

Room-Temperature Electrides: Discovery, Synthesis, and Applications

Edmund Tse

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Electron is generally known as a subatomic particle associated in an orbital of certain energy in atoms and molecules. The energy levels of electrons can also be described using a band structure for bulk materials, such as conductors and semiconductors. However, on rare occasions, solvated electrons have been observed when alkali metals are dissolved in several amine and ether solvents.¹ F-centers, where electrons are trapped in anion vacancies, have been observed for hundreds of years.² In these cases, the electrons do not belong to a well-defined environment, such as a single atom or shared among a collection of atoms.³

Electrides can be viewed as stoichiometric F-center salts in which electrons fill up all the anionic voids in a crystal structure. Alkalides, which closely resemble electrides, are crystals with alkali metal anions as the counterions. With the exception of Li^- , the crystal structures of Na^- , K^- , Rb^- and Cs^- have all been solved by James L. Dye and coworkers.⁴ Although an electron can be viewed as the tiniest anion possible, there is a stark difference between alkalides and electrides. The exact position of each atom in alkalides can be pinpointed, but only the probability density of the electrides can be described. However, alkalides have proven to be useful model systems for studying electrides.

The synthesis process of electrides is rather straightforward. By mixing an alkali metal and a complexant in an appropriate solvent, a solution of the complexed cation and the solvated electron can be obtained. Crystals are then grown using conventional methods, either by solvent layering or slow evaporation. However, as simple as this might sound, the actual procedure is tiresome. As electrons are one of the best reducing agents known to chemists, organic electrides are highly sensitive towards temperature, air and moisture. The complexants used are often crown ethers or cryptands, which are known to decompose due to the highly reducing nature of electrons. Besides, alkali metals are reactive in nature, and thus contamination must be prevented. All these inherent challenges prompted inorganic chemists to look for ways to stabilize such reactive species.

After twenty years of hard work, the first room-temperature organic electride was finally synthesized by J.L. Dye *et al.*⁵ The use of nitrogen instead of oxygen as electron donors rendered a weaker complexant, yet resulting in a more stable framework. By incorporating piperazine rings, the nonreducible tertiary amine groups at the appropriate conformational positions resulted in a thermally stable electride and sodide.

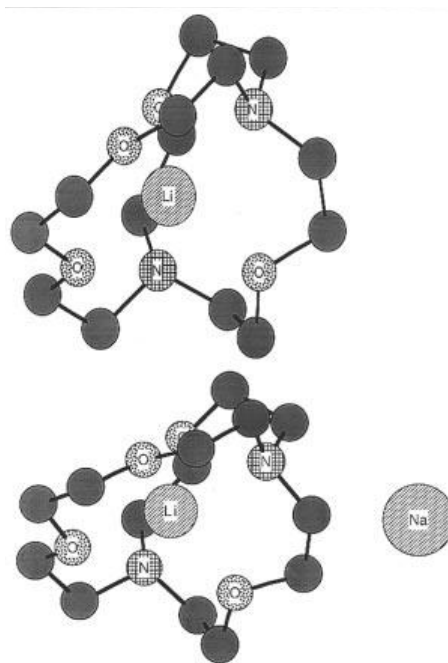


Fig. 1. Comparison between the crystal structures of sodide and electride. The geometric arrangements of the complexed Li^+ and the complexant are essentially the same in both structures, suggesting the excess electron density of the electron does not penetrate into the cryptand cage.

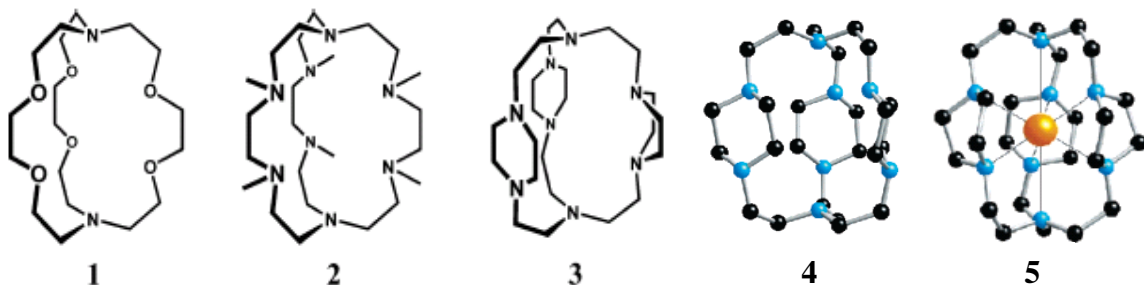


Fig. 2. Development of cryptands over the years (1-3).⁵ Comparison of the crystal structures of the uncomplexed TriPip222 aza-cryptand and the ligand with a trapped Na^+ (4,5). Slight differences can be spotted: the C atoms in the pip-backbone are pushed away from the central Na^+ . The authors suggested the pre-organization of the N atoms in the cryptand favored the coordination of the Na^+ ion.⁵

Characterization is a crucial topic to identify such novel species. Comparing crystal structures between alkaliides and electrides is one of the indirect methods, as the electron density is often less than the noise obtained in X-ray diffraction studies.⁶ Apart from X-ray crystallography, NMR and EPR are useful techniques. ^{133}Cs NMR was used to elucidate the temperature dependence of the calculated chemical shifts and the measured susceptibility of electrides, compared to conventional metal cesium solution in ammonia.⁷ In EPR studies, most powdered electrides consistently give a nearly isotropic signal at the free electron g -value. The EPR spectra of the electride and sodide of $\text{Cs}^+(\text{18-crown-6})_2$ indicated that the unpaired electrons in the electrides are trapped in the same site as the sodides.⁸

To date, all organic electrides are not air-stable. To accomplish this task, chemists resort to inorganic electrides. Alumino-silicate or all-silicate zeolites provide a sturdy, thermally-stable framework, yet cations and electrons share the same channel.⁹ The resultant structure cannot be regarded as an electride, as the electron density is spread throughout the whole structure.¹⁰ Matsuishi *et al.* came up with an ingenious idea to replace all the free oxygen ions in the precursor, $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C12A7) mixed oxide, with electrons.¹¹ Alkali metals are trapped in zigzag chains in the mixed oxide, while electrons are localized in nearby cages to compensate for the charges. Substituting the oxygen ions with electrons resulted in tiny changes in the crystal structure, but a drastic increase in the electron conductivity from an insulating precursor to a near-metallic behavior. As electrons only fill up one-third of the cages, electron hopping gives rise to a new band for enhanced electron transfer. Furthermore, this inorganic electride is air- and moisture-stable, as the authors claimed the pores, being ~ 0.1 nm in diameter, are small enough to render the sites inaccessible.

With an electride that is stable in ambient environment, chemists began to search for useful application for this class of material. Electride films have been reported to exhibit unusual low-temperature, low-voltage thermionic emission.¹² Although light-emitting diodes (LEDs) are now the popular choice for general lighting devices, cold-cathode fluorescent lamps (CCFLs) still have certain practical advantages, such as large-area illumination and low cost. To this end, C12A7 electride has been studied as a CCFL cathode material.¹³ Hosono *et al.* uses C12A7 electride as a pinacol coupling reagent.¹⁴ Also, C12A7 electride is investigated as an electrode material for the hydroxylation of an arylboronic acid.¹⁵ Besides, C12A7 electrides exhibit superconductivity at near 0 K.¹⁶

With the collective effort of several notable chemists, such reactive species has been substantially stabilized. With all these unique properties, electrides hold promise to more exotic applications, and may one day become an indispensable reagent in lab.

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