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Alkali Metals Plus Complexants: From Alkalides and Electrides to Aromatic Anions

James L. Dye

Department of Chemistry and Center for Fundamental Materials Research,
Michigan State University, East Lansing, MI 48824, USA

Abstract: Electron transfer from an alkali metal to a suitable complexant for the cation can yield crystalline ionic solids that contain the complexed cation and either an alkali metal anion (*alkalide*) or a trapped electron (*electride*). The nature and properties of electrides are emphasized in this paper. When the organic complexant contains aromatic groups, the anionic species is an aromatic radical anion. Preliminary work on the addition of alkali metals to LOGEAs (large organic globular electron acceptors) is described and strategies for the synthesis of mixed electride-anion compounds are considered.

INTRODUCTION

Electron transfer in organic chemistry usually refers to electrons that are transferred from a source molecule or ion to an acceptor molecule or ion. *Electrides* are crystalline materials in which the "excess" electron density is centered in a cavity formed by close-packing of large complexed cations (Refs. 1-4). Thus the electron does not "belong" to any single molecule. The cations are alkali cations encapsulated within a cryptand cage or a crown ether sandwich. This paper considers the transfer of these unusual "anions" from one site to another, and the nature and extent of inter-electron coupling. *Hypothetical* source molecules that would form electrides when brought together may be viewed as "expanded atoms" with a large positive ion at the center and an electron far from this center in a Rydberg-like state (Ref. 5). This is illustrated in Figure 1 by a hypothetical "expanded cesium atom" with Cs^+ trapped inside of a complexant cage. As these are brought together, we expect formation first of an "expanded metal" and then of an electride. With cesium atoms, a metal would form, with a half-filled conduction band. If, however, the complexed cations are of sufficient size to form large cavities when brought together, electron-

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trapping in the cavities can be energetically more favorable than delocalization in a conduction band. Weak overlap of the "excess" electron density would result in the formation of a *Mott insulator*, with one electron in each cavity.

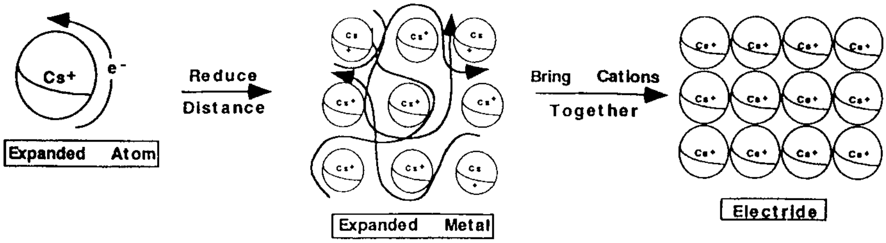


Figure 1. Schematic diagram of the expected sequence of events when "expanded atoms" are brought together to form an electride. Large enough cavities will cause electron localization.

The metallic solid $Li^+(NH_3)_4$ may be considered as an electride with strong enough overlap and small enough cavities to form a 3D metal (Ref. 6). In this case, the conduction band energy lies below that of a cavity-centered localized state. When $Li(NH_3)_4$ melts at 89K it forms a liquid metal. By contrast, liquid $Li(CH_3NH_2)_4$ is a near metal (Ref. 7), with $\sigma \approx 400$ ohm^{-1} cm^{-1}, while the solid is a semiconductor (Ref. 8). The lithium-ethylamine system is non-metallic in both the liquid and solid states (Ref. 9).

Both theory and experiment indicate that the cavity-centered state of electrides lies below the conduction band. Electron transfer between occupied cavities would require formation of doubly-occupied cavities. Coulomb repulsion is too large to make such a process energetically favorable and *pure* electrides are insulators with intrinsic conductivities below 10^{-8} ohm^{-1} cm^{-1} (Ref. 10). However, when defects are present, electrons can transfer to an *empty* cavity with no coulomb repulsion to overcome. Thus, the electride $K^+(C222)e^-$, which has large, short channels between the cavities in a chain-like configuration, has conductivities as high as 30 ohm^{-1} cm^{-1}, probably because defect "holes" can move readily down the chain.

Electrides are a new class of materials with no counterparts to provide a basis for comparison. Research in this area is full of surprises. Irreversible decomposition, the formation of other species such as alkali metal anions, and the existence of several phases for a single electride make these studies difficult. Added to this is the fact that electrides are very reactive towards air and moisture and are thermally unstable above 210-270 K (depending on the electride) because the complexant is reduced by the electron even *in vacuo*.

The addition of alkali metals to organic compounds provides a wide spectrum of compound types, with reduction to form "normal" electron-pair bonds by far the most prevalent. Thus, any acidic compounds, alcohols, amides, disulfides, etc. are simply reduced by the alkali metal. Even ethers are compatible only because of slow reaction kinetics, so that crown ethers and cryptands are *thermodynamically* unstable in the presence of alkali metals. Generally, carbon-hydrogen bonds are robust enough to resist cleavage by alkali metals, making aliphatic hydrocarbons unreactive at ordinary temperatures.

The addition of alkali metals to aromatic hydrocarbons to form aromatic radical anions, $(\mathrm{Arom})^{\dot{-}}$ is a vast field of study. It has not yet been possible to form alkalides or electrides with molecules that contain aromatic groups. It might be possible for complexants that contain aromatic groups with *low* electron affinities to react with alkali metals to form solids that contain mixed $(\mathrm{Arom})^{\dot{-}}$ and trapped electrons or alkali metal anions.

NATURE OF ELECTRIDES AND ALKALIDES

Role of Complexant and Metal

Key to the formation of alkalides and electrides is the strength of the complexant-cation interaction compared to the solvation energy of the cation. For example, cesium is somewhat soluble in methylamine ($MeNH_2$) so that we have the equilibria,

$$\mathrm{Cs(s)} + n\mathrm{MeNH_2} \xrightleftharpoons{\mathrm{MeNH_2}} \mathrm{Cs^+(MeNH_2)_n} + e^-_{solv} \qquad (1)$$

and

$$2\mathrm{Cs(s)} + n\mathrm{MeNH_2} \xrightleftharpoons{\mathrm{MeNH_2}} \mathrm{Cs^+(MeNH_2)_n} + \mathrm{Cs^-} \qquad (2)$$

This implies, of course, the additional equilibrium

$$\mathrm{Cs^-} + n\mathrm{MeNH_2} \xrightleftharpoons{\mathrm{MeNH_2}} \mathrm{Cs^+(MeNH_2)_n} + 2e^-_{solv} \qquad (3)$$

The addition of two moles of the complexant 18-crown-6 (18C6) introduces the complexation equilibrium,

$$Cs^+(MeNH_2)_n + 2(18C6) \xrightleftharpoons{MeNH_2} Cs^+(18C6)_2 + nMeNH_2 \quad (4)$$

which lies far to the right with Cs^+ encapsulated in a crown ether "sandwich". Equilibrium (4) shifts (1) and (2) to the right, greatly increasing the solubility of cesium in methylamine. With excess cesium, predominantly $Cs^+(18C6)_2$ and Cs^- are formed; a solution of the *ceside*. With limited cesium, the solution has primarily $Cs^+(18C6)_2$ and e^-_{solv}; a solution of the *electride*. When a less polar solvent, such as trimethylamine (Me_3N) or diethyl ether (Et_2O) is added to a ceside solution, the crystalline *ceside*, $Cs^+(18C6)_2Cs^-$ precipitates, while addition to an electride solution yields the crystalline *electride*, $Cs^+(18C6)_2e^-$. Thus, the chemistry of formation of alkalides and electrides is inherently simple. The reactivity and instability of the solutions and solids requires, however, rigorous attention to the purity of materials and to the vacuum-line synthesis techniques used.

Alkali metals are nearly insoluble in dimethyl ether (Me_2O) and tetrahydrofuran (THF). In such cases, the complexant presumably acts directly at the metal surface (Ref. 11), according to

$$M(s) + \text{Complexant} \rightleftharpoons M^+(\text{Complexant}) + e^-_{solv} \quad (5)$$

followed by the subsequent process,

$$e^-_{solv} + K(s) \rightleftharpoons K^- \quad (6)$$

Complexants other than crown ethers or cryptands can be used to prepare alkalides, but not electrides. For example, hexamethyl hexacyclen (HMHCY) has been used to form crystalline sodides (IUPAC, *natrides*) with the formula $M^+(HMHCY)Na^-$, with M = Na, K, Rb, Cs (Ref. 12). Other cyclens have also been used. The fully methylated cyclens have the advantage that they are very stable to reduction. Whereas a crown ether can be reduced according to

$$R\text{-}O\text{-}CH_2CH_2\text{-}O\text{-}R + 2e^- \longrightarrow R\text{-}O^- \; ^-O\text{-}R + CH_2 = CH_2 \quad (7)$$

the corresponding reduction at the >N-C- site does not appear to occur at ordinary temperatures. We have been unable to synthesize an electride with any of the methylated cyclens, in spite of numerous attempts. It would be desirable to synthesize a thermally stable electride with a fully methylated aza-cryptand, but we have not had access to such a complexant.

Electron Locales in Electrides

All seven electrides of known structure have the cation encapsulated in a cryptand cage or a crown ether sandwich. These crystalline solids all contain cavities (void spaces with diameters between 3.9 and 4.8Å) between complexed cations. That is, a sphere of this diameter could be centered in the cavity and would just touch the van der Waals surfaces of the nearest complexant hydrogens that line the cavity. Since we expect the partial positive charge of these -CH_2- hydrogens to attract electron density, it is likely that the "effective" diameter of the cavity is at least 0.5Å larger than the "hard sphere" diameter. In addition, the cavities are not spherical, providing still more room for the trapped electron density. Although repulsion from the closed-shell complexant molecules prevents significant electron density from penetrating into the complexant or cation region, we expect non-zero electron density at the boundaries of the cavities and especially in the channels that interconnect the cavities. An extensive quantum mechanical study of the electride $Cs^+(15C5)_2e^-$ confirms these expectations (Ref. 13).

To first order, the "excess" electrons in electrides may be viewed as particles in spherical boxes, with an image positive charge at the center of each cavity, providing "hydrogen-like" stabilization. The evidence for electron-trapping in cavities is overwhelming and has been summarized elsewhere (Refs. 3,4). The closest analogues are F-centers in alkali halide crystals, in which electrons are trapped at halide ion vacancies. However, electrides are *stoichiometric* F-center salts with an electron at *every* anionic site. This permits new phenomena to be encountered as the electrons interact with one another.

Communication Among Electrons

In most electrides, the trapping sites are more or less uniformly distributed in space with inter-cavity distances of 8-11Å (center-to-center). It is clear now, however, that distance alone is not the dominant factor in the electron-electron interactions. Such interactions are strongly influenced by the *channels* that interconnect the cavities. The presence of such channels was emphasized in our first communication on electride structure (Ref. 14), and the influence of channels on magnetic coupling and conductivity has been described in subsequent publications. Recently, we developed computer methodology that permits easy visualization of the sizes and shapes of cavities and channels in any material with known crystal structure (Refs. 3,15). Essentially, the atoms are represented as van der Waals spheres centered at their respective crystallographic sites. The programs permit construction of *isosurfaces* that are at any desired distance from the molecular van der Waals surfaces, making it easy to determine the maximum diameter of a hard sphere that would just fit in a cavity, or of a sphere that would just be able to move from one cavity to another through a connecting channel. In addition, cavity shapes can be determined as well as channel lengths and topologies, adding immeasurably to our understanding of electrides.

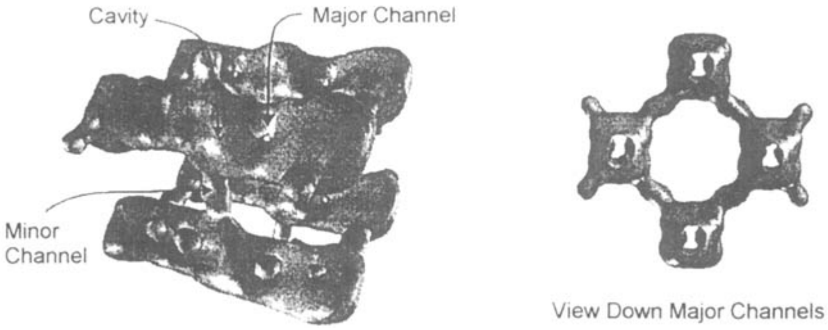


Figure 2. Views of the cavity-channel isosurfaces in $Cs^+(15C5)_2e^-$ at a distance of 0.5 Å from the van der Waals surfaces of the complexant molecules. The major channel has a dumbbell-shaped cross section with dimensions of about 1.9 Å by 4 Å, while each minor channel has a diameter of about 1.5 Å.

Properties of Specific Electrides

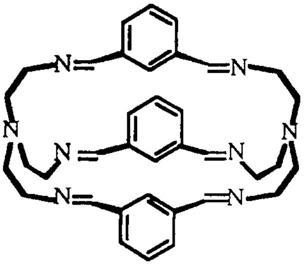
The electrides $Cs^+(15C5)_2e^-$, $Cs^+(18C6)_2e^-$ and $Li^+(C211)e^-$ contain essentialy 1D cavity-channel structures in which the void spaces form chains along a specific direction with much smaller inter-chain channels. These three electrides are insulators with only small, defect-dominated conductances. They all show maxima in their magnetic susceptibilities and the susceptibility data can be quantitatively described by the linear chain Heisenberg antiferromagnetic (LCHA) model, with $-J/k_B$ values of 3.0, 38 and 54 K, respectively (k_B is the Boltzmann constant) (Ref. 4). Figure 2 shows a perspective view of the cavities and channels in $Cs^+(18C6)_2e^-$ as well as a view down the channel axis. Each view represents an isosurface through all points that lie at 0.5 Å from the van der Waals surfaces of the molecule. Views at closer distances would give truer pictures of the actual shapes of the cavities and channels, but they would show every crack and cranny in the structure and the foreground would obscure the inner geometry. When the temperature of a polycrystalline sample of $Cs^+(18C6)_2e^-$ is raised to 230 K or higher for a period of 30 minutes or longer, it converts irreversibly, but without significant decomposition, to form a non-crystalline phase with much reduced J-coupling ($J/k_B < 3K$) (Ref. 16). The most logical explanation is movement of the complexant to block the major channel. This would decrease overlap of the wave functions in adjacent cavities, tending to isolate the trapped electrons in non-connected cavities. Such behavior also occurs with $Cs^+(15C5)_2e^-$ and with $K^+(15C5)_2e^-$. Two phases of $Li^+(C211)e^-$ exist, with $-J/k_B$ values of 54 K and 18 K (Ref. 17). Electride coupling constants correlate well with the cross-sectional areas of the channels (Ref. 4), providing additional evidence for the "electron lattice-gas" model, with maximum electron density in the void spaces.

The electride $K^+(C222)e^-$ has a very different cavity-channel geometry and very different properties (Ref. 18). Its specific conductance is some *10 orders of magnitude* greater than those of $Cs^+(15C5)_2e^-$ and $Cs^+(18C6)_2e^-$ and the inter-electron coupling is much stronger, with $-J/k_B > 300$ K. As with the alkalides $K^+(C222)K^-$ and $Rb^+(C222)Rb^-$, the structure contains dumbbell-shaped *dual* cavities along a very open zigzag chain. The cavities have a diameter of 4.6Å with a center-to-center distance of the pair in the dumbbell of only 5.5Å and a "neck" diameter of 4.0Å. The channel between the cavity pairs has a diameter of 3.3Å. In addition, each chain is connected to two neighboring chains by channels of diameter 2.2Å to form a 2D network. The conductivities of polycrystalline pellets and thin films suggest that defects are responsible for the high conductivity. We propose that these are missing electrons (holes) that can move easily down the chain and can migrate by activation from one chain to another through the inter-chain channels. The strong interaction between electrons in $K^+(C222)e^-$ also affects the optical spectrum of thin films produced by either rapid solvent evaporation or by high-vacuum vapor co-deposition.

While most electrides show a broad absorption peak in the near IR at 1200-1500 nm, annealed $K^+(C222)e^-$ films show either a "localized" peak or a plasma-like absorption, depending on the conditions of deposition.

LARGE ORGANIC GLOBULAR ELECTRON ACCEPTORS

Our study of these LOGEAs was inspired by the behavior of alkali metal-doped fullerenes, in which multiple electrons can be accepted into the LUMOs of C_{60}, with incorporation of alkali cations into the octahedral and tetrahedral holes between close-packed C_{60} molecules. Many such adducts show superconductivity, providing the possibility that reduced solid LOGEAs might also have interesting and useful electronic properties. The synthesis of "cryptatium" by Echegoyen, Lehn and co-workers by alkali metal addition to a cryptand with bipyridal arms (Ref. 19) provided additional stimulus. We reasoned that large molecules with aromatic constituents might react with alkali metals in solution to produce electron-rich molecules and crystalline solids, with the alkali cations either encapsulated by the complexant molecules or externally solvated. Standard aromatic complexants, such as dibenzo-18-crown-6, are not suitable because they decompose rapidly in the presence of solvated electrons, presumably by formation of good phenolate-type leaving groups. The ease of synthesis of large amounts of schiff-base cryptands such as **1** prompted us to investigate these complexants.



An aromatic schiff base cryptand **1**

Extensive (but as yet unpublished) work has been done with these compounds, which readily accept up to three electrons, but crystallization has proved to be difficult and so far the solids have not been completely characterized. Low field microwave absorption

(LFMA), one of the criteria for superconductivity, has been seen with some samples (Ref. 20), but the phase(s) responsible have not been identified. Work with these compounds is continuing.

We consider crystalline electrides and salts of aromatic anions to form the extremes of what might be a continuum of materials. In the former, there are no well-defined molecular orbitals to contain the electron(s) while in the latter, the "excess" electron(s) are delocalized over all or a portion of the molecule. Of particular interest would be complexants in which the electron affinity of the aromatic moieties would be small enough to permit partial occupancy of both the molecule and cavities between molecules. The aromatic-containing complexant must be robust enough to resist reduction, able to encapsulate one or more cations, and large enough to leave cavities of diameter 4Å or larger when close-packed. The proposed molecule would contain one or more low electron affinity groups such as $-CH_2-\phi$. This might form a solid with electron density distributed between cavities and the aromatic groups, leading to interesting electronic properties.

SUMMARY

Until the late 1960s, the chemistry of the alkali metals was thought to be predictable and rather uninteresting. The introduction by Pedersen, Lehn and others of cyclic and bicyclic polyethers as complexants for the alkali cations provided large, well-shielded positive ions that greatly expanded the chemistry of these elements. Recognition that alkali metal *anions* are present in metal solutions in amines and ethers (not in ammonia!) and the isolation of well-defined crystalline salts of Na^-, K^-, Rb^- and Cs^- added completely new and unexpected chemistry to the alkali metal family. The use of solutions of alkali metal anions in organic synthesis is already well-established and growing (Ref. 21).

The synthesis and study of crystalline *electrides* introduced a new and unusual "anion" into the family of ionic solids; namely, the trapped electron. It now appears that electrides provide unique examples of "electron lattice gases" in which the electron density is largely, but not exclusively, confined to the void spaces in the crystal structures. While one might expect electron-transfer to be very facile in electrides, the coulomb barrier to double-occupancy in cavities actually makes *pure* cavity-based electrides insulating. The fact that the 3D solid, $Li(NH_3)_4$, with small cavities is a metal, suggests, however, that *metallic* electrides might be synthesized.

The area of solid materials produced by the addition of alkali metals to organic compounds to yield itinerant electrons is a wide-open field. Its further development will require collaboration among organic chemists, physical-inorganic chemists and physicists. The potential interesting and useful optical, magnetic and electronic properties that may result from materials with such weakly-bound electrons make such studies very attractive. The major barrier to new electride development at this time is the synthesis of suitable complexants. While the treatment with alkali metals requires non-traditional methods, they are straightforward and well-developed and should not pose undue difficulties. I hope that the challenge in this area and the promise of new and different materials will encourage others to enter the fascinating field of electride chemistry.

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