Electrides: Ionic Salts with Electrons as the Anions

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Electrides are ionic compounds that have alkali metal cations complexed by a crown ether or cryptand, with trapped electrons as counterions. The crystal structures and properties of two electrides illustrate the diversity that is encountered. One, Cs^+ (18-crown-6)$_2$$e^-$, has relatively isolated, trapped electrons apparently centered at each anionic site. It has a low conductivity consistent with electron localization, with an activation energy for conductivity of at least 0.45 electron volt. The other, K^+ (cryptand[2.2.2])e^-, has electron pairs trapped in an elongated cavity in a singlet ground state, but there is also a thermally accessible paramagnetic state available. This electride is much more conducting, with an activation energy of only 0.02 electron volt.

CHEMISTS FEEL AT HOME WITH ELECTRONS—THEY STUDY electron-transfer processes, talk about electron-pair bonds, invoke free radicals and radical-ions (when dealing with odd electron molecules) and refer to the oxidation state of an atom in a compound by counting electrons. Delocalization of electrons, either in an aromatic molecule, or in the plane of graphite, or even in a metal, causes few problems, as arguments based on orbital overlap and band formation are invoked.

The picture is not so clear for solvated electrons (e^-_{solv}), or for electrons trapped in organic glasses. In these cases, the extra electron does not "belong" to a single molecule or even to a collection of molecules with a well-defined geometry. Most investigators believe that the solvated electron wave function is centered in a cavity in the solvent and that the cavity size and geometry fluctuate with time, to provide a time-average orientational polarization of the solvent dipoles that helps to stabilize the trapped electron (*1*). Even in glasses, initial electron trapping at a site of favorable bond or molecular dipole orientation is followed by "annealing"—molecular reorientation—that deepens the trap.

This article describes a new class of compounds that we call electrides (*2*). We believe that in common with solvated and trapped electrons, the electron density is centered in "cavities"—in this case, anionic sites—with the positive ends of $^-O–CH_2^+$ dipoles oriented toward the cavity. However, in contrast to solutions that contain solvated electrons, and glasses with trapped electrons, electrides are well-defined crystalline salts whose crystal structures can be determined. The structures and properties of electrides agree with an ionic model in which the positive ions are complexed alkali metal cations and the negative ions are trapped electrons or electron pairs. The mobility of these trapped electrons depends on the structure of the crystal and is apparently influenced by the size and length of channels that interconnect the anionic sites. Thus, electrons in electrides are, on the one hand, the simplest anions. On the other hand, because of the small mass of the electron and the quantum effects that result, trapped electrons exhibit unusual and complex interactions with each other and with the cations. As a result, electrides have proven to be remarkably complex and varied in behavior, providing a rich field for experimental studies and a challenging area for theoretical investigations.

Background

Electrides have their "parentage" in solvated electrons and alkali metal anions. The properties of the former have been studied by many investigators over an 80-year time span, first as the reducing species in solutions of the alkali metals in ammonia, amines, polyethers, and a few other solvents (*3*) and second as a product of the radiolysis and photolysis of liquids (*4*). Alkali metal anions, M^-, are of more recent vintage, having been proposed in the 1960s as the diamagnetic species in metal-ammonia and metal-amine solutions (*5*). Experimental proof of the existence of alkali metal anions in amines and ethers came quickly (*6*), and in 1974 the first crystalline salt of an alkali metal anion was synthesized and characterized (*7*). This class of compounds, called alkalides, has expanded to more than 40 salts of Na^-, K^-, Rb^-, and Cs^- (*2, 8*), and the crystal structures of 16 alkalides have been determined (*9, 10*). Interestingly, in spite of many attempts, lithides have not yet been prepared, nor has Li^- been unequivocally identified in solution.

The key to the preparation of stable solutions that contain solvated electrons or alkali metal anions is to provide a solvent that is resistant to reduction and that strongly solvates the cation. Anion or electron solvation is important but not dominant. Similarly, the key to the synthesis of crystalline alkalides and electrides is a complexant for the cations that is resistant to reduction and is a strong enough complexant to compete with polar solvents for the cation. Crown ethers, first developed by Pedersen (*11*), and cryptands, first synthesized by Lehn and co-workers (*12*), meet these two criteria and were used to prepare the first alkalides and electrides. More recently, aza-analogs of the crown ethers have been used as well (*13*). These complexants are relatively nonvolatile cyclic (or bicyclic) molecules that complex alkali cations by encapsulating them in the hole formed by the ring or rings. The lone-pair electrons of the ether oxygens in the $–CH_2–O–CH_2–$ units or of the aza nitrogens in the $–CH_2–N(CH_3)–CH_2–$ units are oriented toward the positive ion and

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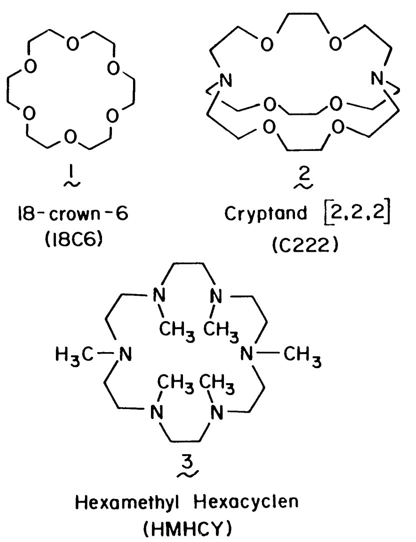

Fig. 1. Typical complexants used to synthesize alkalides and electrides.

provide stabilization. The structural formulas of some complexants used to synthesize alkalides and electrides are shown in Fig. 1.

The complexants play another important role in the synthesis of electrides. In the absence of complexants, alkali metals dissolve only in ammonia, some primary amines, and a few other solvents such as polyethers and hexamethylphosphoric triamide. Except for lithium, which is highly soluble in methylamine and ethylamine and moderately soluble in ethylenediamine, the alkali metals are only slightly soluble in solvents other than ammonia. Complexation of the cation by a crown ether, cryptand, or similar complexant solubilizes the alkali metals in many other solvents (*14*) by shifting the equilibria:

$$\mathrm{M(s)} \rightleftarrows \mathrm{M}^+ + e^-_{\mathrm{solv}} \qquad (1)$$

$$\mathrm{M}^+ + C \rightleftarrows \mathrm{M}^+C \qquad (2)$$

in which C represents the complexant. These equilibria, together with

$$\mathrm{M(s)} + e^-_{\mathrm{solv}} \rightleftarrows \mathrm{M}^- \qquad (3)$$

permit one to prepare concentrated alkali metal solutions in a solvent such as dimethyl ether ($\mathrm{Me_2O}$) that contain M^+C with either M^- or e^-_{solv} (or a mixture of the two) as the counterion. In many cases, the relative concentrations of M^- and e^-_{solv} can be controlled simply by adjusting the ratio of complexant to metal. Sometimes, however, stoichiometric solutions contain appreciable concentrations of both M^- and e^-_{solv} as well as free complexant. When the solubility of the metal in the absence of complexant is very small and the cation complexation constant is very large, the solubility behavior may be described by two simple equilibria

$$\mathrm{M(s)} + C \rightleftarrows \mathrm{M}^+C + e^-_{\mathrm{solv}} \qquad (4)$$

and

$$2\mathrm{M(s)} + \mathrm{C} \rightleftarrows \mathrm{M}^+C + \mathrm{M}^- \qquad (5)$$

Crystalline alkalides or electrides are prepared from solutions that contain primarily M^- or e^-_{solv}, respectively, by adding a less polar cosolvent such as trimethylamine or diethyl ether and cooling the solution.

The preparation of alkali metal solutions and solid alkalides and electrides would be far simpler were it not for the highly reactive nature of solvated and trapped electrons and alkali metal anions. Not only must one exclude reducible substances such as oxygen, water, alcohols, and such, but one must also keep the temperature below about −40°C during electride synthesis, storage, and use. This is because the solvents and complexants are themselves reducible, leading to decomposition of the solution or solid. The main advantage of dimethyl ether as a solvent is its extreme resistance to reduction. Apparently, the absence of both ionizable hydrogens (present in primary and secondary amines for example) and hydrogens that are beta to O or N makes $\mathrm{Me_2O}$ particularly robust. For the same reasons, trimethylamine is the preferred cosolvent.

Solvent-free crystalline electrides are also subject to irreversible decomposition that becomes more pronounced as the temperature is raised. Most can be stored at −75°C indefinitely, but decompose rapidly above about 0°C. The mechanism is not known, but initiation may occur by deprotonation of the $-\mathrm{CH_2}-$ groups. A promising recent finding is that aza-crowns, such as hexamethyl hexacyclen (HMHCY), Fig. 1, are more resistant to irreversible decomposition. Since aza-crowns form weaker complexes with the alkali metals than do oxa-crowns, however, decomplexation to regenerate the free complexant and metal tends to occur as the temperature is increased (*13*). Initial work with poly-aza bicyclic complexants similar to the cryptands suggests that it might be possible to synthesize electrides that are stable to both decomposition and decomplexation. An important goal is to synthesize electrides that can be stored indefinitely at room temperature under vacuum or under an inert atmosphere.

Experimental Methods

The synthesis of electrides is straightforward, but care must be taken to use solvents that are free of oxidants, to exclude air and moisture, and to keep the solutions and solids cold. My research group has worked out solvent and complexant purification and handling procedures and has designed synthesis vessels that minimize decomposition during solution formation and electride crystallization. Only vacuum-line synthesis methods have been used thus far, although it might be possible to be less rigorous and work under an inert atmosphere by using more conventional Schlenk-line techniques (*15*).

After synthesis, polycrystalline electride samples are stored until needed in sealed tubes at −75°C or in liquid nitrogen. When it is necessary to transfer powdered samples or single crystals to an instrument, it suffices to open the ampoule in a nitrogen-filled polyethylene glove bag, as long as the sample is kept cold. It is also possible to prepare solid pellets by keeping the die and anvil at or near liquid-nitrogen temperatures. To study surface properties of single crystals, such as reflectance spectra, it is necessary to grow the crystals and transfer them to the measurement system in a vacuum-tight apparatus.

Characterization of alkalides and electrides requires many different techniques. In addition to direct analysis, they have been studied by the following methods: (i) magnetic susceptibility from 2 to 300 K with a SQUID susceptometer (*16*); (ii) two- and four-probe dc conductivity and ac impedance spectroscopy (to 13 MHz) (*17*); (iii) solid-state alkali metal nuclear magnetic resonance spectroscopy (NMR), including static and magic-angle sample spinning (MAS), spin-echo and relaxation methods, and single crystal studies (*18*); (iv) electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR) spectroscopy, including the study of electrons at low concentrations in alkalides (*16*, *19*); (v) differential scanning calorimetry (*13*); (vi) optical transmission (films), reflectance (single crystals) and fluorescence spectroscopy (films, powders, and single crystals) (*20*); (vii) powder and single crystal x-ray diffraction (*9*, *10*); and (viii) photoelectron and thermionic electron emission (*21*).

As a result of all these methods, a large amount of information about the behavior of electrides, including the crystal structures of three of them, has been obtained (*22–24*). In spite of continuing problems with mixed alkalide-electride samples and with decomposition and decomplexation, much can be said about the structure and properties of several electrides, and the relation of properties to structure can be inferred. In what follows, particular attention is paid to two electrides of known structure, Cs^+ (18-crown-6)$_2$e$^-$ (abbreviated CsC6), and K^+ (cryptand[2.2.2])e$^-$ (KCrypt). The members of the class of compounds called electrides have different properties. This makes the detailed investigation of electrides other than the two considered here even more inviting.

Crystal Structures

In each of the two electrides the structure of the complex is remarkably similar to that of the same complexed cation in the corresponding alkalides or, indeed, in "ordinary" salts that contain the same complexed cation and an anion such as iodide. This provides strong evidence for the presence of the complexed cation in electrides rather than, for example, complexed atoms or complexed cations in which a substantial portion of the charge within the complex is neutralized by the electron.

If the metal is present as the complexed cation, then where is the electron? The answer cannot be obtained from the structure alone, but once again, comparison with the structures of alkalides provides a clue. The electride, CsC6, is isostructural with the sodide, Cs^+ (18-crown-6)$_2$Na$^-$ (*22*). The main difference is that in the electride, the Na^- site is vacant—each anionic site is now a hole! The resolution of the structure is not high enough to tell whether there is an electron in the hole or just empty space. However, consider the attraction of the cavity for an electron. The surrounding cations produce an image-positive charge at the center of the hole that would provide Coulomb attraction for the electron. The image charge would be further enhanced by substantial dipole orientation of the surrounding crown ether molecules. The electronegative oxygens in each –O–CH$_2$– unit produce a dipole moment with the positive end oriented toward the cavity. For example, a substantial portion of the solvation energy of the solvated electron has its origin in orientation polarization of the solvent molecules or bond dipoles. Thus, the observed arrangement of the complexed cations in electrides, packed as closely together as possible, provides a natural trap for electronic charge at each anionic site. The situation is analogous to F-centers in alkali halides (*25*), in which electrons are trapped at anionic vacancies. According to this view, electrides are pictured as salts in which all of the anionic sites participate in electron trapping.

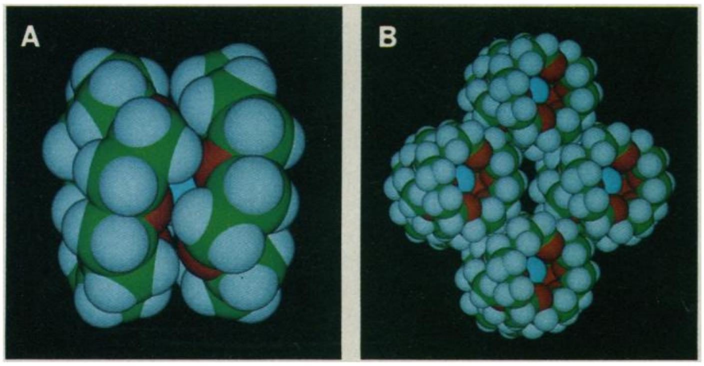

Fig. 2. Space-filling representations of the packing in Cs^+ (18-crown-6)$_2$e$^-$. Color code: green, carbon; red, oxygen; blue, cesium; and white, hydrogen. (**A**) View of the complexed sandwich cation Cs^+ (18-crown-6)$_2$ that shows how well the cesium cation is protected by the crown ether. This view is nearly perpendicular to that in (B). (**B**) View down the most open channel. The anionic site lies between two sets of these units so that it is nearly equidistant from eight complexed cesium cations. [Prepared directly from the crystal structure data by F. A. Momany of Polygen Corporation]

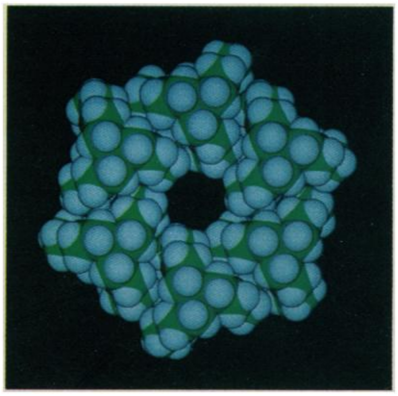

Fig. 3. Space-filling representation of the packing in K^+ (cryptand[2.2.2])e$^-$. Color code: green, carbon; red, oxygen; and white, hydrogen. The nitrogen and potassium atoms are hidden from view in this display. The central hole connects elongated cavities that contain electron pairs. [Prepared directly from the crystal structure data by F. A. Momany of the Polygen Corporation]

A word of caution is in order here. Electrons are not like massive anions—they are free to move beyond the boundaries of the cavity, with nonzero density in the regions occupied by the atoms of the complexant. Indeed, it is claimed (*26*) that the optical spectrum demands extension of the electron density out to at least the hydrogens of the surrounding crown ether molecules. A challenging experimental problem is to map the electron density distribution in electrides. An even more challenging theoretical problem is to calculate it!

The picture that emerges from the structure of CsC6 (monoclinic, space group *C2/c*, four molecules per unit cell) is then as follows. (i) Cs^+ is embedded in a sandwich complex with coordination to 12 crown ether oxygens and has the structure of a "normal" complexed cation. A view of this sandwich structure is shown in Fig. 2A. (ii) Each complexed Cs^+ is surrounded by eight anionic sites, empty except for electronic charge. Conversely, each anionic site is surrounded by eight complexed cesium cations. (iii) The shortest center-to-center distance of the anionic sites is 8.68 Å along the *c*-axis. Each site has six neighboring sites, two at 8.68 Å and four at 10.2 Å. (iv) The region between anionic sites is "pinched off" by packing of the complexed cations to produce channels. The channel along the *c*-axis is rather short and open. The others are longer and smaller in diameter.

The boundaries of the cavities and channels are determined by the location of the van der Waals surfaces of the complexant. In Fig. 2B the view is down the *c*-axis channel through a "dog bone"–shaped opening. This channel and the anionic vacancies form a one-dimensional chain of cavities 8.68 Å apart and similar to beads on a string. The channels that connect separate chains are longer and more constricted. The four cavities that serve as neighbors in these directions are 10.2 Å apart.

The electride K^+ (cryptand[2.2.2])e$^-$ or KCrypt has a structure that is very similar to those of the corresponding potasside, K^+ (cryptand[2.2.2])K^- and rubidide, Rb^+ (cryptand[2.2.2])Rb^-. Instead of having individual anionic cavities, these alkalides contain elongated dumbbell-shaped cavities, each holding a pair of anions in close contact; they seem to contain the implausible dimers K_2^{2-} and Rb_2^{2-}, respectively.

In a fashion similar to that of the alkalides, the electride, KCrypt, contains interlocking sheets of complexed cations with open channels that connect very large vacancies (~12 Å by 4 Å by 6 Å), each presumably capable of trapping a pair of electrons (*23*). A view down the most open channels, perpendicular to the sheets, is shown in Fig. 3. Each channel has a minimum diameter (between hydrogen van der Waals surfaces) of about 4 Å. Adjacent anionic sites between a given pair of sheets are also connected by somewhat more constricted channels in one direction but are nearly completely blocked in the third direction. A schematic drawing of the channels and vacancies is shown in Fig. 4 (*27*).

In summary, the electride prepared from potassium and cryptand [2.2.2], which also belongs to the monoclinic space group (*C2/c* and has eight molecules per unit cell, contains elongated anionic sites, each of which could accommodate two trapped electrons. The center-to-center distance within a two-electron site is about 5.3 Å. Two other sites are connected by channels and are located about 7.8 and 8.4 Å away, with the former distance corresponding to a large open channel. Other trapping sites are separated by closely packed complexed cations from this system of roughly two-dimensional channels. The distance to the closest pair of such sites from a given trapping site is about 10.9 Å. It is not possible to give precise distances for the electride because the zigzag nature of the channels and the complex shape of the cavities makes it difficult to locate the "centers" of the trapping sites. In the corresponding potasside, which has similar packing but a different space group, the closest K^- to K^- distances are 4.90, 7.95, 9.26, and 10.67 Å (*9*).

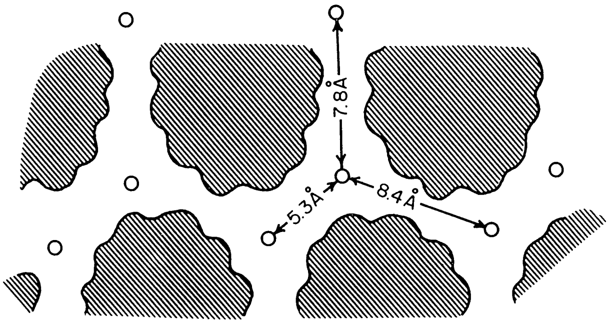

Fig. 4. Schematic diagram of the open channels in K^+ (cryptand[2.2.2])e^- showing probable locations of the centers of trapped electron charge density.

Correlation of Structures and Properties

The striking difference between the structures of CsC6 and KCrypt is matched by great differences in their properties. Early in our work on electrides, my research group used the optical absorption spectra of thin films to place electrides into two classes that correspond to "localized" and "delocalized" electrons. The former class, to which most electrides synthesized to date belong, is characterized by a distinct infrared electronic absorption peak at wavelengths between 1.2 and 1.6 μm, similar to that of solvated electrons in liquids and trapped electrons in glasses. The onset energy of 0.5 to 0.7 eV defines the minimum trap depth.

Several electrides, including KCrypt, have high absorbance out to at least 3.0 μm with a broad decreasing absorbance throughout the visible region of the spectrum. The close similarity to the reflectance and transmittance spectra of metallic metal-ammonia solutions prompted the assignment of these electrides as delocalized or "metallic," with absorption spectra that are dominated by plasmon absorption. The extremely broad visible "tail" would demand, however, a short electron mean–free path (*28*). An alternative explanation of the absorption spectrum of KCrypt is that the electronic ground state lies only slightly below the conduction band, so that the observed spectrum is just the "tail" of a peak that lies far enough in the infrared to be obscured by cryptand absorptions. Quantitative reflectance spectra of single crystals will probably be required to determine the origin of this absorption.

It might seem that simply measuring electrical conductivities would tell us immediately whether an electride is a metal, semiconductor, or insulator. Indeed, if four-probe measurements on single crystals as a function of temperature could be made, not only could this question be answered but also the anisotropy of the conductivity could be measured and related to the crystal structure. This remains a major research goal, but the technical problems are formidable. The difficulty in growing and handling large electride single crystals, their thermal instability, and the problems involved in attaching suitable electrodes, have so far combined to prevent single-crystal conductivity studies of electrides.

It is relatively easy to measure the conductivity of packed powders or pellets as a function of temperature. When the intrinsic resistivity is high enough to mask effects caused by the electrode-sample resistance, two-probe dc methods are often satisfactory. For example, initial measurements on CsC6 indicated that it is a semiconductor with an activation energy of 0.45 eV, a value that is large enough to overwhelm any non-ohmic behavior at the electrodes (*16*). Grain-boundary effects could still be important but they tend not to affect the activation energy (*17*). Recent measurements indicate that ionic contributions to the conductivity and the presence of small amounts of Cs^- may be important in this case (*29*).

The situation is different with KCrypt. The conductivity is at least a million times as high as that of CsC6, but the current-voltage (*I-V*) curves are markedly non-ohmic, with *I* increasing approximately as V^2. Such nonlinearity shows that effects at the electrode-sample interface are important. The cause was eventually shown to be a "Schottky barrier" at the electrodes, whose origin is the difference in the work functions of the electrode metal (steel or gold) and the electride. This leads to a depletion layer near the electrode and results in non-ohmic behavior. The effect was nearly eliminated by coating the electrodes with potassium metal, whereby the *I-V* curves were linear through the origin and the resistivity was more than three orders of magnitude lower than that in the absence of potassium (*29*).

Finally, impedance spectroscopy [the measurement of the frequency dependence of the complex impedance (*29, 30*)], was used to identify electrode and grain-boundary effects, four-probe cells were employed to eliminate effects caused by the lead wires, and potassium-coated electrodes were used to remove the Schottky barrier. KCrypt has a dc powder conductivity that ranges from about 0.7 $\text{ohm}^{-1}\ \text{cm}^{-1}$ at 100 K to about 1.0 $\text{ohm}^{-1}\ \text{cm}^{-1}$ at 140 K, with an activation energy of only 0.02 eV. Thus, it appears to be nonmetallic with a small activation barrier for electron migration. It is possible that the conductivity is highly anisotropic and that the observed powder conductivity is dominated by high resistivity in one or two directions, leading to residual grain-boundary resistance. Single-crystal conductivity studies will be required to settle this question.

Interactions among the trapped electrons in an electride can affect the magnetic susceptibility. Individual electrons have an intrinsic magnetic moment which, in the absence of electron-electron interactions, will yield a Curie law contribution $\chi = 0.37/T$ to the molar magnetic susceptibility. Strong pairwise spin coupling would cancel this paramagnetic contribution, leading to diamagnetism. The cooperative phenomena of ferromagnetism and antiferromagnetism involve alignment or anti-alignment of adjacent electron spins below a critical temperature known as the Curie temperature (ferromagnetism) or the Néel temperature (antiferromagnetism). At temperatures well above such transitions or with weak coupling, one obtains deviations from the Curie law contribution of the form $\chi = 0.37/(T - \theta)$ in which the Weiss constant, θ, is positive or negative for ferromagnetic or antiferromagnetic interactions, respectively.

The localized electride CsC6, and most others whose optical spectra suggest electron localization, nearly obey the Curie law, with, however, small negative Weiss constants. For example,

$\theta = -1.5$ K for CsC6 and ranges from -5 to -20 K for other electrides of this class. This suggests that the electrons interact only weakly with one another, with a slight tendency toward antiferromagnetism. In one case, that of Cs^+ (15-crown-5)$_2e^-$ a Néel transition to an antiferromagnetic state occurs at 4.3 K.

As with other characteristics, KCrypt has strikingly different magnetic properties. The electronic contribution to the molar susceptibility approaches a small negative value as T approaches zero, indicating spin-pairing. The pairing is weak enough, however, that the susceptibility increases with increasing temperature, reaching a value that corresponds to about 15% unpaired spins at 200 K, the highest temperature examined. This suggests that the electronic ground state is a singlet state in which electrons exist as pairs, but that a thermally accessible triplet (or dissociated) state lies only about 0.05 eV above the singlet ground state. Recall that the structure of this electride shows large dumbbell-shaped cavities (Fig. 4) that are assumed to be occupied by electron pairs. The susceptibility data are consistent with the picture of an electron pair trapped in each large cavity in a singlet ground state. The conductivity data suggest that thermal excitation to a triplet or dissociated state may lead to high conductivity. By contrast, the electrons in CsC6 lie at least 0.9 eV below the conducting state in localized traps and interact only weakly with each other.

Data from NMR are also in accord with the presumed electronic structures of these two electrides. Solid-state ^{133}Cs NMR studies of CsC6, both pure and with Na^- substitution for some of the electrons (*22*), yield a small paramagnetic chemical shift of Cs^+ that corresponds to about 0.04% 6*s* character. This presumably arises from some overlap of the wave function of the trapped electron with the complexed cation. Substitution of one, two, or three Na^- ions for electrons in the eight anionic sites around each complexed cesium cation yields three new ^{133}Cs NMR peaks shifted diamagnetically 1/8, 2/8, and 3/8 of the way toward the chemical shift of Cs^+ in the isostructural diamagnetic sodide, Cs^+ (18-crown-6)$_2Na^-$.

Because of extreme line broadening caused by the large quadrupolar coupling of ^{39}K to its surroundings, solid-state ^{39}K NMR does not yield accurate chemical shifts. Spin-echo methods show, however, that the static NMR pattern of KCrypt is the same as that of the cation in K^+ (cryptand[2.2.2])K^-, again illustrating that the cation environment is similar in the electride and the potasside (*31*). From the perspective of a K^+ ion inside the cryptand cage, the electron pair in the electride cavity looks like the pair of K^- ions in the potasside cavity.

The EPR spectra of pure electrides do not provide much information because of rapid electron exchange. Exchange narrowing leads to a single narrow line at the free electron *g*-value. Thus, when we refer to "localized" electrons, the time scale of localization becomes important. On the electronic or optical time scale of picoseconds or less the electrons are localized, while on the EPR time scale of nanoseconds to microseconds they undergo exchange. EPR studies of KCrypt are extremely difficult because of the high microwave conductivity of this electride. Only the tiniest speck of sample can be used without degrading the cavity "Q" and losing the EPR signal.

Although the EPR spectra of pure electrides do not provide local information, it is possible to slow down electron exchange by "diluting" the electrons in a diamagnetic host lattice. Such samples are easy to produce from alkalides that have crystal structures similar to the electride being studied. In fact, it is difficult to avoid "contamination" of alkalides by trapped electrons. The solutions always contain some e^-_{solv} along with M^- and, as a result, defect electrons are present in some of the anionic sites.

Studies of the detailed EPR behavior of electron-doped alkalides are currently in progress, and they show the following general behavior:

1) When the cation is encapsulated in a crown-ether sandwich [for example, Cs^+ (18-crown-6)$_2Na^-$] or a cryptand cage [Cs^+ (cryptand[2.2.2]Na^-], the EPR spectrum shows only a broad signal with no evident hyperfine coupling to the cation. This is what we expect for electron trapping at the anionic site with only weak overlap with not one, but a number (six or eight) of adjacent cations.

2) When the cation is complexed by only a single crown-ether molecule [for example, Rb^+ (18-crown-6)Na^- or Cs^+ (HMHCY)Na^-], the EPR spectrum shows strong hyperfine coupling to a single cation. This result is expected for substitution of the alkalide ion by an electron—a tendency for the electron to interact strongly with the exposed face of the complexed cation. It is interesting that a pure electride of this type has yet to be isolated—such systems tend to dissociate into the metal and the free complexant when the solvent is removed.

Future Directions

Studies to date have provided intriguing glimpses into the nature of electrides. Only a few of the many possible complexants for the cations have been explored. Would binuclear complexes, in which two cations are trapped within the same molecule, provide new hosts? Could a polymeric backbone of cation complexants provide an "electride ion exchanger" in which exchange resulted also in reduction? Could electrons be introduced into anion-exchange sites in a zeolite or layered oxide to provide "inorganic electrides"? Could a single complexant for a divalent cation such as Ca^{2+} provide electrides with double the electron density, leading to new metallic compounds, or would the intriguing monovalent cation Ca^+ be formed? These are a few of the synthetic challenges provided by research on electrides.

Equally intriguing are the unanswered theoretical questions about electrides. Are the electrons really free from localization in a chemical bond or on an atom? What combination of wave functions best describes the electron density distribution? Can electrides be used to model distance effects in electron exchange? What, if any, are the consequences of the presence or absence of channels that interconnect electron-trapping sites? What are the band structures of electrides? What factors affect the conductivity? the spin-pairing? Clearly a combination of experiment and theory needs to be brought to bear on these problems. Now that crystal structures can be determined, studies of the properties of oriented electride single crystals will provide the most detailed information about electrides.

Finally, a question always addressed to researchers by journalists and the general public is "What are the practical consequences of this work?" In a field so filled with uncertainties about properties, stabilities, and economic factors, this question is not easily answered, and one can only speculate about possible uses of electrides. The most obvious application would be to use the strong reducing power of solvated electrons in inorganic and organic reductions. The advantage of electrides in this application is their high solubility in aprotic solvents such as dimethyl ether. Organic chemists have already used crown ethers and cryptands extensively in "dissolving metal reductions" in various solvents (*32*). Usually the reactions were heterogeneous with the complexant acting as a transfer agent for an alkali metal. Electrides provide the opportunity for fast, homogeneous aprotic reductions.

Whether electrides have a future in device applications is a more difficult question. One unusual feature of electrides is their very low electron-binding energies. We have observed not only photoelectron emission, but also thermionic electron emission at the picoampere-to-nanoampere level at temperatures as low as −80°C (*21*). In principle, these "cold" electron emitters could provide a new class of near-infrared detectors, but the mechanism of photoelectron and thermionic electron emission is not yet understood. Clearly, if we are able to synthesize thermally stable electrides, the prospects for device applications will brighten perceptibly.

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