

Electrides: Early Examples of Quantum Confinement

JAMES L. DYE*

*Department of Chemistry, Michigan State University, East Lansing,
Michigan 48824*

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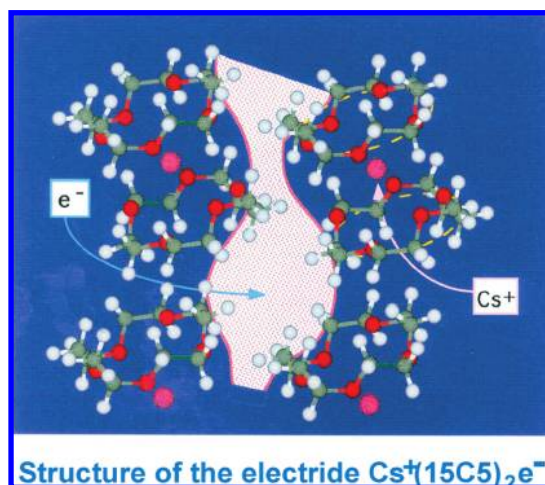
Electrides are ionic solids with cavity-trapped electrons, which serve as the anions. Localization of electrons in well-defined trapping sites and their mutual interactions provide early examples of quantum confinement, a subject of intense current interest. We synthesized the first crystalline electride, $\text{Cs}^+(18\text{-crown-6})_2\text{e}^-$, in 1983 and determined its structure in 1986; seven others have been made since. This Account describes progress in the synthesis of both organic and inorganic electrides and points to their promise as new electronic materials.

Combined studies of solvated electrons in alkali metal solutions and the complexation of alkali cations by crown ethers and cryptands made electride synthesis possible. After our synthesis of crystalline alkaliides, in which alkali metal anions and encapsulated alkali cations are present, we managed to grow crystalline electrides from solutions that contained complexed alkali cations and solvated electrons. Electride research is complicated by thermal instability. Above approximately $-30\text{ }^\circ\text{C}$, trapped electrons react with the ether groups of crown ethers and cryptands. Aza-cryptands replace ether oxygens with less reactive tertiary amine groups, and using those compounds, we recently synthesized the first room-temperature-stable organic electride.

The magnetic and electronic properties of electrides depend on the geometry of the trapping sites and the size of the open channels that connect them. Two extremes are $\text{Cs}^+(15\text{-crown-5})_2\text{e}^-$ with nearly isolated trapped electrons and $\text{K}^+(\text{cryptand } 2.2.2)\text{e}^-$, in which spin-pairing of electrons in adjacent cavities predominates below 400 K. These two electrides also differ in their electrical conductivity by nearly 10 orders of magnitude. The pronounced effect of defects on conductivity and on thermionic electron emission suggests that holes as well as electrons play important roles. Now that thermally stable organic electrides can be made, it should be possible to control the electron–hole ratio by incorporation of neutral complexant molecules. We expect that in further syntheses researchers will elaborate the parent aza-cryptands to produce new organic electrides.

The promise of electrides as new electronic materials with low work functions led us and others to search for inorganic electrides. The body of extensive research studies of alkali metal inclusion in the pores of aluminosilicate zeolites provided the background for our studies of pure silica zeolites as hosts for M^+ and e^- and our later use of nanoporous silica gel as a carrier of high concentrations of alkali metals. Both systems have some of the characteristics of inorganic electrides, but the electrons and cations share the same space.

In 2003, researchers at the Tokyo Institute of Technology synthesized an inorganic electride that has separated electrons and counterions. This thermally stable electride has a number of potentially useful properties, such as air-stability, low work function, and metallic conductivity. Now that both organic and inorganic electrides have been synthesized, we expect that experimental and theoretical research on this interesting class of materials will accelerate.



Introduction

Quantum confinement occurs when an electron or hole is trapped in a potential well of diameter comparable to the electron's wavelength. Perhaps the earliest examples are F-centers in ionic crystals in which a small number of defect anion vacancies are occupied by trapped electrons.¹ *Electrides* are *stoichiometric* ionic crystals in which electrons are trapped in cavities and serve as the counteranions to an equal number of positive charges in a regular crystalline array. Although alkali metals added to zeolites to produce stoichiometric trapped electrons in an inorganic host have been studied for decades and the adducts have some electrone features, the "excess" electrons share the same space as the alkali cations and are coupled to them. Thus, they do not strictly meet the electrone definition given above. The only *inorganic electrone* in which trapped electrons and counteranions occupy separate sites was synthesized in 2003.² All other electrines that meet this criterion were synthesized in our laboratory and have organic building blocks.

We synthesized the first crystalline organic electrone in 1983³ and determined its crystal structure in 1986.⁴ Since then, we have made and fully characterized seven other crystalline organic electrines. The challenge for electrone synthesis is to find solvents and *cation* complexants that can coexist with solvated electrons and yield high enough concentrations of dissolved alkali metals to permit crystallization of pure electrines. Since solvated electrons are the world's best reducing agents, decomposition of the solvent and complexant are thermodynamically favored and frequently catalyzed by impurities or decomposition products. Preventing decomposition during synthesis or after crystallization requires high-purity materials and low temperatures, usually below $-30\text{ }^{\circ}\text{C}$. Otherwise, the synthesis is straightforward. One simply dissolves the pure alkali metal in a solvent such as dimethyl ether or methylamine at $-30\text{ }^{\circ}\text{C}$ or below in the presence of a dissolved complexant and cools the solution slowly to grow crystals. Rapid cooling forms electrone powders. Competing formation of *alkalides*, salts of alkali metal anions, will be considered later.

The key to cavity formation and the isolation of the electrons from the counteranions is the complete encapsulation of the alkali *cation* within a complexant structure such as a crown ether "sandwich" or inside a cryptand molecule. The complexants used to synthesize seven of the eight electrines described in this Account are shown in Figure 1. The resulting complexed cation is so large that close-packing leaves large voids that serve as the electron-trapping sites. Six of the

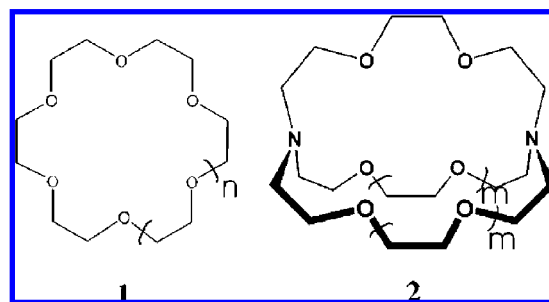


FIGURE 1. Crown ethers and cryptands used to prepare electrines: **1**, ($n = 0$) 15-crown-5 (15C5); ($n = 1$) 18-crown-6 (18C6); **2**, ($m = 0$) cryptand[2.1.1] (C211); ($m = 1$) cryptand[2.2.2] (C222).

eight organic electrines made to date have pseudo-1D chains of electron-trapping cavities connected along the chain by constricting channels. The cavities, of diameter 0.4–0.6 nm, are uniformly spaced along the chain, with center-to-center distances of 0.7–0.9 nm. The strength of the spin–spin antiferromagnetic coupling between adjacent electrons, obtained by fitting the temperature dependence of the magnetic susceptibility, depends strongly on the cross-sectional area of the connecting channels. Thus, these electrines have "particle in box" characteristics with some "leakage" from one box to another along the chain. The remaining two organic electrines have more complex arrangements of cavities and channels that will be described later.

The study and utilization of electrines has been limited by their thermal instability. This has prevented the development of such possible applications as thermionic electron emission,^{5,6} infrared photoelectron emission, and their use as n-doped and cathodic materials. Recently, a combination of theory and experiment provided an organic electrone that is thermally stable at room temperature and above.⁷ The key was the design and synthesis of a complexant that combined the internal cation-trapping site of a cryptand with replacement of ether oxygens by more robust tertiary amine linkages. Each of the three arms of this aza-cryptand contains a piperazine ring. The result is a complexant that is resistant to both decomplexation and decomposition. The ability to finally synthesize an electrone that is stable at room temperature, and the relative ease with which organic chemists should be able to elaborate the complexant or to synthesize similar ones, opens the door to the synthesis of new electrines and to electrines with designed electron–hole combinations.

The 2003 preparation of the first inorganic electrone in which cavity-trapped electrons balance the lattice positive charges² opened a new chapter in electrone synthesis and utilization. Thermal stability and low reactivity with air make this material suitable for possible application. The search for other inorganic electrines is a very promising area of study.

Solvated Electrons as Electrider Precursors

The first indication that alkali metals dissolve in ammonia is an unpublished notebook entry⁸ by Sir Humphry Davy in 1808. "When 8 grains of potassium were heated in ammoniacal gas - it assumed a beautiful metallic appearance and gradually became of a fine blue colour". This observation lay dormant for a half-century until Weyl published a paper on sodium–ammonia solutions.⁹ The work of Charles Kraus in the period 1907–1930 established the modern picture of metal–ammonia solutions and introduced the concept of solvated electrons as distinct species in solution.¹⁰ It was his studies of the electromotive force (emf) of concentration cells¹¹ that prompted my entry into the field in 1954 and ushered in a half-century of work with alkali metals. We measured electron mobilities directly by a moving boundary method,¹² activity coefficients,¹³ and optical spectra.¹⁴ The model for solvated electrons at that time and since involves the formation of a cavity in the solvent in which the electron is trapped and stabilized by solvent dipole orientation and polarization.¹⁵ As the solution concentration is increased, neutral M^+e^- species are formed by ion-pairing, diamagnetic electron pairs are formed, presumably by clustering, and finally at high concentrations the electrons become delocalized and form liquid metals.¹⁶ Solvated electrons can be produced in many solvents other than ammonia. Early studies of metastable alkali metal solutions were made in primary amines and polyethers.^{17–19}

The advent of pulse-radiolysis techniques and fast detection methods opened the floodgates to transient solvated electron studies in nearly any polar liquid. So many reactions were involved that the solvated electron became the second most kinetically studied species in chemistry (next to the solvated proton). When the existence of the solvated electron in water was proposed in the early 1960s, we measured the rate of reaction of solutions of cesium in ethylenediamine with dissolved water by a stopped-flow method.²⁰ The reaction was slow enough to predict a hydrated electron lifetime of 0.5 ms in pure water. At about the same time, hydrated electrons were observed spectroscopically in pure water and their lifetime was determined directly.²¹ In addition to kinetics studies, we also measured alkali metal solubilities and optical spectra in ethylenediamine.^{22,23} Previous optical studies of alkali metal solutions in amines as well as our spectra of Li through Cs were confusing because of the appearance of a new, apparently metal-independent peak at 650 nm. This unexplained peak was present in addition to that of the solvated electron at about 1250 nm and intermediate peaks for K, Rb, and Cs. The confusion was finally cleared up in 1968

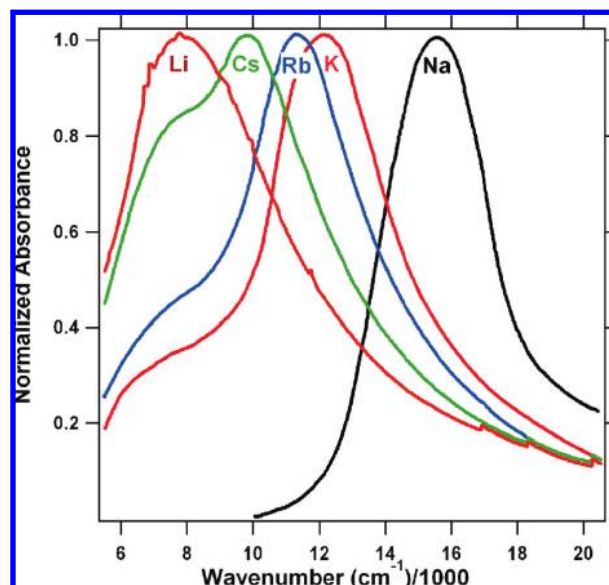
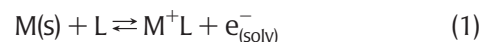


FIGURE 2. Optical spectra of alkali metals in ethylenediamine.²³ The spectrum of Li and the IR shoulders on K, Cs, and Rb are due to solvated electrons. The other metal-dependent peaks are from alkali metal anions. The original spectra have been corrected by removing the contribution of Na^+ .

when Hurley, Tuttle, and Golden showed that Na^+ , obtained by exchange of other alkali cations with the sodium borosilicate glass used to prepare solutions, was responsible for the 650 nm band.²⁴ The corrected optical spectra are shown in Figure 2. It quickly became evident that *alkali metal anions*, M^- , were responsible for the metal-dependent bands.^{25,26} Thus, after 160 years of alkali metal research, a third oxidation state of the group I elements, -1 , was added to the usual 0 and $+1$ states that had been universally considered to be the only states available for these elements.

Although the identification of alkali metal anions in solution was a major breakthrough, another development was essential to the preparation of crystalline electrideres and alkalides (salts of alkali metal anions). Except for Li, the solubilities of alkali metals in amines are generally low. For example, solubilities in ethylenediamine at room temperature range from 2.39×10^{-3} M for Na to 5.4×10^{-2} M for Cs.²² Solubilities in other amine and ether solutions are even lower. With the development of crown ethers by Pedersen²⁷ and cryptands by Lehn^{28,29} (Figure 1), the situation changed markedly. Complexation of the cation by the complexant, L, according to

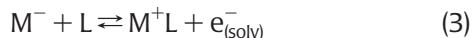


or



enhanced metal solubility by many orders of magnitude³⁰ and set the stage for subsequent crystallization of $M^+L \cdot e^-$ and

$M^+L \cdot M^-$ from saturated solutions. An additional advantage provided by the complexants is the ability, in favorable cases, to alter the relative amounts of $e_{(\text{soln})}^-$ and M^- in solution by the reaction



The use of various crown ethers and cryptands provides yet another way to control the species present in solution and available for alkali/electride synthesis. The selectivity for complexation of various cations depends on the structure of the complexant, primarily the size of the cation-trapping cage.³¹ Thus, for example, the crown ether 15-crown-5 (15C5) in contact with K and Cs metals in the solvent dimethyl ether forms the sandwich complex $Cs^+(15C5)_2$ and the anion K^- rather than the reverse. Similarly, K and Na metals with 12C4 form $K^+(12C4)_2$ and Na^- . An important contributor to the species formed is also the stability of M^- relative to M^+L and $e_{(\text{soln})}^-$. For example, the remarkable stability of Na^- insures that in mixed systems of Na and another alkali metal, the sodide will form preferentially. Reaction 3 lies far to the left when M is sodium. On the other hand, when M is lithium, no Li^- is observed and reaction 3 lies far to the right.

Crystalline Organic Electrides

The first crystalline *alkalide*, $Na^+(C222)Na^-$, was synthesized in 1974.³² To date, 40 crystalline alkalides have been made and structurally characterized.^{33,34} The stability of Na^- relative to $e_{(\text{soln})}^-$ and the tendency of the exchange reaction



to lie far to the right (in which $M = K, Rb,$ or Cs) make sodides much easier to synthesize than other alkalides. Of the 40 crystalline alkalides, 28 are sodides, 5 are potassides, 5 are rubidides, and 2 are cesides. No lithides have been synthesized to date. Although the -1 oxidation state of alkali metals has been firmly established for 35 years, it is still not common knowledge. For example, many General Chemistry textbooks in use today state that alkali metals have only the oxidation states 0 and $+1$.

Although electride powders and films were identified as early as 1978, the structure of the first crystalline electride, $Cs^+(18C6)_2e^-$, was not determined until 1986.⁴ The need to maintain cold anaerobic conditions during synthesis, crystal selection, and structure determination presented problems that were difficult to overcome. In addition, it was necessary to suppress the formation of M^- and to grow crystals by slow cooling of saturated solutions. Despite these problems, we now have the crystal structures of eight electrides.^{7,33,35} The excess electron density is too low to be directly observed by

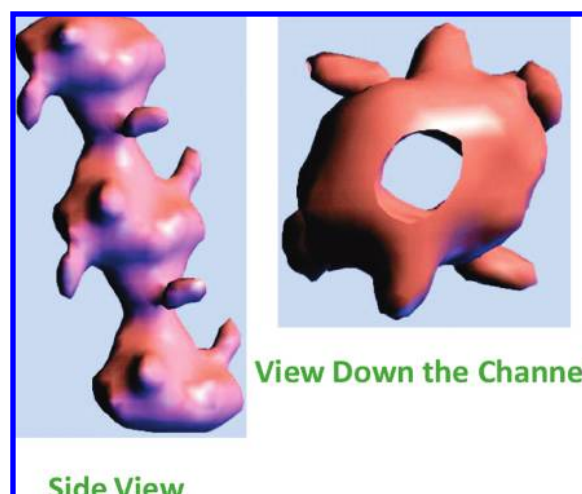


FIGURE 3. Geometry of the cavities and channels in the electride $Cs^+(15C5)_2e^-$.

X-ray diffraction, but the comparison with corresponding alkalides, the very low unpaired spin density on the trapped cations as determined by alkali metal NMR studies,³⁶ and theoretical calculations³⁷ leave little doubt that the maximum unpaired electron density occurs in the cavities that are formed by close-packing of the complexed cations.

Because electrons tend to occupy the voids in electride crystals rather than being attached to the molecules, we are interested in the geometry of the empty spaces. It is possible to use the crystal structures and the van der Waals radii of the atoms to construct 3D computer images of the void spaces.³⁸ Although it is likely that some “excess” electron density is present on the molecules that line the cavities and channels, a reasonable picture is attraction of the electron to the image positive charge at the center of the cavity to form “hydrogen atom-like” states, similar to those proposed for solvated electrons in metal–ammonia solutions.¹⁵ Thus, the ground state of the trapped electron has largely $1s$ character, although asymmetry of the cavity might introduce some p -character. The intense near-IR optical absorption that is characteristic of electrides would then be largely the result of an $s \rightarrow p$ transition. Of interest in this connection is the observation of *three* near-IR peaks in a thin film of $Cs^+(15C5)_2e^-$.³⁹ One possible explanation is anisotropy of the excited p -states because of nonspherical symmetry of the trapping cavity. The geometry of the empty space in the electride $Cs^+(15C5)_2e^-$ is shown in Figure 3. Each cavity contains a trapped electron, which can interact with electrons in adjacent cavities along the chain.

A consequence of the cavity–channel structure of electrides is the magnitude of the interelectron coupling. The six electrides with uniform pseudo-1D cavity–channel geome-

tries have nearly the same center-to-center distances but different channel sizes. The cross-sectional areas at the channel centers (halfway between the cavities) range from 0.023 nm² for Cs⁺(15C5)e⁻ to 0.125 nm² for Li⁺(C211)e⁻. The coupling constant, $-J/k_B$ (in which k_B is the Boltzmann constant) changes from 3 to 54 K for this pair. The coupling constant was determined by fitting the magnetic susceptibilities to the linear chain Heisenberg antiferromagnetic (LCHA) model.³⁵ The strongest interelectron interaction occurs in K⁺(C222)e⁻, which has $-J/k_B = 440$ K for nearest neighbors and 378 K for next-nearest neighbors, as determined by a fit of the magnetic susceptibility to the Heisenberg alternating linear chain (ALCHA) model.⁴⁰ The cavity–channel structure of K⁺(C222)e⁻ is much more open than that of other electrides and electron pairs are trapped in dumbbell-shaped cavities.^{41,42} The eighth electride, [Cs⁺(15C5)(18C6)e⁻]₆ · 18C6 has each Cs⁺ ion complexed by a mixed 15C5–18C6 “sandwich” with electrons trapped in a ring of six cavities.⁴³ The electrons are spin-coupled with $-J/k_B = 410$ K.⁴⁴ Excess defect cesium can be included, with Cs⁺ coordinated to the central free 18C6 and the excess electron occupying an otherwise empty cavity.

The temperature variation of the magnetic susceptibility of three electrides with 1D channel–cavity geometries and the dependence of the coupling constants of six electrides on the cross-sectional area of the connecting channels are shown in Figure 4.⁴⁵ The eight crystalline organic electrides synthesized to date are listed in Table 1.

In summary, organic electrides are crystalline compounds in which electrons occupy cavities of diameter 0.4–0.6 nm. Connecting these cavities are empty channels, usually along one direction, which permit antiferromagnetic coupling of the electron spins. More open channels lead to stronger coupling. A theoretical challenge is to model this coupling as a function of geometry.

Defects play important roles in electrides. The specific conductances span a range of more than 10 orders of magnitude from Cs⁺(15C5)₂e⁻ to K⁺(C222)e⁻.^{42,46} A pure electride with small channels has low conductivity, probably because of small overlap of adjacent electrons and the energy cost to put two electrons in the same cavity. The high and anisotropic conductivity of K⁺(C222)e⁻ was attributed to the presence of defect holes along the open chains, combined with random 2D interchain hopping.⁴² Another effect of defects is the observation of thermionic electron emission. Remarkably, electride films of K⁺(C222)e⁻ and Rb⁺(C222)e⁻, produced by high vacuum co-deposition of the metal and C222, show low-voltage, low-temperature electron emission that apparently results from surface defect sites.⁶ Sample decomposition upon

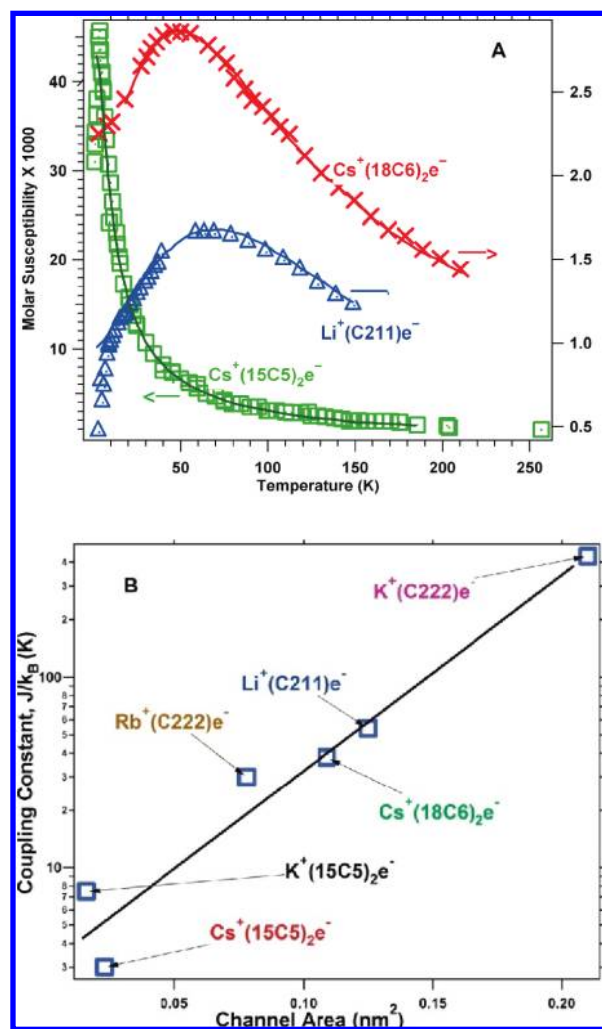


FIGURE 4. (A) The molar magnetic susceptibilities of three electrides as a function of temperature. Solid lines are fits to the LCHA model. (B) The interelectron coupling constant, $-J/k_B$, as a function of the minimum cross-sectional area of the channels that connect the electron-trapping cavities.³⁵

increasing the film temperature first increases the thermionic emission, presumably by creating new defect sites, and then the emission decreases as the sites are destroyed. Characterization and control of such sites could lead to materials with unusually small electron binding energies.

The preparation and study of crystalline organic electrides has been done only in our laboratory. This is probably because the thermal instability of organic electrides makes such studies difficult. Decomposition occurs through rupture of the O–C ether linkage in crown ethers and cryptands. For example, reductive decomposition of cryptand [2.2.2] yields ethylene and a glycolate.⁴⁷ It has been known for some time that tertiary amines are more resistant to reduction than are ethers. Thus, a strategy that uses aza-crowns or aza-cryptands with tertiary amine linkages instead of the ether linkages of crown ethers and cryptands should yield more stable elec-

TABLE 1. Structural Data and Coupling Constants for Eight Crystalline Organic Electrides

compound	space group (Z)	cell parameters (pm)	coupling constant, $-J/k_B$ (K)	refs
$\text{Cs}^+(18\text{C6})_2\text{e}^-$	monoclinic $C2/c$ (4)	1307.5, 1584.0, 1735.9; $\beta = 92.30^\circ$	38.3	4
$\text{K}^+(\text{C222})\text{e}^-$	monoclinic $C2/c$ (8)	1212.9, 2069.2, 2151.9 $\beta = 95.23^\circ$	440, 378 ^a	41,42
$\text{Cs}^+(15\text{C5})_2\text{e}^-$	tridinic $P1$ (1)	859.7, 888.6, 994.1; $\alpha = 102.9^\circ, \beta = 90.06^\circ, \gamma = 97.74^\circ$	1.6	39
$\text{Cs}^+[(15\text{C5})(18\text{C6})]_6 \cdot (18\text{C6})$	hexagonal $R3$ (18)	3310.8, 3310.8, 1626.6	410 ^b	43,44
$\text{K}^+(15\text{C5})_2\text{e}^-$	tridinic $P1$ (1)	862.8, 891.4, 912.6; $\alpha = 76.31^\circ, \beta = 89.16^\circ, \gamma = 80.99^\circ$	7.7	c
$\text{Li}^+(\text{C211})\text{e}^-$	orthorhombic $Pbcn$ (4)	1006.0, 2313.4, 838.0	54.1	45
$\text{Rb}^+(\text{C222})\text{e}^-$	tridinic $P1$ (2)	873.0, 1156.5, 1394.7; $\alpha = 64.20^\circ, \beta = 71.93^\circ, \gamma = 84.74^\circ$	30.7	35
$\text{Na}^+[\text{tri-pip-aza}(222)]\text{e}^-$	orthorhombic $Pccn$ (8)	1070.3, 1460.8, 1860.6	11.1	7

^a Nearest-neighbor and next-nearest-neighbor coupling constants. ^b Coupling constant for a large ring of six trapped electrons. ^c Unpublished results, this laboratory.

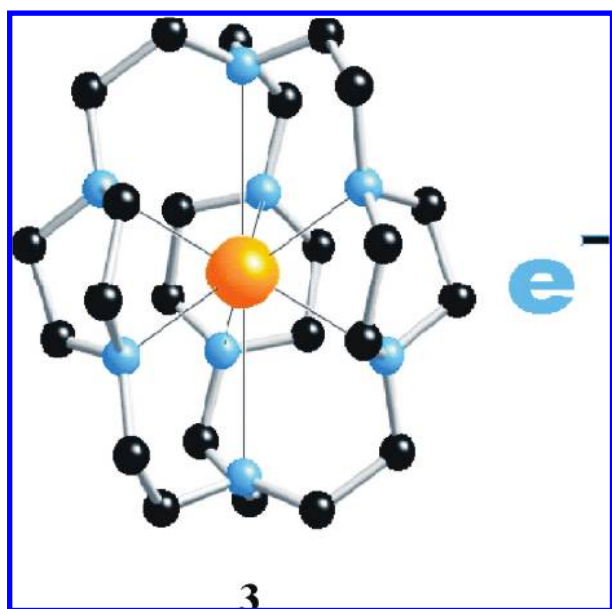


FIGURE 5. The first crystalline organic electride, $\text{Na}^+ \cdot (\text{tri-pip-aza } 222) \cdot \text{e}^-$, that is stable up to room temperature. Nitrogens are shown in blue, carbons in black, and Na^+ in orange.

trides. But the single electron-pair tertiary amine nitrogens are less effective complexants for alkali cations than are the two electron pairs of ether oxygens. The result is that most aza-crown- and aza-cryptand-based alkalides and electrides tend to *dissociate* rather than *decompose* as the temperature is increased.⁴⁸ Generally, the entropy of complexation of M^+ by an encapsulating ligand is unfavorable because the free ligand has more available conformations than the complex. In addition, the enthalpy of complexation is more sensitive to the lone-pair orientations of the amine nitrogens than is the case for the two lone pairs on each ether oxygen.

We sought an aza-cryptand whose structure minimized these destabilizing features. By a combination of molecular modeling and theoretical calculations, the aza-cryptand labeled **3** in Figure 5 and abbreviated tri-pip-aza (2.2.2), was predicted to complex an internal sodium cation strongly enough to prevent its dissociation and subsequent combination with an electron.⁷ The synthesis was a chal-

lenge and competition with Na^- required that the electride be formed by replacement of the anion of a preformed salt of **3** with an electron via a metathesis reaction. The resulting crystalline salt, $\text{Na}^+ \cdot \mathbf{3} \cdot \text{e}^-$, was the first organic electride to be stable at room temperature. ²³Na NMR spectra showed that decomplexation began at about 35 °C to form free **3** and the sodide $\text{Na}^+ \cdot \mathbf{3} \cdot \text{Na}^-$. This sodide was stable to 100 °C, at which temperature it formed the free ligand and sodium metal. The released aza-cryptand was stable to reduction up to 120 °C.⁷

The features that led to the first thermally stable organic electride could be used to develop modified aza-complexants that are designed to alter the electronic properties of electrides. In addition to obvious extensions, such as incorporation of longer “arms” it should be possible to add pendant groups to the carbon backbone of the aza-cryptand. For example, the addition of aromatic substituents would provide alternate locales for electron attachment, leading to possible hopping of cavity-trapped electrons to an aromatic site. A similar 3D hopping mechanism between aromatic sites was observed for single crystals of neutral $[\text{Ru}(\text{bpy})_3]$.⁴⁹ The ultimate modification would be polymerization of the aza-cryptands to form a “polymer electride”. Even in the absence of complexant modification, the similarity in the conformations of free and Na^+ -containing tri-pip-aza (2.2.2), **3**, suggest that empty cavities might be formed by “doping” the electride with neutral ligand. This would introduce “holes” along the electride chain and might provide a 1D conduction mechanism as well as long-lived defect states with low work functions that could lead to thermionic electron emission.

Inorganic Electrides

The thermal instability and air sensitivity of organic electrides prompted us and others to explore inorganic materials as possible electrides. The essential structural requirement is the presence of voids that carry image positive charges, either from positive lattice constituents or

from trapped countercations. Void spaces are characteristic of zeolites, and studies by Kasai in 1966 showed that alkali metals could be introduced into aluminosilica zeolites with resultant ionization to form M^+ and electrons.⁵⁰ The released electrons were not completely free of the cations however and formed species such as $(Na_4)^{3+}$ with a single electron shared by four sodium cations.⁵¹ Aluminosilicates have *negative* lattice charges because of substitution of Al(III) for Si(IV). A large number of studies of alkali metals added to aluminosilicate zeolites have been made.⁵² While they have some of the characteristics of electrides, the essential feature of cavity-trapped electrons separated from the cations is missing.

The advent of all-silica zeolites without lattice negative charges made possible the addition of alkali metals to give a 1:1 ratio of cations to electrons.⁵³ In several such zeolites, we showed that at least partial ionization occurred to yield alkali cations bound at the silica surface and electrons released into the channels.⁵⁴ These materials are closer to "true electrides" and have similar optical properties, but the cations and electrons still occupy the same void space, in contrast to organic electrides. Theoretical calculations indicated that Cs ionizes to give Cs^+ at the walls and electrons in the channels, while sodium forms 1D metallic chains in the all-silica zeolite used.^{55,56}

In 2003, a paper in *Science* by Matsuishi et al. of the Tokyo Institute of Technology reported the synthesis of an inorganic electride in which a lattice positive charge is balanced by electrons trapped in vacancies of diameter ~ 0.4 nm.² The host lattice is a calcium aluminum oxide, whose positive charge is balanced by anions in otherwise empty cages. The electride is made by reductive replacement of cavity-trapped O^{2-} ions by electrons. The reduction is carried out at high temperatures with a reducing element such as Ca, C, or Ti. The unit cell has the composition $[Ca_{24}Al_{28}O_{64}]^{4+} \cdot (4e^-)$, such that one-third of the 12 vacancies per unit cell contain electrons. The name "mayenite electride" is frequently used, based on the name of the mineral precursor. Partial replacement of O^{2-} by e^- produces a semiconductor in which the conduction mechanism is cage-to-cage hopping. As the electron concentration increases, the conductivity becomes more metallic, until full replacement yields metallic conductivity, even becoming a superconductor below 1 K.⁵⁷ This inorganic electride is stable in air for long periods at ambient temperatures. It has a low work function and may be useful in a number of device applications.

Although alkali metals in zeolites did not provide "true" electrides with complete separation of electrons and cat-

ions, they did lead to new and useful reducing materials. The tendency of alkali metals to bind to porous silica and to ionize, at least partially, provided the impetus for our recent preparation of alkali metal–silica gel (M–SG) materials.⁵⁸ These large-pore (3–15 nm pore diameter) silica gels can absorb up to 40 wt % alkali metal from the molten state. Both pure alkali metals and liquid alloys (such as Na–K alloys) can be used. Lithium cannot be used with silica gel because it reduces the silica even at room temperature. The relation to metal–zeolite behavior is evidenced by partial ionization of the alkali metal, presumably by ion–lattice interactions at the walls.⁵⁹ Whether electron delocalization occurs as with zeolites or there is electron addition to the silica framework is not known at this time. It is clear that in large pores, alkali metal nanocrystals form with coherence lengths of at least 3–4 nm. These powdered materials have been developed commercially as convenient, easily handled reducing agents.⁶⁰ Appropriate heat treatment makes them unreactive toward dry air, thus improving their utility as reductants for organic synthesis.⁶⁰

Summary

The trapping of electrons at anion vacancies (F-centers) in alkali halides has been observed for more than a century. Likewise, electrons solvated in vacancies in ammonia and other solvents have a long history. The unique feature of electrides is that they are *stoichiometric* crystalline solids in which an elementary particle serves as the anion and does not "belong" to any particular atom, molecule, or bond. Electrides could thus be viewed as regular stoichiometric arrays of quantum dots. Spin-coupling between the electrons varies from practically nonexistent to having a strength comparable to $k_B T$ at room temperature.

The development of electride research was certainly held up by the difficulties of synthesis and study of these unstable and reactive materials. However, the interest in possible applications of electrides is high, as exemplified by the appearance of more than 25 papers about the mayenite electride that was first described in 2003.² Now that both organic and inorganic electrides that are thermally stable have been made, we anticipate increased study, both theoretical and experimental, of this interesting class of materials.

BIOGRAPHICAL INFORMATION

James L. Dye was born in Soudan, Minnesota, in 1927. He received his A.B. degree from Gustavus Adolphus College in 1949 and his Ph.D. degree with Professor Frank Spedding from Iowa State University in 1953. He joined the Department of Chemis-

try at Michigan State University in 1953, where he is now Emeritus Professor of Chemistry. His research interests include physical, inorganic, and materials chemistry, with emphasis on alkali metal anions, solvated and trapped electrons, and alkali metals in porous metal oxides.

FOOTNOTES

*E-mail: dye@msu.edu.

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