

Macrocyclic chemistry in reducing environments: From concentrated metal solutions to crystalline electrides

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Abstract - Macrocyclic and macrobicyclic complexants for the alkali metal cations can be used to greatly enhance alkali metal solubilities in a variety of amine and ether solvents. This provides concentrated solutions that contain alkali metal anions and/or solvated electrons which should be useful in organic and inorganic synthesis. The solvent dimethyl ether and fully methylated macrocyclic aza-analogs of crown ethers provide exceptionally stable solutions. Crystalline alkalides and electrides can be prepared by slow cooling or dimethyl ether evaporation from dimethyl ether-trimethylamine mixtures. The crystal structures of 12 alkalides and two electrides have been determined and are correlated with such measurements as optical spectra, powder conductivities, magnetic susceptibilities and alkali metal NMR spectra. The factors that determine stabilities of solutions and solid alkalides and electrides are discussed.

INTRODUCTION

Crown ethers and cryptands have had a profound effect on alkali metal solution chemistry. Since the first report of metal solubility enhancement by dicyclohexano-18-crown-6 (ref. 1) in 1970, macrocyclic and macrobicyclic polyethers and polyamines have been used for the study of metal solutions (refs. 2-10), as neat solvents for the alkali metals (refs. 11-14) and in dissolving metal reductions (refs. 15-20).

The ability of alkali cation complexants to greatly increase the concentrations of M^+C (C = complexant), M^- and e^- in solution led directly to the synthesis of solvent-free crystalline salts of the alkali metal anions (alkalides, refs. 21-32), over 30 of which have now been synthesized and characterized. These include salts in which the anion is Na^- , K^- , Rb^- or Cs^- . No salts of Li^- have yet been synthesized. A number of mixed compounds have been made in which the complexed cation and the alkali metal anion are different alkali metals. The crystal structures of a dozen alkalides have been determined (refs. 22, 30-33).

Since alkali metal solutions in amines and ethers, with or without a cation complexant present, contain either solvated alkali metal anions, or solvated electrons, or both, the synthesis of alkalides prompted us to attempt to prepare salts in which the anions are all trapped electrons. Early work on such electrides (refs. 34-37) was carried out on powders or films formed by rapid solvent evaporation. More recently (refs. 30, 38-40) we have been able to crystallize electrides from solution and have determined the crystal structures of two of them (refs. 41, 42).

Macrocyclic and macrobicyclic complexants for the cations can be thought of as replacements for the first solvation shell of metal solutions. Indeed, the metal-ammonia compounds $Li(NH_3)_4$ and $M(NH_3)_6$, in which M is an alkaline earth or Eu or Yb , have been known for years (ref. 43), and $Li(CH_3NH_2)_4$ has properties (refs. 44,45) akin to those of electrides. The simplest sodide, $Li^+(en)_2 \cdot Na^-$, in which en represents ethylenediamine, was synthesized recently (ref. 46). Unpublished results from our laboratory show that methylamine and ethylamine can form similar compounds with lithium and sodium.

The developments described above now provide us with a variety of concentrated alkali metal solutions in both protic and aprotic solvents that contain alkali metal anions and/or solvated electrons. The study of such solutions and their use in "dissolving metal reductions" is a promising area of research that has just begun to be exploited. The wide-ranging optical, electronic and magnetic properties of crystalline alkalides and electrides make them attractive targets for possible use in solid-state devices.

The major difficulty in utilizing these materials is their thermal instability, which results from autocatalytic reduction of the complexant or solvent by M^- or e^- . In this paper, we examine the structures and properties of alkalides and electrides, the factors that influence stability, and the promise that new tertiary amine complexants provide for the synthesis of thermally stable compounds and solutions.

STRUCTURAL FEATURES

General - Although the structures of alkaliides and electrides are extremely varied, two features are common. First, the cation complexation is "normal"; that is, the $M^+ - O$ and/or $M^+ - N$ distances and the arrangement of the complexant around the cation are similar to those in which conventional anions such as Br^- , SCN^- , etc. are present. Second, closest-packing of the cations and anions occurs. When the complexed cations are much larger than the anions, as with sodides and electrides, the complexed cations are in close contact over a large fraction of their van der Waals surfaces. This is illustrated in Fig. 1, which shows three views of the cation packing in $Cs^+(18C6)_2 \cdot Na^-$ (ref. 38). (See ref. 47 for abbreviations used in this paper.)

The close similarity of the sodide and the electride, and the ability to replace some of the electrons in the electride with Na^- ions, provide the strongest evidence that the electrons occupy the anionic sites in $Cs^+(18C6)_2 \cdot e^-$. This conclusion has been questioned (ref. 48) on the grounds that the optical spectrum is not compatible with complete electron localization within the anion vacancy. In our model of localized electrides, in which the electrons are trapped at anionic sites, we certainly expect electron density to spill onto the hydrogens that line the cavity. "Electron trapping" at the anionic sites in electrides, does not mean complete confinement of the wavefunction within the vacancy. The same terminology is used to describe F-centers (ref. 49), yet it is understood that the trapped electron wavefunction overlaps strongly with the cations and even to some extent with neighboring anions.

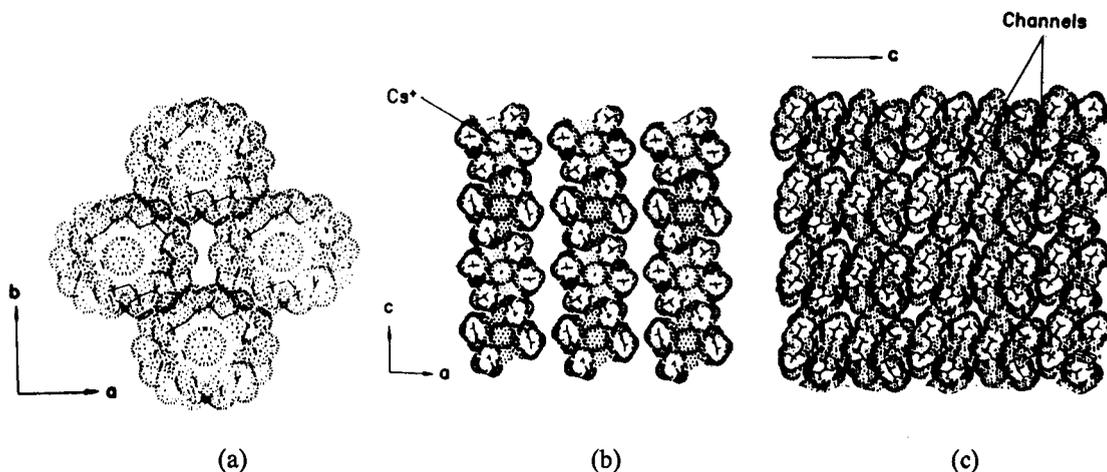


Fig. 1. Three views of the cation packing in $Cs^+(18C6)_2 \cdot e^-$ and $Cs^+(18C6)_2 \cdot Na^-$. The cavities visible in view (b) are the anionic sites. They are separated by 8.68Å along the c -axis through the "dog-bone"-shaped channels shown in view (a), and by 10.27Å along the $[1,1,0]$ and $[-1,1,0]$ directions through the "bow-tie" and "diamond"-shaped channels shown in view (c).

Alkaliides - For each of the alkali metal anions, Na^- , K^- , Rb^- and Cs^- there is at least one alkaliide salt of known structure in which the anions are isolated from each other. This gives us the opportunity to estimate the sizes of these anions. Since we expect them to be highly polarizable, it is likely that the nearest hydrogens from $-CH_2-$ groups of the complexant can penetrate into the region occupied by the outer s orbitals of the anion. This means that the distance between M^- and the nearest hydrogen, minus the van der Waals radius of H gives the minimum radius of the alkali metal anion. We use the average distance to hydrogens that line the cavity to define an effective radius of the anion. Table 1 gives the minimum and effective radii of the alkali metal anions together with those estimated for M^- by the method of Matalon, Golden and Ottolenghi (ref. 50) from the metallic and cationic radii. The complexed cations are generally not spherical but have "average radii" (estimated from space-filling models) that range from 3.5Å for $Li^+(en)_2$ to 5Å for $Cs^+(18C6)_2$. (Actually the latter is a cylinder $\sim 11Å$ diameter by 8Å high.) Thus, typical cation-anion distances in alkaliides whose cations are well-shielded by the complexants can be expected to vary from 4.5Å in $Li^+(en)_2 \cdot Na^-$ (structure unknown) to 8-9Å in $Cs^+(18C6)_2 \cdot Cs^-$ (structure known). In the latter salt, Cs^- is so large that the cations are not closest packed with each other, although closest-packing is achieved when both cations and anions are considered (ref. 31).

The alkalides described above could be considered "normal" salts, albeit with large and strongly reducing anions. The structures of $\text{Rb}^+(\text{C222})\cdot\text{Rb}^-$ (refs. 42 and 51) and that of the corresponding salt with K^+ and K^- present (ref. 51) are not normal. In these salts, the anions are trapped as pairs. For example, the Rb^- to Rb^- distance in the pair is 1.3Å shorter than twice the effective radius of Rb^- . A similar shorter distance is also present in the potasside. Either packing forces distort K^- and Rb^- , permitting them to approach closer to each other than expected, or dimers Rb_2^{2-} and K_2^{2-} are formed. Since the bond order in such dimers is zero, any net bonding would be expected to be very weak. It is interesting to note that well-isolated Na^- ions are present in both $\text{Na}^+(\text{C222})\cdot\text{Na}^-$ (ref. 22) and $\text{K}^+(\text{C222})\cdot\text{Na}^-$ (ref. 51).

Shortened M^- to M^- distances also occur in $\text{Cs}^+(\text{C222})\cdot\text{Cs}^-$ (ref. 31) in which zig-zag chains of Cs^- ions in contact are present. The Cs^- to Cs^- distances are shortened by 0.6Å from that expected on the basis of the effective size of Cs^- . Similar chains of Rb^- ions in which each Rb^- to Rb^- distance is shortened by 1.3Å have recently been observed in $\text{Rb}^+(\text{18C6})\cdot\text{Rb}^-$ (ref. 51).

TABLE 1. Radii (in Angstroms) of alkali metal anions

Anion ^a	Compound ^b	Minimum radius ^c	Effective radius ^d
Na^- (2.72)	$\text{Cs}^+(\text{18C6})_2\text{Na}^-$	2.47	2.87 (18H)
	$\text{Rb}^+(\text{15C5})_2\text{Na}^-$	2.60	2.99 (20H)
	$\text{Cs}^+(\text{HMHCY})\text{Na}^-$	2.39	2.83 (13H)
	$\text{K}^+(\text{HMHCY})\text{Na}^-$	2.48	2.99 (20H)
	$\text{K}^+(\text{C222})\text{Na}^-$	2.55	2.73 (14H)
K^- (3.27)	$\text{Cs}^+(\text{15C5})_2\text{K}^-$	2.77	3.14 (16H)
	$\text{K}^+(\text{C222})\text{K}^-$	2.96	3.24 (17H)
Rb^- (3.39)	$\text{Rb}^+(\text{C222})\text{Rb}^-$	3.0	3.2 (14H)
	$\text{Rb}^+(\text{18C6})\text{Rb}^-$	3.0	3.23 (9H)
Cs^- (3.55)	$\text{Cs}^+(\text{18C6})_2\text{Cs}^-$	3.09	3.46 (15H)
	$\text{Cs}^+(\text{C222})\text{Cs}^-$	3.17	3.50 (15H)

^aEstimated radius (ref. 26) given in parentheses

^bAbbreviations: 18C6 = 18-crown-6; 15C5 = 15-crown-5; HMHCY = hexamethyl hexacyclen; C222 = cryptand [2.2.2]

^cDistance to nearest H atom minus 1.20Å

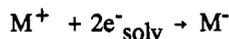
^dAverage distance to neighboring H atoms minus 1.20Å. The number of H atoms included is given in parentheses

The effect of close anion-anion contacts on the properties of alkalides is uncertain. It apparently broadens the Cs^- NMR spectrum in $\text{Cs}^+(\text{C222})\cdot\text{Cs}^-$ so severely that no signal can be detected (refs. 31, 52). Similarly, the Rb^- signal in $\text{Rb}^+(\text{C222})\text{Rb}^-$ was not detected (ref. 53). Yet, the K^- NMR signal in polycrystalline $\text{K}^+(\text{C222})\cdot\text{K}^-$, while difficult to detect in normal static and MAS-NMR experiments (ref. 54), is readily detected by spin-echo methods (unpublished). The optical spectra of thin polycrystalline films do not seem to be out of line with those of the corresponding isolated anions in solution or in other alkalide compounds that do not form anionic pairs or chains (refs. 34-36).

It is interesting that in the six known structures that contain Na^- , no pairs or chains of anions are present. It is tempting to speculate that the low-lying empty d-orbitals in K^- , Rb^- and Cs^- may mix with the ground state s wavefunctions of the electron pair, causing a large paramagnetic and highly anisotropic NMR chemical shift and resulting in some net bonding character to the dimer or polymeric chain. Alternatively, the large size and consequent high polarizability of the anions could make them distort under crystal packing forces so that a "hard-sphere" radius has little meaning.

Another interesting feature of alkalide structures occurs in two sodides when the cation is only partially encapsulated by the ligand. In $\text{K}^+(\text{HMHCY})\cdot\text{Na}^-$ (ref. 55), the cation is essentially in contact with Na^- on the open side of the complexant "basket" (Fig. 2). In spite of the close proximity of the cation in this "contact ion-pair", the optical and NMR spectra of Na^- are normal, indicating very little charge transfer from Na^- to K^+ or Cs^+ . The effect on the cation may be more pronounced, however. For example, although Cs^+ is easily detected by MAS-NMR methods in other alkalides and in electrides, no cesium signal has yet been detected in $\text{Cs}^+(\text{HMHCY})\cdot\text{Na}^-$ samples.

Electrides - Electride crystallization and structure determination presented challenges that were difficult to overcome. First, solvated electrons in most amine and ether solvents are chemically "hot" and the solutions tend to decompose readily. Second, it is difficult to prepare solutions that contain only complexed cations and solvated electrons since, except in the case of lithium solutions, the reaction



tends to lie far to the right so that crystals of electrides are often contaminated with alkaliides. Third, many electrides tend to form very tiny crystals unsuitable for structure determination by x-ray diffraction. Finally, crystalline electrides tend to decompose thermally at lower temperatures than alkaliides, increasing the difficulty of working with them.

In spite of the difficulties involved in the study of electrides, this class of compounds deserves intensive investigation because of the nature and diversity of the optical, electronic and magnetic properties. Unlike alkali metal anions, which are more or less locked in place, electrons as anions are able to move readily through the crystal and to interact with each other and with the alkali cations and the complexant molecules. Fortunately, the two electrides whose structures have been determined represent two extremes of behavior and permit us to speculate about the relationship between structure and properties of electrides.

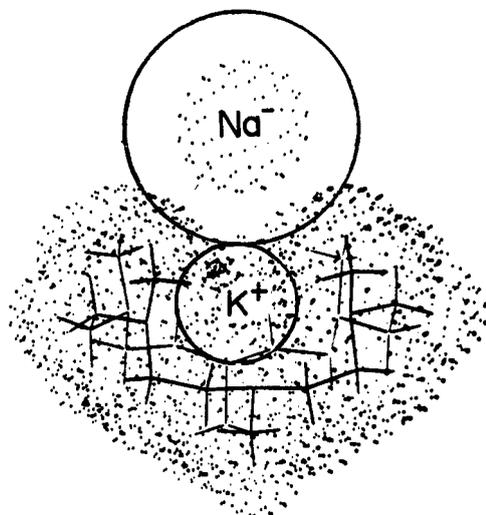


Fig. 2. Computer-generated display of the "ion pair" unit in crystalline $K^+(HMHCY) \cdot Na^-$. The two circles represent the sizes of Na^- and K^+ . The shaded areas (except for Na^-) represent the van der Waals surfaces, while the stick diagram shows the bonding geometry of the complexant.

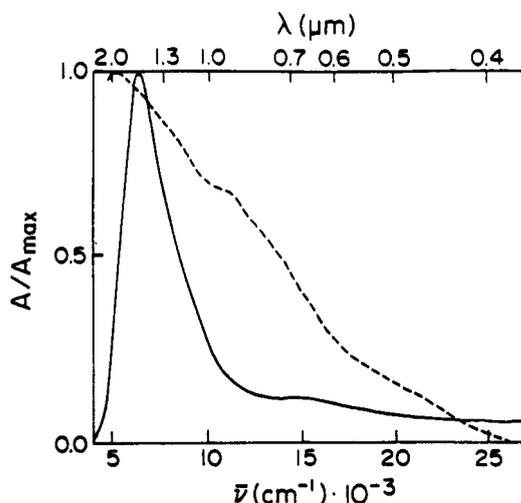


Fig. 3. Optical absorption spectra of thin films of $K^+(C222) \cdot e^-$ (dashed) and $Cs^+(18C6)_2 \cdot e^-$ (solid). Reprinted with permission from *Nature* Vol. 331, No. 6157. Copyright 1988, Macmillan Journals Limited.

The first electride, $Cs^+(18C6)_2 \cdot e^-$, (refs. 38-41) contains electrons that are trapped in a relatively deep (~ 0.9 eV) potential well, interact only weakly with each other, and have very low spin density at the cesium nucleus. These features are deduced from a number of different measurements. The optical absorption spectrum of thin films (Fig. 3) has a distinct absorption maximum at 6000 cm^{-1} (0.75 eV) and essentially no electronic absorption below 4000 cm^{-1} (0.50 eV). This establishes a lower limit to the trap depth. Powder conductivity studies show that this electride is a semiconductor with an activation energy of 0.45 eV, corresponding to a band-gap of 0.90 eV. The magnetic susceptibility (ref. 56) obeys the Curie-Weiss law with a Weiss constant of only -1.2 K indicating very weak antiferromagnetic coupling between the electrons. The temperature dependent ^{133}Cs NMR chemical shift (ref. 52) shows that the unpaired electron density at the cesium cation is only 0.03% of the free atom value. This proves that overlap of the trapped electron wavefunction with the complexed cesium cation is very small. Furthermore, the cesium NMR spectra of mixed electride-sodide crystals show that up to three of the eight anionic sites around a complexed cesium cation can be occupied by Na^- rather than e^- (refs. 41,52).

All of these properties are consistent with localization of the electrons at anionic sites in $\text{Cs}^+(18\text{C}6)_2\cdot\text{e}^-$. We refer to such compounds as localized electriles. This does not mean, however, that electron-exchange is absent. Indeed, the narrow (0.5G) ESR line, independent of temperature down to 2 K shows that electron-exchange is rapid on the ESR time scale (ref. 56).

The crystal structure of $\text{Cs}^+(18\text{C}6)_2\cdot\text{e}^-$, characterized by the cation packing shown in Fig. 1, is nearly identical to that of $\text{Cs}^+(18\text{C}6)_2\cdot\text{Na}^+$, except that the anionic sites are x-ray empty; i.e. at the background noise level. This is expected, since even if all the electron density were in the anionic cavity, it would correspond to an average density of only 0.026 electrons per cubic Å, below the noise level in the final electron density difference map (ref. 41). Since we expect the electronic wavefunction to spread at least into the region occupied by the $-\text{CH}_2-$ hydrogens, the actual average electron density would be even lower than this.

Although we cannot "locate" the electrons by x-ray diffraction, the evidence for electron trapping at the anionic sites is overwhelming. This localized electrile is probably best described as a compound with "stoichiometric F-centers"; that is, one in which all anionic sites are occupied by trapped electrons. Remaining questions that need to be explored are, "What is the unpaired electron density at various atoms in the structure?", and "What role, if any, is played by the empty channels that interconnect the anionic sites?". Because of exchange narrowing we cannot probe the electron density in pure electriles by ESR or ENDOR techniques. We are, however, currently using these methods to study isolated electrons trapped at anionic sites in alkaliides (F-centers in alkaliides).

As illustrated in Fig. 1, the electrile $\text{Cs}^+(18\text{C}6)_2\cdot\text{e}^-$ has anionic trapping sites similar to "beads on a string", connected along the *c*-axis by short but constricted channels. The center-to-center distance of 8.68 Å along this direction is much shorter than the value 10.27 Å along the [1,1,0] and [-1,1,0] directions, which have long and constricted channels. We anticipate that this structure would give considerable anisotropy and a one-dimensional character to the properties of this electrile. Single crystal studies are being carried out to test this hypothesis.

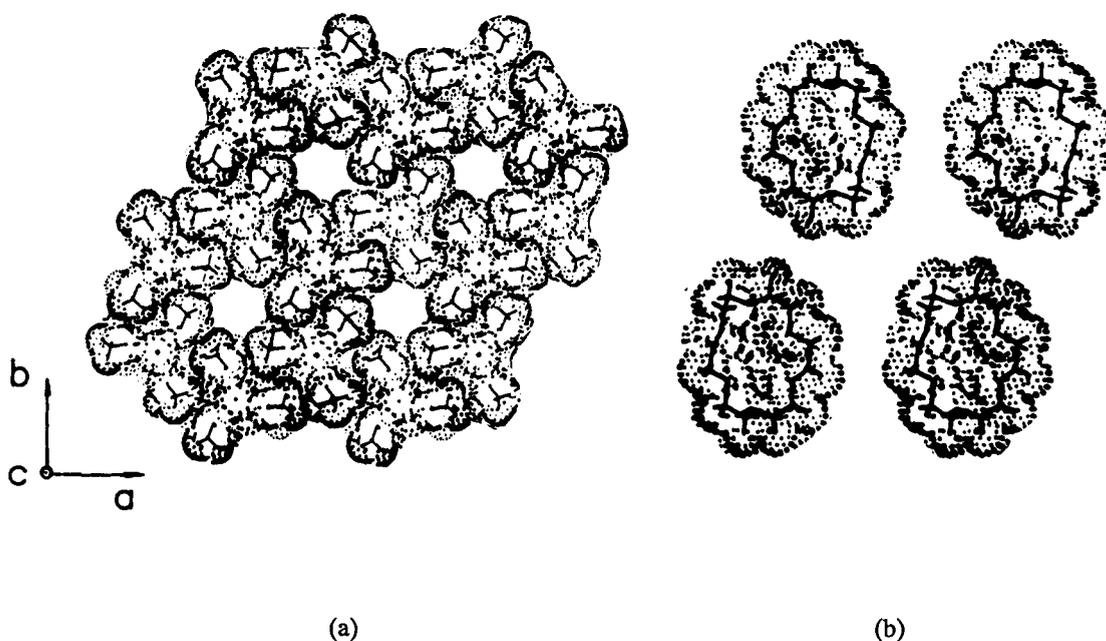


Fig. 4. Two cutaway views of the cation packing in $\text{K}^+(\text{C}222)\cdot\text{e}^-$. View (a) is down the *c*-axis and shows an end view of the channels that connect the electron-pair trapping sites. Note the interlocking nature of the cryptand strands. View (b) is with the *c*-axis vertical and the *a* axis horizontal and illustrates the "dumbbell" shape of the electron-pair trapping site and the two-dimensional nature of the channels. The vacancy is about 12 Å long and 4 Å across at its midpoint.

The second electrider, $\text{K}^+(\text{C222})\cdot\text{e}^-$, has very different properties (ref. 42) from the localized electrider, $\text{Cs}^+(\text{18C6})_2\cdot\text{e}^-$. The optical spectrum of thin, solvent-free films (Fig. 3) consists of a broad absorption edge, extending throughout the visible and near infrared with a slight maximum at $5,000\text{ cm}^{-1}$ but nearly as high absorbance down to $4,000\text{ cm}^{-1}$ (the low energy limit of our studies). Because of its very close similarity to the spectrum of concentrated metal-ammonia solutions, which are metallic, we refer to this as a "plasma edge" spectrum, although the electrider is probably not a true metal. The powder conductivity has an activation energy of only $\sim 0.02\text{ eV}$ and is 2×10^5 times larger than that of $\text{Cs}^+(\text{18C6})_2\cdot\text{e}^-$ at 200 K. Recent impedance spectroscopy studies (ref. 57) indicate that the dc powder conductivity measurements on $\text{K}^+(\text{C222})\cdot\text{e}^-$ are dominated by grain-boundary effects. The magnetic susceptibility as a function of temperature shows that the ground state is diamagnetic, with an activation energy for spin-unpairing of 0.05 to 0.10 eV. The uncertainty in this value arises because we can only study the susceptibility up to 200 K before decomposition sets in, whereas the predicted maximum in the susceptibility is some 150-200° above this temperature.

These data, together with the crystal structure of $\text{K}^+(\text{C222})\cdot\text{e}^-$, led us to conclude (ref. 42) that the electrons are weakly trapped as singlet-state pairs in the large dumbbell-shaped cavities that exist between adjacent layers of closest-packed $\text{K}^+(\text{C222})$ ions. The shape of this trapping site is illustrated in Fig. 4, which also shows a view down the c -axis. The latter view shows clearly how the cryptand strands of one complex ion fit into the clefts in neighboring complex ions. It also shows the rather open ($\sim 4\text{ \AA}$ diameter) channel that connects one anion-pair site with a neighboring site along c .

The supposition that electron-pairs are trapped is further strengthened by the structures of $\text{Rb}^+(\text{C222})\cdot\text{Rb}^-$ and $\text{K}^+(\text{C222})\cdot\text{K}^-$ (ref. 51) in which, as described earlier, similar sites contain pairs of anions with shortened M^+ to M^- distances. The channel structure of $\text{K}^+(\text{C222})\cdot\text{e}^-$ is two-dimensional, with channels along the a -axis intersecting the c -axis channels at the anion-pair trapping sites. The open nature of both sets of channels suggests that the high electron mobility may result from facile electron exchange between adjacent pairs of electrons. An intriguing alternative is high conductivity of a thermally accessible triplet state.

The two electrideres described here represent the extremes in the behavior of electrideres. Many intermediate types exist although most appear to be localized. Electron spin pairing is common and several electrideres have magnetic susceptibilities that indicate the presence of antiferromagnetic transitions. As additional crystal structures are determined it will be interesting to see whether the structure-property correlations suggested here are general.

THERMAL STABILITIES

Our major concern has been to prepare and study alkalides and electrideres and to avoid irreversible decomposition by keeping the samples at low temperatures. We have not carried out systematic studies of decomposition, and most of the observations described here are therefore anecdotal in nature. The observation that a sample decomposes does not a priori mean that the compound is unstable at that temperature. Impurities in the metal, complexant or solvent, leaks in the system, and photochemical initiation of decomposition can all trigger the autocatalytic processes that lead to irreversible reduction of the complexant. In spite of these uncertainties, we report here some general trends that relate to the nature of the decomposition process.

The mechanisms of ether reductions by alkali metals are complex and can proceed by several pathways, including H-atom abstraction or deprotonation at the α and β carbon atoms (see ref. 58 for a recent comprehensive review). Deprotonation by e^- , M^- , or metal would lead to the formation of hydrogen atoms and carbanions, a process that could readily lead to radical chain decomposition. Some observations tend to support the hypothesis that deprotonation of the $-\text{CH}_2-$ groups is an important step. Complexation of a cation by a crown ether or cryptand or their aza-analogs would tend to make the C-H bonds more acidic by withdrawal of electrons. When this effect is accentuated by the presence of a dipositive cation such as Ba^{2+} , decomposition occurs even at $-70\text{ }^\circ\text{C}$ when solvent is removed. Conversely, spreading the charge over a large number of ligating oxygens such as in $\text{Cs}^+(\text{18C6})_2$ tends to enhance the stability. Finally, substitution of all of the ether oxygens by less charge-withdrawing tertiary amine nitrogens greatly enhances the stability (refs. 16, 17, 19, 55).

An important aspect of the synthesis of alkalides and electrideres and their use in solution is the choice of solvents. Our early work used primary amine solvents such as methylamine, ethylamine and 2-aminopropane. The latter two solvents, especially 2-aminopropane led to rapid decomposition of electrideres. Curiously, this was largely prevented when dissolved lithium metal was present (ref. 59). The reasons for this are unclear, but to this day we find that lithium tends to prevent decomposition during crystal growth, even when it is not incorporated into the crystal.

The best solvent found to date, insofar as stability is concerned, is dimethyl ether (ref. 28) with trimethylamine as a co-solvent for crystal growth. Often methylamine is used first to speed the solution process. Apparently, avoiding β hydrogens, and the acidic hydrogens on primary or secondary amines is the key to solvent stability. Metal solutions in dimethyl ether in the presence of a tertiary amine poly-aza complexant such as HMHCY are very stable and make the synthesis of alkalides and electrides much easier.

When complexants such as HMHCY are used, the stabilities are remarkable (ref. 55) with no signs of irreversible decomposition of the complexant over periods of weeks. Another problem occurs, however, with such complexants. A sodide such as K^+ (HMHCY) $\cdot Na^-$ can be crystallized at, say, $-50^\circ C$, that is thermodynamically stable to decomplexation and kinetically stable to irreversible decomposition. The enthalpy of formation is sufficiently negative to overcome the negative $T\Delta S$ term, so that ΔG for the formation process is negative and the compound is stable. When, however, the crystals are allowed to remain in vacuo at room temperatures for several days, decomplexation occurs to yield the alkali metals and undecomposed HMHCY. By redissolving the mixture at low temperatures, the compound can be made again. Evidently at the higher temperature ΔG for the formation process becomes positive because of the $T\Delta S$ term. We are currently synthesizing complexants that are designed to overcome this problem. The goal is to prepare alkalides and electrides that are stable at room temperatures to both decomposition and decomplexation. If successful, these two new classes of compounds may find uses that are currently prevented by problems with stability.

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