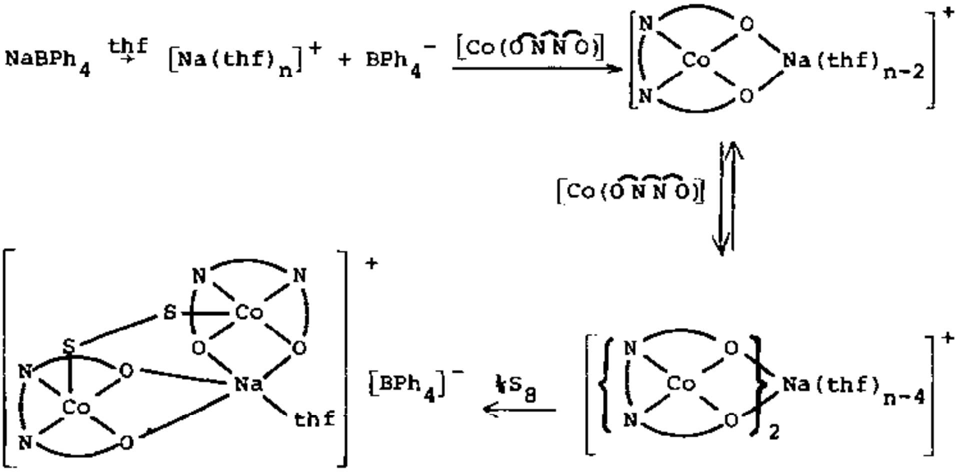
The complexation of Li^+-K^+ and Cs^+ by the multidentate phosphoryl containing ligands (88)-(92) has been studied in thf/chloroform (4/1)[269] or acetonitrile/chloroform (1/1)[270] mixtures by electrical conductivity methods. The effective stability constants of the complexes $[ML]^+$ have been determined and the influence of the solvent on both the solution behaviour of the alkali metal cations and the stability of the complexes assessed.[269,270]

The imidodisulphates, $HN(SO_3M)_2$ (M = Li,Cs), $LiN(SO_3Li)_2,3H_2O$ and $CsN(SO_3Cs)_2,2H_2O$ have been prepared and characterised.[271] T.g.a. and d.t.a. studies of the hydrates have shown that whereas the lithium salt loses its three water molecules in two stages, the caesium salt loses its two water molecules simultaneously. Similar studies of $HN(SO_3M)_2$ (M = Li,Cs) show that the thermal decomposition of the caesium salt follows a different route to that of the lithium salt which is similar to those of the other alkali metals.[271]

1.5.8 Sodium Derivatives

Acetylcyclopentadienylsodium has been isolated as a thf adduct from reaction between cyclopentadienylsodium and methyl acetate in thf.[272] The product was characterised by means of a single crystal X-ray diffraction study. The coordination sphere around each sodium atom consists of the oxygen atoms from two ligands, r(Na...O) = 229.5, 232.9 pm, the thf oxygen molecule, r(Na...O) = 235.4 pm, and an ion contact pair between the sodium and the five ring carbons of the ligand, r(Na...C) = 269-294 pm. The geometry of the Na^+ coordination sphere is pseudo tetrahedral if the ring is assumed to occupy a single coordination position.[272]

[Co(salophen)] has been shown to dissolve in thf on addition of $NaBPh_4$.[273] The resulting solution reacts with elemental sulphur giving maroon crystals of {[(thf)(salophen)Co-S_2-Co(salophen)]-[Na(thf)]}[BPh_4] (<u>93</u>), the reactive species being a [Co(salophen)]-Na^+ adduct (<u>94</u>). The proposed reaction sequence based on a single crystal structural analysis of (<u>93</u>), is given in Scheme 3:

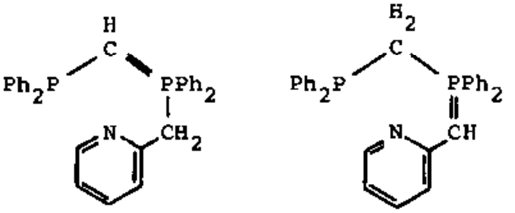


(<u>93</u>) (<u>94</u>)

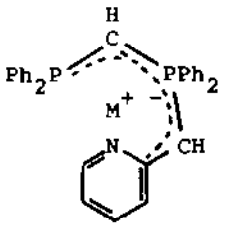
<u>Scheme 3</u>

The coordination properties of various phosphorus ylides towards Na^+, K^+ and Ba^{2+} have been reported by Schmidbaur et al.[274,275]

The reaction[274] of a mixture if ylide isomers (95) with $NaNH_2$ or KH in thf or with barium in liquid NH_3 leads to the ylide complexes (96)-(98). The complexes have been characterised in solution by multinuclear (^{1}H, ^{13}C, ^{23}Na and ^{31}P) n.m.r. spectroscopy. Single crystal X-ray diffraction analysis of (97) revealed a centrosymmetric binuclear structure with pyridine rings in an unusual bridge position between K^+ ions. Each cation is surrounded by two pyridine nitrogens, r(K...N) = 277.9, 295.6 pm, two thf molecules, r(K...O) = 262.0, 274.5 pm and the phosphane phosphorus atom, r(K...P) = 345.4 pm. Contacts to the ylide carbon atom at the pyridine ring and to the ring carbon atoms of the pyridine are less important.[274] The ferrocenyl-substituted ylide complexes

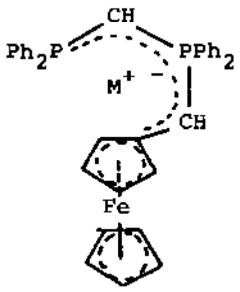


(95)

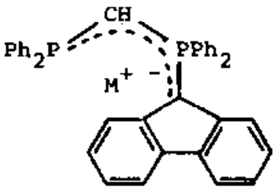


(96) M = Na(thf)
(97) M = $K(thf)_2$
(98) M = ½Ba

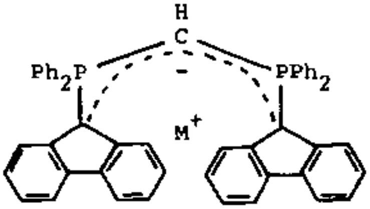
(99) and (100) are readily obtained on treatment of the appropriate ylide with $NaNH_2$ or KH in thf, respectively. Similarly, the complexes (101)-(105) are derived by reaction of the corresponding ylides with $NaNH_2$ or KH in thf or with barium in liquid NH_3, as appropriate. Finally further treatment of (105) with KH yields the potassium complex (106). All the ylide complex products were



(99) M = $Na(thf)_2$
(100) M = K

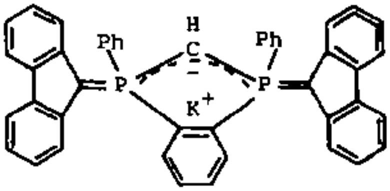


(101) M = $Na(thf)_2$
(102) M = $K(thf)_2$
(103) M = ½Ba



(104) M = Na(thf)

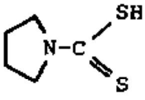
(105) M = $K(thf)_2$



(106)

characterised primarily by multinuclear n.m.r. methods.[275]

Single crystal neutron[276] and X-ray[277-281] diffraction studies have been undertaken on a number of unrelated sodium salts. The structures of the monosodium salt of (107) dihydrate[276] and of sodium (tert)-butoxide[277] have been refined; those of the monosodium salts of (108) monohydrate,[278] (109) trihydrate,[279] (110) monohydrate[280] and (111) dihydrate,[281] have been determined for the first time. The structure of sodium (tert)-butoxide, originally solved in the monoclinic space group Cc,[282] has been re-refined in the true trigonal space group R3c.[277] The modified unit cell contains six hexameric and six nonameric C_4H_9ONa units, the centre of each oligomeric unit lying on a triad axis; no significant alterations in molecular geometry arose on re-refinement. The neutron diffraction study of the monosodium salt of (107) dihydrate was effected[276] to refine the O-H...S hydrogen bonding in the structure, previously solved by X-ray



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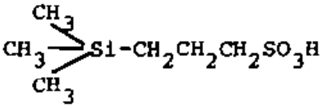
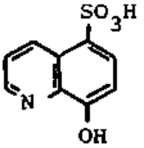
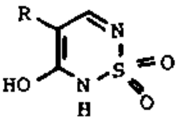


$(CH_3)_3Si-CH_2CH_2CH_2SO_3H$

(108)



(109)



(110) R = NO_2

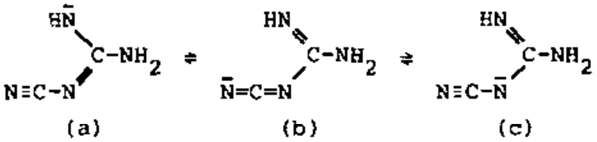
(111) R = CN

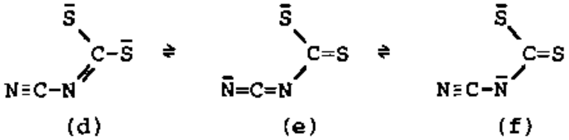
methods.[283] The Na^+ cation in the salt is situated in a distorted octahedral environment comprising two sulphur atoms from monodentate anions, r(Na...S) = 294.9, 300.7 pm and four water molecules, r(Na...O) = 234.9-250.0 pm. Similar six-fold coordination polyhedra are observed for the Na^+ cations in the four novel structures.[278-281] Two crystallographically distinct Na^+ cations occur in the monosodium salt of (108) monohydrate;[278] they are both surrounded by four oxygens from sulphate moieties and by two water molecules, r(Na...O) values lying in the range 230-250 pm. The Na^+ cation in the monosodium salt of (109) trihydrate[279] is coordinated to one nitrogen atom, r(Na...N) = 244.5 pm, one hydroxyl oxygen, r(Na...O) = 240.2 pm, and one sulphate oxygen r(Na...O) = 239.0 pm from three separate anions and to three water molecules, r(Na...O) = 237.6-243.1 pm. In the monosodium salt of (110) monohydrate,[280] the Na^+ ions are located in octahedral coordination polyhedra comprising one hydroxyl oxygen, r(Na...O) = 240.8 pm, one nitro oxygen, r(Na...O) = 240.2 pm and two S-dioxo oxygens r(Na...O) = 236.6, 238.0 pm from three distinct anions and two water molecules, r(Na...O) = 233.7, 248.7 pm. In the closely related monosodium salt of (111) dihydrate,[281] the octahedral geometry of the Na^+ coordination sphere is generated by the nitrile nitrogen atom, r(Na...N) = 246.7 pm, and three S-dioxo oxygens, r(Na...O) = 244.9-253.7 pm from four separate anions and two water molecules, r(Na...O) = 235.3, 238.6 pm.

The structures of the corresponding monopotassium salts of (110) monohydrate,[280] and of (111) monohydrate[281] have also been derived. The K^+ ions adopt seven fold coordination polyhedra in both salts; that in the (110) derivative is described as a laterally capped trigonal prism and that in the (111) derivative as a pentagonal bipyramid. The coordination sphere in the former salt is composed of one hydroxyl oxygen, r(K...O) = 287.9 pm, one nitro oxygen r(K...O) = 289.6 pm, and three S-dioxo oxygens, r(K...O) = 282.4-301.1 pm, from five different anions and two water molecules, r(K...O) = 278.3, 280.6 pm; that in the latter salt is composed of one nitrile nitrogen, r(K...N) = 291.6 pm and four S-dioxo oxygens, r(K...O) = 283.0-293.4 pm from five different anions and two water molecules, r(K...O) = 275.2, 281.0 pm.

1.5.9 Potassium, Rubidium and Caesium Derivatives

As for the 1981 Review, the papers abstracted for this subsection deal almost exclusively with structural aspects of the chemistry of these metals. The crystal and molecular structures of five potassium salts, $K[(NH_2)C(NH)NCN]$,[284] $K_2[S_2CNCN],H_2O$,[285] $K_2[CH_3N(SO_3)_2]$,[286] $K[CH_3NH(SO_3)]$[286] and $K[(CH_3)_2N(SO_3)]$[287] have been elucidated. The K^+ ions in the slats of the related N-cyanoguanidine and N-cyanodithiocarbimate moieties have surprisingly different coordination geometries; that in $K[(NH_2)C(NH)NCN]$[284] is intermediate between octahedral and trigonal prismatic whereas that in $K[S_2CNCN],H_2O$[285] is square antiprismatic. The six coordinating atoms in the former salt are all nitrogen atoms, two nitrile nitrogens, two imino nitrogens and two amino nitrogens, each from a different anion, with r(K...N) = 280.8-301.2 pm. The eight coordinating atoms in the latter salt consist of four sulphur atoms from one bidentate and two monodentate $-CS_2$ moieties, r(K...S) = 321.8-338.0 pm, three nitrogen atoms, two nitrile nitrogens and one imino nitrogen, r(K...N) = 293.9, 294.9, 380.3 pm, and a single water molecule, r(K...O) = 275.0 pm. The coordinating properties of the two anions are in excellent agreement with the resonance structures:


(a) (b) (c)


(d) (e) (f)

[NB. (e) and (f) may be duplicated by putting the negative charge on the alternative S atom]

Kennard et al[286,287] have reported the crystal and molecular structures of the potassium salts of the trioxosulphate derivatives of methylamine and dimethylamine. Their primary interest in these compounds is in the anion geometry and there is minimal discussion of the cation coordination polyhedra. Indeed, for $K[(CH_3)_2N(SO_3)],0.66H_2O$[287] there is no information on the K^+ coordination sphere - this may be due to the very high R value of

0.149 - and there is a dichotomy between the text and the tabulated data for the K^+ coordination spheres in $K[CH_3N(SO_3)_2]$ and in $K[CH_3NH(SO_3)]$.[286] According to the text, the K^+ ion in $K[CH_3N(SO_3)_2]$ is surrounded by eight oxygen atoms from neighbouring anions with r(K...O) = 272-313 pm, while the two crystallographically distinct K^+ ions in $K[CH_3NH(SO_3)]$ are surrounded by eight and six oxygen atoms, respectively, in irregular arrangements with r(K...O) = 275-320 pm. According to the tables, the situation is reversed with minor differences in the interionic distances.

K_2SN_2 has been prepared in high yield (85-96%) by reaction of $S(NR)_2$ (R = $SiMe_3$) with C_4H_9OK in boiling dme.[288] It is stable upto 453K and above. It reacts explosively with H_2O, MeOH or halomethanes, bursting into flames. It is insoluble in hydrocarbons, ethers and liquid ammonia.

Finally, Raman spectra of single crystals of K[TCNQ] and of its deuterated analogue have been recorded as a function of temperature.[289] The intensities of the intra- and intermolecular vibrations exhibit marked variations at the dimer-monomer phase transition temperature (396K). A simple model is presented to interpret and correlate these results with previously observed i.r. intensity anomalies in this and other organic semiconductors.[289]

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