

Solutions of alkali metals in liquid ammonia have been developed as versatile reducing agents which effect reactions with organic compounds that are otherwise difficult or impossible.⁽¹⁵⁾ Aromatic systems are reduced smoothly to cyclic mono- or di-olefins and alkynes are reduced stereospecifically to *trans*-alkenes (in contrast to Pd/H₂ which gives *cis*-alkenes).

The alkali metals are also soluble in aliphatic amines and hexamethylphosphoramide, P(NMe₂)₃ to give coloured solutions which are strong reducing agents. These solutions appear to be similar in many respects to the dilute solutions in liquid ammonia though they are less stable with respect to decomposition into amide and H₂. Likewise, fairly stable solutions of the larger alkali metals K, Rb and Cs have been obtained in tetrahydrofuran, ethylene glycol dimethyl ether and other polyethers. These and similar solutions have been successfully used as strong reducing agents in situations where protonic solvents would have caused solvolysis. For example, naphthalene reacts with Na in tetrahydrofuran to form deep-green solutions of the paramagnetic sodium naphthenide, NaC₁₀H₈, which can be used directly in the presence of a bis(tertiary phosphine) ligand to reduce the anhydrous chlorides VCl₃, CrCl₃, MoCl₅ and WCl₆ to the zerovalent octahedral complexes [M(Me₂PCH₂CH₂PMe₂)₃], where M = V, Cr, Mo, W. Similarly the planar complex [Fe(Me₂PCH₂CH₂PMe₂)₂] was obtained from *trans*-[Fe(Me₂PCH₂CH₂PMe₂)₂Cl₂], and the corresponding tetrahedral Co(0) compound from CoCl₂.⁽¹⁶⁾

4.3 Compounds⁽¹⁷⁾

4.3.1 Introduction: the ionic-bond model⁽¹⁸⁾

The alkali metals form a complete range of compounds with all the common anions and have long been used to illustrate group similarities and trends. It has been customary to discuss the simple binary compounds in terms of the ionic bond model and there is little doubt that there is substantial separation of charge between the cationic and anionic components of the crystal lattice. On this model the ions are considered as hard, undeformable spheres carrying charges which are integral multiples of the electronic charge z_1e^+ . Corrections can be incorporated for zero-point energies, London dispersion energies, ligand-field stabilization energies and non-spherical ions (such as NO₃⁻, etc.). The attractive simplicity of this model, and its considerable success during the past 70 y in interpreting many of the properties of simple salts, should not, however, be allowed to obscure the growing realization of its inadequacy.^(18,19) In particular, as already noted, success in calculating lattice energies and hence enthalpy of formation via the Born–Haber cycle, does not establish the correctness of the model but merely indicates that it is consistent with these particular observations. For example, the ionic model is quite successful in reproducing the enthalpy of formation of BF₃, SiF₄, PF₅ and even SF₆ on the assumption that they are assemblies of point charges at the known interatomic distance, i.e. B³⁺(F⁻)₃, etc.,⁽²⁰⁾ but this is not a sound reason

¹⁷ W. A. HART and O. F. BEUMEL, Lithium and its compounds, *Comprehensive Inorganic Chemistry*, Vol. 1, Chap. 7, Pergamon Press, Oxford, 1973. T. P. WHALEY, Sodium, potassium, rubidium, caesium and francium, *ibid.*, Chap. 8.

¹⁸ N. N. GREENWOOD, *Ionic Crystals, Lattice Defects and Nonstoichiometry*, Butterworths, London, 1968, 194 pp.

¹⁹ D. M. ADAMS, *Inorganic Solids: An Introduction to Concepts in Solid-State Structural Chemistry*, Wiley, London, 1974, 336 pp.

²⁰ F. J. GARRICK, *Phil. Mag.* **14**, 914–37 (1932). It is instructive to repeat some of these calculations with more recent values for the constants and properties used.

¹⁵ A. J. BIRCH, *Qt. Rev.* **4**, 69–93 (1950); A. J. BIRCH and H. SMITH, *Qt. Rev.* **12**, 17–33 (1958).

¹⁶ J. CHATT and H. R. WATSON, Complexes of zero-valent transition metals with the ditertiary phosphine, Me₂PCH₂CH₂PMe₂, *J. Chem. Soc.* 2545–9 (1962).

for considering these molecular compounds as ionic. Likewise, the known lattice energy of lithium metal can be reproduced quite well by assuming that the observed bcc arrangement of atoms is made up from alternating ions Li^+Li^- in the CsCl structure;⁽²¹⁾ the discrepancy is no worse than that obtained using the same model for AgCl (which has the NaCl structure). It appears that the ionic-bond model is self compensating and that the decrease in the hypothetical binding energy which accompanies the diminution of formal charges on the atoms is accompanied by an equivalent increase in binding energy which could be described as "covalent" (BF_3) or "metallic" (Li metal).

Indeed, the inherent improbability of the ionic bond model can be appreciated when it is realized that all simple cations have a positive charge and several vacant orbitals (and are therefore potentially electron pair acceptors) whereas all simple anions have a negative charge and several lone pairs of electrons (and are therefore potentially electron pair donors). The close juxtaposition of these electron-pair donor and acceptor species is thus likely to result in the transfer of at least some charge density by coordination, thereby introducing a substantial measure of covalency into the bonding of the alkali metal halides and related compounds. A more satisfactory procedure, at least conceptually, would be to describe crystalline salts and other solid compounds in terms of molecular orbitals. Quantitative calculations are difficult to carry out but the model allows flexibility in placing "partial ionic charges" on atoms by modifying orbital coefficients and populations, and it can also incorporate metallic behaviour by modifying the extent to which partly filled individual molecular orbitals are either separated by energy gaps or overlap.

The compounds which most nearly fit the classical conception of ionic bonding are the alkali metal halides. However, even here, one must ask to what extent it is reasonable to maintain that positively charged cations M^+ with favourably

directed vacant p orbitals remain uncoordinated by the surrounding anionic ligands X^- to form extended (bridged) complexes. Such interaction would be expected to increase from Cs^+ to Li^+ and from F^- to I^- (why?) and would place some electron density between the cation and anion. Some evidence on this comes from very precise electron density plots obtained by X-ray diffraction experiments on LiF, NaCl, KCl, MgO and CaF_2 .⁽²²⁾ Data for LiF are shown in Fig. 4.2a from which it is clear that the Li^+ ion is no longer spherical and that the electron density, while it falls to a low value between the ions, does not become zero. Even more significantly, as shown in Fig. 4.2b, the minimum does not occur at the position to be expected from the conventional ionic radii: whatever set of tabulated values is used the cation is always larger than expected and the anion smaller. This is consistent with a transfer of some electronic density from anion to cation since the smaller resultant positive charge on the cation exerts smaller coulombic attraction for the electrons and the ion expands. The opposite holds for the anion. These results also call into question the use of radius-ratio rules to calculate the coordination number of cations and leave undecided the numerical value of the ionic radii to be used (see also p. 66, hydrides). In fact, the radius-ratio rules are particularly unhelpful for the alkali halides, since they predict (incorrectly) that LiCl, LiBr and LiI should have tetrahedral coordination and that NaF, KF, KCl, RbF, RbCl, RbBr and CsF should all have the CsCl structure. It may be significant that adoption of the NaCl structure by all these compounds maximizes the p orbital overlap along the orthogonal x-, y- and z-directions, and so favours molecular orbital formation in these directions. Further information on the variation in apparent radius of the hydride, halide and other anions in compounds with the alkali metals and other cations is in ref. 23.

²² H. WITTE and E. WÖLFEL, *Z. phys. Chem.* **3**, 296–329 (1955). J. KRUG, H. WITTE and E. WÖLFEL, *ibid.* **4**, 36–64 (1955). H. WITTE and E. WÖLFEL, *Rev. Mod. Phys.* **30**, 51–5 (1958).

²³ O. JOHNSON, *Inorg. Chem.* **12**, 780–5 (1973).

²¹ C. S. G. PHILLIPS and R. J. P. WILLIAMS, *Inorganic Chemistry*, Vol. 1, Chap. 5, "The ionic model", pp. 142–87, Oxford University Press, Oxford, 1965.

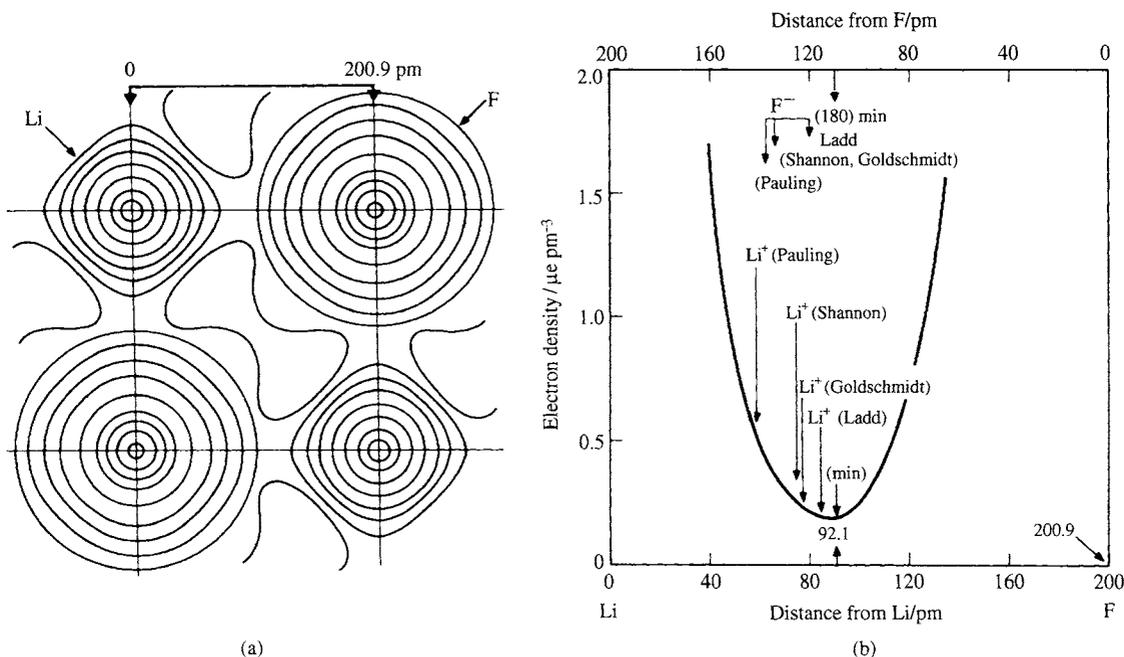


Figure 4.2 (a) Distribution of electron density ($\mu\text{e}/\text{pm}^3$) in the xy plane of LiF , and (b) variation of electron density along the Li-F direction near the minimum. The electron density rises to $17.99 \mu\text{e pm}^{-3}$ at Li and to $115.63 \mu\text{e pm}^{-3}$ at F. (The unit $\mu\text{e pm}^{-3}$ is numerically identical to e \AA^{-3} .)

Deviations from the simple ionic model are expected to increase with increasing formal charge on the cation or anion and with increasing size and ease of distortion of the anion. Again, deviations tend to be greater for smaller cations and for those (such as Cu^+ , Ag^+ , etc.) which do not have an inert-gas configuration.⁽¹⁸⁾ The gradual transition from predominantly ionic to covalent is illustrated by the “isoelectronic” series:



A similar transition towards metallic bonding is illustrated by the series:



Alkali metal alloys with gold have the CsCl structure and, whilst NaAu and KAu are essentially metallic, RbAu and CsAu have partial ionic bonding and are n-type semiconductors. These factors

should constantly be borne in mind during the discussion of compounds in later chapters.

The extent to which charge is transferred back from the anion towards the cation in the alkali metal halides themselves is difficult to determine precisely. Calculations indicate that it is probably only a few percent for some salts such as NaCl , whereas for others (e.g. LiI) it may amount to more than $0.33 e^-$ per atom. Direct experimental evidence on these matters is available for some other elements from techniques such as Mössbauer spectroscopy,⁽²⁴⁾ electron spin resonance spectroscopy,⁽²⁵⁾ and neutron scattering form factors.⁽²⁶⁾

²⁴ N. N. GREENWOOD and T. C. GIBB, *Mössbauer Spectroscopy*, Chapman & Hall, London, 1971, 659 pp.

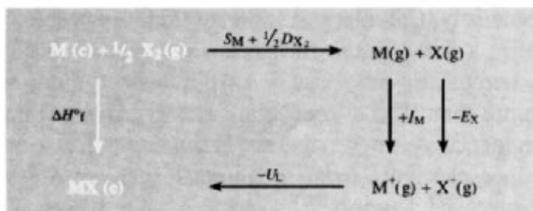
²⁵ P. B. AYSOUGH, *Electron Spin Resonance in Chemistry*, pp. 300–1, Methuen, London, 1967. P. W. ATKINS and M. C. R. SYMONS, *The Structure of Inorganic Radicals*, pp. 51–73, Elsevier, Amsterdam, 1967.

²⁶ G. E. BACON, *Neutron Diffraction*, 3rd edn., Oxford University Press, Oxford, 1975, 636 pp.

4.3.2 Halides and hydrides

The alkali metal halides are all high-melting, colourless crystalline solids which can be conveniently prepared by reaction of the appropriate hydroxide (MOH) or carbonate (M_2CO_3) with aqueous hydrohalic acid (HX), followed by recrystallization. Vast quantities of NaCl and KCl are available in nature and can be purified if necessary by simple crystallization. The hydrides have already been discussed (p. 65).

Trends in the properties of MX have been much studied and typical examples are illustrated in Figs. 4.3 and 4.4. The mp and bp always follow the trend $F > Cl > Br > I$ except perhaps for some of the Cs salts where the data are uncertain. Figure 4.3 also shows that the mp and bp of LiX are always below those of NaX and that (with the exception of the mp of KI) the values for NaX are the maximum for each series. Trends in enthalpy of formation ΔH_f° and lattice energy U_L are even more regular (Fig. 4.4) and can readily be interpreted in terms of the Born-Haber cycle, providing one assumes an invariant charge corresponding to loss or gain of one complete electron per ion, M^+X^- . The Born-Haber cycle considers two possible routes to the formation of MX and equates the corresponding enthalpy changes by applying Hess's law.⁽¹⁸⁾



Hence

$$\Delta H_f^\circ(MX) = S_M + \frac{1}{2} D_{X_2} + I_M - E_X - U_L$$

where S_M is the heat of sublimation of $M(c)$ to a monatomic gas (Table 4.2), D_{X_2} is the dissociation energy of $X_2(g)$ (Table 4.2), I_M is the ionization energy of $M(g)$ (Table 4.2), and E_X the electron affinity of $X(g)$ (Table 17.3, p. 800). The

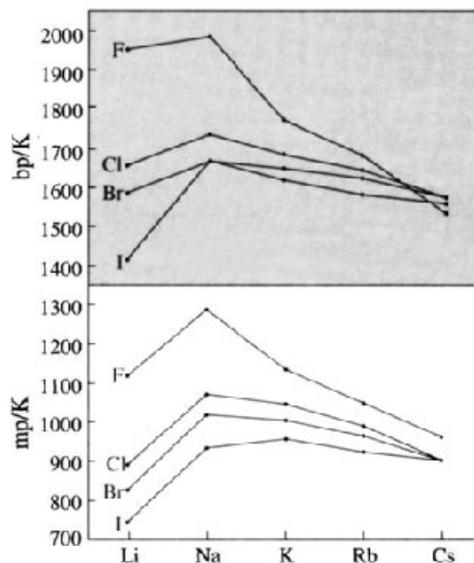


Figure 4.3 Melting point and boiling point of alkali metal halides.

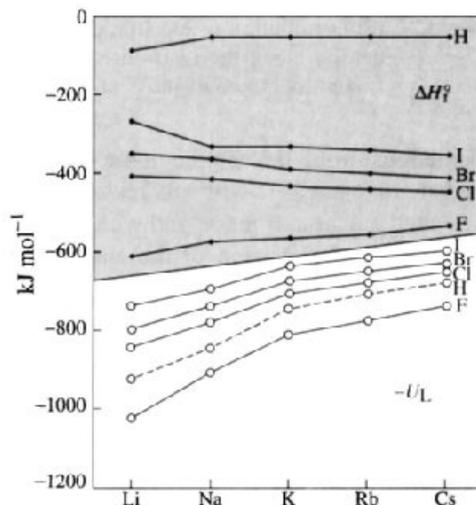


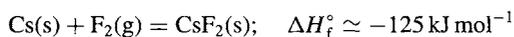
Figure 4.4 Standard enthalpies of formation (ΔH_f°) and lattice energies (plotted as $-U_L$) for alkali metal halides and hydrides.

lattice energy U_L is given approximately by the expression

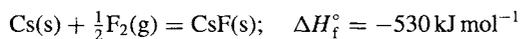
$$U_L = \frac{N_0 A e^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{\rho}{r_0}\right)$$

where N_0 is the Avogadro constant, A is a geometrical factor, the Madelung constant (which has the value of 1.7627 for the CsCl structure and 1.7476 for the NaCl structure), r_0 is the shortest internuclear distance between M^+ and X^- in the crystal, and ρ is a measure of the close-range repulsion force which resists mutual interpenetration of the ions. It is clear that the sequence of lattice energies is determined primarily by r_0 , so that the lattice energy is greatest for LiF and smallest for CsI, as shown in Fig. 4.4. In the Born-Haber expression for ΔH_f° this factor predominates for the fluorides and there is a trend to smaller enthalpies of formation from LiF to CsF (Fig. 4.4). The same incipient trend is noted for the hydrides MH, though here the numerical values of ΔH_f° are all much smaller than those for MX because of the much higher heat of dissociation of H_2 compared to X_2 . By contrast with the fluorides, the lattice energy for the larger halides is smaller and less dominant, and the resultant trend of ΔH_f° is to larger values, thus reflecting the greater ease of subliming and ionizing the heavier alkali metals.

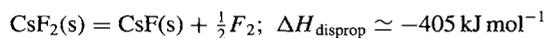
The Born-Haber cycle is also useful in examining the possibility of forming alkali-metal halides of stoichiometry MX_2 . The dominant term will clearly be the very large second-stage ionization energy for the process $M^+(g) \longrightarrow M^{2+}(g) + e^-$; this is 7297 kJ mol^{-1} for Li but drops to 2255 kJ mol^{-1} for Cs. The largest possible lattice energy to compensate for this would be obtained with the smallest halogen F and (making plausible assumptions on lattice structure and ionic radius) calculations indicate that CsF_2 could indeed be formed exothermically from its elements:



However, the compound cannot be prepared because of the much greater enthalpy of formation of CsF which makes CsF_2 unstable with respect to decomposition:



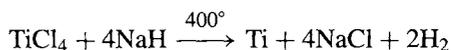
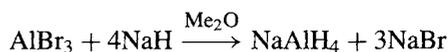
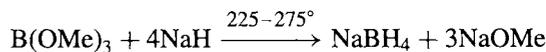
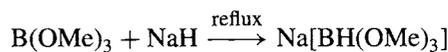
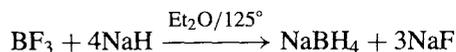
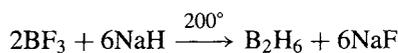
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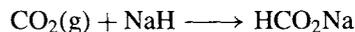
There is some evidence that Cs^{3+} can be formed by cyclic voltammetry of $Cs^+[OTeF_5]^-$ in pure MeCN at the extremely high oxidizing potential of 3 V, and that Cs^{3+} might be stabilized by 18-crown-6 and cryptand (see pp. 96 and 97 for nomenclature).⁽²⁷⁾ However, the isolation of pure compounds containing Cs^{3+} has so far not been reported.

Ternary alkali-metal halide oxides are known and have the expected structures. Thus Na_3ClO and the yellow K_3BrO have the anti-perovskite structure (p. 963) whereas Na_4Br_2O , Na_4I_2O and K_4Br_2O have the tetragonal anti- K_2NiF_4 structure.⁽²⁸⁾

The alkali metal halides, particularly NaCl and KCl, find extensive application in industry (pp. 71 and 73). The hydrides are frequently used as reducing agents, the product being a hydride or complex metal hydride depending on the conditions used, or the free element if the hydride is unstable. Illustrative examples using NaH are:



Sulfur dioxide is uniquely reduced to dithionite (a process useful in bleaching paper pulp, p. 720). CO_2 gives the formate:



Particularly reactive (pyrophoric) forms of LiH, NaH and KH can be prepared simply and in high yield by the direct hydrogenation of

²⁷ K. MOOCK and K. SEPPELT, *Angew. Chem. Int. Edn. Engl.* **28**, 1676-8 (1989).

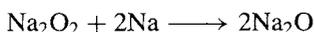
²⁸ S. SITTA, K. HIPPLER, P. VOGT and H. SABROWSKY, *Z. anorg. allg. Chem.* **597**, 197-200 (1991).

hexane solutions of MBu^n in the presence of tetramethylethylenediamine (tmeda) and these have proved extremely useful reagents for the metalation of organic compounds which have an active hydrogen site.⁽²⁹⁾

4.3.3 Oxides, peroxides, superoxides and suboxides

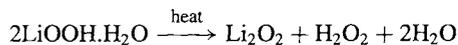
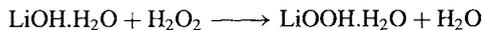
The alkali metals form a fascinating variety of binary compounds with oxygen, the most versatile being Cs which forms 9 compounds with stoichiometries ranging from Cs_7O to CsO_3 . When the metals are burned in a free supply of air the predominant product depends on the metal: Li forms the oxide Li_2O (plus some Li_2O_2), Na forms the peroxide Na_2O_2 (plus some Na_2O) whilst K, Rb and Cs form the superoxide MO_2 . Under the appropriate conditions pure compounds M_2O , M_2O_2 and MO_2 can be prepared for all five metals.

The "normal" oxides M_2O (Li, Na, K, Rb) have the antifluorite structure as do many of the corresponding sulfides, selenides and tellurides. This structure is related to the CaF_2 structure (p. 118) but with the sites occupied by the cations and anions interchanged so that M replaces F and O replaces Ca in the structure. Cs_2O has the anti- CdCl_2 layer structure (p. 1211). There is a trend to increasing coloration with increasing atomic number, Li_2O and Na_2O being pure white, K_2O yellowish white, Rb_2O bright yellow and Cs_2O orange. The compounds are fairly stable towards heat, and thermal decomposition is not extensive below about 500° . Pure Li_2O is best prepared by thermal decomposition of Li_2O_2 (see below) at 450°C . Na_2O is obtained by reaction of Na_2O_2 , NaOH or preferably NaNO_2 with the Na metal:



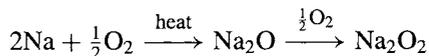
In this last reaction Na can be replaced by the azide NaN_3 to give the same products. The normal oxides of the other alkali metals can be prepared similarly.

The peroxides M_2O_2 contain the peroxide ion O_2^{2-} which is isoelectronic with F_2 . Li_2O_2 is prepared industrially by the reaction of $\text{LiOH}\cdot\text{H}_2\text{O}$ with hydrogen peroxide, followed by dehydration of the hydroperoxide by gentle heating under reduced pressure:

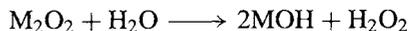


It is a thermodynamically stable, white, crystalline solid which decomposes to Li_2O on being heated above 195°C .

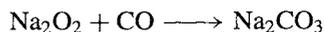
Na_2O_2 , is prepared as pale-yellow powder by first oxidizing Na to Na_2O in a limited supply of dry oxygen (air) and then reacting this further to give Na_2O_2 :



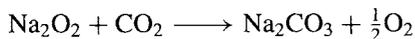
Preparation of pure K_2O_2 , Rb_2O_2 and Cs_2O_2 by this route is difficult because of the ease with which they oxidize further to the superoxides MO_2 . Oxidation of the metals with NO has been used but the best method is the quantitative oxidation of the metals in liquid ammonia solution (p. 78). The peroxides can be regarded as salts of the dibasic acid H_2O_2 . Thus reaction with acids or water quantitatively liberates H_2O_2 :



Sodium peroxide finds widespread use industrially as a bleaching agent for fabrics, paper pulp, wood, etc., and as a powerful oxidant; it explodes with powdered aluminium or charcoal, reacts with sulfur with incandescence and ignites many organic liquids. Carbon monoxide forms the carbonate, and CO_2 liberates oxygen (an important application in breathing apparatus for divers, firemen, and in submarines — space capsules use the lighter Li_2O_2):



²⁹ P. A. A. KLUSENER, L. BRANDSMA, H. D. VERKRUJSE, P. V. R. SCHLEYER, T. FRIEDL and R. PI, *Angew. Chem. Int. Edn. Engl.* **25**, 465 (1986).

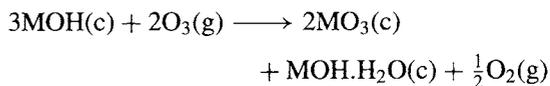


In the absence of oxygen or oxidizable material, the peroxides (except Li_2O_2) are stable towards thermal decomposition up to quite high temperatures, e.g. $\text{Na}_2\text{O}_2 \sim 675^\circ\text{C}$, $\text{Cs}_2\text{O}_2 \sim 590^\circ\text{C}$.

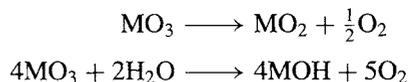
The superoxides MO_2 contain the paramagnetic ion O_2^- which is stable only in the presence of large cations such as K, Rb, Cs (and Sr, Ba, etc.). LiO_2 has only been prepared by matrix isolation experiments at 15 K and positive evidence for NaO_2 was first obtained by reaction of O_2 with Na dissolved in liquid NH_3 ; it can be obtained pure by reacting Na with O_2 at 450°C and 150 atm pressure. By contrast, the normal products of combustion of the heavier alkali metals in air are KO_2 (orange), mp 380°C , RbO_2 (dark brown), mp 412°C and CsO_2 (orange), mp 432°C . NaO_2 is trimorphic, having the marcasite structure (p. 680) at low temperatures, the pyrite structure (p. 680) between -77° and -50°C and a pseudo- NaCl structure above this, due to disordering of the O_2^- ions by rotation. The heavier congeners adopt the tetragonal CaC_2 structure (p. 298) at room temperature and the pseudo- NaCl structure at high temperature.

Sesquioxides " M_2O_3 " have been prepared as dark-coloured paramagnetic powders by careful thermal decomposition of MO_2 (K, Rb, Cs). They can also be obtained by oxidation of liquid ammonia solutions of the metals or by controlled oxidation of the peroxides, and are considered to be peroxide disuperoxides $[(\text{M}^+)_4(\text{O}_2^{2-})_2(\text{O}_2^-)_2]$. Indeed, pure Rb_4O_6 , prepared by solid-state reaction between Rb_2O_2 and 2RbO_2 , has recently been shown to be $[\text{Rb}_4(\text{O}_2^{2-})_2(\text{O}_2^-)_2]$ by single-crystal diffractometry, although the two types of diatomic anion could not be distinguished in the cubic unit cell even at -60°C ; the compound is thermodynamically stable and melts at 461°C ⁽³⁰⁾

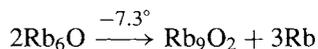
Ozonides MO_3 have been prepared for Na, K, Rb and Cs by the reaction of O_3 on powdered anhydrous MOH at low temperature and extraction of the red MO_3 by liquid NH_3 :



Under similar conditions Li gives $[\text{Li}(\text{NH}_3)_4]\text{O}_3$ which decomposes on attempted removal of the coordinated NH_3 , again emphasizing the important role of cation size in stabilizing catenated oxygen anions. Improved techniques involving the reaction of oxygen/ozone mixtures on the preformed peroxide, followed by extraction with liquid ammonia, now permit gram amounts of the pure crystalline ozonides of K, Rb and Cs to be prepared.⁽³¹⁾ (See also p. 98, p. 610.) The ozonides, on standing, slowly decompose to oxygen and the superoxide MO_2 , but on hydrolysis they appear to go directly to the hydroxide:



In addition to the above oxides M_2O , M_2O_2 , M_4O_6 , MO_2 and MO_3 in which the alkali metal has the constant oxidation state +1, rubidium and caesium also form suboxides in which the formal oxidation state of the metal is considerably lower. Some of these intriguing compounds have been known since the turn of the century but only recently have their structures been elucidated by single crystal X-ray analysis.⁽³²⁾ Partial oxidation of Rb at low temperatures gives Rb_6O which decomposes above -7.3°C to give copper-coloured metallic crystals of Rb_9O_2 :



Rb_9O_2 inflames with H_2O and melts incongruently at 40.2° to give $2\text{Rb}_2\text{O} + 5\text{Rb}$. The structure of Rb_9O_2 comprises two ORb_6 octahedra sharing a common face (Fig. 4.5). It thus has the anti- $[\text{Ti}_2\text{Cl}_9]^{3-}$ structure. The Rb-Rb distance within this unit is only 352 pm (compared with 485 pm in Rb metal) and the nearest Rb-Rb distance

³¹ W. SCHNICK and M. JANSEN, *Z. anorg. allg. Chem.* **532**, 37-46 (1986).

³² A. SIMON, *Naturwiss.* **58**, 622-3 (1971); *Z. anorg. allg. Chem.* **395**, 301 (1973); *Struct. Bonding* **36**, 81-127 (1979); *Angew. Chem. Int. Edn. Engl.* **27**, 159-83 (1988).

³⁰ M. JANSEN and N. KORBER, *Z. anorg. allg. Chem.* **598/599**, 163-73 (1991).

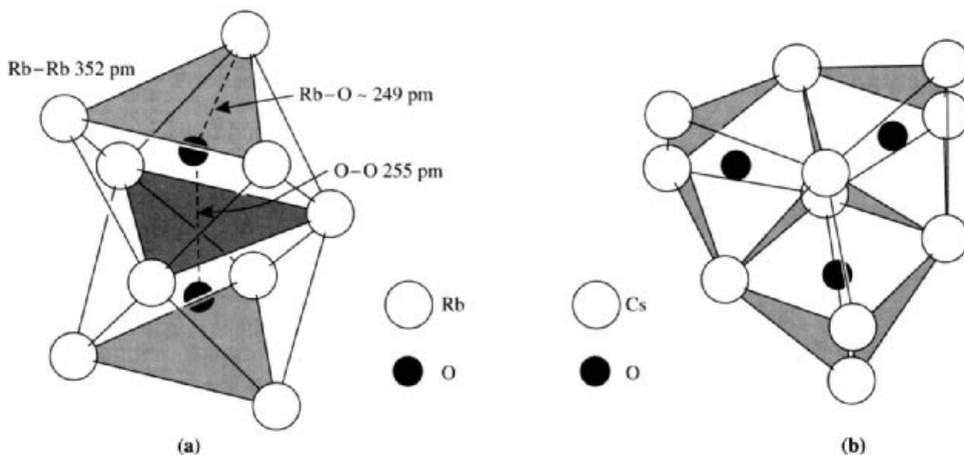


Figure 4.5 (a) The confacial bioctahedral Rb_9O_2 group in Rb_9O_2 and Rb_6O , and (b) the confacial trioctahedral $Cs_{11}O_3$ group in Cs_7O .

between groups is 511 pm. The Rb–O distance is ~ 249 pm, much less than the sum of the conventional ionic radii (289 pm) and the metallic character of the oxide comes from the excess of at least 5 electrons above that required for simple bookkeeping. Crystalline Rb_6O has a unit cell containing 4 formula units, i.e. $Rb_{24}O_4$, and the structure consists of alternating layers of Rb_9O_2 and close-packed metal atoms parallel to (001) to give the structural formula $[(Rb_9O_2)Rb_3]$.

Caesium forms an even more extensive series of suboxides:⁽³²⁾ Cs_7O , bronze-coloured, mp $+4.3^\circ C$; Cs_4O , red-violet, decomposes $>10.5^\circ C$; $Cs_{11}O_3$, violet crystals, mp (incongruent) $52.5^\circ C$; and $Cs_{3+x}O$, a nonstoichiometric phase up to Cs_4O , which decomposes at $166^\circ C$. Cs_7O reacts vigorously with O_2 and H_2O and the unit cell is found to be $Cs_{21}O_3$, i.e. $[(Cs_{11}O_3)Cs_{10}]$. The unit $Cs_{11}O_3$ comprises 3 octahedral OCs_6 groups each sharing 2 adjacent faces to form the trigonal group shown in Fig. 4.5b. These groups form chains along (001) and are also surrounded by the other Cs atoms. The Cs–Cs distance within the $Cs_{11}O_3$ group is only 376 pm, whereas between groups it is 527 pm; this latter distance is also the shortest distance between Cs in a group and the other 10 Cs atoms, and is similar to the interatomic distance in Cs metal. The structures of the other 3 suboxides are more complex

but it is salutary to realize that Cs forms at least 9 crystalline oxides whose structures can be rationalized in terms of general bonding systematics.

4.3.4 Hydroxides

Evaporation of aqueous solutions of LiOH under normal conditions produces the monohydrate, and this can be readily dehydrated by heating in an inert atmosphere or under reduced pressure. $LiOH \cdot H_2O$ has a crystal structure built up of double chains in which both Li and H_2O have 4 nearest neighbours (Fig. 4.6a); Li is tetrahedrally coordinated by 2OH and 2 H_2O , and each tetrahedron shares an edge (2OH) and two corners (2 H_2O) to produce double chains which are held laterally by H bonds. Each H_2O molecule is tetrahedrally coordinated by 2Li from the same chain and 2OH from other chains. Anhydrous LiOH has a layer lattice of edge-shared $Li(OH)_4$ tetrahedra (Fig. 4.6b) in which each Li in a plane is surrounded tetrahedrally by 4OH, and each OH has 4Li neighbours all lying on one side; neutron diffraction shows that the OH bonds are normal to the layer plane and there is no H bonding between layers.

Numerous hydrates have been prepared from aqueous solutions of the heavier alkali metal

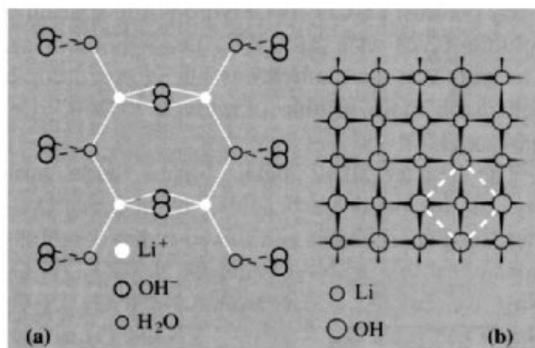


Figure 4.6 (a) The double-chain structure of $\text{LiOH}\cdot\text{H}_2\text{O}$, and (b) the layer structure of anhydrous LiOH (see text).

hydroxides (e.g. $\text{NaOH}\cdot n\text{H}_2\text{O}$, where $n = 1, 2, 2.5, 3.5, 4, 5.25$ and 7) but little detailed structural information is available.⁽³³⁾ The anhydrous compounds all show the influence of oriented OH groups on the structure,⁽¹³⁾ and there is evidence of weak $\text{O}-\text{H}\cdots\text{O}$ bonding for KOH and RbOH . Melting points are substantially lower than those of the halides, decreasing from 471°C for LiOH to 272° for CsOH , and the mp of the hydrates is even lower, e.g. 2.5°C (incongr.) for $\text{CsOH}\cdot 2\text{H}_2\text{O}$ and -5.5°C for the trihydrate.

The alkali metal hydroxides are the most basic of all hydroxides. They react with acids to form salts and with alcohols to form alkoxides. The alkoxides are oligomeric and the degree of polymerization can vary depending on the particular metal and the state of aggregation. The *tert*-butoxides, MOBu' , ($\text{Bu}' = \text{OCMe}_3$) can be considered as an example. Crystalline $(\text{KOBu}')_4$ has a cubane-like structure and the tetramer persists in tetrahydrofuran solution and in the gas phase.^(34,35) By contrast, $(\text{NaOBu}')_4$ is exclusively tetrameric in *thf*, but is a mixture of hexamers and nonamers

in the crystalline state and of hexamers and heptamers in the vapour phase. The lithium analogue is tetrameric in *thf* but is hexameric in benzene, toluene or cyclohexane and in the gas phase. The degree of polymerization can also be influenced by the nature of the organic residue. Thus X-ray crystallography shows that lithium 2,6-di-*tert*-butyl-4-methylphenolate is dimeric whereas the closely related phenolate $\{\text{LiOC}_6\text{H}_2(\text{CH}_2\text{NMe}_2)_2\text{-2,6-Me-4}\}_3$ provides the first example of a trimeric structure, with an essentially planar central Li_3O_3 heterocyclic ring.⁽³⁶⁾ The trimer, like the dimer, features unusually short $\text{Li}-\text{O}$ and $\text{C}_{ipso}-\text{O}$ bonds (186.5 and 130.1 pm, respectively) perhaps suggesting quasi-aromaticity of the Li_3O_3 ring, the delocalized π -electrons originating from the lone pairs on the oxygen atoms.

The alkali metal hydroxides are also readily absorb CO_2 and H_2S to form carbonates (or hydrogencarbonates) and sulfides (or hydrogensulfides), and are extensively used to remove mercaptans from petroleum products. Amphoteric oxides such as those of Al , Zn , Sn and Pb react with MOH to form aluminates, zincates, stannates and plumbates, and even SiO_2 (and silicate glasses) are attacked.

Production and uses of LiOH have already been discussed (p. 70). Huge tonnages of NaOH and KOH are produced by electrolysis of brine (pp. 71, 73) and the enormous industrial importance of these chemicals has already been alluded to.

4.3.5 Oxoacid salts and other compounds

Many binary and pseudo-binary compounds of the alkali metals are more conveniently treated within the context of the chemistry of the other element and for this reason discussion is deferred to later chapters, e.g. borides (p. 145),

³³ H. JACOBS and U. METZNER, *Z. anorg. allg. Chem.* **597**, 97–106 (1991). D. MOOTZ and H. RUTTER, *Z. anorg. allg. Chem.* **608**, 123–30 (1992).

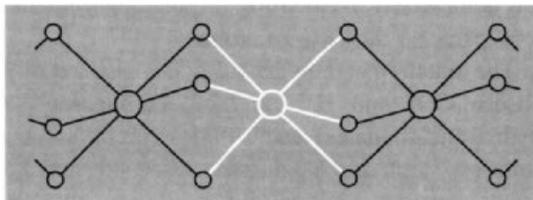
³⁴ M. H. CHISHOLM, S. R. DRAKE, A. A. NAIINI and W. E. STREIB, *Polyhedron* **10**, 337–43 (1991).

³⁵ M. BRAUN, D. WALDMÜLLER and B. MAYER, *Angew. Chem. Int. Edn. Engl.* **28**, 895–6 (1989).

³⁶ P. A. VAN DER SCHAAF, M. P. HOGGERHEIDE, D. M. GROVE, A. L. SPEK and G. VAN KOTEN, *J. Chem. Soc., Chem. Commun.*, 1703–5 (1992).

graphite intercalation compounds (p. 293), carbides, cyanides, cyanates, etc. (pp. 297, 319), silicides (p. 335), germanides (p. 393), nitrides, azides and amides (p. 417), phosphides (p. 489), arsenides (p. 554), sulfides (p. 676), selenides and tellurides (p. 765), polyhalides (p. 835), etc. Likewise, the alkali metals form stable salts with virtually all oxoacids and these are also discussed in later chapters.

Lithium salts show a great propensity to crystallize as hydrates, the trihydrates being particularly common, e.g. $\text{LiX} \cdot 3\text{H}_2\text{O}$, $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{ClO}_3, \text{ClO}_4, \text{MnO}_4, \text{NO}_3, \text{BF}_4$, etc. In most of these Li is coordinated by $6\text{H}_2\text{O}$ to form chains of face-sharing octahedra:



By contrast Li_2CO_3 is anhydrous and sparingly soluble (1.28 wt% at 25°C , i.e. 0.17 mol l^{-1}). The nitrate is also anhydrous but is hygroscopic and much more soluble (45.8 wt% at 25°C , i.e. 6.64 mol l^{-1}).

The heavier alkali metals form a wide variety of hydrated carbonates, hydrogencarbonates, sesquicarbonates and mixed-metal combinations of these, e.g. $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$, $\text{NaKCO}_3 \cdot n\text{H}_2\text{O}$, $\text{K}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$, etc. These systems have been studied in great detail because of their industrial and geochemical significance (see Panel). Some solubility data are in Fig. 4.7, which indicates the considerable solubility of Rb_2CO_3 and Cs_2CO_3 and the lower solubility of the hydrogencarbonates. The various stoichiometries reflect differing ways of achieving charge balance, preferred coordination polyhedra, and H bonding. Thus $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ has two types of 6-coordinate Na, half being surrounded by $1\text{H}_2\text{O}$ plus 5 oxygen atoms from CO_3 groups and half by

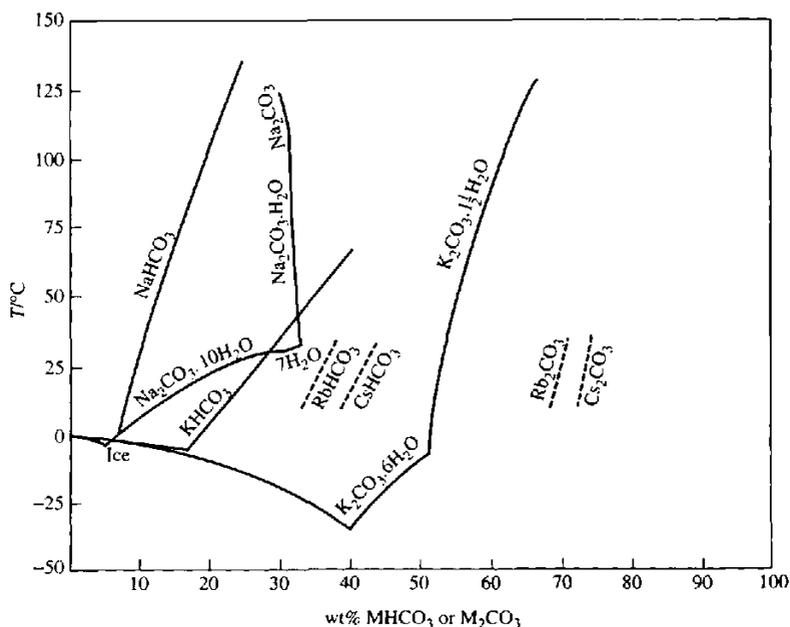


Figure 4.7 Solubilities of alkali carbonates and bicarbonates (hydrogencarbonates). (H. Stephen and T. Stephen, *Solubilities of Inorganic and Organic Compounds*, Vol. 1, Part 1, Macmillan, New York.).

Industrial Production and Uses of Sodium Carbonate, Hydroxide and Sulfate⁽³⁷⁾

Na_2CO_3 (soda ash) is interchangeable with NaOH in many of its applications (e.g. paper pulping, soap, detergents) and this gives a valuable flexibility to the chlor-alkali industry. About half the Na_2CO_3 produced is used in the glass industry. One developing application is in the reduction of sulfur pollution resulting from stack gases of power plants and other large furnaces: powdered Na_2CO_3 is injected with the fuel and reacts with SO_2 to give solids such as Na_2SO_3 which can be removed by filtration or precipitation. World production of Na_2CO_3 was 28.7 million tonnes in 1985: the five leading countries were the USA, the USSR, China, Bulgaria and the Federal Republic of Germany, and they accounted for over 70% of production. Most of this material was synthetic (Solvay), but the increasing use of natural carbonate (trona) is notable, particularly in the USA where it is now the sole source of Na_2CO_3 , the last synthetic unit having been closed in 1985: reserves in the Green River, Wyoming, deposit alone exceed 10^{10} tonnes and occur in beds up to 3 m thick over an area of 2300 km^2 . About one third of the world production is now from natural deposits.

Formerly Na_2CO_3 found extensive use as "washing soda" but this market has now disappeared due to the domestic use of detergents. The related compound NaHCO_3 is, however, still used, particularly because of its ready decomposition in the temperature range 50–100°C:



Production in the USA is ~350 000 tonnes annually of which 30% is used in baking-powder formulations, 20% in animal feedstuffs, 15% in chemicals manufacture, 11% in pharmaceuticals, 9% in fire extinguishers and the remaining 15% in the textile, leather and paper industries and in soaps, detergents and neutralizing agents.

Caustic soda (NaOH) is industry's most important alkali. It is manufactured on a huge scale by the electrolysis of brine (p. 72) and annual production in the USA alone is over 10 million tonnes. Electrolysis is followed by concentration of the alkali in huge tandem evaporators such as those at PPG Industries' Lake Charles plant. The evaporators, which are perhaps the world's largest, are 41 m high and 12 m in diameter. About half the caustic produced is used directly in chemical production; a detailed breakdown of usage (USA, 1985) is: organic chemicals 30%, inorganic chemicals 20%, paper and pulp 20%, export 10%, soap and detergents 5%, oil industry 5%, textiles 4%, bauxite digestion 3% and miscellaneous 3%. Principal applications are in acid neutralization, the manufacture of phenol, resorcinol, β -naphthol, etc., and the production of sodium hypochlorite, phosphate, sulfide, aluminates, etc.

Salt cake (Na_2SO_4) is a byproduct of HCl manufacture using H_2SO_4 and is also the end-product of hundreds of industrial operations in which H_2SO_4 used for processing is neutralized by NaOH . For long it had few uses, but now it is the mainstay of the paper industry, being a key chemical in the kraft process for making brown wrapping paper and corrugated boxes: digestion of wood chips or saw-mill waste in very hot alkaline solutions of Na_2SO_4 dissolves the lignin (the brown resinous component of wood which cements the fibres together) and liberates the cellulose fibres as pulp which then goes to the paper-making screens. The remaining solution is evaporated until it can be burned, thereby producing steam for the plant and heat for the evaporation: the fused Na_2SO_4 and NaOH survive the flames and can be reused. Total world production of Na_2SO_4 (1985) was ~4.5 million tonnes (45% natural, 55% synthetic). Most of this (~70%) is used in the paper industry and smaller amounts are used in glass manufacture and detergents (~10% each). The hydrated form, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, Glauber's salt, is now less used than formerly. Further information on the industrial production and uses of Na_2CO_3 , NaOH and Na_2SO_4 are given in *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn., Vol. 1, 1991, pp. 1025–39 and Vol. 22, 1997, pp. 354–419.

$2\text{H}_2\text{O}$ plus 4 oxygen atoms from CO_3 groups. The decahydrate has octahedral $\text{Na}(\text{H}_2\text{O})_6$ groups associated in pairs by edge sharing to give $[\text{Na}_2(\text{H}_2\text{O})_{10}]$. The hydrogencarbonate NaHCO_3 has infinite one-dimensional chains of HCO_3 formed by unsymmetrical $\text{O}-\text{H}\cdots\text{O}$ bonds (261 pm) which are held laterally by Na ions. The sesquicarbonates $\text{Na}_3\text{H}(\text{CO}_3)_2 \cdot 2\text{H}_2\text{O}$ have short,

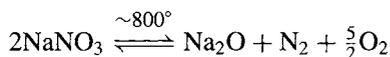
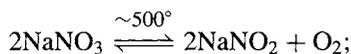
symmetrical $\text{O}-\text{H}-\text{O}$ bonds (253 pm) which link the carbonate ions in pairs, and longer $\text{O}-\text{H}\cdots\text{O}$ bonds (275 pm) which link these pairs to water molecules. Similar phases are known for the other alkali metals.

Alkali metal nitrates can be prepared by direct reaction of aqueous nitric acid on the appropriate hydroxide or carbonate. LiNO_3 is used for scarlet flares and pyrotechnic displays. Large deposits of NaNO_3 (saltpetre) are found in Chile and were probably formed by bacterial decay of small marine organisms: the NH_3 initially produced

³⁷ Ref. 4, pp. 149–63 and 219–25. See also *Kirk-Othmer Encyclopedia of Chemical Technology*, 4th edn., Vol. 1, 1991, Chlorine and sodium hydroxide, pp. 938–1025. Sodium carbonate, pp. 1025–39.

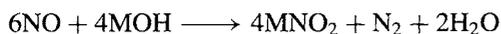
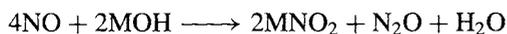
presumably oxidized to nitrous acid and nitric acid which would then react with dissolved NaCl. KNO_3 was formerly prepared by metathesis of NaNO_3 and KCl but is now obtained directly as part of the synthetic ammonia/nitric acid industry (p. 421).

Alkali metal nitrates are low-melting salts that decompose with evolution of oxygen above about 500°C , e.g.

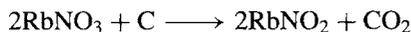
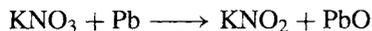


Thermal stability increases with increasing atomic weight, as expected. Nitrates have been widely used as molten salt baths and heat transfer media, e.g. the 1:1 mixture $\text{LiNO}_3:\text{KNO}_3$ melts at 125°C and the ternary mixture of 40% NaNO_2 , 7% NaNO_3 and 53% KNO_3 can be used from its mp 142° up to about 600°C .

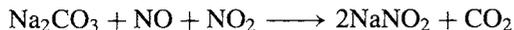
The corresponding nitrites, MNO_2 , can be prepared by thermal decomposition of MNO_3 as indicated above or by reaction of NO with the hydroxide:



Chemical reduction of nitrates has also been employed:



The commercial production of NaNO_2 is achieved by absorbing oxides of nitrogen in aqueous Na_2CO_3 solution:



Nitrites are white, crystalline hygroscopic salts that are very soluble in water. When heated in the absence of air they disproportionate:



NaNO_2 , in addition to its use with nitrates in heat-transfer molten-salt baths, is much used in the production of azo dyes and other organo-nitrogen compounds, as a corrosion inhibitor and in curing meats.

Other oxoacid salts of the alkali metals are discussed in later chapters, e.g. borates (p. 205), silicates (p. 347), phosphites and phosphates (p. 510), sulfites, hydrogensulfates, thiosulfates, etc. (p. 706) selenites, selenates, tellurites and tellurates (p. 781), hypohalites, halites, halates and perhalates (p. 853), etc.

4.3.6 Coordination chemistry ⁽³⁸⁻⁴²⁾

Exciting developments have occurred in the coordination chemistry of the alkali metals during the last few years that have completely rejuvenated what appeared to be a largely predictable and worked-out area of chemistry. Conventional beliefs had reinforced the predominant impression of very weak coordinating ability, and had rationalized this in terms of the relatively large size and low charge of the cations M^+ . On this view, stability of coordination complexes should diminish in the sequence $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$, and this is frequently observed, though the reverse sequence is also known for the formation constants of, for example, the weak complexes with sulfate, peroxosulfate, thiosulfate and the hexacyanoferrates in aqueous solutions.⁽³⁹⁾ It was also known that the alkali metal cations formed numerous hydrates, or aqua-complexes, as discussed in the preceding section, and there is a definite, though smaller tendency to form ammine complexes such as $[\text{Li}(\text{NH}_3)_4]\text{I}$. Other well-defined complexes include the extremely stable adducts $\text{LiX}\cdot 5\text{Ph}_3\text{PO}$, $\text{LiX}\cdot 4\text{Ph}_3\text{PO}$ and $\text{NaX}\cdot 5\text{Ph}_3\text{PO}$, where X is a large anion such as I, NO_3 , ClO_4 , BPh_4 , SbF_6 , AuCl_4 , etc.; these compounds melt in the range $200\text{--}315^\circ$ and are stable to air and water (in which they are insoluble).

³⁸ P. N. KAPOOR and R. C. MEHROTRA, *Coord. Chem. Rev.* **14**, 1-27 (1974).

³⁹ D. MIDGLEY, *Chem. Soc. Revs.* **4**, 549-68 (1975).

⁴⁰ N. S. POONIA and A. V. BAJAJ, *Chem. Revs.* **79**, 389-445 (1979).

⁴¹ W. SETZER and P. v. R. SCHLEYER, *Adv. Organomet. Chem.* **24**, 353-451 (1985).

⁴² C. SCHADE and P. v. R. SCHLEYER, *Adv. Organomet. Chem.* **27**, 169-278 (1987).

They probably all contain the tetrahedral ion $[\text{Li}(\text{OPPh}_3)_4]^+$ which was established by X-ray crystallography for the compound $\text{LiI} \cdot 5\text{Ph}_3\text{PO}$; the fifth molecule of Ph_3PO is uncoordinated.

In recent years this simple picture has been completely transformed and it is now recognized that the alkali metals have a rich and extremely varied coordination chemistry which frequently transcends even that of the transition metals. The efflorescence is due to several factors such as the emerging molecular chemistry of lithium in particular, the imaginative use of bulky ligands, the burgeoning numbers of metal amides, alkoxides, enolates and organometallic compounds, and the exploitation of multidentate

crown and cryptand ligands. Some of these aspects will be dealt with more fully in subsequent subsections (4.3.7 and 4.3.8).

Lithium is now known in at least 20 coordination geometries with coordination numbers ranging from 1–12. Some illustrative examples are in Table 4.3 and in the accompanying Figs. 4.8 and 4.9 which will repay close attention. The bulky ligand bis(trimethylsilyl)methyl forms a derivative in which Li is 1-coordinate in the gas phase but which polymerizes in the crystalline form to give bent 2-coordinate Li (and 5-coordinate carbon). The related ligand tris(trimethylsilyl)methyl gives an anionic complex in which Li is linear 2-coordinate, and the

Table 4.3 Stereochemistry of lithium

CN and shape	Examples	Remarks	Ref.
1	$[\text{LiCH}(\text{SiMe}_3)_2]$	Gas-phase electron diffr. Li–C 203 pm	43
2 linear	$[\text{Li}\{\text{C}(\text{SiMe}_3)_3\}_2]^-$	Li–C 216 pm, C–Li–C 180°. Cation is $[\text{Li}(\text{thf})_4]^+$	44
bent	Li_3N	$\text{Li}_1\text{–N}$ 194 pm. See Fig. 4.8a	45
	$\{\text{LiCH}(\text{SiMe}_3)_2\}_\infty$	Note 5-Coord C_α , Li–C 214, 222 pm; C–Li–C 147–152°, Li–C–Li 152°	43
3 planar	$\{\{\text{Li}(\mu\text{-OCBu}_3')_2\}\}_2$	Li–O 167.7 pm, O–Li–O 103°	46
	$\{\{\text{Li}(\mu\text{-NR}_2)(\text{OEt}_2)\}_2\}$	R = SiMe_3 ; Li–N 206 pm, Li–O 195 pm; N–Li–N 105°, N–Li–O 127.5°. See also Fig. 4.13 below	47
pyramidal angular	$[\text{Li}_5(\text{N}=\text{CPh}_2)_6(\text{O}=\text{P}(\text{NMe}_2)_3)]^-$	Cluster anion, see Fig. 4.8b	48
	$[\text{LiEt}]_4$	Cubane-like cluster, See Fig. 4.8c	49
4 tetrahedral	$[(\text{LiOCMe}_2\text{Ph})_6]$; $[\{\text{Li}(\text{c-hexyl})\}_6]$	Hexagonal prism, see Fig. 4.8d	50
	$[\text{Li}(\text{MeOH})_4]\text{I}$	See also $[\text{Li}(\text{thf})_4]^+$ in line 3, above, and Fig. 4.8b	51
5 trigonal-bipyramidal	$\{\text{LiAl}(\mu\text{-C}_2\text{H}_5)_4\}_\infty$		
	$[\text{LiBr}(\text{phen})_2] \cdot \text{Pr}^t\text{OH}$	Br equatorial, one N from each phen axial; N–Li–N 169°; Pr^tOH uncoordinated	52
	$[\text{LiL}][\text{ClO}_4]$	L is the aza cage shown in Fig. 4.8e	53

⁴³J. L. ATWOOD, T. FJELDBERG, M. F. LAPPERT, N. T. LUONG-THI, R. SHAKIR and A. J. THORNE, *J. Chem. Soc., Chem. Commun.*, 1163–5 (1984).

⁴⁴C. EABORN, P. B. HITCHOCK, J. D. SMITH and A. C. SULLIVAN, *J. Chem. Soc., Chem. Commun.*, 827–8 (1983).

⁴⁵U. v. ALPEN, *J. Solid State Chem.* **29**, 379–92 (1979), and refs. therein.

⁴⁶G. BECK, P. B. HITCHOCK, M. F. LAPPERT and I. A. MACKINNON, *J. Chem. Soc., Chem. Commun.*, 1313–4 (1989); see also ref. d.

⁴⁷T. FJELDBERG, P. B. HITCHOCK, M. F. LAPPERT and A. J. THORNE, *J. Chem. Soc., Chem. Commun.*, 822–4 (1984).

⁴⁸D. BARR, W. CLEGG, R. E. MULVEY and R. SNAITH, *J. Chem. Soc., Chem. Commun.*, 226–7 (1984).

⁴⁹H. DIETRICH, *J. Organomet. Chem.* **205**, 291–9 (1981).

⁵⁰M. H. CHISHOLM, S. R. DRAKE, A. A. NAINI and W. E. STRIEB, *Polyhedron* **10**, 805–10 (1991).

⁵¹W. WEPPNER, W. WELZEL, R. KNIEP and A. RABENAU, *Angew. Chem. Int. Edn. Engl.* **25**, 1087–9 (1986).

⁵²W. C. PATALINGHUG, C. R. WHITAKER and A. H. WHITE, *Aust. J. Chem.* **43**, 635–7 (1990).

⁵³A. BENCINI, A. BIANCHI, A. BORSELLI, M. CIAMPOLINI, M. MICHELONI, N. NARDI, P. PAOLI, B. VALTANCOLI, S. CHIMICHI and P. DAPPORTO, *J. Chem. Soc., Chem. Commun.*, 174–5 (1990).

Table 4.3 continued

CN and shape	Examples	Remarks	Ref.
sq. pyramidal	[LiL'] [BPh ₄]	L' is the aza cage shown in Fig. 4.8f	54
	[(Li(thf)) ₄ (C ₄ Bu' ₂) ₂]	Dimeric dilithiobutatriene complex, Fig. 4.8g	55
planar	[LiL''] [PF ₆]	L'' is the pentadentate ligand in Fig. 4.8h	56
6 octahedral	LiX	NaCl-type, X = H, F, Cl, Br, I. Also LiIO ₃ ; LiNO ₃ (calcite-type); LiAlSi ₂ O ₆ (spodumene)	
planar	Li ₃ N	See Fig. 4.8a. Li _{II} has 3 Li _I and 3 N at 213 pm	45
pentag. pyram.	[LiL*(MeOH)] [PF ₆]	See Fig. 4.8i	57
irregular	[Li ₂ (μ-η ⁴ , η ⁴ -C ₆ H ₈ (tmeda) ₂)]	See Fig. 4.9a	58
7 irregular	[Li(η ⁵ -C ₅ H ₄ SiMe ₃)(tmeda)]	5C at 227 pm, 2N at 215 pm. See Fig. 4.9b	59
	[Li ₂ (μ-η ⁵ , η ⁵ -C ₈ H ₆)(dme) ₂]	Pentalene-dimethoxyethane complex, Fig. 4.9c	60
8 cubic	Li metal	Body-centered cubic	
	LiHg, LiTl	CsCl-type	
irregular	[Li ₂ (μ-η ⁶ , η ⁶ -C ₁₀ H ₈)(tmeda) ₂]	Dilithionaphthalene complex, Fig. 4.9d	61
9 irregular	[Na ₂ Ph(Et ₂ O ₂ (Ph ₂ Ni) ₂ N ₂ Na-Li ₆ (OEt) ₄ (Et ₂ O) ₂)]	Fig. 4.9e. 4Li are 9-coord (1, 2, 5, 6), Li(4) is 7-coord and Li(3) is 6 coord	62
12 cuboctahedron	Li metal (cold worked, ccp)	Below 78 K Li is hcp (12 coord)	
hexag. prism.	[Li ₂ (μ-C ₁₉ H ₁₂) ₂]	Lithium 7bH-indenofluorene dimer, see Fig. 4.9f	63

⁵⁴A. BENCINI, A. BIANCHI, M. CIAMPOLINI, E. GARCIA-ESPANA, P. DAPPORTO, M. MICHELONI, P. PAOLI, J. A. RAMIREZ and B. VALTANCOLI, *J. Chem. Soc., Chem. Commun.*, 701-3 (1989).

⁵⁵W. NEUGEBAUER, G. A. P. GEIGER, A. J. KOS, J. J. STEZOWSKI and P. v. R. SCHLEYER, *Chem. Ber.* **118**, 1504-16 (1985).

⁵⁶E. C. CONSTABLE, M. J. DOYLE, J. HEALY and P. R. RAITHBY, *J. Chem. Soc., Chem. Commun.*, 1262-4 (1988).

⁵⁷E. C. CONSTABLE, L.-Y. CHUNG, J. LEWIS and P. R. RAITHBY, *J. Chem. Soc., Chem. Commun.*, 1719-20 (1986).

⁵⁸S. K. ARORA, R. B. BATES, W. A. BEAVERS and R. S. CUTLER, *J. Am. Chem. Soc.* **97**, 6271-2 (1975).

⁵⁹M. F. LAPPERT, A. SINGH, L. M. ENGELHART and A. H. WHITE, *J. Organomet. Chem.* **262**, 271-8 (1984).

⁶⁰J. J. STEZOWSKI, H. OIER, D. WILHELM, T. CLARK and P. v. R. SCHLEYER, *J. Chem. Soc., Chem. Commun.*, 1263-4 (1985).

⁶¹J. J. BROOKS, W. RHINE, G. D. STUCKY *J. Am. Chem. Soc.* **94**, 7346-51 (1972).

⁶²K. JONAS, D. J. BRAUER, C. KRÜGER, P. J. ROBERTS and Y.-H. TSAY *J. Am. Chem. Soc.* **98**, 74-81 (1976).

⁶³D. BLADAUSKI, H. DIETRICH, H.-J. HECHT and D. REWICKI, *Angew. Chem. Int. Edn. Engl.* **16**, 474-5 (1977).

same stereochemistry is observed in the unique structure of Li₃N (Fig. 4.8a) which also features the highly unusual planar 6-coordination mode; the structure comprises hexagonal sheets of overall composition Li₂N stacked alternately with planes containing the 2-coordinate Li. The coordination number of N is 8 (hexagonal bipyramidal). Three-coordinate Li is known in planar, pyramidal and angular geometries, the latter two modes being illustrated in Fig. 4.8b, c and d. Numerous examples of 4-coordinate Li have already been mentioned. Five-coordinate Li can be trigonal bipyramidal as in [LiBr(phen)₂]

and the aza cage cation shown in Fig. 4.8e, square pyramidal (Fig. 4.8f and g) or planar (Fig. 4.8h).

Table 4.3 indicates that octahedral coordination is a common mode for Li. Less usual is planar 6-fold coordination (Fig. 4.8a), pentagonal pyramidal coordination (Fig. 4.8i) or irregular 6-fold coordination (Fig. 4.9a). Examples of 7-fold coordination are in Fig. 4.9b and c. Lithium has cubic 8-fold coordination in the metallic form and in several of its alloys with metals of large radius. It is also 8-coordinate in the dilithionaphthalene complex shown in Fig. 4.9d; here the aromatic

hydrocarbon bonds to two lithium atoms in a bis-hexahapto bridging mode and each lithium is also coordinated by a chelating diamine. A much more complicated dimeric cluster compound, whose central ($\text{Li}_6\text{Na}_2\text{Ni}_2$) core is shown schematically in Fig. 4.9e, includes 9-coordinate lithium among its many fascinating structural features.

When Li metal is cold-worked it transforms from body-centred cubic to cubic close-packed in which each atom is surrounded by 12 others in twinned cuboctahedral coordination; below 78 K the stable crystalline modification is hexagonal close-packed in which each lithium atom has 12 nearest neighbours in the form of a cuboctahedron. This very high coordination

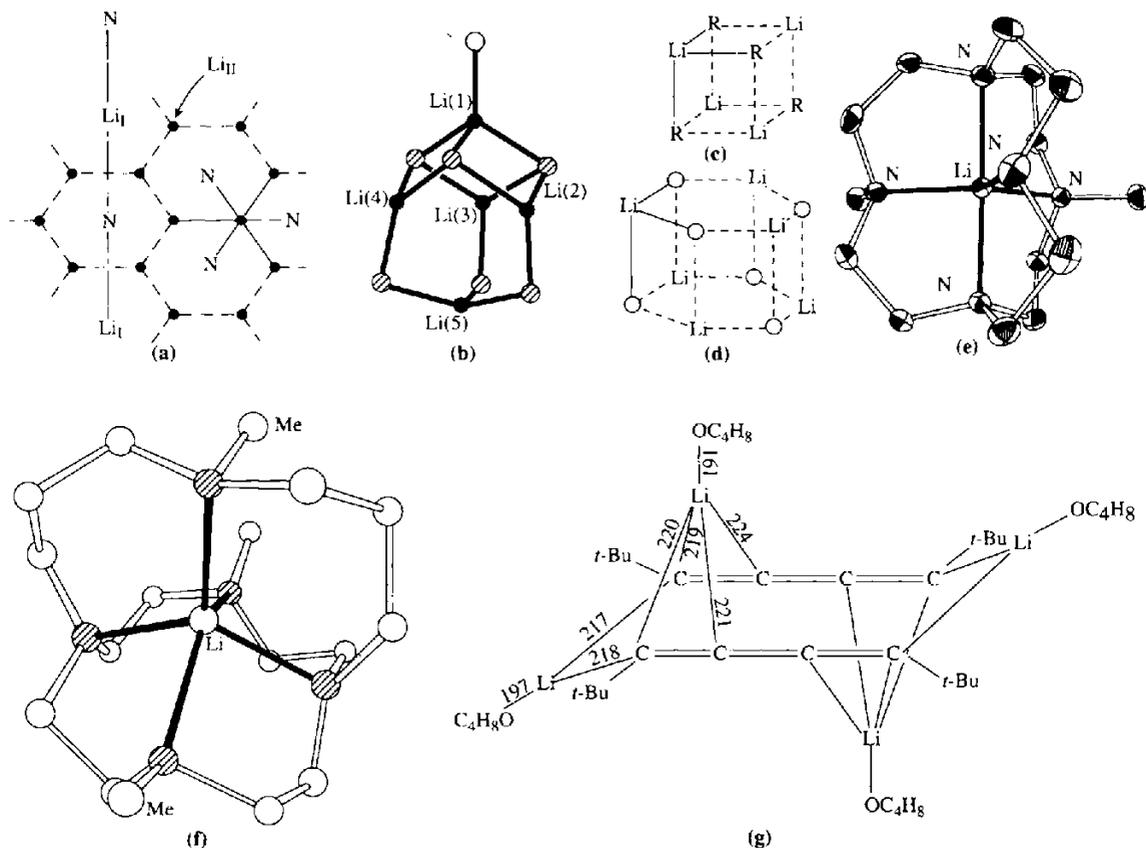


Figure 4.8 Structures of selected lithium compounds having coordination numbers ranging from 2 to 6. (a) The unique structure of Li_3N .⁽⁴⁵⁾ (b) The cluster anion $[\text{Li}_5(\text{N}=\text{CPh}_2)_6(\text{O}=\text{P}(\text{NMe}_2)_3)]^-$ showing four pyramidal and one tetrahedral Li^{48} [● = Li, ○ = $(\text{Me}_2\text{N})_3\text{P}=\text{O}$, ⊗ = $\text{Ph}_2\text{C}=\text{N}$]. (c) Schematic structure of the cubane-like cluster $[(\text{LiEt})_4]$ (rings are puckered).⁽⁴⁹⁾ (d) Schematic structure of the hexagonal prismatic cluster $[(\text{LiOCMe})_2\text{Ph}_6]$ (rings puckered).⁽⁵⁰⁾ (e) Li^+ encapsulated trigonal-bipyramidally by the cryptand dimethylpentaaza[5.5.5]heptadecane (L).⁽⁵³⁾ (f) Li^+ encapsulated square-pyramidally by the cryptand trimethylpentaazabicyclo[7.5.5]nonadecane (L').⁽⁵⁴⁾ (g) The dimeric dilithiobutatriene complex showing square-pyramidal coordination of two Li and trigonal coordination of the other two Li.⁽⁵⁵⁾ (h) Coordination of Li^+ by the planar pentadentate macrocycle dimethyltetraaza[6.0.0]pyridinophanediene (L'').⁽⁵⁶⁾ (i) Pentagonal-pyramidal coordination of Li^+ by the pentadentate macrocycle (L*) and an apical MeOH ligand; L* = (bis-2-hydroxyethyl)-6H,13H-tripyrrodoheptaazapentadecine.⁽⁵⁷⁾

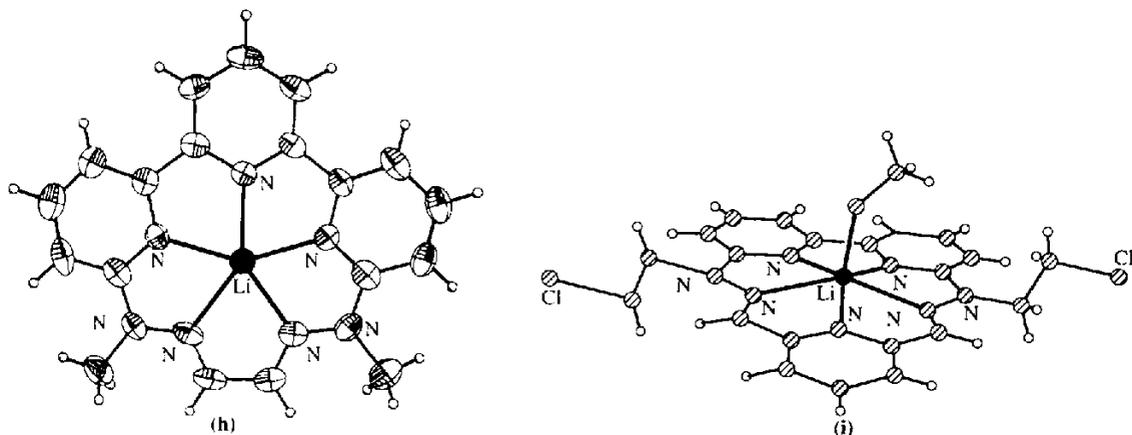


Figure 4.8 continued

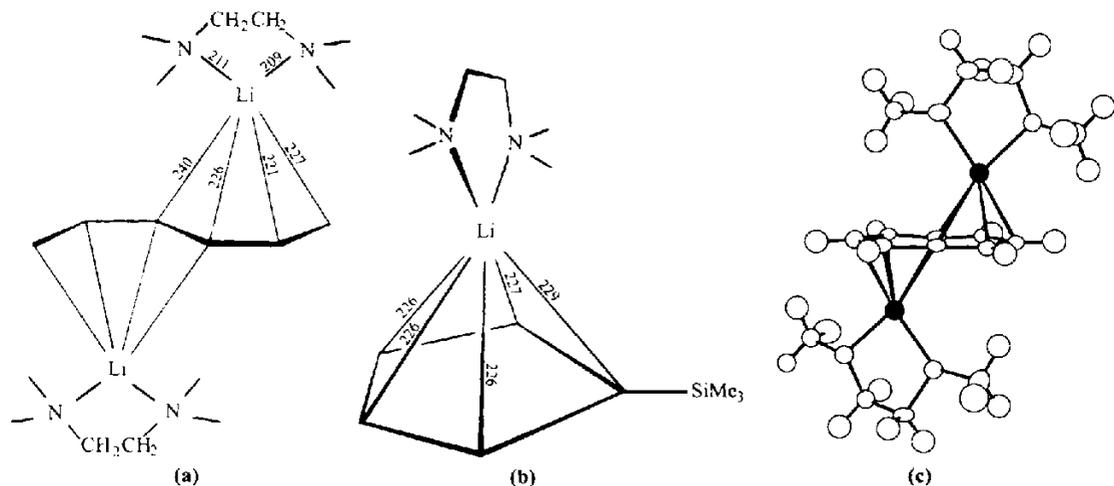


Figure 4.9 Structures of selected organolithium compounds illustrating coordination numbers ranging from 6 to 12. (a) The dilithiobis(tetramethylethylenediamine)hexatriene complex; each Li is coordinated by the bridging bistetrahapto triene and by one chelating tmeda ligand.⁽⁵⁸⁾ (b) The trimethylsilylcyclopentadienyllithium complex with tmeda.⁽⁵⁹⁾ (c) The dilithiopentalene-dimethoxyethane complex.⁽⁶⁰⁾ (d) The dilithionaphthalene complex with tmeda.⁽⁶¹⁾ (e) The $\text{Li}_6\text{Na}_2\text{Ni}_2$ core in the cluster $[(\text{Na}_2\text{Ph}(\text{Et}_2\text{O})_2(\text{Ph}_2\text{Ni})_2\text{N}_2\text{NaLi}_6(\text{OEt})_4(\text{Et}_2\text{O}))_2]$ showing the four 9-coordinate Li atoms (1, 2, 5, 6), together with the 7-coordinate Li(4) and 6-coordinate Li(3) atoms.⁽⁶²⁾ (f) Hexagonal-prismatic 12-fold coordination of Li in its *H*-indenofluorene dimer.⁽⁶³⁾

number is also found in the dimeric sandwich compound that Li forms with the extended planar hydrocarbon 7*bH*-indeno[1,2,3-*jk*]fluorene; in this case, as can be seen from Fig. 4.9f, the coordination geometry about the metal atoms is hexagonal prismatic.

Similar structural diversity has been established for the heavier alkali metals also but it is unnecessary to deal with this in detail. The structural chemistry of the organometallic compounds in particular, and of related complexes, has been well reviewed.^(41,42)

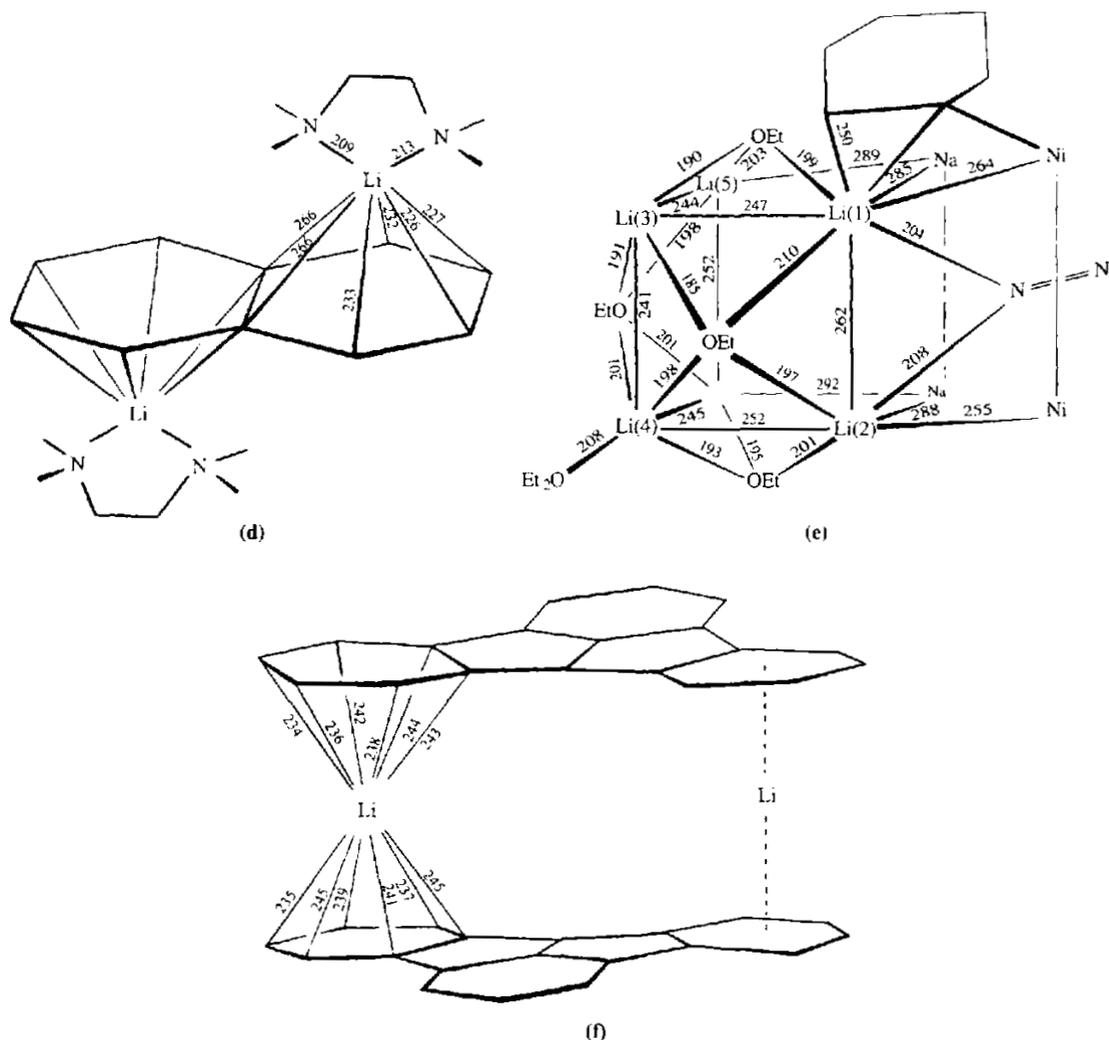


Figure 4.9 continued

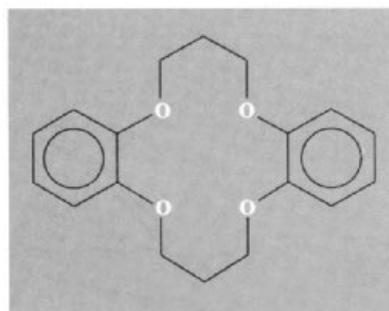
Complexes with chelating organic reagents such as salicylaldehyde and β -diketonates were first prepared by N. V. Sidgwick and his students in 1925, and many more have since been characterized. Stability, as measured by equilibrium formation constants, is rather low and almost invariably decreases in the sequence $\text{Li} > \text{Na} > \text{K}$. This situation changed dramatically in 1967 when C. J. Pedersen announced the synthesis of several macrocyclic polyethers which were shown to form stable complexes with

alkali metal and other cations.⁽⁶⁴⁾ The stability of the complexes was found to depend on the number and geometrical disposition of the ether oxygen atoms and in particular on the size and shape of potential coordination polyhedra relative to the size of the cation. For this reason stability could peak at any particular cation

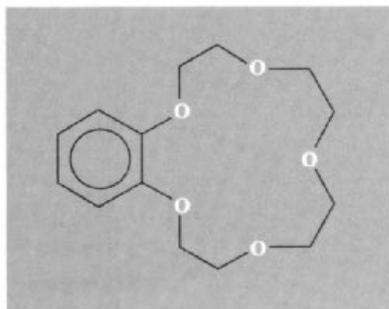
⁶⁴ C. J. PEDERSEN, *J. Am. Chem. Soc.* **89**, 2495, 7017–36 (1967). See also C. J. PEDERSEN and H. K. FRENSDORF, *Angew. Chem. Int. Edn. Engl.* **11**, 16–25 (1972).

and, for M^I , this was often K and sometimes Na or Rb rather than Li. Pedersen, who was awarded a Nobel Prize for these discoveries, coined the epithet "crown" for this class of macrocyclic polyethers because, as he said "the molecular structure looked like one and, with it, cations could be crowned and uncrowned without physical damage to either".⁽⁶⁵⁾ Typical examples of such "crown" ethers are given in Fig. 4.10, the numerical prefix indicating the number of atoms in the heterocycle and the suffix the number of ether oxygens. The aromatic rings can be substituted, replaced by naphthalene residues, or reduced to cyclohexyl derivatives. The "hole size" for coordination depends on the number of atoms in the ring and is compared with conventional ionic diameters in Table 4.4. The best complexing agents are rings of 15–24 atoms including 5 to eight oxygen atoms. Nitrogen and sulfur can also serve as the donor atoms in analogous macroheterocycles.

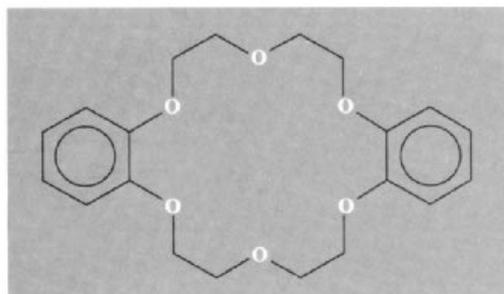
The X-ray crystal structures of many of these complexes have now been determined: representative examples are shown in Fig. 4.11 from which it is clear that, at least for the larger cations, coordinative saturation and bond directionality are far less significant factors than in many transition element complexes.^(66,67) Further interest in these ligands stems from their use in biochemical modelling since they sometimes mimic the behaviour of naturally occurring, neutral, macrocyclic antibiotics such as valinomycin, monactin, nonactin, nigericin



Dibenzo-14-crown-4



Benzo-15-crown-5



Dibenzo-18-crown-6

Figure 4.10 Schematic representation of the (non-planar) structure of some typical crown ethers.

⁶⁵ C. J. PEDERSON, Nobel Lecture, *Angew. Chem. Int. Edn. Engl.* **27**, 1021–7 (1988).

⁶⁶ J.-M. LEHN, *Struct. Bonding* **16**, 1–69 (1973).

⁶⁷ M. R. TRUTER, *Struct. Bonding* **16**, 71–111 (1973).

Table 4.4 Comparison of ionic diameters and crown ether "hole sizes"

Cation	Ionic diam/pm	Cation	Ionic diam/pm	Polyether ring	"Hole size"/pm
Li ⁺	152	Mg ²⁺	144	14-crown-4	120–150
Na ⁺	204	Ca ²⁺	200	15-crown-5	170–220
K ⁺	276	Sr ²⁺	236	18-crown-6	260–320
Rb ⁺	304	Ba ²⁺	270	21-crown-7	340–430
Cs ⁺	334	Ra ²⁺	296	—	—

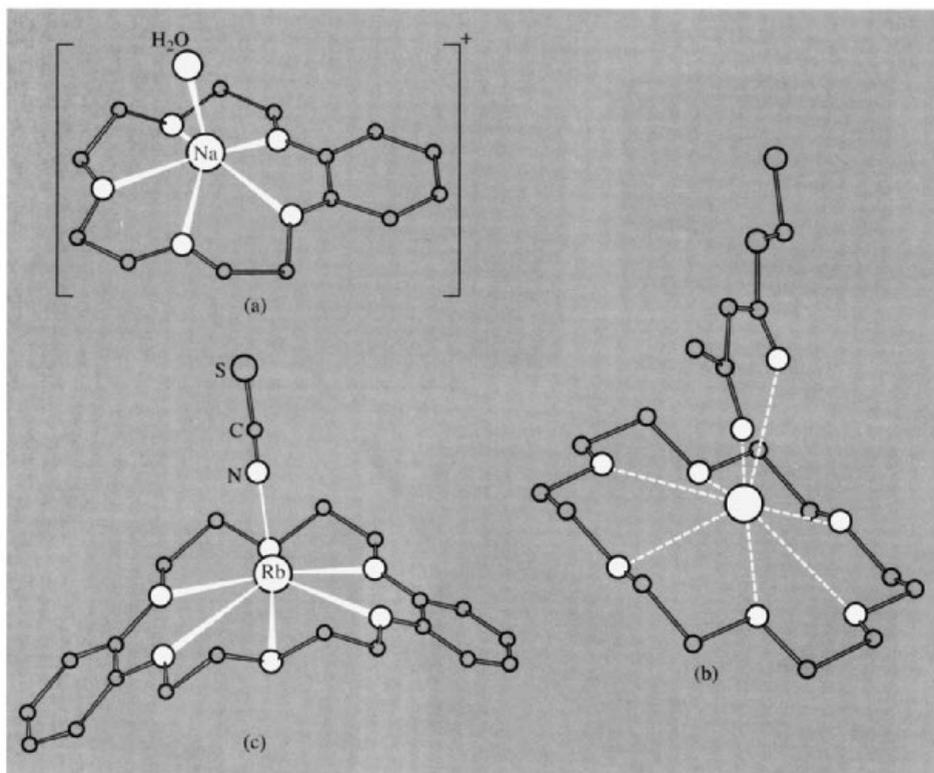


Figure 4.11 Molecular structures of typical crown-ether complexes with alkali metal cations: (a) sodium-water-benzo-15-crown-5 showing pentagonal-pyramidal coordination of Na by 6 oxygen atoms; (b) 18-crown-6-potassium-ethyl acetoacetate enolate showing unsymmetrical coordination of K by 8 oxygen atoms; and (c) the RbNCS ion pair coordinated by dibenzo-18-crown-6 to give seven-fold coordination about Rb.

and enneatin.^(68,69) They may also shed some light on the perplexing and remarkably efficient selectivity between Na and K in biological systems.^(68–70)

Another group of very effective ligands that have recently been employed to coordinate alkali metal cations are the macrobicyclic polydentate ligands that J.-M. Lehn has termed

“cryptands”,⁽⁷¹⁾ e.g. $N\{(CH_2CH_2O)_2CH_2CH_2\}_3N$ (Fig. 4.13a, b). This forms a complex $[Rb(\text{crypt})]CNS.H_2O$ in which the ligand encapsulates the cation with a bicapped trigonal prismatic coordination polyhedron (Fig. 4.12c, d). Such complexes are finding increasing use in solvent extraction, phase-transfer catalysis,⁽⁷²⁾ the

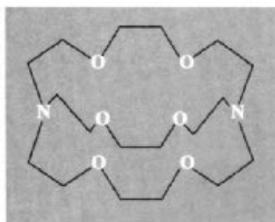
⁶⁸ W. SIMON, W. E. MORF and P. Ch. MEIER, *Struct. Bonding* **16**, 113–60 (1973).

⁶⁹ D. J. CRAM, Nobel Lecture, *Angew. Chem. Int. Edn. Engl.* **27**, 1009–20 (1988). See also F. VÖGTLE (ed.) *Host Guest Complex Chemistry, I, II and III*, Springer-Verlag, *Topics in Current Chemistry* **98**, 1–197 (1981); **101**, 1–203 (1982); **121**, 1–224 (1984).

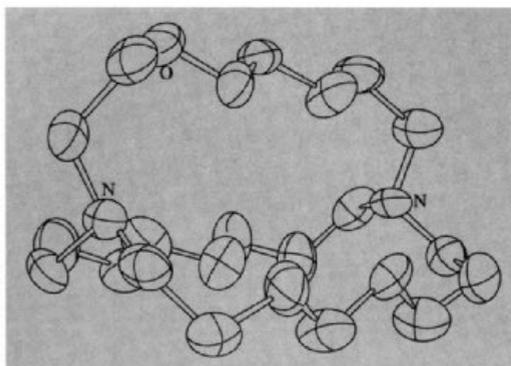
⁷⁰ R. M. IZATT, D. J. EATOUGH, and J. J. CHRISTENSEN, *Struct. Bonding* **16**, 161–89 (1973).

⁷¹ J.-M. LEHN, Nobel Lecture, *Angew. Chem. Int. Edn. Engl.* **27**, 89–112. (1988).

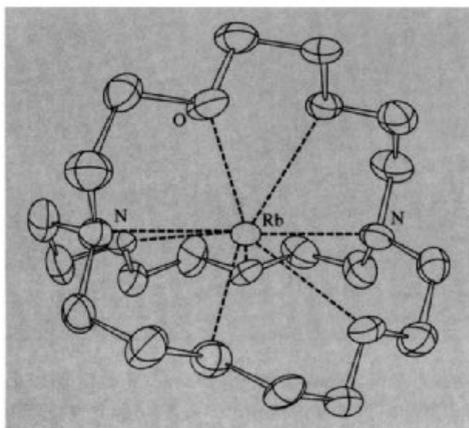
⁷² W. P. WEBER and G. W. GOKEL, *Phase Transfer Catalysis in Organic Synthesis*, Vol. 4 of *Reactivity and Structure*, Springer-Verlag, 1977, 250 pp. C. M. STARKS and C. LIOTTA, *Phase Transfer Catalysis*, Academic Press, New York, 1978, 365 pp. F. MONTANARI, D. LANDINI and F. ROLLA, *Topics in Current Chemistry* **101**, 149–201 (1982). E. V. DEHMLOW and S. S. DEHMLOW, *Phase Transfer Catalysis* (2nd edn.), VCH Publishers, London 1983, 386 pp. T. G. SOUTHERN, *Polyhedron* **8**, 407–13 (1989).



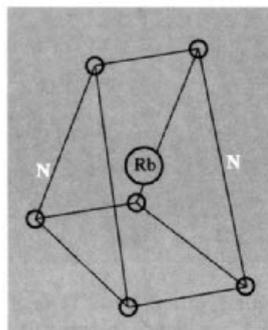
(a) Cryptand



(b) Molecular structure and conformation of the free macrobicyclic cryptand ligand



(c) Molecular structure of complex cation of RbSCN with cryptand.

(d) Schematic representation of bicapped trigonal prismatic coordination about Rb⁺.**Figure 4.12** A typical cryptand and its complex.

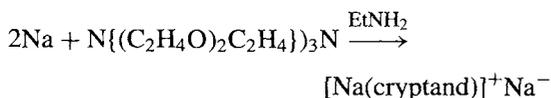
stabilization of uncommon or reactive oxidation states and the promotion of otherwise improbable reactions. Extraordinarily pronounced selectivity in complexation can be achieved by suitably designed ligands, some of the more spectacular being $K^+/Na^+ \sim 10^5$, $Cu^{2+}/Zn^{2+} \sim 10^8$, $Cd^{2+}/Zn^{2+} \sim 10^9$.

A growing application of cryptands and other macrocyclic polydentate ligands is in protecting sensitive anions from the polarizing and destabilizing effect of cationic charges, by encapsulating or crowning the cation and so preventing its close approach to the anion. For example, ozonides of K, Rb and Cs form

stable solutions in typical organic solvents (such as CH_2Cl_2 , tetrahydrofuran or MeCN) when the cation is coordinated by crown ethers or cryptands, thus enabling the previously unstudied solution chemistry of O_3^- to be investigated at room temperature.⁽⁷³⁾ Slow evaporation of ammonia solutions of such complexes yields red crystalline products and an X-ray structure of $[Rb(\eta^6-18\text{-crown-6})(\eta^2-O_3)(NH_3)]$ reveals 9-coordinate Rb, the chelating ozonide ion itself having O–O distances of 129 and 130 pm and an O–O–O angle of 117° .

⁷³ N. KORBER and M. JANSEN, *J. Chem. Soc., Chem. Commun.*, 1654–5 (1990).

A particularly imaginative application of this concept has led to the isolation of compounds which contain monatomic alkali metal *anions*. For example, Na was reacted with cryptand in the presence of EtNH₂ to give the first example of a sodide salt of Na⁻.⁽⁷⁴⁾



The Na⁻ is 555 pm from the nearest N and 516 pm from the nearest O, indicating that it is a separate entity in the structure. Potasides, rubidides and caesides have similarly been prepared.⁽⁷⁴⁾ The same technique has been used to prepare solutions and even crystals of electrides, in which trapped electrons can play the role of anion. Typical examples are [K(cryptand)]⁺e⁻ and [Cs(18-crown-6)]⁺e⁻.^(74,75)

Macrocycles, though extremely effective as polydentate ligands, are not essential for the production of stable alkali metal complexes; additional conformational flexibility without loss of coordinating power can be achieved by synthesizing benzene derivatives with 2–6 pendant mercapto-polyether groups C₆H_{6-n}R_n, where R is —SC₂H₄OC₂H₄OMe, —S(C₂H₄O)₃Bu, etc. Such “octopus” ligands are more effective than crowns and often equally as effective as cryptands in sequestering alkali metal cations.⁽⁷⁶⁾ Indeed, it is not even essential to invoke organic ligands at all since an inorganic cryptate which completely surrounds Na has been identified in the heteropolytungstate (NH₄)₁₇Na[NaW₂₁Sb₉O₈₆].14H₂O; the compound was also found to have pronounced antiviral activity.⁽⁷⁷⁾

⁷⁴ J. L. DYE, J. M. CERASE, M. T. LOK, B. L. BARNETT and F. J. TEHAN, *J. Am. Chem. Soc.* **96**, 608–9, 7203–8 (1974).
J. L. DYE, *Angew. Chem. Int. Edn. Engl.* **18**, 587–98 (1979).

⁷⁵ J. L. DYE, *Prog. Inorg. Chem.* **32**, 327–441 (1984);
J. L. DYE and R.-H. HUANG, *Chem. in Britain* March, 239–44 (1990).

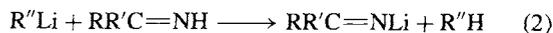
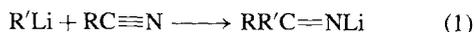
⁷⁶ F. VÖGTLE and E. WEBER, *Angew. Chem. Int. Edn. Engl.* **13**, 814–5 (1974).

⁷⁷ J. FISCHER, L. RICHARD and R. WEISS, *J. Am. Chem. Soc.* **98**, 3050–2 (1976).

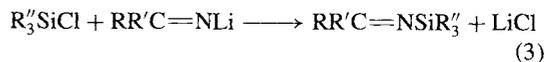
4.3.7 Imides, amides and related compounds^(78,79)

Before discussing the organometallic compounds of the alkali metals (which contain direct M–C bonds, Section 4.3.8) it is convenient to mention another important class of compounds: those which involve M–N bonds. In this way we shall resume the sequence of compounds which started with those having M–X bonds (i.e. halides, Section 4.3.2), through those with M–O bonds (oxides, hydroxides etc., Sections 4.3.3–4.3.5) to those with M–N and finally those with M–C bonds. As we shall see, several significant perceptions have emerged in this field during the past decade. For example, it is now generally agreed that in all these classes of compound the bond from the main group element to the alkali metal is predominantly ionic. Furthermore, structural studies of compounds with Li–N bonds in particular have led to the seminal concepts of *ring-stacking* and *ring-laddering* which, in turn, have permitted the rationalization of many otherwise puzzling structural features.

Lithium imides (imidolithiums) are air-sensitive compounds of general formula (RR'C=NLi)_n. They can be prepared in high yield either by the addition of an organolithium compound across the triple bond of a nitrile (equation (1)) or by lithiation of a ketimine (equation (2)).



Lithium imides have proved to be useful reagents for the synthesis of imino derivatives of a wide variety of other elements, e.g. Be, B, Al, Si, P, Mo, W and Fe as in equation (3).



When R and R' are both aryl groups the resulting lithium imides are amorphous, insoluble

⁷⁸ R. E. MULVEY, *Chem. Soc. Rev.* **20**, 167–209 (1991).

⁷⁹ K. GREGORY, P. V. R. SCHLEYER and R. SNAITH, *Adv. Inorg. Chem.* **37**, 47–142 (1991).

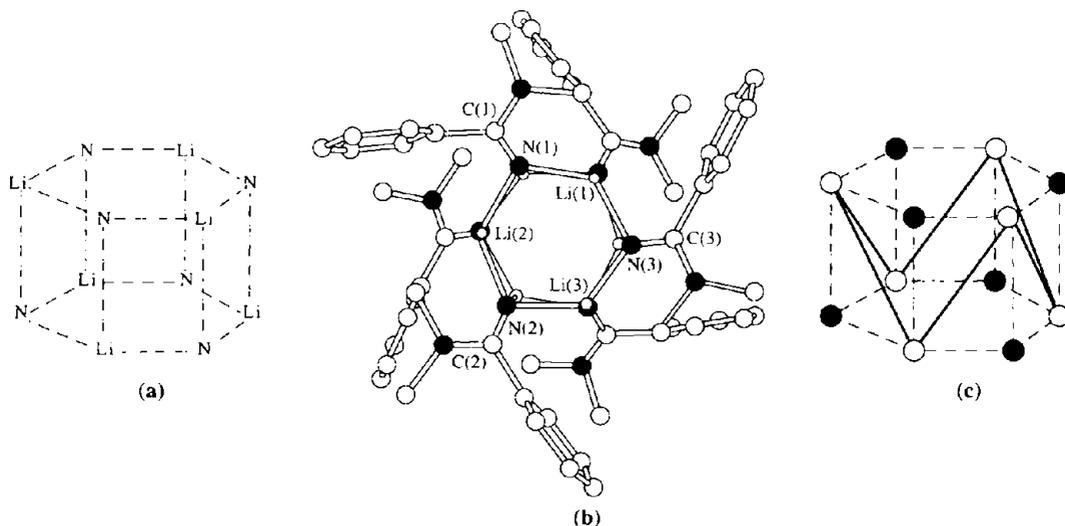


Figure 4.13 (a) Schematic representation of the Li_6N_6 core cluster in hexameric lithium imides. (b) The X-ray structure of $[\text{Me}_2\text{N}(\text{Ph})\text{C}=\text{NLi}]_6$ viewed from above showing the stacking of two 6-membered Li_3N_3 rings. (c) Each Li atom has two nearest-neighbour Li atoms in the adjacent ring at 248 pm, shown here joined by full lines; the mean Li-N distances (broken lines) are 198 pm within each ring and 206 pm between rings.⁽⁸⁰⁾

(presumably polymeric) solids, but if only one or neither of R, R' is an aryl group, soluble crystalline hexamers are obtained. The skeletal structure of these hexamers comprises an Li_6N_6 cluster formed by the stacking of two slightly puckered heterocyclic Li_3N_3 rings so that the Li atoms in each ring are almost directly above or below the N atoms in the adjacent ring. This is illustrated schematically in Fig. 4.13a (cf. Fig. 4.8d for the analogous hexameric alkoxide structure). An alternative view, looking down onto the open 6-membered face of the stack, is shown in Fig. 4.13b for the case of $[\text{Me}_2\text{N}(\text{Ph})\text{C}=\text{NLi}]_6$. Formation of such hexamers can be viewed as a stepwise process. Initially formed ion-pairs (monomers), $\text{Li}^+[\text{N}=\text{CRR}']^-$, with 1-coordinate Li^+ , associate at first to cyclic trimers, $(\text{LiN}=\text{CRR}')_3$, containing 2-coordinate Li^+ centres. Such rings are essentially planar systems [the planarity of the $(\text{LiN})_3$ ring itself extending outwards through the imido C up to

and including the α -atoms of R and R'] and so two such rings can come together, sharing their $(\text{LiN})_3$ faces and so raising the Li^+ coordination number to 3. Such stacking necessitates a loss in planarity of the original trimeric rings thus normally preventing more extensive stacking. A further feature of the stacked hexameric structure is the close approach of neighbouring Li atoms across the diagonals of the square faces (Fig. 4.13c), each Li atom being only 248 pm from its two nearest neighbours. This is much less than the Li-Li distance in Li metal (304 pm) or even in the necessarily covalent diatomic molecule Li_2 (274 pm), but this does not imply either metallic or covalent metal-metal bonding. Such close approaches merely reflect the small size of the Li^+ ion. For example, the Li-Li distance in LiF (which has the NaCl-type crystal structure) is 284 pm, which is 7% less than the Li-Li distance in Li metal itself.

The ring-stacking concept used in the preceding paragraph to explain the occurrence and structure of lithium imide hexamers can be applied more widely to Li-C, Li-N and Li-O rings and

⁸⁰ D. BARR, W. CLEGG, R. E. MULVEY, R. SNAITH and K. WADE, *J. Chem. Soc., Chem. Commun.*, 295-7 (1986).

clusters of various sizes.^(78,79) but the details lie outside the scope of the present treatment.

In contrast to the planar (sp^2) nitrogen centres in lithium imides, lithium amides, $(RR'NLi)_n$, feature tetrahedral (sp^3) nitrogen. The exocyclic R groups are thus above and below the $(LiN)_n$ plane and this prevents ring stacking. Rings of varying size are known, with $n = 2, 3$ or 4 depending on the nature of the substituents (Fig. 4.14a, b and c). In the important case of $n = 2$, the 4-membered Li_2N_2 heterocycles can associate further by edge fusion (rather than by face fusion) to form ladder-like structures as shown schematically in Fig. 4.14d. Specific examples of amidolithium heterocycles are $[(Me_3Si)_2NLi]_2$ (gas-phase), $[(PhCH_2)_2NLi]_3$ (Fig. 4.15a) and the tetramethylpiperidinolithium tetramer $[Me_2\bar{C}(CH)_2]_3CMe_2NLi_4$ (Fig. 4.15b). By contrast, lithiation of the cyclic amine pyrrolidine

in the presence of the chelating ligand tetramethylethylenediamine (tmeda) affords the

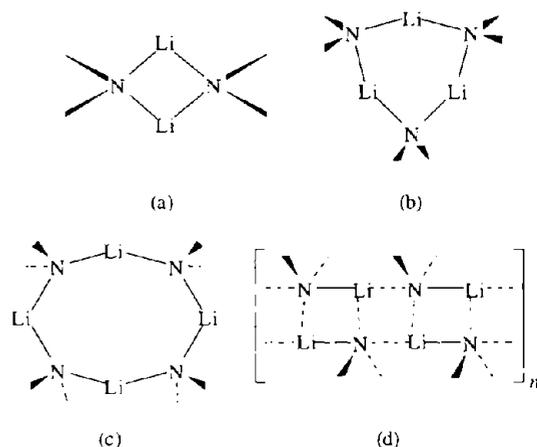


Figure 4.14 Schematic representation of (a) 4-membered, (b) 6-membered and (c) 8-membered $(LiN)_n$ heterocycles showing pendant groups on N lying both above and below the plane of the ring. (d) the ladder-like structure formed by lateral bonding of two Li_2N_2 units.

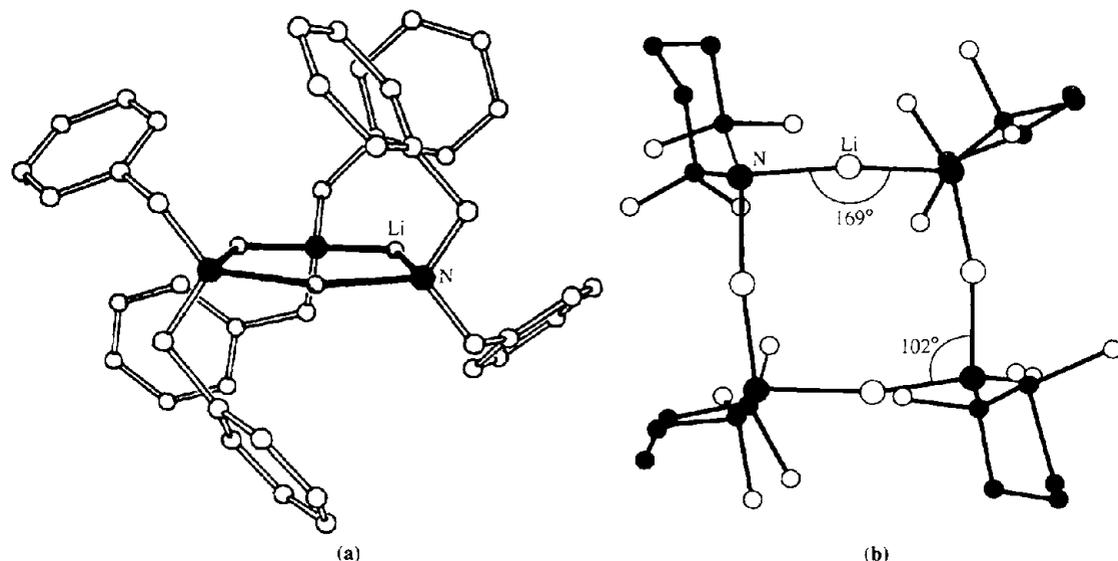


Figure 4.15 X-ray structure of (a) dibenzylamidolithium, $[(PhCH_2)_2NLi]_3$ ⁽⁸¹⁾ and (b) tetramethylpiperidinolithium, $[Me_2\bar{C}(CH)_2]_3CMe_2NLi_4$.⁽⁸²⁾

⁸¹ D. R. ARMSTRONG, R. E. MULVEY, G. T. WALKER, D. BARR, R. SNAITH, W. CLEGG and D. REED, *J. Chem. Soc., Dalton Trans.*, 617–28 (1988).

⁸² M. F. LAPPERT, M. J. SLADE, A. SINGH, J. L. ATWOOD, R. D. ROGERS and R. SHAKIR, *J. Am. Chem. Soc.* **105**, 302–3 (1983).

laddered complex $[(\text{H}_2\overline{\text{C}}(\text{CH}_2)_3\text{NLi})_2\text{tmeda}]_2$ (Fig. 4.16). Detailed examination of the interatomic distances in this structure clearly indicate that laddering is achieved by the lateral connection of the two outer Li_2N_2 rings. The Li–N bonds in all these compounds are considered to be predominantly ionic.

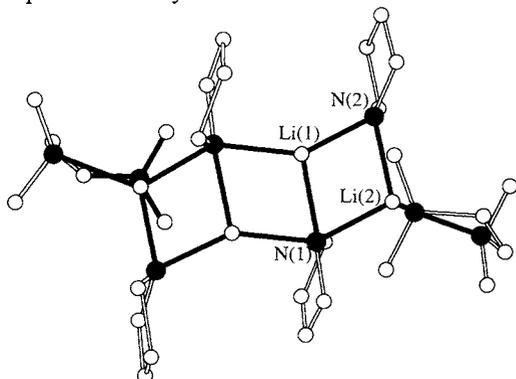


Figure 4.16 X-ray structure of the laddered complex $[(\text{H}_2\overline{\text{C}}(\text{CH}_2)_3\text{NLi})_2\text{tmeda}]_2$ where tmeda is tetramethylethylenediamine.⁽⁸³⁾

4.3.8 Organometallic compounds^(41,42,84,85)

Some structural aspects of the organometallic compounds of the alkali metals have already been briefly mentioned in Section 4.3.6. The diagonal relation of Li with Mg (p. 76), coupled with the known synthetic utility of Grignard reagents (pp. 132–5), suggests that Li, and perhaps the other alkali metals, might afford synthetically

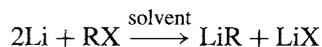
⁸³ D. R. ARMSTRONG, D. BARR, W. CLEGG, R. E. MULVEY, D. REED, R. SNAITH and K. WADE, *J. Chem. Soc., Chem. Commun.*, 869–70 (1986). D. R. ARMSTRONG, D. BARR, W. CLEGG, S. M. HODGSON, R. E. MULVEY, D. REED, R. SNAITH and D. S. WRIGHT, *J. Am. Chem. Soc.*, **111**, 4719–27 (1989).

⁸⁴ G. E. COATES, M. L. H. GREEN and K. WADE, *Organometallic Compounds*, Vol. 1, *The Main Group Elements*, 3rd edn., Chap. 1, The alkali metals, pp. 1–70, Methuen, London, 1967.

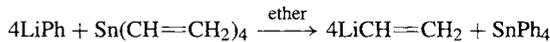
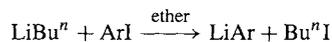
⁸⁵ G. WILKINSON, F. G. A. STONE and E. W. ABEL (eds.) *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982. Vol. 1, Chap. 2. J. L. WARDELL, Alkali Metals, pp. 43–120.

useful organometallic reagents. Such is found to be the case.⁽⁸⁶⁾

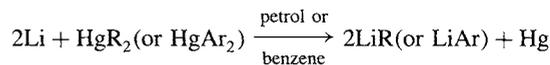
Organolithium compounds can readily be prepared from metallic Li and this is one of the major uses of the metal. Because of the great reactivity both of the reactants and the products, air and moisture must be rigorously excluded by use of an inert atmosphere. Lithium can be reacted directly with alkyl halides in light petroleum, cyclohexane, benzene or ether, the chlorides generally being preferred:



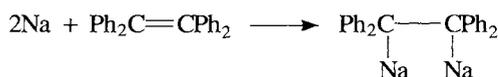
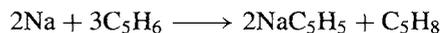
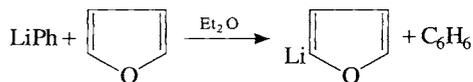
Reactivity and yields are greatly enhanced by the presence of 0.5–1% Na in the Li. The reaction is also generally available for the preparation of metal alkyls of the heavier Group 1 metals. Lithium aryls are best prepared by metal–halogen exchange using LiBu^n and an aryl iodide, and transmetalation is the most convenient route to vinyl, allyl and other unsaturated derivatives:



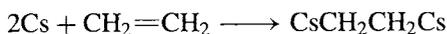
The reaction between an excess of Li and an organomercury compound is a useful alternative when isolation of the product is required, rather than its direct use in further synthetic work:



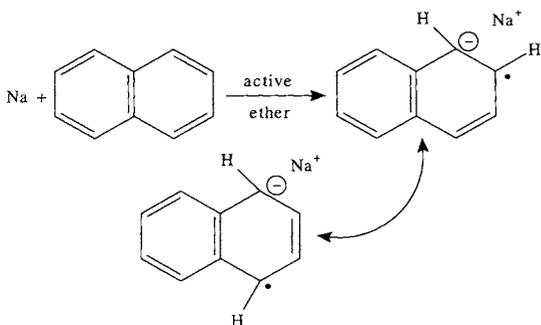
Similar reactions are available for the other alkali metals. Metalation (metal–hydrogen exchange) and metal addition to alkenes provide further routes, e.g.



⁸⁶ B. J. WAKEFIELD, *Organolithium Methods*, Academic Press, New York, 1988, 189 pp.

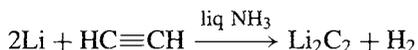
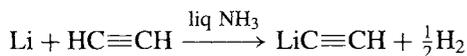


In the presence of certain ethers such as Me_2O , $\text{MeOCH}_2\text{CH}_2\text{OMe}$ or tetrahydrofuran, Na forms deep-green highly reactive paramagnetic adducts with polynuclear aromatic hydrocarbons such as naphthalene, phenanthrene, anthracene, etc.:

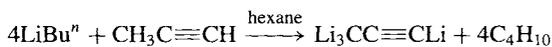


These compounds are in many ways analogous to the solutions of alkali metals in liquid ammonia (p. 77).

The most ionic of the organometallic derivatives of Group 1 elements are the acetylides and dicarbides formed by the deprotonation of alkynes in liquid ammonia solutions:



The largest industrial use of LiC_2H is in the production of vitamin A, where it effects ethynylation of methyl vinyl ketone to produce a key tertiary carbinol intermediate. The acetylides and dicarbides of the other alkali metals are prepared similarly. It is not always necessary to prepare this type of compound in liquid ammonia and, indeed, further substitution to give the bright red perliithiopropyne Li_4C_3 can be effected in hexane under reflux:⁽⁸⁷⁾



⁸⁷ R. WEST, P. A. CARNEY and I. C. MINEO, *J. Am. Chem. Soc.* **87**, 3788–9 (1965).

Organolithium compounds tend to be thermally unstable and most of them decompose to LiH and an alkene on standing at room temperature or above. Among the more stable compounds are the colourless, crystalline solids LiMe (decomp above 200°C), LiBu^n and LiBu^t (which shows little decomposition over a period of days at 100°C). Common lithium alkyls have unusual tetrameric or hexameric structures (see preceding sections). The physical properties of these oligomers are similar to those often associated with covalent compounds (e.g. moderately high volatility, high solubility in organic solvents and low electrical conductivity when fused). Despite this it is now generally agreed that the central $(\text{LiC})_n$ core is held together by predominantly ionic forces, though estimates of the precise extent of charge separation vary from about 55 to 95%.^(88–91) The resolution of this apparent paradox lies in the realization that continued polymerization of (Li^+R^-) monomers into infinite ionic arrays, such as are found in the alkali-metal halides, is hindered by the bulky nature of the R groups. Furthermore, these organic groups, which are covalently bonded within themselves, almost completely surround the ionic core and so dominate the bulk physical properties. Such ionic/covalent oligomers have been termed “supramolecules”.⁽⁹²⁾

The structure and bonding in lithium methyl have been particularly fully studied. The crystal structure consists of interconnected tetrameric units $(\text{LiMe})_4$ as shown in Fig. 4.17: the individual Li_4C_4 clusters consist of a tetrahedron

⁸⁸ A. STREITWIESER, J. E. WILLIAMS, S. ALEXANDRATOS and J. M. MCKELVEY, *J. Am. Chem. Soc.* **98**, 4778–84 (1976). A. STREITWIESER, *Acc. Chem. Res.* **17**, 353–7 (1984).

⁸⁹ E. D. JEMMIS, J. CHANDRASEKHAR and P. v. R. SCHLEYER, *J. Am. Chem. Soc.* **101**, 2848–56 (1979). P. v. R. SCHLEYER, *Pure Appl. Chem.* **55**, 355–62 (1983); **56**, 151–62 (1984).

⁹⁰ G. D. GRAHAM, D. S. MARYNICK and W. N. LIPSCOMB, *J. Am. Chem. Soc.* **102**, 4572–8 (1980).

⁹¹ D. BARR, R. SNAITH, R. E. MULVEY and P. G. PERKINS, *Polyhedron* **7**, 2119–28 (1988).

⁹² D. SEEBACH, *Angew. Chem. Int. Edn. Engl.* **27**, 1624–54 (1988).

⁹³ K. WADE, *Electron Deficient Compounds*, Nelson, London, 1971, 203 pp.

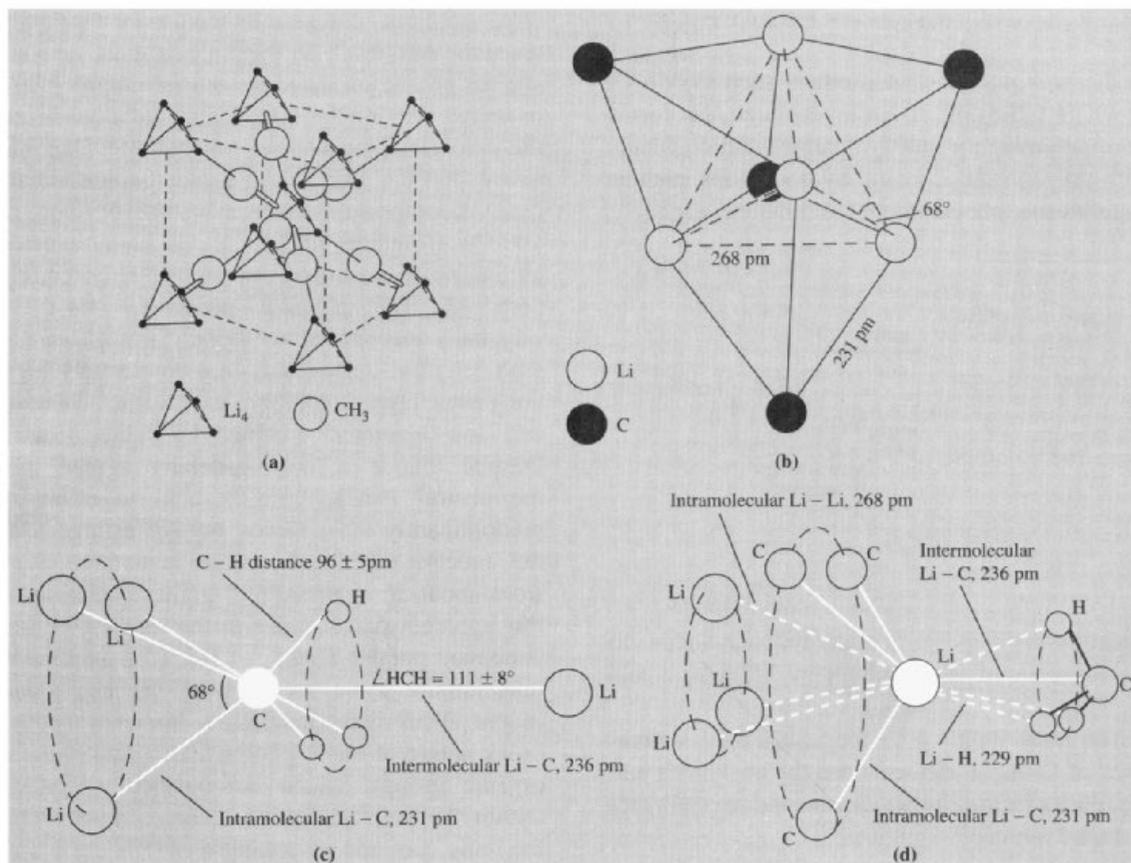


Figure 4.17 Crystal and molecular structure of $(\text{LiMe})_4$ showing (a) the unit cell of lithium methyl, (b) the Li_4C_4 skeleton of the tetramer viewed approximately along one of the threefold axes, (c) the 7-coordinate environment of each C atom, and (d) the $(4+3+3)$ -coordinate environment of each Li atom. After ref. 93, modified to include Li—H contacts.

of 4Li with a triply-bridging C above the centre of each face to complete a distorted cube. The clusters are interconnected along cube diagonals via the bridging CH_3 groups and the intercluster Li—C distance (236 pm) is very similar to the Li—C distance within each cluster (231 pm). The carbon atoms are thus essentially 7-coordinate being bonded directly to 3H and 4Li. The Li—Li distance within the cluster is 268 pm , which is virtually identical with the value of 267.3 pm for the gaseous Li_2 molecule and substantially smaller than the value of 304 pm in Li metal (where each Li has 8 nearest neighbours). Each Li atom is

therefore closely associated with three other Li atoms and three C atoms within its own cluster and with one C and three H atoms in an adjoining cluster. Detailed calculations show that the C—H \cdots Li interactions make a substantial contribution to the overall bonding.⁽⁹¹⁾ Such “agostic” interactions were indeed first noted in lithium methyl long before their importance in transition metal organometallic compounds was recognized. The effect is most pronounced in $(\text{LiEt})_4$ where the α -H on the ethyl group comes within 198 pm of its neighbouring Li atom;^(79,91) cf. 204.3 pm in solid LiH, which has the NaCl structure (pp. 65, 82).

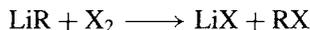
Higher alkyls of lithium adopt similar structures in which polyhedral clusters of metal atoms are bridged by alkyl groups located over the triangular faces of these clusters. For example, crystalline lithium *t*-butyl is tetrameric and the structural units $(\text{LiBu}^t)_4$ persist in solution; by contrast lithium ethyl, which is tetrameric in the solid state, dissolves in hydrocarbons as the hexamer $(\text{LiEt})_6$ which probably consists of octahedra of Li_6 with triply bridging $-\text{CH}_2\text{CH}_3$ groups above 6 of the 8 faces. As the atomic number of the alkali metal increases there is a gradual trend away from these oligomeric structures towards structures which are more typical of polarized ionic compounds. Thus, although NaMe is tetrameric like LiMe , NaEt adopts a layer structure in which the CH_2 groups have a trigonal pyramidal array of Na neighbours, and KMe adopts a NiAs-type structure (p. 679) in which each Me is surrounded by a trigonal prismatic array of K. The extent to which this is considered to be K^+CH_3^- is a matter for discussion though it will be noted that CH_3^- is isoelectronic with the molecule NH_3 .

The structure of the organometallic complex lithium tetramethylborate LiBMe_4 is discussed on pp. 127–8 alongside that of polymeric BeMe_2 with which it is isoelectronic.

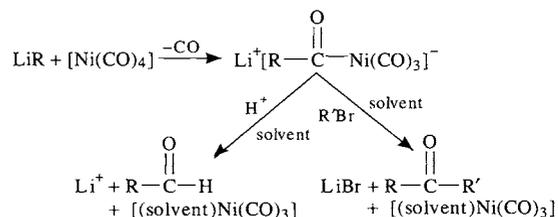
Organometallic compounds of the alkali metals (particularly LiMe and LiBu^n) are valuable synthetic reagents and have been increasingly used in industrial and laboratory-scale organic syntheses during the past 20 y.^(86,94,95) The annual production of LiBu^n alone has leapt from a few kilograms to about 1000 tonnes. Large scale applications are as a polymerization catalyst, alkylating agent and precursor to metalated organic reagents. Many of the synthetic reactions parallel those of Grignard reagents over which they sometimes have distinct advantages in terms of speed of reaction, freedom from complicating side reactions or convenience of handling. Reactions are

those to be expected for carbanions, though free-radical mechanisms occasionally occur.

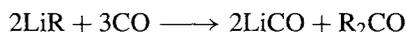
Halogens regenerate the parent alkyl (or aryl) halide and proton donors give the corresponding hydrocarbon:



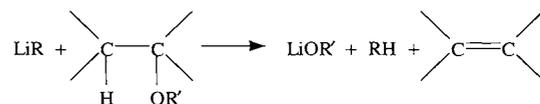
C–C bonds can be formed by reaction with alkyl iodides or more usefully by reaction with metal carbonyls to give aldehydes and ketones: e.g. $\text{Ni}(\text{CO})_4$ reacts with LiR to form an unstable acyl nickel carbonyl complex which can be attacked by electrophiles such as H^+ or $\text{R}'\text{Br}$ to give aldehydes or ketones by solvent-induced reductive elimination:



$[\text{Fe}(\text{CO})_5]$ reacts similarly. Aldehydes and ketones can also be obtained from *N,N*-disubstituted amides, and symmetrical ketones are formed by reaction with CO:



Thermal decomposition of LiR eliminates a β -hydrogen atom to give an olefin and LiH , a process of industrial importance for long-chain terminal alkenes. Alkenes can also be produced by treatment of ethers, the organometallic reacting here as a very strong base (proton acceptor):

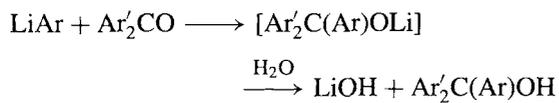
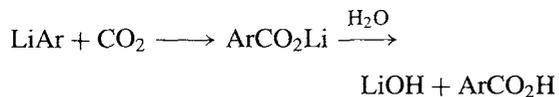


⁹⁴ B. J. WAKEFIELD, *The Chemistry of Organolithium Compounds*, Pergamon Press, Oxford, 1976, 337 pp.

⁹⁵ K. SMITH, Lithiation and organic synthesis, *Chem. in Br.* **18**(1), 29–32 (1982)

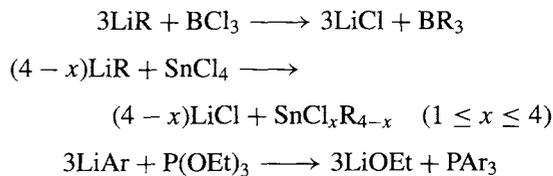
Lithium aryls react as typical carbanions in non-polar solvents giving carboxylic acids with CO_2

and tertiary carbinols with aryl ketones:



Organolithium reagents are also valuable in the synthesis of other organometallic compounds via

metal-halogen exchange:



Similar reactions have been used to produce organo derivatives of As, Sb, Bi; Si, Ge and many other elements.