Chapter 10

THE GROUP IA(1) ELEMENTS: LITHIUM, SODIUM, POTASSIUM, RUBIDIUM, AND CESIUM

10-1 Introduction

Sodium and potassium are abundant (2.6 and 2.4%, respectively) in the lithosphere. There are vast deposits of rock salt (NaCl) and $KCl \cdot MgCl_2 \cdot 6\,H_2O$ (carnallite) resulting from evaporation of lagoons over geologic time. The Great Salt Lake of Utah and the Dead Sea in Israel are examples of evaporative processes at work today. The elements Li, Rb, and Cs have much lower abundances and occur in a few silicate minerals.

The element Fr has only very short-lived isotopes that are formed in natural radioactive decay series or in nuclear reactors. Tracer studies show that the ion behaves as expected from the position it holds in Group IA(1).

Sodium and its compounds are of great importance. The metal, as Na—Pb alloy, is used to make tetraalkylleads (Section 29-9), and there are other industrial uses. The hydroxide, carbonate, sulfate, tripolyphosphate, and silicate are among the top 50 industrial chemicals.

Potassium salts, usually sulfate, are used in fertilizers. The main use for Li is as a metal in the synthesis of lithium alkyls (Section 29-3).

Both Na^+ and K^+ are of physiological importance in animals and plants; cells probably differentiate between Na^+ and K^+ by some type of complexing mechanism. Lithium salts are used in the treatment of certain mental disorders.

Some properties of the elements were given in Table 8-1. The low ionization enthalpies and the fact that the resulting M^+ ions are spherical and of low polarizability leads to a chemistry of +1 ions. The high second ionization enthalpies preclude the formation of +2 ions. Despite the essentially ionic nature of Group IA(1) compounds, some degree of covalent bonding can occur. The diatomic molecules of the elements (e.g., Na_2) are covalent. In some chelate and organometallic compounds, the M—O, M—N, and M—C bonds have a slight covalent nature. The tendency to covalency is greatest for the ion with the greatest polarizing power, that is, Li^+. The charge/radius ratio for Li^+, which is similar to that for Mg^{2+}, accounts for the similarities in their chemistry, where Li^+ differs from the other members.

Some other ions that have +1 charge and radii similar to those of the alkalis may have similar chemistry. The most important are

1. Ammonium and substituted ammonium ions. The solubilities and crystal structures of salts of NH_4^+ resemble those of K^+.
2. The Tl^+ ion can resemble either Rb^+ or Ag^+; its ionic radius is similar to that of Rb^+, but it is more polarizable.
3. Spherical +1 complex ions, such as $(\eta^5\text{-}C_5H_5)_2Co^+$ (Chapter 29).

10-2 Preparation and Properties of the Elements

Both Li and Na are obtained by electrolysis of fused salts or of low-melting eutectics such as $CaCl_2 + NaCl$. Because of their low melting points and ready vaporization K, Rb, and Cs cannot readily be made by electrolysis, but are obtained by treating molten chlorides with Na vapor. The metals are purified by distillation. The elements Li, Na, K, and Rb are silvery but Cs has a golden-yellow cast. Because there is only one valence electron per metal atom, the binding energies in the close-packed metal lattices are relatively weak. Hence, the metals are very soft with low melting points. The Na—K alloy, with 77.2% K, has a melting point of −12.3 °C.

The elements Li, Na, or K may be dispersed on various solid supports, such as Na_2CO_3 or kieselguhr, by melting. They are used as catalysts for various reactions of alkenes, notably the dimerization of propene to 4-methyl-1-pentene. Dispersions in hydrocarbons result from high-speed stirring of a suspension of the melted metal. These dispersions may be poured in air, and they react with water with effervescence. They may be used where sodium shot or lumps would react too slowly.

The metals are highly electropositive (Table 8-1) and react directly with most other elements and many compounds on heating. Lithium is usually the least, and Cs the most, reactive.

Lithium is only slowly attacked by water at 25 °C and will not replace the weakly acidic hydrogen in $C_6H_5C{\equiv}CH$, whereas the other alkali metals will do so. However, Li is uniquely reactive with N_2 (slowly at 25 °C, but rapidly at 400 °C) forming a ruby-red crystalline nitride (Li_3N). Like Mg, which gives Mg_3N_2, lithium can be used to absorb N_2.

With water, Na reacts vigorously, K inflames, and Rb and Cs react explosively; large lumps of Na may also react explosively. The elements Li, Na, and K can be handled in air although they tarnish rapidly. The others must be handled under Ar.

A fundamental difference, which is attributable to cation size, is shown by the reaction with O_2. In air (or O_2) at 1 atm the metals burn. Lithium gives only Li_2O with a trace of Li_2O_2. Sodium normally gives the peroxide, Na_2O_2, but it will take up further O_2 under pressure and heat to give the superoxide, NaO_2. The elements K, Rb, and Cs form the superoxides MO_2. The increasing stability of the per- and superoxides as the size of the alkali ions increases is a typical example of the stabilization of larger anions by larger cations through lattice-energy effects, as is explained in Section 4-6.

The metals react with alcohols to give the alkoxides, and Na or K in ethanol or *tert*-butanol is commonly used in organic chemistry as a reducing agent and a source of the nucleophilic RO^- ions.

Sodium and the other metals dissolve with much vigor in mercury. Sodium amalgam (Na/Hg) is a liquid when low in sodium, but is solid when rich in sodium. It is a useful reducing agent and can be used for aqueous solutions.

10-3 Solutions of the Metals in Liquid Ammonia and Other Solvents

The Group IA(1) metals, and to a lesser extent Ca, Sr, Ba, Eu, and Yb, are soluble in ammonia giving solutions that are blue when dilute. These solutions conduct electricity and the main current carrier is the solvated electron. While the lifetime of the solvated electron in water is very short, in very pure liquid ammonia it may be quite long (<1% decomposition per day).

In *dilute solutions* the main species are metal ions (M^+) and electrons, which are both solvated. The broad absorption around 15,000 Å, which accounts for the common blue color, is due to the solvated electrons. Magnetic and electron spin resonance studies show the presence of individual electrons, but the decrease in paramagnetism with increasing concentration suggests that the electrons can associate to form diamagnetic electron pairs. Although there may be other equilibria, the data can be accommodated by the equilibria

$$\mathrm{Na(s)\ (dispersed)} \rightleftharpoons \mathrm{Na\ (in\ solution)} \rightleftharpoons \mathrm{Na^+ + e^-} \quad (10\text{-}3.1)$$

$$2\,e^- \rightleftharpoons e_2^{2-} \quad (10\text{-}3.2)$$

The most satisfactory models of the solvated electron assume that the electron is not localized but is "smeared out" over a large volume so that the surrounding molecules experience electronic and orientational polarization. The electron is trapped in the resultant polarization field, and repulsion between the electron and the electrons of the solvent molecules leads to the formation of a cavity within which the electron has the highest probability of being found. In ammonia this is estimated to be approximately 3.0–3.4 Å in diameter; this cavity concept is based on the fact that solutions are of much lower density than the pure solvent, that is, they occupy far greater volume than that expected from the sum of the volumes of metal and solvent.

As the concentration of metal increases, metal ion clusters are formed. Above 3 *M* concentration, the solutions are copper colored with a metallic luster. Physical properties, such as their exceedingly high electrical conductivities, resemble those of liquid metals. More is said about this in Section 10-7.

The metals are also soluble to varying degrees in other amines, hexamethylphosphoramide, $OP(NMe_2)_3$, and in ethers such as THF or diglyme, giving blue solutions.

The ammonia and amine solutions are widely used in organic and inorganic synthesis. (Lithium in methylamine or ethylenediamine can reduce aromatic rings to cyclic monoalkenes.) Sodium in liquid ammonia is the most widely used of such reducing agents. The blue solution is moderately stable at temperatures where ammonia is still a liquid, but reaction to give the amide (Reaction 10-3.3),

$$\mathrm{Na + NH_3(\ell) = NaNH_2 + \tfrac{1}{2}\,H_2} \quad (10\text{-}3.3)$$

can occur photochemically and is catalyzed by transition metal salts. Thus sodium amide is prepared by treatment of Na with ammonia in the presence of a trace of iron(III) chloride. Primary and secondary amines react similarly, giving alkylamides (Reaction 10-3.4),

$$\mathrm{Li(s)} + \mathrm{CH_3NH_2}(\ell) \longrightarrow \mathrm{LiNHCH_3(s)} + \tfrac{1}{2}\,\mathrm{H_2} \qquad (10\text{-}3.4)$$

and dialkylamides (Reaction 10-3.5), respectively.

$$\mathrm{Li(s)} + \mathrm{(C_2H_5)_2NH}(\ell) \longrightarrow \mathrm{LiN(C_2H_5)_2(s)} + \tfrac{1}{2}\,\mathrm{H_2} \qquad (10\text{-}3.5)$$

The lithium dialkylamides are used to make compounds with M—NR$_2$ bonds (Section 24-7).

The formation of the amides of K, Rb, and Cs is reversible owing to the favorable potential for half-reaction 10-3.6.

$$e^- + \mathrm{NH_3} = \mathrm{NH_2^-} + \tfrac{1}{2}\,\mathrm{H_2} \qquad K = 5 \times 10^4 \qquad (10\text{-}3.6)$$

The similar reactions for Li and Na are irreversible, owing to the insolubility of the latter amides in ammonia:

$$\mathrm{Na^+(am)} + e^-(\mathrm{am}) + \mathrm{NH_3}(\ell) = \mathrm{NaNH_2(s)} + \tfrac{1}{2}\,\mathrm{H_2} \qquad K = 3 \times 10^9 \qquad (10\text{-}3.7)$$

where am denotes a solution in ammonia.

COMPOUNDS OF THE GROUP IA(1) ELEMENTS

10-4 Binary Compounds

The metals of Group IA(1) react directly with most other elements to give binary compounds or alloys. Many of these compounds are described under the appropriate element. The most important are the oxides (M_2O), peroxides (M_2O_2), and superoxides (MO_2). Although all three types can be obtained for each alkali metal, indirect methods are often required. The direct reactions of the metals with an excess of O_2 give different products, depending on the metal: lithium predominantly forms the oxide, along with traces of the peroxide; sodium preferentially forms the peroxide, with traces of the oxide; potassium, rubidium, and cesium form superoxides.

All three types of compounds between oxygen and an alkali metal are readily hydrolyzed:

$$\text{Oxides} \qquad \mathrm{M_2O + H_2O = 2\,M^+ + 2\,OH^-} \qquad (10\text{-}4.1)$$

$$\text{Peroxides} \qquad \mathrm{M_2O_2 + 2\,H_2O = 2\,M^+ + 2\,OH^- + H_2O_2} \qquad (10\text{-}4.2)$$

$$\text{Superoxides} \qquad \mathrm{2\,MO_2 + 2\,H_2O = O_2 + 2\,M^+ + 2\,OH^- + H_2O_2} \qquad (10\text{-}4.3)$$

10-5 Hydroxides

These are white, very deliquescent crystalline solids: NaOH (mp 318 °C) and KOH (mp 360 °C). The solids and their aqueous solutions absorb CO_2 from the atmosphere. Hydroxides are freely soluble exothermically in water and in alcohols and are used whenever strong alkali bases are required.

10-6 Ionic Salts

Salts of virtually all acids are known; they are usually colorless, crystalline, ionic solids. Color arises from colored anions, except where defects induced in the lattice (e.g., by radiation) may cause *color centers,* through electrons being trapped in holes (cf. ammonia solutions cited previously).

The properties of a number of *lithium compounds* differ from those of the other Group IA(1) elements but resemble those of Mg^{2+} compounds. Many of these anomalous properties arise from the very small size of Li^+ and its effect on lattice energies, as explained in Section 4-6. In addition to examples cited there, we note that LiH is stable to approximately 900 °C, while NaH decomposes at 350 °C. The compound Li_3N is stable, whereas Na_3N does not exist at 25 °C. Lithium hydroxide decomposes at red heat to Li_2O, whereas the other hydroxides MOH sublime unchanged; LiOH is also considerably less soluble than the other hydroxides. The carbonate (Li_2CO_3) is thermally less stable relative to Li_2O and CO_2 than are other alkali metal carbonates. The solubilities of Li^+ salts resemble those of Mg^{2+}. Thus LiF is sparingly soluble (0.27 g/100 g H_2O at 18 °C) and is precipitated from ammoniacal NH_4F solutions; LiCl, LiBr, LiI and, especially $LiClO_4$ are soluble in ethanol, acetone, and ethyl acetate; LiCl is soluble in pyridine.

The alkali metal salts are generally characterized by high melting points, by electrical conductivity of the melts, and by ready solubility in water. These salts are seldom hydrated when the anions are small, as in the halides, because the hydration energies of the ions are insufficient to compensate for the energy required to expand the lattice. The Li^+ ion has a large hydration energy, and it is often hydrated in its solid salts when the same salts of other alkalis are unhydrated, e.g., $LiClO_4 \cdot 3\ H_2O$. For salts of *strong* acids, the Li salt is usually the *most* soluble in water of the alkali metal salts, whereas for *weak* acids the Li salts are usually *less* soluble than those of the other elements.

There are few important *precipitation reactions* of the ions. One example is the precipitation by methanolic solutions of 4,4′-diaminodiphenylmethane (L) of Li and Na salts (e.g., NaL_3Cl). Generally, the larger the M^+ ion the more numerous are its insoluble salts. Thus Na has few insoluble salts; the mixed Na—Zn and Na—Mg uranyl acetates [e.g., $NaZn(UO_2)_3(CH_3CO_2)_9 \cdot 6\ H_2O$], which may be precipitated almost quantitatively from dilute acetic acid solutions, are useful for analysis. Salts of the heavier ions, K^+, Rb^+, and Cs^+, with large anions such as $ClO^-{}_4$, $[PtCl_6]^{2-}$, $[Co(NO_2)_6]^{3-}$, and $B(C_6H_5)_4^-$, are relatively insoluble and form the basis for gravimetric analysis.

10-7 Solvation and Complexation of Alkali Metal Ions

Hydration of Alkali Metal Cations

For alkali metal cations, as well as for others, solvation must be considered from two points of view. First, each ion in solution possesses a primary solvation shell (termed hydration shell when the solvent is water), which is the number of solvent (water) molecules directly coordinated to the metal ion, as described for ligands in Chapter 6. The discussion of water exchange rates in Section 6-5 (in particular Fig. 6-6) concerned precisely this first solvation, or coordination layer. Second, there is also the overall solvation number, which is the total number of solvent molecules on which the ion exercises a substantial restraining influence. Thus, although the first solvation shell or coordination sphere of a solvated metal ion is the most important, other layers of solvent molecules are organized and influenced by the cation. As an example, consider the aqueous lithium cation which, as shown in Table 10-1, has a hydration number of about 25. This means that a total of 25 water molecules operate in aqueous solution under the restraining influence of the cation's positive charge to such an extent as to be considered bound to the cation.

In the case of Li^+, a primary coordination number of four tetrahedrally arranged water molecules is observed in numerous crystalline salts, and a similar arrangement of four water molecules probably exists in aqueous solutions. The ions Na^+ and K^+ may also have fourfold primary hydration in aqueous solutions. The primary hydration numbers of Rb^+ and Cs^+ are probably equal to six. However, as mentioned earlier, electrostatic forces operate beyond the primary hydration sphere of an ion, and additional layers of water molecules are bound to metal ions in water solution. These successive layers of bound solvent molecules are collectively termed the secondary solvation (hydration) layers. The extent of the secondary solvation layers appears to vary *inversely* with the size of the bare ion, that is, inversely with the size of the crystal radii of the ions. Thus as the crystal radii increase, the total hydration numbers, the hydrated radii, and the hydration energies all decrease. Apparently, the greater charge density of the smaller cation (i.e., Li^+) produces a greater organizing influence on secondary hydration layers in $Li^+(aq)$ than is the case for the successively larger monocations of the Group IA(1) metals. As a result, the aqueous lithium cation is effectively larger than that of sodium, and so on, as shown in Table 10-1. Correspondingly, as hydrated radii decrease, the ionic mobilities of the aqueous alkali metal ions are found to increase, as shown in Table 10-1.

These trends play a role in the behavior of the alkali metal cations in ion exchange materials and in their passage through cell walls and other biological membranes, although doubtless other factors than size and hydration numbers are also important. In a cation exchange resin, two cations compete for attachment at anionic sites on the resin, as shown by equilibrium 10-7.1:

Table 10-1 Data on the Hydration of Aqueous Group IA(I) Ions

	Li^+	Na^+	K^+	Rb^+	Cs^+
Ionic radii[a] (Å)	0.90	1.16	1.52	1.66	1.81
Approximate hydrated radii (Å)	3.40	2.76	2.32	2.28	2.28
Approximate hydration numbers[b]	25.3	16.6	10.5	10.0	9.9
Hydration enthalpies (kJ mol^{-1})	519	406	322	293	264
Ionic mobilities[c]	33.5	43.5	64.6	67.5	68

[a] Values by Shannon and Prewitt as listed in Appendix IIC, for coordination number 6.

[b] From transference data.

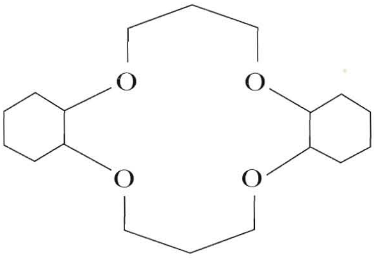
[c] At 18 °C and infinite dilution.

$$A^+(aq) + [B^+R^-](s) = B^+(aq) + [A^+R^-](s) \qquad (10\text{-}7.1)$$

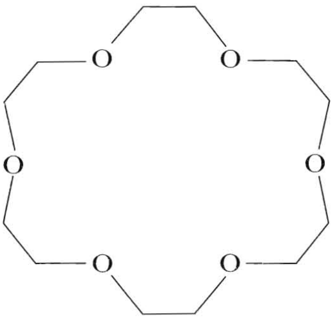
where R represents the solid resin and A^+ and B^+ are the cations. The value of the equilibrium constants for such equilibria can be measured quite accurately, and the order of preference of the alkali cations is usually $Li^+ < Na^+ < K^+ < Rb^+ < Cs^+$, although irregular behavior does occur in some cases. The usual order may be explained if we assume that the bonding force that holds the cation to the anionic site on the resin is essentially electrostatic, and that under ordinary conditions, the ions within the waterlogged resin are hydrated approximately to the same extent as they are in dilute aqueous solution. Then the ion with the smallest hydrated radius (which is the one with the largest "naked" radius) will be able to approach most closely to the negative site of attachment on the resin. Hence, according to Coulomb's law, this ion will be held most strongly.

Complexation of Cations by Crowns and Cryptates

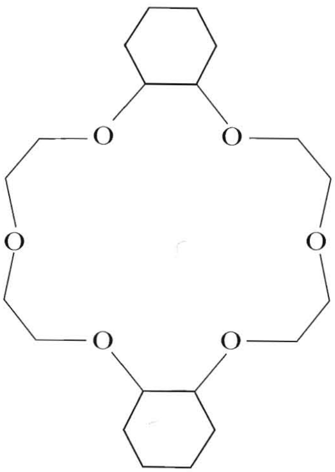
Alkali metal cations may be brought into solution in solvents other than water by use of two types of special complexation ligands: *crown ethers* and *cryptates.* Ethers, polyethers, and especially cyclic polyethers are particularly suited to solvate Na^+ and other alkali metal cations. Examples are tetrahydrofuran (THF), the "glyme" solvents [which are linear polyethers such as $CH_3O(CH_2CH_2O)_nCH_3$], and the macrocyclic *crown ethers.* Five of the more common crown ethers are shown in Structures 10-I through 10-V, along with their customary names. In such crown ethers, the number of oxygen atoms and the total number of atoms



dicyclohexyl-14-crown-4
10-I

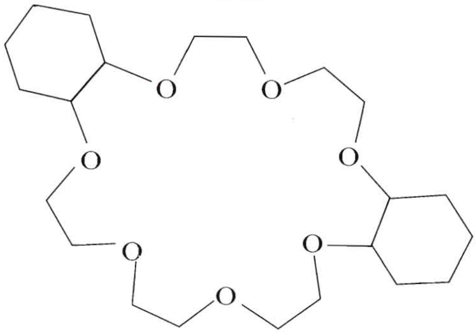


18-crown-6
10-II



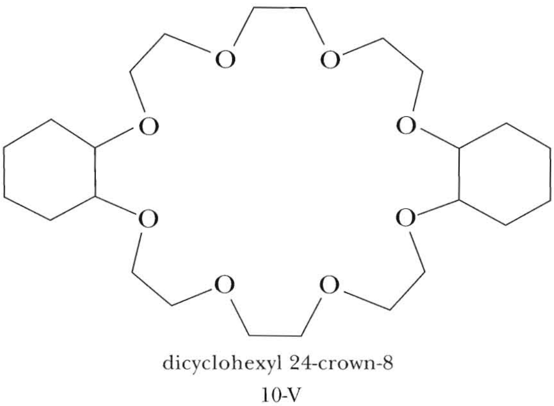
dicyclohexyl 18-crown-6

10-III



dicyclohexyl 21-crown-7

10-IV

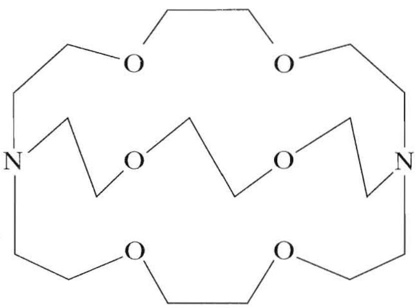


dicyclohexyl 24-crown-8

10-V

in the ring are both specified within the name of the polyether. As an example, 18-crown-6 is a symmetrical cyclic polyether containing 6 oxygen atoms and a total of 18 ring atoms, as shown in Structure 10-II. The name of crown ether 10-III is dicyclohexyl-18-crown-6.

The bonding of an alkali metal cation within the cavity of a cyclic polyether is largely electrostatic, and a close match between the size of the cation and the



10-VI
2,2,2-crypt

size of the crown is important if the cation is to be tightly bound in the cavity created by the oxygen donor atoms. For 18-crown-6, the binding constants increase in the order $Li^+ < Na^+$, $Cs^+ < Rb^+ < K^+$. In other words, the strongest binding is achieved by K, principally because this ion possesses the best match in size to the cavity of 18-crown-6. In comparison, Rb^+ is preferentially bound by the larger dicyclohexyl-21-crown-7, and Cs^+ by dicyclohexyl-24-crown-8. In contrast, the small Li^+ ion finds its greatest binding with small crown ethers such as dicyclohexyl-14-crown-4. In each of these cases, the size ratio of the cation to that of the crown's cavity is in the optimum range of about 0.80–0.97. Obviously, a cation radius/crown cavity size ratio greater than 1 would be undesirable, since the crown ring would then be too small to surround the cation effectively.

Other factors have been found to influence the stability of a crown ether complex with an alkali metal cation. First of all, the greater the number of oxygen atoms in the crown ring, the greater the magnitude of the ion–dipole interaction. Binding is enhanced in cases where the crown donor oxygen atoms are coplanar. Also, for greatest affinity, the crown ether should not be sterically hindered, and the oxygen atoms should be symmetrically placed around the ring. Finally, for maximum binding to a given alkali metal cation, the crown ring should not contain electron-withdrawing substituents, which would decrease the basicity of the oxygen atoms.

The *cryptates* are even more potent and selective agents for binding alkali metal ions (and others). However, they differ from the crown ethers in two ways. First, they incorporate nitrogen as well as oxygen donor atoms, as shown in Structure 10-VI. Second, the cryptates are polycyclic, and hence are able more fully to surround a metal cation, thereby taking greater advantage of the chelate effect mentioned in Section 6-4. The cryptate shown in Structure 10-VI is called 2,2,2-crypt (often abbreviated C_{222}), and the structure of a representative complex is shown in Fig. 10-1.

Alkali Metal Anions

When a solution of sodium in ethylamine is cooled in the presence of 2,2,2-crypt, the compound shown in Fig. 10-2, $[Na(2,2,2\text{-crypt})]^+Na^-$, which is stable only below −10 °C, crystallizes. This fascinating compound is one of a number of known *sodide* (i.e., Na^- containing) compounds. Although Reaction 10-7.2

$$2\,Na(g) = Na^+(g) + Na^-(g) \qquad (10\text{-}7.2)$$

is endothermic by 438 kJ mol^{-1}, the lattice energy for the formation of the crys-

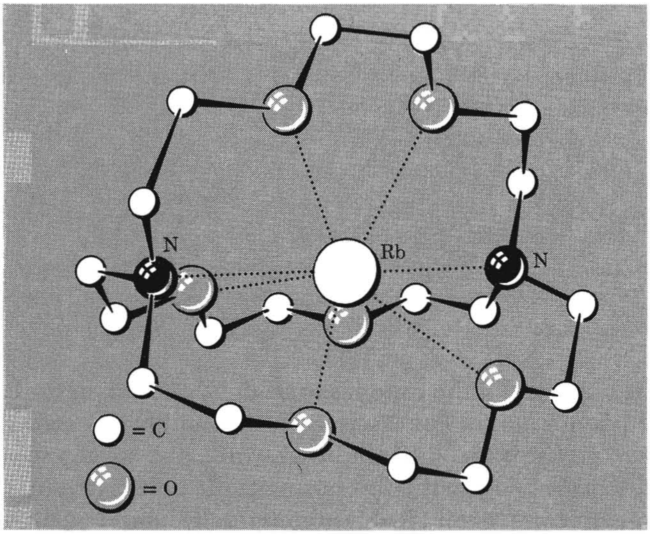


Figure 10-1 The structure of the cation in the thiocyanate salt [Rb(2,2,2-crypt)]SCN·H_2O. [Reproduced by permission from M. R. Truter, *Chem. Br.* **1971,** 203.]

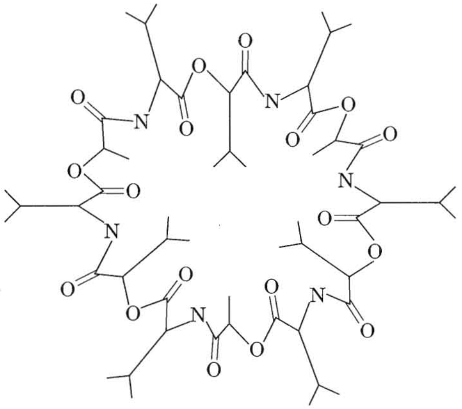
talline sodide compound and the complexation of the sodium cation by the cryptate overcome this endothermicity, thereby stabilizing the sodide (Na^-) ion. Other less stable *alkalides* have been prepared by J. L. Dye and co-workers, for example, the potasside $[K(2,2,2\text{-crypt})]^+K^-$, and similar cesides. The alkalides are brown or gold-brown solids that are extremely air and water sensitive, thermally unstable, diamagnetic solids.

The structure of the sodide shown in Fig. 10-2 warrants comment. The crystal structure is best described as alternating layers of $[Na(2,2,2\text{-crypt})]^+$ and Na^- ions in what is essentially a hcp array, as described in Chapter 4. The unusually large cryptated cations form a hcp array in which the octahedral sites are occupied by sodide ions. Furthermore, this structure is nearly identical to that of the simple cryptated salt $[Na(2,2,2\text{-crypt})]^+I^-$, which contains the common iodide anion. The sodide anion in $[Na(2,2,2\text{-crypt})]^+Na^-$ is located as far as possible from the negative oxygen and nitrogen atoms of the cryptate, and the shortest distance between sodide ions in the same layer is 8.83 Å. The separation between adjacent layers of sodide ions is 11.0 Å, and the distance between the Na^- and the Na^+ ions is 7.06 Å.

Interestingly, a similar series of *electrides* is known. These are black, paramagnetic solids that have the general formula $[M(\text{crypt})]^+e^-$, and which adopt structures similar to those of the alkalides. In electrides, it is the electrons rather than the alkali metal anions that are held in the cavities formed by the cryptated metal cations. For instance, in the case of the electride $[Cs(\text{crypt})]^+e^-$, the electrons are located in cavities of diameter 2.4 Å between the cryptated cations.

Encapsulated Metal Ions in Biology

Naturally occurring small cyclic polypeptides can also act to encapsulate metal ions. These cyclic polypeptides play a role in transporting alkali and alkaline



10-VII

earth ions across membranes in living systems. More is presented on this topic in Chapter 31. Perhaps the best known examples of such cyclic polypeptides are valinomycin (Structure 10-VII) and nonactin (shown in Fig. 10-3 as the potassium complex).

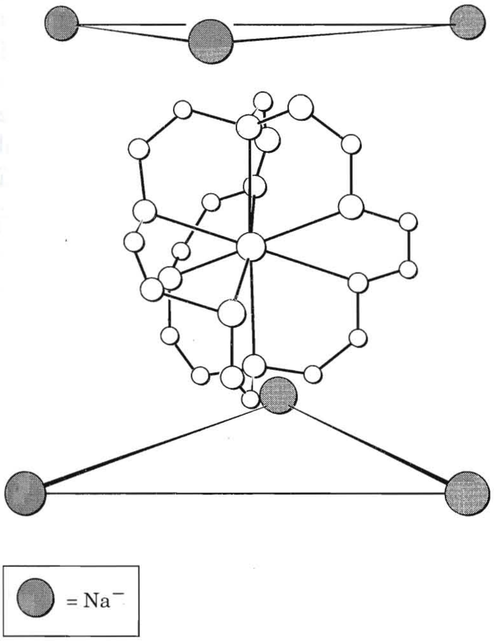


Figure 10-2 Part of the unit cell of the crystalline sodide $[Na(2,2,2\text{-crypt})]^+Na^-$ showing a single sodium cation at the center of the 2,2,2-crypt ligand and the six nearest neighbor Na^- (sodide) anions. [Reprinted in part with permission from F. J. Tehan, B. L. Barnett, and J. L. Dye, *J. Am. Chem. Soc., 96,* 7203–7208 (1974). Copyright © (1974) American Chemical Society.]

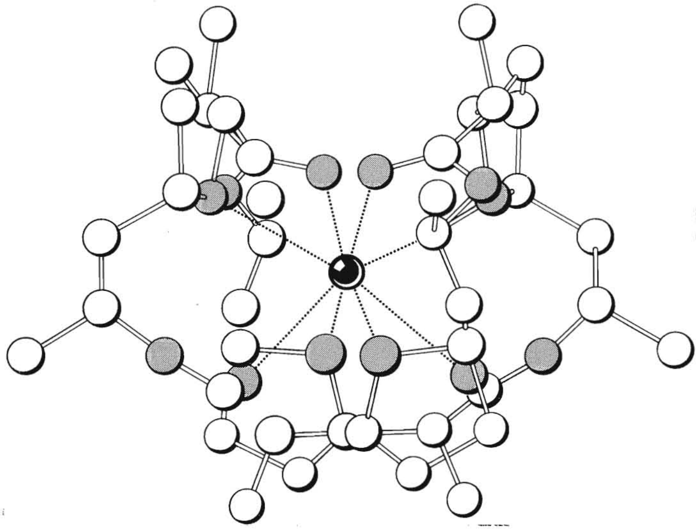


Figure 10-3 The structure of the nonactin complex of K$^+$. [Reproduced by permission from D. A. Fenton, *Chem. Soc. Rev.*, **1977,** *6,* 325–343.]

10-8 Organometallic Compounds

Lithium Alkyls and Aryls

One of the most important areas of chemistry for the Group IA(1) elements is that of their organic compounds. This is especially true of Li, whose alkyls and aryls find extensive use as alkylating and arylating agents. Organolithium compounds resemble Grignard reagents in their reactions, although the lithium reagents are generally more reactive.

Lithium alkyls and aryls are best prepared as in Reaction 10-8.1

$$C_2H_5Cl + 2\ Li \longrightarrow C_2H_5Li + LiCl \qquad (10\text{-}8.1)$$

using alkyl or aryl chlorides in benzene or petroleum solvents. Methyllithium may also be prepared at low temperatures in hexane as insoluble white crystals from the exchange between butyllithium and methyl iodide.

$$C_4H_9Li + CH_3I \longrightarrow CH_3Li(s) + C_4H_9I \qquad (10\text{-}8.2)$$

Organolithium compounds all react rapidly with oxygen and water, and are usually spontaneously flammable in air.

Organolithium compounds are among the few alkali metal compounds that have properties—solubility in hydrocarbons and other nonpolar liquids and high volatility—typical of covalent substances. These compounds are generally liquids or low melting solids, and molecular association is an important structural feature. For example, in the crystals of methyllithium (Fig. 10-4), the lithium atoms are associated in a tetrahedral unit with methyl groups symmetrically capping each triangular face of the Li_4 tetrahedron. A similar aggregation occurs for lithium alkoxides (LiOR) and dialkylamides ($LiNR_2$).

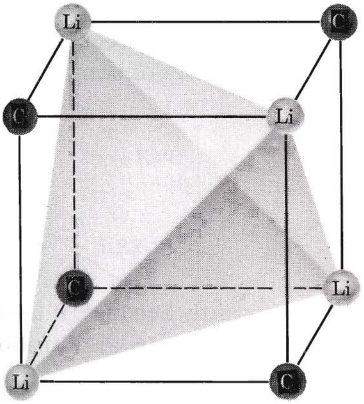


Figure 10-4 The structure of solid $(CH_3Li)_4$, showing the tetrahedral arrangement of Li atoms and the face-capping positions of the methyl groups. The structure may be regarded to be roughly that of a cube.

In solution, the lithium alkyls are also aggregated, but the extent of aggregation depends on the solvent and the steric nature of the organic group. It is not surprising, then, that the wide variations in reactivities of Li alkyls depend on these differences in aggregation and other ion pairing interactions. An example is benzyllithium, which is monomeric in THF and reacts as a benzylating agent some 10^4 times as fast as methylation by the tetrameric methyllithium.

Organosodium and Organopotassium Compounds

These compounds are all appreciably ionic and are not soluble to any extent in hydrocarbons. They are exceedingly reactive, being sensitive to air and water. Although alkyl and aryl derivatives can be prepared *in situ* for use as reactive intermediates, they are seldom isolated.

Some of the most important compounds are those formed by the more acidic hydrocarbons such as cyclopentadiene (Reaction 10-8.3),

$$3\,C_5H_6 + 2\,Na \longrightarrow 2\,C_5H_5^-\,Na^+ + C_5H_8 \qquad (10\text{-}8.3)$$

and acetylenes (Reaction 10-8.4).

$$RC{\equiv}CH + Na \longrightarrow RC{\equiv}C^-Na^+ + \tfrac{1}{2}\,H_2 \qquad (10\text{-}8.4)$$

Reactions 10-8.3 and 10-8.4 are best performed using sodium dispersed in THF, glyme, or DMF. The ionic products of Reactions 10-8.3 and 10-8.4 are useful as reagents for the synthesis of transition metal organometallic derivatives.

Other Alkali Metal Compounds

A large number of alkali metal compounds that are commonly volatile and soluble in hydrocarbon or ether solvents is known. The most important of these are the alkyls and aryls that were discussed in Section 10-8. These compounds have much in common, however, especially the tendency to aggregate into dimers, tetramers, hexamers, and so on, with the following classes of compounds, where R = alkyl or aryl:

Alkoxides	MOR
Amides	MNHR, MNR_2
Phosphides	MPHR, MPR_2
Thiolates	MSR

Such compounds have been extensively studied recently because, if the R group is very bulky, the alkali metal compound can be used to make transition metal complexes with very low coordination numbers.

Some typical syntheses are given in Reactions 10-9.1 and 10-9.2, which should be compared with the syntheses of the alkyls (Section 10-8).

$$i\text{-}Pr_2NH + n\text{-}BuLi \longrightarrow i\text{-}Pr_2NLi + C_4H_{10} \tag{10-9.1}$$

$$2\ t\text{-}BuOH + 2\ Na \longrightarrow 2\ t\text{-}BuONa + H_2 \tag{10-9.2}$$

Reaction 10-9.1 illustrates the utility of alkyl lithiums as deprotonating agents; the resulting dialkyl amides can similarly act as strong bases.

A characteristic feature, especially of lithium compounds [although not restricted to them, since $(NaO\text{-}t\text{-}Bu)_6$ is a hexamer both in the solid and in benzene], is aggregation, as discussed for the alkyls in Section 10-8. The extent of aggregation typically depends on the compound, the nature of the attached groups, and on the solvent.

Other important compounds of the alkali metals include those with the transition metal carbonylates (Chapter 28), which are made in THF solvent by reactions such as 10-9.3 through 10-9.5.

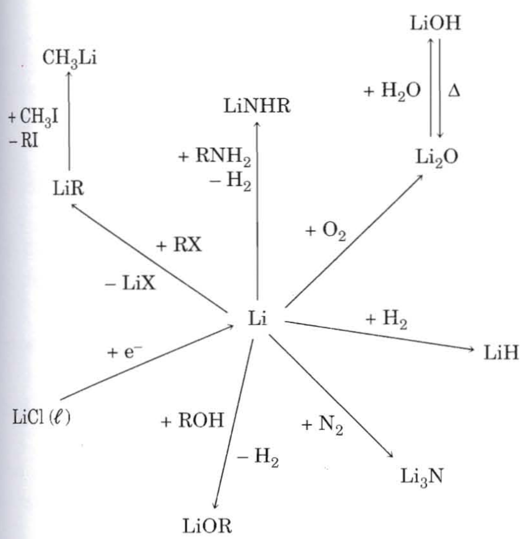
$$Mn_2(CO)_{10} + 2\ Na/Hg \longrightarrow 2\ NaMn(CO)_5 \tag{10-9.3}$$

$$Co_2(CO)_8 + 2\ Na/Hg \longrightarrow 2\ NaCo(CO)_4 \tag{10-9.4}$$

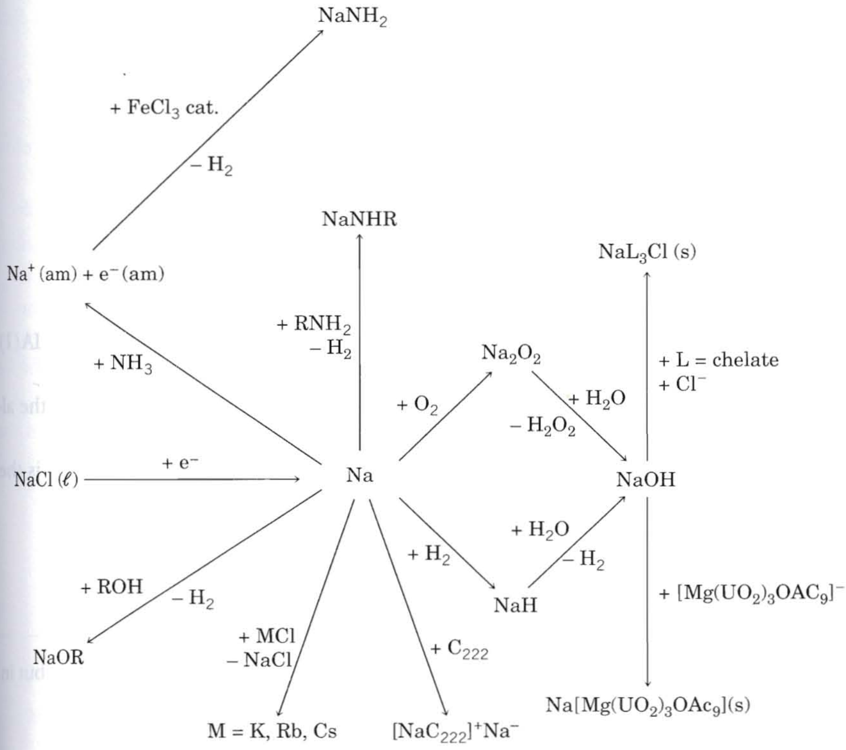
$$Cr(CO)_6 + 2\ Na \longrightarrow Na_2Cr(CO)_5 + CO \tag{10-9.5}$$

10-10 Reaction Summary

As a study aid, and in order to compare the chemistry of lithium with that of the other members of the group, the reactions of the Group IA(1) metals are listed in Fig. 10-5(*a–c*). Rather than being a comprehensive list of reactions, Fig. 10-5 is meant to be only an overview of the important types of reactions that the alkali metals typically undergo. The student should note the metal ion precipitation reactions, as well as the differences between lithium (and to some extent sodium) and the other members of the group.


CH_3Li
$+CH_3I$
$-RI$
LiR
$LiNHR$
$+RNH_2$
$-H_2$
$LiOH$
$+H_2O$
Δ
Li_2O
$+O_2$
$+RX$
$-LiX$
Li
$+H_2$
LiH
$+e^-$
$LiCl(\ell)$
$+ROH$
$-H_2$
$+N_2$
Li_3N
$LiOR$

(a)


$NaNH_2$
$+FeCl_3$ cat.
$-H_2$
$NaNHR$
$Na^+(am) + e^-(am)$
$+RNH_2$
$-H_2$
$NaL_3Cl(s)$
$+NH_3$
Na_2O_2
$+L =$ chelate
$+Cl^-$
$+O_2$
$+H_2O$
$-H_2O_2$
$NaCl(\ell)$
$+e^-$
Na
$NaOH$
$+H_2O$
$+H_2$
$-H_2$
NaH
$+ROH$
$-H_2$
$+[Mg(UO_2)_3OAC_9]^-$
$NaOR$
$+MCl$
$-NaCl$
$+C_{222}$
$Na[Mg(UO_2)_3OAc_9](s)$
$M = K, Rb, Cs$
$[NaC_{222}]^+Na^-$

(b)

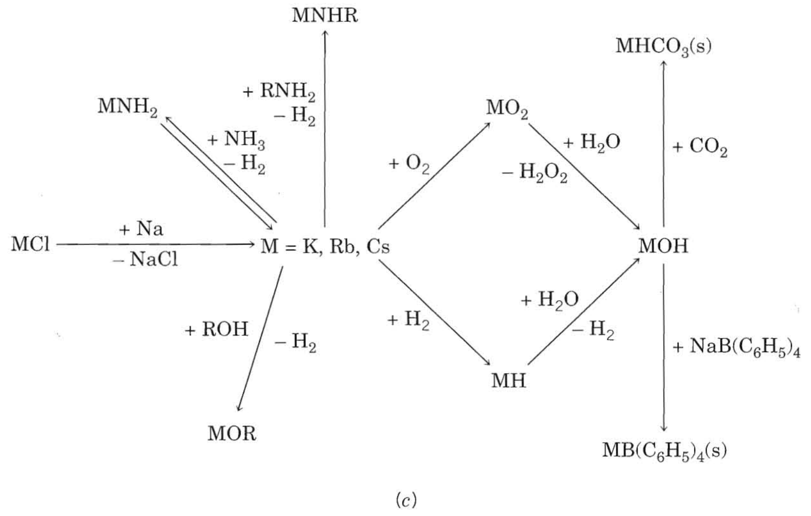


Figure 10-5 Reactions of the alkali metals.

STUDY GUIDE

Study Questions

A. Review

1. Why are the alkali metals soft and volatile?
2. Why are they highly electropositive?
3. Write down the electronic structure of francium.
4. Why are the first ionization energies of the Group IA(1) atoms low?
5. Why does the chemical reactivity of the metals increase from Li to Cs?
6. What other ions have properties similar to the alkali metal ions?
7. How does the charge-radius ratio of Li^+ differ from those of the other Group IA(1) ions? List some consequences of this difference.
8. How do the reactivity and the nature of the products vary from Li to Cs when the alkali metals react with oxygen?
9. What is the nature of the solutions of alkali metals in liquid ammonia? What is the chief reaction by which they decompose?
10. How would you make lithium hydride? Why is it more stable than NaH?
11. Draw the crystal structures of NaCl and CsCl. Why do they differ?
12. Why is sodium peroxide a useful oxidizing agent in aqueous solution?
13. In what order are the M^+ ions eluted from a cation exchange resin column?
14. Why is LiF almost insoluble in water, whereas LiCl is soluble, not only in water, but in acetone?
15. What is (a) a crown ether, (b) a cryptate?
16. Why are lithium salts commonly hydrated and those of the other alkali ions usually anhydrous?
17. How would you extinguish a sodium fire in the laboratory?

B. Additional Exercises

1. Vapors of the alkali metals contain about 1% diatomic molecules. Discuss the bonding in such molecules using the MO approach. Why do the dissociation energies of the diatomic alkali metal molecules decrease with increasing Z?
2. Anhydrous KOH in THF is one of the strongest known bases and will deprotonate exceedingly weak acids. Why? (Compare the solvation of KOH by water and by THF.)
3. The formation constant for the 1:1 complex between K^+ and cyclohexyl-18-crown-6 is much larger than the values for the other alkali metal cations. Estimate from this the size of the "hole" available for the cations in this ligand.
4. Why is there so little variation in the standard potentials for reduction of the Group IA(1) cations?
5. Which ligand would you expect more favorably to complex with K^+, cyclohexyl-18-crown-6 or 2,2,2-crypt? Why?
6. Write balanced chemical equations for the electrolysis of (a) NaCl in water, (b) molten NaCl, (c) tetraethylammonium chloride in water, (d) molten tetraethylammonium chloride.
7. Complete and balance equations for the following reactions involving the metals and the ions of Group IA(1).
   - (a) $KCl + Na$
   - (b) $Li + N_2$
   - (c) $Na + O_2$
   - (d) $Cs + O_2$
   - (e) $K + C_2H_5OH$
   - (f) $Li + HN(C_2H_5)_2$
   - (g) $Li + HN(SiMe_3)_2$
   - (h) $RbO_2 + H_2O$
   - (i) $Li_2O + H_2O$
   - (j) $KOH + CO_2$
   - (k) $K^+ + B(C_6H_5)_4^-$
   - (l) $Li + ClC_6H_5$
   - (m) $C_4H_9Li + CH_3I$
   - (n) $CH_3Li + [W(CO)_5Cl]^-$
8. If a crown ether were to be modified by replacing some or all oxygen atoms with sulfur, would such a complexing agent favor K^+ or Ag^+? Explain.
9. Make a thorough list of all of the ways in which the structure and reactivity of lithium and its compounds differ from those of the other alkali metals.
10. Why do alkoxides, amides, and alkyls of lithium [as opposed to other metals of Group IA(1)] have largely covalent rather than ionic nature?
11. Suggest a reason why 14-crown-4 is able to catalyze reactions of $LiCH_3$ in organic solvents.
12. Why is butyllithium more reactive in hexane as an R^- donor (nucleophile) than CH_3Li?
13. Make a careful drawing of each of the following:
    - (a) $Li^+(aq)$
    - (b) $[Na(2,2,2\text{-crypt})]^+$
    - (c) 24-crown-8
    - (d) Methyllithium (solid state)
14. Give balanced equations for the reaction of sodium with diethylamine, hydrogen, ethanol, water, and oxygen. Repeat for lithium and for potassium.
15. Lithium hydride adopts the NaCl-type structure, having a unit cell edge of 4.08 Å. Use this information and the effective nuclear charges for each ion to determine the Pauling radius of Li^+ and H^-, as described in Chapter 4.
16. Write out the Born–Haber cycle for the formation of KH.
17. Write out the Born–Haber cycle for the formation of Na_2O_2.
18. Suggest the product on reaction of BuLi and $HN(SiMe_3)_2$.

C. Questions from the Literature of Inorganic Chemistry

1. Consider the paper by H. K. Frendsdorf, *J. Am. Chem. Soc.*, **1971,** *93,* 600–606, and references cited therein, regarding the stability constants of cyclic polyether complexes with alkali cations.
   (a) Draw the structures of the crown ethers in Table II of this paper.
   (b) What relationship exists between stability constants for the complexes in methanol, cation radius, and ring size of the various crown ethers?
   (c) How do the potassium complexes of nonactin and valinomycin compare with the potassium complexes of 24-crown-8 and 30-crown-10, as inferred with stability constants?
   (d) Why are the stability constants for crown ether–alkali metal complexes in water lower than stability constants in methanol?
2. Consider the paper by B. Van Eck, Dinh Le Long, D. Issa, and J. L. Dye, *Inorg. Chem.*, **1982,** *21,* 1966–1970.
   (a) The analysis of the crystalline alkalides that are featured in this work was performed by reacting the samples with water. Write a balanced chemical equation for the reaction that takes place.
   (b) The H_2 evolved during analysis was compared with the total titratable base that was present after reaction with water. Why? For K^+ crypt-2,2,2·Na^-, how many equivalents of titratable base are released per equivalent of hydrogen upon reaction with water?
   (c) Why are the sodides the easiest crystals to prepare and the most stable of the alkalide compounds?
3. Consider the work: E. C. Alyea, D. C. Bradley, and R. G. Copperthwaite, *J. Chem. Soc., Dalton Trans.*, **1972,** *1580–1584.*
   (a) Draw Lewis diagrams for the lithium derivatives of $[N(SiMe_3)_2]^-$, which are used as reagents in this paper.
   (b) Suggest a synthesis of the lithium bis(trimethylsilyl)amido reagents, $Li[N(SiMe_3)_2]$.
   (c) What is the likely coordination geometry of the metal complexes of Table 2?
   (d) What reactions were used to synthesize the complexes of Table 2? Write balanced chemical equations.
   (e) What π delocalizations do the authors mention involving the N and Si atoms of the silylamide ligands? Show with orbital diagrams how π overlap within the $(Si)_2N—M$ framework may take place. To what extent is Sc^{3+} believed to be involved in such π bonding? Why?
   (f) Show, with orbital diagrams, both the M π donation and π acceptance that the authors discuss. For which metals is each form of π bonding apparent?
   (g) What would be the likely reaction of such ML_3 complexes with water?

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