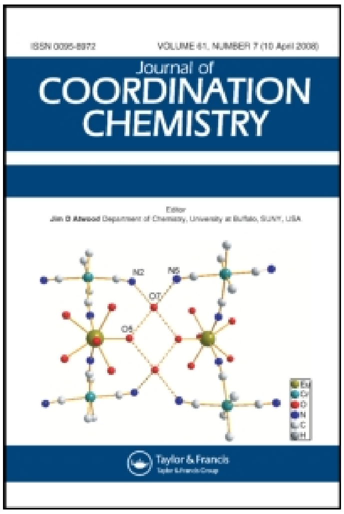

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CORRELATION OF THE STRUCTURE AND PROPERTIES OF ALKALIDES AND ELECTRIDES THAT CONTAIN CRYPTANDS OR CROWN ETHERS

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Abstract The structures of several salts that contain alkali metal anions (alkalides) and two that contain trapped electrons (electrides) are correlated with their optical and NMR spectra, and magnetic susceptibilities. The nature of the channels and trapping sites in the two electrides are described.

Keywords: Cryptands, crown ethers, alkalides, electrides

INTRODUCTION

Alkalides and electrides are ionic salts in which alkali metal anions (Na^-, K^-, Rb^-, or Cs^-) or trapped electrons serve to balance the charge of complexed alkali cations.[1-7]

Alkali anions are known in the gas phase and in solution.[8-10] Trapped electrons in F-Centers and solvated electrons in solution have been studied for a long time. The synthesis of alkalides and electrides was made possible in the late 60's and early 70's when two new types of cation complexing agents, crown ethers and cryptands were synthesized.[12,13]

The first alkalide, $Na^+(C222){\bullet}Na^-$, (C222 = cryptand[2.2.2]) was synthesized and characterized in 1974[1] and the crystal structure was determined soon after the synthesis.[2] Since then over 30 alkalides and 8 electrides have been synthesized. Many attempts to determine the crystal structures of other alkalides and electrides failed because of the high reactivity of these compounds with air and moisture and the tendency towards irreversible decomposition at temperatures above about -40 °C.[14] In 1985 a new technique for growing and handling suitable single crystals was established in our lab that has led to the determination of the crystal structures of 2 electrides[15,16] and 10 alkalides.[17,18]

RELATION OF ALKALIDE NMR SPECTRA TO STRUCTURE

Since the first alkalide $Na^+(C222)\bullet Na^-$ was synthesized, alkali metal -C222 systems have been studied extensively. A puzzling feature was that the optical spectra of thin films[5] revealed the presence of K^-, Rb^- and Cs^- in the K-C222, Rb-C222 and Cs-C222 systems, but we were unable to obtain any solid state NMR signals for the anions in these compounds,[19-21] whereas the anions could easily be detected when the cations were contained in sandwiched crown ether complexes. This, together with the absence of accurate microscopic analytical data, had led us to believe that the polycrystalline samples used in the NMR studies contained mixtures of electrides and metals rather than alkali metal anions. However, single crystal x-ray crystallography[18] confirmed the existence of the ceside $Cs^+(C222)\bullet Cs^-$ and provided a possible explanation of the absence of the NMR signal of Cs^-. In $Cs^+(C222)\bullet Cs^-$ the Cs^- ions form chains along the b-axis with uniform distances of 6.38 Å, which is 0.62 Å shorter than the "effective diameter" of the Cs^+ ion (7.0 Å). This means that the anions are in contact with each other, which, by mixing excited state character into the ground-state wavefunction, can broaden the NMR signal beyond the detection limit. In contrast to $Cs^+(C222)\bullet Cs^-$, another ceside, $Cs^+(18C6)_2\bullet Cs^-$ gives a clear solid state NMR signal of Cs^- at -228 ppm (with respect to Cs^+ in aqueous solution).[24] The crystal structure of this compound [18] shows that Cs^- ions also form chains along the b-axis but with a much larger uniform distance of 8.86 Å, which means that the Cs^-

ions are rather isolated from each other. With the help of an Evans and Sutherland PS-300 computer display system we can study the packing of the complexed cations and alkali metal anions in such crystals. Figure 1 shows the chain-like arrangement of the ceside anions in these two crystals.

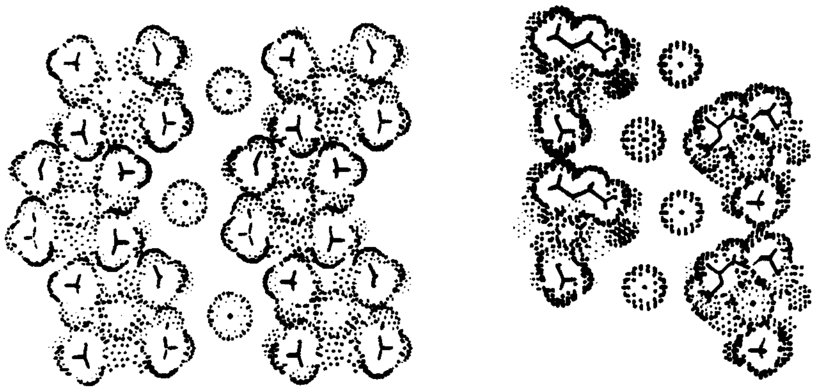

FIGURE 1 Cross-sectional views of the structures of $Cs^+(18C6)_2{\bullet}Cs^-$ (left) and $Cs^+(C222){\bullet}Cs^-$ (right). The Cs^- ions are represented by the isolated circular patterns and are not drawn to scale. Representations of the complexed cations are drawn to scale based upon atomic positions and appropriate van der Waals radii.

A similar situation occurs in the Rb-C222 system. X-ray crystallography[22] demonstrated that the rubidide, $Rb^+(C222){\bullet}Rb^-$ formed. However, the anions are trapped in pairs between planes of complexed Rb^+ cations. The Rb^- to Rb^- distance in a pair is only 5.13 Å, while the effective diameter of Rb^- is 6.4 Å. The distance of Rb^- to a third Rb^- ion is much longer (7.9 Å). Again the Rb^- NMR signal is absent in this compound although it can be observed in other rubidides.[20]

ELECTRIDE PROPERTIES AND STRUCTURES

Eight electrides have been identified to date,[23-27] and the crystal structures of two have been determined.[15,16] According to their spectroscopic, electronic and magnetic properties, they fall into two categories: electrides with localized, weakly interacting trapped electrons and those with strong interactions between trapped electrons in which the electrons are either delocalized or more weakly bound.

The first type of electride is represented by $Cs^+(18C6)_2 \cdot e^-$. Its optical spectrum shows a peak at about 1500 nm[24] and its magnetic properties are characterized by Curie-Weiss paramagnetism with about 85% unpaired electrons.[28]

The second is represented by $K^+(C222) \cdot e^-$. The optical spectrum of this compound has a plasma-type shape[7,29] and its magnetic susceptibility shows a weak Curie tail at low temperatures (< 5 K) that corresponds to less than 1% free spins and depends on the preparation.[16] The susceptibility increases slightly with temperature in the region of 40 to 200 K. Figure 2 compares the magnetic susceptibilities of these two electrides.

As we might expect from their different properties, these two electrides are also quite different in their structures. In $Cs^+(18C6)_2 \cdot e^-$, the space between the sandwiched cations consists of elongated cavities with narrow channels connecting them to six neighboring cavities.[15] Since this electride is isostructural to the corresponding sodide $Cs^+(18C6)_2 \cdot Na^-$, it is reasonable to assume that the trapped electrons occupy the anionic sites where Na^- ions are located in $Cs^+(18C6)_2 \cdot Na^-$. Of course, wavefunctions of the trapped electrons defined by the van der Waals radii of surrounding atoms, extend beyond the edges of the cavities and penetrate into the neighborhood. The cavities are about 4.5 Å across and 7 Å long. The shortest distance between adjacent

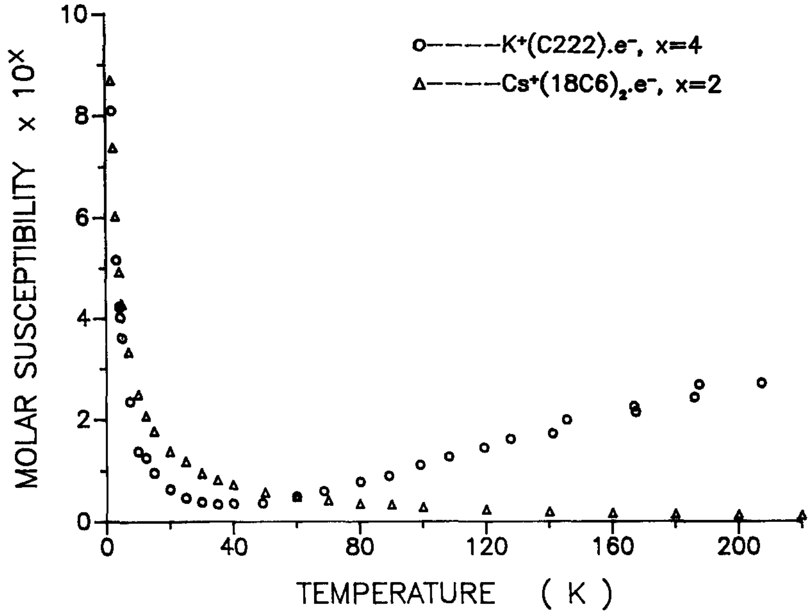

FIGURE 2 Comparison of the electronic contribution to the molar magnetic susceptibility of $Cs^+(18C6)_2{\bullet}e^-$ (solid line) and $K^+(C222){\bullet}e^-$ (dashed line). The diamagnetic contribution has been removed by subtracting the susceptibility of the decomposed sample as described in ref. 23.

cavities is 8.68 Å in the direction of elongation. The distance to each of the four other cavities is 10.2 Å. Thus the trapped electrons are relatively isolated from each other.

The structure of $K^+(C222){\bullet}e^-$ shows a very different type of packing.[16] The space available to trap electrons consists of rather open two-dimensional, intersecting channels that form large vacancies at the intersections. There are no similar channels along the b-axis. This structure is consistent with the strong interactions between trapped electrons shown by the magnetic susceptibility data. Figure 3 compares the channel structures in $Cs^+(18C6)_2{\bullet}e^-$ and $K^+(C222){\bullet}e^-$.

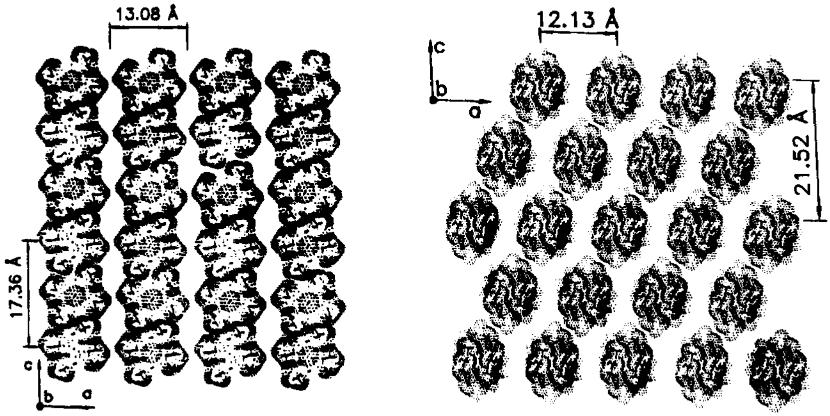

FIGURE 3 Comparison of the channel structures of $Cs^+(18C6)_2\cdot e^-$ (left) and $K^+(C222)\cdot e^-$ (right). Trapped electrons and electron pairs, respectively, are presumed to occupy the x-ray "empty" vacancies and channels with some penetration into the surrounding regions.

AN NMR INSIGHT INTO THE NATURE OF ELECTRON TRAPPING

Since $Cs^+(18C6)_2\cdot Na^-$ and $Cs^+(18C6)_2\cdot e^-$ are isostructural, it is possible to "dope" $Cs^+(18C6)_2\cdot e^-$ with Na^- ions and study the effect on the electron-nuclear interaction. A ^{133}Cs NMR study[21] showed that one can substitute up to three Na^- ions for electrons in the eight trapping sites around each complexed cesium cation. The substitution of the diamagnetic Na^- ions for electrons decreases the paramagnetic shift of the neighboring Cs^+. This causes a multiple peak NMR spectrum with separate NMR peaks for cesium cations surrounded by eight, seven, six and five electrons (0,1,2 and 3 sodide ions). There are five peaks that occur at chemical shifts of -61, 25, 42, 57 and 73 ppm.[21] The peak at -61 ppm is from the pure sodide, $Cs^+(18C6)_2\cdot Na^-$ while the others are from electrides substituted by 3, 2, 1 and 0 sodides, respectively. The spacing between the peaks from 25 to 73 ppm is roughly 1/8 of the distance between -61 and +73 ppm in agreement with the assumption that each Cs^+ ion interacts with 8 trapped electrons.

SUMMARY

The recently developed capability for determination of the crystal structures of alkalides and electrides has provided a breakthrough in interpreting the properties of these two new classes of materials. Neither the structures alone nor the properties can give a complete picture of electron trapping in electrides. But the combination of structure and properties is beginning to yield an understanding of the nature of the anionic traps and of the electron - electron and electron - cation interactions.

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