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ALKALI METAL NMR AND MAGNETIC SUSCEPTIBILITIES OF ALKALIDES AND ELECTRIDES

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Judith Lynne Eglin

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Ph. D. degree in Chemistry

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### ALKALI METAL NMR AND MAGNETIC SUSCEPTIBILITIES OF ALKALIDES AND ELECTRIDES

bу

Judith Lynne Eglin

## A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

## DOCTOR OF PHILOSOPHY

Department of Chemistry

#### ABSTRACT

### ALKALI METAL NMR AND MAGNETIC SUSCEPTIBILITIES OF ALKALIDES AND ELECTRIDES

bу

Judith Lynne Eglin

The electride  $Cs^+(15C5)_2e^-$  undergoes an antiferromagnetic Neel transition at 4.6 K. At higher temperatures, the susceptibility follows the Curie-Weiss law until the temperature of a first-order phase transition at 266 K. This transition can be observed by both magnetic susceptibility and 133Cs NMR studies. Below 240 K, the 133Cs chemical shift is linear in 1/T with an intercept of 180 ± 10 ppm. The slope of the line and the magnetic susceptibility data yield a Fermi contact density at Cs<sup>+</sup> that corresponds to 0.063% atomic character.

The physical properties of  $Cs^+(HMHCY)Na^-$  at two different electron dopant levels were studied and the <sup>133</sup>Cs MAS NMR spectra were observed for the first time. The compound,  $Li_2^+(TMTCY)_2Na^ \cdot CH_3NH^-$  was characterized and the crystal structure obtained. Since solvent is incorporated in the crystal structure, a method was developed to test for its presence.

The complexant TMPAND, a fully methylated aza analog of a cryptand was used to synthesize a sodide and an electride. The temperature dependence of the quadrupole coupling constant for  $^{7}L_{i}$  in the sodide was studied above and below the observed phase transition. The phase transition could also be detected by

conductivity measurements and  $^{23}$ Na NMR spectra, but not by optical absorption studies.

The systems  $Li^+(CH_3CH_2NH_2)_4Na^-$ ,  $Li^+(CH_3CH_2NH_2)_4K^-$ , and  $Li^+(CH_3CH_2NH_2)_4Cs^-$  were characterized by magnetic susceptibility measurements and <sup>7</sup>Li NMR studies. While the sodide appears to be a diamagnetic compound, the potasside and ceside are paramagnetic. The <sup>7</sup>Li chemical shift value is temperature dependent and increases with temperature. The intriguing properties of these systems suggest that further characterization might verify a new class of "metallic" compounds.

The spin-echo NMR technique with phase cycling is a powerful tool in the determination of the environment of  $^{87}$ Rb nuclei in alkalides and electrides. Computer simulations of the experimental powder patterns yielded the quadrupole coupling constants for the complexed rubidium cation as well as values of the asymmetry parameter.

### ACKNOWLEDGEMENTS

For his guidance and support throughout the course of this work, I would like to express my appreciation to Dr. James L. Dye. For their helpful advice, I would like to thank Dr. William Pratt, Dr. Jerry Cowan, and Dr. Carl Foiles of the Physics Department as well as Dr. Kim Dunbar of the Chemistry Department.

I appreciate all of the advice and support that I received from all of the members of the Dye research group with whom I have worked, in particular Rui Huang, Jineun Kim, Lauren Hill McMills, Mark Kuchenmeister, Marc DeBacker, Sylvie Doueff, Mike Wagner, Evy Jackson, Erik Hendrickson and especially Kevin Moeggenborg. I would also like to thank the Master Glassblowers at Michigan State University, Keki Mistry, Manfred Langer, and Scott Bancroft, for the numerous pieces of glassware that they have designed, built, and repaired for me. I am grateful for Kermit Johnson's help with the NMR instruments, Marty Rabb for his aid in the repair of the SQUID and Dr. Don Ward for his help in my many attempts to obtain single crystal X-ray data. Special thanks go to all of my professors in the Department of Chemistry at The College of Wooster for all of their encouragement and enthusiasm. Finally, I would like to thank "our class" of fifth year students for all of their help and moral support.

I also appreciate the support I received from the National Science Foundation Solid State Chemistry Grant DMR-87-14751 and the Michigan State University Center for Fundamental Research.

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## TABLE OF ABBREVIATIONS

•

DMICY	dimethyltricyclen
TMICY	trimethyltricyclen
РМРСҮ	pentamethylpentacyclen
HMHCY	hexamethylhexacyclen
TMPAND	5,12,17-trimethyl-1,5,9,12,17-penta- azabicyclo[7.5.5]nonadecane
18C6	18-Crown-6
15C5	15-Crown-5
C222	Cryptand [2.2.2]
NMR	Nuclear Magnetic Resonance
MAS	Magic Angle Spinning
QCC	Quadrupole Coupling Constant
MHz	MegaHertz
ppm	Chemical shift referenced to $M^+(aq)$ at infinite dilution
т <sub>1</sub>	Spin-lattice relaxation time
т <sub>2</sub>	Spin-spin relaxation time
DSC	Differential Scanning Calorimetry
kG	kiloGauss
EPR	Electron Paramagnetic Resonance
Т	Temperature

### I. INTRODUCTION

Since Weyl first discovered that alkali metals dissolve in liquid ammonia<sup>1</sup>, these solutions have been of interest to chemists. The dilute blue metal ammonia solutions, which become bronze upon an increase in mole percent metal, are intriguing. Not only do these solutions provide information about the metal-nonmetal transition, but they also allow the investigation of the solvation of a fundamental particle, the electron.

The description "solvated electron" was first applied by Kraus<sup>2</sup> and was later elaborated on by Jortner.<sup>3,4</sup> Jortner described the metal ammonia system with the electron density of the solvated electron symmetric about the center of a cavity of radius 3.2 to 3.4 angstroms in the solvent. The liquid ammonia in the vicinity of the cavity is polarized by the electron. The major species present in dilute solutions are the solvated electron and the metal cation formed according to the following equation:

 $M^{o} + NH_{3} \longrightarrow M^{+}(solv.) + e^{-}(solv.)$  (1.1)

Over the intermediate concentration range, 1 to 7 mole percent metal, a metal-nonmetal transition takes place with changes in the electronic, thermodynamic and mechanical properties of the metal ammonia solutions.<sup>5</sup> The transition to metallic behavior as the metal concentration is increased is not unique to metal-ammonia systems. The transition to metallic behavior has been observed in both

supercritical fluid mercury and cesium.6,7,8,9,10,11 In the case of metal-ammonia systems the change is a first order Mott transition in which one can consider the metal to non-metal transition as essentially due to a competition between the kinetic and potential energies of electrons. While the potential energy localizes electrons, the kinetic energy delocalizes them until the metal concentration is high enough to permit significant overlap of the electronic wavefunction.<sup>12</sup>

In the lithium-ammonia system, a eutectic point occurs at 20 mole percent metal and 89 K.<sup>13</sup> A great deal of evidence has accumulated which suggests that a compound,  $Li(NH_3)_4$ , is formed at or near this composition.<sup>14</sup> Upon freezing solutions of stoichiometry  $Li(NH_3)_4$ , a homogeneous, bronze-colored metallic solid results which is, in fact, polycrystalline. In particular, the powder X-ray diffraction patterns obtained for this solid are neither those of Li nor NH<sub>3</sub>, a verification of the formation of the compound,  $Li(NH_3)4$ .<sup>15</sup> The original work in ammonia has been expanded to include other solvents, in particular, methylamine.

Lithium is soluble in methylamine up to 20 mole percent metal, where the metallic liquid compound  $Li(CH_3NH_2)_4$  is formed<sup>16,17</sup>, and freezes at 155 K.  $Li(CH_3NH_2)_4$  appears to be right at the metalnonmetal transition, and in fact goes from metallic to nonmetallic as the temperature is lowered.<sup>18</sup> Lithium methylamine solutions are the only nonammonia metal solutions in which the metal solubilities are large enough to permit a transition to the metallic state. The increase in mole percent metal at the transition from 1 to 7 mole percent of lithium in ammonia to 15 to 20 mole percent in

methylamine is in accord with the expectation that the larger size of  $Li^+(CH_3NH_2)_4$  compared with that of  $Li^+(NH_3)_4$  results in weaker electron-electron overlap.

The compound,  $Li(CH_3NH_2)_4$ , has been shown to assist the solubilization of lithium and sodium metals in various amine and ether solvents.<sup>19</sup> Upon addition of diethylether (DEE), trimethylamine (TMA), or dimethoxyethane (DME) to  $Li(CH_3NH_2)_4$ , dark blue solutions were initially formed which became light blue over a period of minutes.

 $Li(CH_3NH_2)_4$ , which is believed to form  $Li^+(CH_3NH_2)_4$  and  $e^-(solv.)$  upon dilution, increases the solubilization of Na<sup>O</sup> in methylamine. This is believed to follow the reaction:

$$e^{-}(solv.) + Na_{(s)} \longrightarrow Na^{-}$$
 (1.2)

The solvation of alkali metals in tetrahydrofuran (THF) and diethylether (DEE) can also be increased by the use of crown ethers which complex the cation, as reported in 1970 using dicyclohexano-18-crown-6.20 The extension of this work to other solvents, metals, and macrocyclic or macrobicyclic polyethers and polyamines led to the synthesis of alkalide and electride salts.<sup>21,22,23</sup>

Alkalides are ionic salts that consist of an alkali metal cation, complexant, and alkali metal anion. Electrides have an alkali metal cation, but the anion is a trapped electron. In both cases, the cation is complexed by macrobicyclic or macrocyclic polyethers or polyamines.<sup>24,25,26</sup> The structural formulas of 18-crown-6, cryptand [2.2.2] and pentamethylpentacyclen are shown in Figure 1.



Cryptand [2.2.2]

Figure 1. Representative Complexants.

Alkalides and electrides are extremely air and temperature sensitive and therefore must be handled at low temperatures (T<253 K) and under inert atmosphere or vacuum.<sup>27,28,29</sup> Syntheses of alkalides and electrides consist of the introduction of stoichiometric amounts of alkali metals and complexant in a helium glove box into a synthesis apparatus. The synthesis cell is then placed on a vacuum line, evacuated, and the metals Cs, Rb, K, or Na distilled.<sup>30</sup> Lithium is manipulated directly in a helium glove box and never distilled.<sup>31</sup> A nonreacting solvent such as dimethylether or methylamine is then added by vacuum distillation to dissolve either the complexant, alkali metal or both. The solution is usually kept at temperatures of 253 K or below throughout this process. The powdered alkalide or electride sample is then obtained by removal of solvent or the addition of a cosolvent such as trimethylamine or diethylether to precipitate crystals. Once all solvent has been removed, a washing solvent is added and excess complexant is removed through several cycles of washing and filtrations.<sup>32,33,34</sup>

It has been known for some time that alkali anions are stable in the gas phase, the electron affinity of the sodium atom is +0.54eV.35,36 Stabilization of the alkali metal cation by complex formation allowed the first sodide, Na<sup>+</sup>(C222)Na<sup>-</sup>, a stable salt with a sodium anion, to be synthesized.<sup>33</sup>

The characterization of alkalides and electrides includes pressed powder d.c. conductivity<sup>28,37</sup>, EPR spectroscopy, magnetic susceptibility<sup>38</sup>, X-ray crystallography<sup>39,40,41</sup>, and optical absorption spectra of thin films produced by rapid solvent evaporation<sup>42,43,44</sup> or vapor deposition.<sup>45</sup> The optical absorption spectrum has been used to identify the alkali metal anion in heteronuclear alkalides since it has been shown<sup>42</sup> that the peak position in M<sup>+</sup>(C222)M<sup>-</sup> corresponds closely to that observed for the respective anion in solution. Na<sup>-</sup>, K<sup>-</sup>, Rb<sup>-</sup>, and Cs<sup>-</sup> in M<sup>+</sup>(C222)M<sup>-</sup> have absorption peaks at 15400, 11900, 11600 and 10500 cm<sup>-1</sup> respectively, while in ethylenediamine Na<sup>-</sup>, K<sup>-</sup>, Rb<sup>-</sup>, and Cs<sup>-</sup> have

comparable values of 15400, 12000, 11200, and 9800 cm<sup>-1.46</sup> Due to the sensitivity of the peak position to the surroundings, assignments are not completely unambiguous for the identification of heteronuclear films of the stoichiometry MLNa where L is the complexant.<sup>47</sup>

In contrast, alkali metal anions can be unequivocally identified in the solid state by NMR methods due to their unique chemical shifts. In the absence of unpaired electrons, the primary contributor to the chemical shift of the alkali metal nuclei, M<sup>+</sup> or M<sup>-</sup> (except lithium), is one of the paramagnetic terms in the general Ramsey shift expression.<sup>48</sup> Values obtained are relative to the values for the isolated gaseous ions. The paramagnetic term is:

$$\sigma_{\rm p} = \frac{-e^2}{m^2 c^2 \Delta E} \left\langle \Psi_{\rm o} \right| \sum_{{\bf k},{\bf k}'} \frac{1_{\bf k} 1_{\bf k}'}{r_{\bf k}^3} \left| \Psi_{\rm o} \right\rangle \quad (1.3)$$

in which  $\Delta E$  is the average outer p electron excitation energy,  $\psi_0$  is the groundstate wave function,  $l_k$  and  $l_k$ , are orbital angular momentum operators, and  $r_k$  is the distance of the kth electron from the nucleus. The Ramsey shift is the result of the introduction of orbital angular momentum due to the interaction of the filled outer p shell with electron pairs from surrounding molecules or ions. Only nearest neighbor electron-pair donors contribute significantly, therefore the large radius of the alkali metal anion and its weak interactions with surrounding electrons make the Ramsey shifts of Na<sup>-</sup> and K<sup>-</sup> negligible. While not negligible, the Ramsey shifts of Rb<sup>-</sup> and Cs<sup>-</sup> are much smaller than for the cations.

Static solid state NMR generally results in rather broad featureless spectra for most powders. Absence of sufficient nuclear motion in crystalline solids results in substantial broadening of the NMR line relative to those in fluids. The line broadening is the result of a distribution of crystalline orientations and is due to magnetic dipolar and quadrupolar interactions as well as chemical shift anisotropy.

A technique called magic angle sample spinning nuclear magnetic resonance (MAS-NMR) was introduced by Andrew and Lowe in 1959.49,50,51 In some cases when this technique is used, one can obtain solid state spectra that rival those obtained in solution. Line narrowing is achieved by rapidly spinning a sample about an axis inclined at or near the "magic angle" of 54.740 to the Zeeman field. By rotating the sample about the magic angle, the first order quadrupolar, dipolar and chemical shift interactions can be removed from the center of the spectrum and appear as spinning side bands.

In the static spectrum of Na<sup>+</sup>(C222)Na<sup>-</sup>, a broad peak of width 2600 Hz centered at -60 ppm relative to Na<sup>+</sup><sub>(aq.)</sub> is observed with a barely discernable broad shoulder on the low-field side of this peak.<sup>52</sup> Figure 2 demonstrates the dramatic reduction in line width and the resultant improvement of the signal to noise ratio for the same sample of Na<sup>+</sup>(C222)Na<sup>-</sup> run on a Bruker CXP 200 spectrometer in the nonspinning and spinning modes.<sup>44</sup> The chemical shift of



Figure 2. Magic angle sample spinning <sup>23</sup>Na NMR spectrum of Na<sup>+</sup>(C222)Na<sup>-</sup>. Also shown is the nonspinning spectrum of the same sample.<sup>52</sup>

Na<sup>+</sup>(C222) at -23.7 ppm is clearly resolved. The substantial paramagnetic shifts of Na<sup>+</sup> in crystalline salts from that expected for Na<sup>+</sup>(g) is caused by interactions with electron pairs on atoms in the cryptand with the p orbitals of Na<sup>+</sup>.52,53

Through a combination of the results of static and MAS studies at several frequencies, it is possible to determine the sources of line broadening. This may be achieved by lineshape analysis of the static spectra and proton decoupling experiments. In the compound  $Na^+(C222)Na^-$ , as for all the quadrupolar alkali metal nuclei, only the central transition (1/2  $\leftarrow$  -1/2) can be observed since the central transition is unshifted to first order, unlike the other transitions. With second-order perturbation theory, the shift of the central transition with frequency can be represented by the equation<sup>54</sup>:

$$v - v_{\rm L} = \frac{-v_{\rm Q}}{30v_{\rm L}} [I(I+1) - 3/2] (1 + \eta^2/3) (1.4)$$

where  $v_L$  is the is the isotropic Larmor frequency,  $v_Q$  is the nuclear quadrupolar frequency, I is the spin of the nucleus and  $\eta$  is the asymmetry parameter. Figure 3 shows the proton coupled and decoupled <sup>23</sup>Na MAS-NMR spectrum of Na<sup>+</sup>(C222)Na<sup>-</sup> and the variation with frequency.<sup>55</sup> The inset is that of the protondecoupled peak of Na<sup>+</sup>(C222) (*solid line*) overlayed with the calculated lineshape for  $2v_Q = e^2 qQ/h = 1.2 + 0.1$  MHz (*dashed line*). The value of the quadrupole coupling constant is an indication of



Figure 3. 23Na MAS-NMR spectra of Na<sup>+</sup>(C222)Na<sup>-</sup> at three frequencies. Inset shows an expansion of a portion of the bottom spectrum due to Na<sup>+</sup>(C222) (solid line) and its computer simulation (dashed line).55

why the observed chemical shift of Na<sup>+</sup>(C222) varies with frequency. The complexed cation has an isotropic chemical shift of  $-6.5 \pm 0.5$  ppm with respect to aqueous Na<sup>+</sup> as zero.

The observed static line width of the complexed cation, Na<sup>+</sup>(C222), is 3700  $\pm$  300 Hz. The quadrupolar contribution to the linewidth is 320 Hz with the difference, 3400  $\pm$  300 Hz, due to dipolar coupling between the -CH<sub>2</sub>- protons on the cryptand and Na<sup>+</sup>. The second moment can be calculated from the Van Vleck expression with atomic distances obtained from the crystal structure.<sup>55</sup> The Van Vleck equation, in which  $\gamma_{\rm H}$  and  $\gamma_{\rm Na}$  are the magnetogyric ratios and  $r_{\rm k}$  is the distance of the kth hydrogen from the sodium cation, is shown below:

$$\left< \Delta v^2 \right> = \frac{1}{20\pi^2} \gamma_{Na}^2 \gamma_{H}^2 h^2 \sum_{k} \left[ \frac{1}{r_k} \right]^6$$
 (1.5)

For Na<sup>+</sup>(C222), the calculated Gaussian dipolar contribution to the linewidth is 3340 Hz, in excellent agreement with that observed.<sup>55</sup>

Studies have been extended to other alkali metal cations and anions through the use of  $^{87}$ Rb,  $^{133}$ Cs,  $^{7}$ Li and  $^{39}$ K magic angle spinning and static NMR techniques. $^{33,52,56,57,58}$  For the compound Cs<sup>+</sup>(18C6)<sub>2</sub>Rb<sup>-</sup>, Figure 4 demonstrates the ability of alkali metal MAS-NMR to identify the alkali metal species present. $^{58}$  In the  $^{133}$ Cs NMR spectrum, only the peak for the complexed cesium cation, Cs<sup>+</sup>(18C6)<sub>2</sub>, is present and only the Rb<sup>-</sup> peak is present in the



Figure 4. 133Cs (65.61 MHz) and <sup>87</sup>Rb (163.6 MHz) MAS-NMR spectra of polycrystalline Cs<sup>+</sup>(18C6)<sub>2</sub>Rb<sup>-</sup>. 58

 $^{87}$ Rb spectrum. These chemical shifts, -57 ppm for the "sandwich" cation Cs<sup>+</sup>(18C6)<sub>2</sub><sup>59,60</sup> and -187 ppm for the Rb<sup>-</sup> anion<sup>61,62</sup>, are characteristic for these nuclei in the environment described. Table 1 gives values of characteristic NMR shifts of some alkali metal anions and complexed cations. The conclusion drawn from NMR data, that this salt of stoichiometry CsRb(18C6)<sub>2</sub> is a pure rubidide, is supported by X-ray absorption studies.<sup>63</sup> In contrast to the <sup>23</sup>N a NMR studies of alkalides where the quadrupolar and dipolar interactions dominate, <sup>133</sup>Cs NMR central transitions are dominated by chemical shift anisotropy and dipolar interactions. The <sup>133</sup>Cs nuclei possesses a small quadrupole moment.

The low sensitivity and large quadrupolar broadening of the  $^{39}$ K and  $^{87}$ Rb NMR linewidths have limited the detection of potassium and rubidium cation signals in alkalides and electrides. $^{57,56}$  Recently, the first observation of K<sup>+</sup> in compounds other than simple salts was published by Oldfield and coworkers. $^{64}$  Through the use of spin echo techniques used by Oldfield et. al., it has been possible to detect potassium and rubidium cation signals in alkalides and electrides. $^{65,66}$  Data from the spin echo studies of rubidium salts will be presented in Chapter 5.

Although NMR has proven to be an excellent tool in the characterization of alkalides and electrides, the utility of these compounds has been limited due to their extreme sensitivity to air and temperature. While extensive use has been made of crown ethers and cryptands as complexants, all of the compounds studied to date undergo irreversible thermal decomposition at elevated

Species	Chemical shift (ppm) <sup>a</sup>
Na-	-57 to -63
К-	-105
Rb-	-185 to -198
Cs-	-212 to -240 (In Cs <sup>+</sup> (18C6) <sub>2</sub> Cs <sup>-</sup> temperature dependent)
Na+C222	-7 (High field limit)
Cs+(18C6) <sub>2</sub>	-40 to -62
Cs+(15C5) <sub>2</sub>	+24 to +29
Cs+(C222)	+238 to +275 (Inclusive complex)

<sup>a</sup>Chemical shifts are referenced to  $M^+(aq)$  at infinite dilution.

temperatures.<sup>67</sup> Studies done with differential scanning calorimetry (DSC) have indicated that the peak of the trace of the decomposition exotherm increased with the heating rate<sup>68</sup> and this phenomenon can be used to derive kinetic parameters of decomposition.<sup>69,70</sup>

In order to overcome the thermal instability, research has been directed towards the search for more stable complexing agents to be used in the synthesis of alkalides and electrides. Although the instability of the crown ether and cryptand complexants is believed to result from reductive attack on the ether complexant by the unbound or weakly bound electrons, the cleavage of ethers by alkali metals is a complex phenomenon.<sup>71</sup>

Research has led to the investigation of complexants in which nitrogen donor atoms have been substituted for oxygen in crown ethers and cryptands. The first complexant of this type to be used was hexamethylhexacyclen, HMHCY, the fully methylated aza analog of 18-crown-6.72 The complexant appears to be extremely resistant to decomposition to temperatures exceeding 393 K, even in the presence of alkali metals. The compounds synthesized with this complexant, Cs<sup>+</sup>(HMHCY)Na<sup>-</sup>, Rb<sup>+</sup>(HMHCY)Na<sup>-</sup>, and K<sup>+</sup>(HMHCY)Na<sup>-</sup> do not undergo decomposition; however, irreversible decomplexation occurs at temperatures as low as 310 K when the sample is ramped in a differential scanning calorimeter at 5 K/min. The decomplexation correlates with studies done on the complexation of  $K^+$ . When nitrogen is substituted for oxygen in a crown ether, the stability of the potassium complex in methanol decreases with an increase in the number of nitrogen donor atoms.73

Aside from the unique thermal properties of the compounds synthesized with the complexant HMHCY, the crystal structure of these compounds provided the first evidence for contact ion pair formation between an alkali metal cation and an alkali metal anion.<sup>72</sup> The promising results obtained with the first aza complexant led to the use of other complexants with nitrogen donor The smaller aza ring systems, pentamethylpentacyclen and atoms. trimethyltricyclen, have been studied as complexing agents for the Li cation.<sup>74,75</sup> Since early studies of crown ether ligands reported that stronger complexation occurs for those metal cations whose ionic radii best match the radius of the cavity formed by the polyether ring, lithium was chosen as the cation in these complexes based on "fit".<sup>24</sup> Data will be be presented on the compounds synthesized with the complexant trimethyltricyclen in Chapter 3. The results of work that has been initiated in the study of the aza analogs of cryptands will be discussed as well.

### **II. COMPLEXED CESIUM CATION**

### **II.A.** Introduction

The chemical shift of the cesium cation is extremely sensitive to the electron density at the nucleus. Combined with the fact that the nucleus has a relatively high sensitivity and small quadrupole moment, this makes the NMR spectrum of 133Cs a very useful tool in the study of the influence of the surroundings on the chemical shift and line shape of cesium in alkalides and electrides.

The chemical shifts of complexed cesium cations of both the 18C6 and 15C5 alkalide sandwich systems are nearly independent of the anion and agree with values found for halides and thiocynates.<sup>76.77</sup> The resonance peak of the complex,  $Cs^+(18C6)_2$  occurs at -60 ± 2 ppm for all salts except the ceside.<sup>76</sup>

The relatively constant chemical shift of the cesium cation coordinated by 12 crown ether oxygen atoms, implies that neither the structure of the complex nor the electron density at the cesium cation differ significantly in the sodide, potasside and rubidide salts. The chemical shift of Cs<sup>+</sup>, believed to be strongly influenced by the degree of Cs-O overlap, is inversely related to the mean Cs-O distance.<sup>76</sup>

Although the electride,  $Cs^+(18C6)_2e^-$ , is nearly isostructural to the sodide,  $Cs^+(18C6)_2Na^-$  41,78, the 133Cs MAS NMR spectra of the electride consists of a single temperature dependent peak at +81 ppm, a significant paramagnetic chemical shift compared to that of
other  $Cs^+(18C6)_2$  complexes.<sup>76</sup> The origin of the paramagnetic chemical shift in  $Cs^+(18C6)_2e^-$  is the Knight or contact shift.<sup>76</sup>

The fractional atomic character of the cesium ion in  $Cs^+(18C6)_2e^-$  may be calculated from the magnetic susceptibility and the slope of the Knight shift versus 1/T for this Curie-Weiss paramagnet. The trapped electron in  $Cs^+(18C6)_2e^-$  has a very low cesium s-orbital character relative to other electron-cesium systems such as Cs-ammonia solutions.<sup>79,80</sup> The fractional atomic character of  $Cs^+(18C6)_2e^-$  is 3.3 X 10<sup>-4</sup>, while Cs/ammonia solutions that contain 2 to 20 mole percent metal have fractional atomic characters that range from 0.04 to 0.60.

The chemical shift of  $Cs^+(18C6)_2e^-$  extrapolated to infinite temperatures is -61 ± 10 ppm, which is within experimental error of the chemical shift of  $Cs^+(18C6)_2$  observed in alkalides. The plot of chemical shift versus 1/T for  $Cs^+(18C6)_2e^-$  is shown in Figure 5. The study of  $Cs^+(18C6)_2e^-$  has yielded evidence that the trapped electrons in this compound show only weak overlap with the complexed cation, as evidenced by the Knight shift, as well as the absence of any spin pairing or magnetic ordering. In order to compare the  $Cs^+(18C6)_2e^-$  data to other electrides, a study was undertaken of the  $Cs^+(15C5)_2e^-$  system in which the cesium is coordinated to 10 crown ether oxygens. The crystal structure of this compound is known and the magnetic susceptibility obeys the Curie-Weiss law above approximately 15 K. In contrast to  $Cs^+(18C6)_2e^$ with no magnetic ordering, annealed polycrystalline samples of  $Cs^+(15C5)_2e^-$  show an antiferromagnetic transition at 4.6 K.



Figure 5. Plot of chemical shift versus 1/T for  $Cs^+(18C6)_2^{e-.76}$  The temperatures of points marked with an x were calibrated with methanol.

Also of interest was a system intermediate between the pure  $Cs^+(18C6)_2e^-$  and  $Cs^+(15C5)_2e^-$  systems. Syntheses of the mixed crown ether sandwich compounds in which the cesium cation is complexed by a 15C5 molecule and an 18C6 molecule,  $Cs^+(18C6)(15C5)$ , were attempted and the resultant compounds characterized. The investigation of mixed crown ether sandwich compounds offered the potential to fine tune the characteristics, such as magnetic susceptibility or alkali metal NMR chemical shift values, of an alkalide or electride based on the appropriate choice of crown ethers and the alkali metal cation.

### II.B. Theory

The primary contributor to the chemical shift of the alkali metal nuclei in the absence of unpaired electrons is one of the paramagnetic terms in the Ramsey shift.<sup>48</sup> This paramagnetic term is given in equation (1.3). The origin of the extra paramagnetic chemical shift in  $Cs^+(15C5)_2e^-$  is a contact or Knight shift. The Knight shift is the result of a strong local magnetic field generated at the nucleus of interest by paramagnetic electron density. Chemical shifts exist in the atoms themselves with contributions from the ion cores and from surrounding atoms, but changes in chemical shifts from one compound to another are usually much smaller than the Knight shift. The cesium cation should be very sensitive to any overlap with the paramagnetic trapped electron since the lowest energy unoccupied orbital in  $Cs^+$  is the 6s orbital with a non-zero electron density at the nucleus. The Knight shift is given by<sup>81</sup>:

$$K(T) = \frac{\delta \pi}{3N_{av}} \left\langle \left| \Psi_{(o)} \right|^2 \right\rangle \chi(T) \quad (2.1)$$

where  $\langle | \Psi_{(0)} |^2 \rangle$  is the average electron density at the nucleus, and  $\chi(T)$  is the magnetic susceptibility of the paramagnetic species. In the case of a Curie-Weiss paramagnet, K(T) is proportional to 1/T since  $\chi(T)$  varies inversely with temperature.

The value of the chemical shift in ppm at low temperatures fits the equation:

$$\delta(T) = \delta(00) + K(T) \qquad (2.2)$$

Where  $\delta(T)$  is the chemical shift at a specific temperature, T, and  $\delta(\infty)$  is the chemical shift at infinite temperature. The fraction of atomic s-orbital character of the trapped electron can be calculated from information obtained from the slope of the Knight shift versus 1/T and the magnetic susceptibility. The fractional atomic character is defined as:



where  $\langle | \Psi_0 |^2 \rangle_{atom}$  is the electron density at the nucleus for an isolated gas atom and has been estimated to be 2.645 x 10<sup>25</sup> e<sup>-</sup>cm<sup>-3</sup>.79

Although the overall magnetic behavior of  $Cs^+(15C5)_2e^-$  is that of a Curie-Weiss paramagnet, the magnetic moment of a free atom has three principle sources. The spin that the electrons are endowed with and their orbital angular momentum about the nucleus yield two paramagnetic contributions to the magnetization while the change in the orbital moment induced by an applied magnetic field gives a single diamagnetic contribution. The magnetic susceptibility per unit volume is defined as:

$$X = \frac{M}{H} \qquad (2.4)$$

where H is the macroscopic magnetic field intensity and M is defined as the magnetic moment per unit volume. Substances with negative magnetic susceptibility are called diamagnetic, the tendency of electrical charges partially to shield the interior of a body from an applied magnetic field. Substances with positive susceptibility are paramagnetic. Paramagnetism is a property exhibited by substances that contain unpaired electrons. Paramagnetic susceptibilities are temperature dependent and to first order (high T) approximation, the susceptibility  $\chi$  varies inversely with temperature. For a spin 1/2 system, the magnetic susceptibility is given by:

$$\chi = \frac{M}{H} = \frac{Ng^2 \mu_B^2}{4kT} = \frac{C}{T} \quad (2.5)$$

which is in the form of the Curie law where the Curie constant is given by:

$$C = \frac{Ng^2 \mu_B^2}{4k} \quad (2.6)$$

where N is Avogadro's number, k is the Boltzman constant,  $\mu_B$  is the Bohr magneton and g is a constant characteristic of each system. For the case J=S=1/2, the value of the Curie constant is 0.376. This applies to a system that consists of 100 percent independent unpaired spins in which the orbital angular momentum is quenched.

Deviations from Curie law behavior occur because of magnetic interactions that occur between paramagnetic species. In the simplest approximation, this behavior is expressed by the Curie-Weiss law:

$$X = \frac{C}{T-\Theta} \quad (2.7)$$

where the correction term,  $\Theta$ , has units of temperature. The value of  $\Theta$ , the Weiss constant, can be used to indicate whether a material is purely paramagnetic ( $\Theta$ =0), antiferromagnetic ( $\Theta$ <0) or ferromagnetic ( $\Theta$ >0).

A ferromagnetic state is one in which the moments on a given lattice are aligned spontaneously in the same direction. Even in zero applied magnetic field, a ferromagnet has a nonvanishing magnetic moment. Magnetization is at the maximum possible value at T=0. As temperature is increased, magnetization decreases as the spins become uncorrelated until spontaneous magnetization becomes zero at a characteristic temperature,  $\Theta$ , the Curie temperature. The susceptibility of a ferromagnet obeys the Curie-Weiss law at temperatures where T >>  $\Theta$ .

A typical antiferromagnet consists of two interpenetrating sublattices. Each sublattice is uniformly magnetized with its spins aligned parallel, and the spins on one sublattice are aligned antiparallel to the spins on the other sublattice. The transition from antiparallel nonalignment to parallel alignment of neighboring spins is a cooperative one that is accompanied by a characteristic longrange ordering temperature called the Néel temperature,  $\Theta$ . Characterized by a decrease in susceptibility with increasing temperature, the spins are ordered below the Néel temperature. At temperatures well above the Néel temperature, the susceptibility follows the Curie-Weiss law.

### II.C. Experimental

## 1. Synthesis

The synthesis of alkalides and electrides has been described in detail<sup>29,34</sup>, and these techniques were used in the synthesis of  $Cs^+(15C5)_2e^-$ . Approximately 20 percent excess crown ether was used in the synthesis in order to avoid contamination of the compound by ceside. The mixed crown ether compounds,  $Cs^+(18C6)(15C5)Na^-$ ,  $Cs^+(18C6)(15C5)e^-$  and  $Cs^+(18C6)(15C5)Cs^-$  were synthesized under more stringent conditions.

The synthesis of the mixed crown ether compounds required stoichiometric amounts of each crown ether be added to the synthesis apparatus, a K-cell. A very slight excess of the crown ether 15-crown-5 was added since this complexant is the more volatile of the two complexants used and a small amount can be lost during the flame seal-offs on the K-cell, which were made under active vacuum. This problem was minimized by freezing the complexing agents in liquid nitrogen or dry ice during the flame seal-offs on the cell. Dimethylether was then added to the metal(s) mirror and crown ethers to allow the complexation of the alkali metal cation. When all of the complexant had been dissolved and no more of the metal mirror would visibly dissolve over a two to three hour period, the cosolvent trimethylamine was added. No crystals were immediately visible; however, the slow removal of the solvent and cosolvent over a six hour period yielded an apparent homogeneous phase. Rapid precipitation of crystals from the synthesis must be avoided since this leads to multiple <sup>133</sup>Cs MAS NMR lines, an indication that more than one phase is present. The crystals, once precipitated, were washed with trimethylamine then harvested.

Attempts were made to grow single crystals for X-ray structure determination. Crystals of  $Cs^+(18C6)(15C5)Na^-$  and  $Cs^+(18C6)(15C5)e^-$  were grown from saturated solutions of dimethylether and trimethylamine by slowly cooling the temperature of the solution from approximately 233 K to 203 K over a three day period. Slow solvent evaporation of a solution of the sodide in dimethylether and trimethylamine over a period of several days was also attempted. Crystals of suitable quality to perform X-ray structure determinations were not obtained.

# 2. NMR

 $Cs^{+}(15C5)_{2}e^{-}$ 

Magic Angle Sample Spinning (MAS)  $^{133}$ Cs NMR spectra were obtained at 23.6 MHz on a Bruker WH 180 MHz (proton frequency) NMR spectrometer operating at a field strength of 4.2277 T, with 4-5 µsec pulse lengths and 0.5 to 2 second delay times. The temperature was controlled by flowing the nitrogen spinning gas through a liquid nitrogen heat exchanger and then warming the gas with an in-line heater. After the samples had been loaded into the rotor in a nitrogen-filled glove bag at liquid nitrogen temperatures, the sapphire rotor that contained the sample was loaded into a precooled NMR probe. Although the temperature was monitored with a thermocouple placed in the gas stream at a point just ahead of where the gas entered the spinner, it proved to be difficult to determine the actual sample temperature. Unfortunately, there seem to be only a few reliable methods for the determination of the sample temperature, especially the temperature of the sample where the NMR signal is detected.<sup>82</sup>

The temperature can be obtained by measuring the temperature-dependent chemical shift of a standard sample such as acidified methanol. At low temperatures, more hydrogen bonding occurs and the <sup>1</sup>H peak of the OH group in methanol shifts downfield. The chemical shift,  $\Delta v$  in Hz, between the CH<sub>3</sub> and OH groups can be fit with the following quadratic equation with an error (RMS) of 0.8 K over the temperature range from 175 to 330 K:<sup>83</sup>

T=403.0 - 0.491 | 
$$\Delta v$$
 | - 6.62 (10<sup>-3</sup>  $\Delta v$ )<sup>2</sup>

In order to incorporate the methanol sample into a MAS sapphire sample rotor, the Kel-F bolt used to attach the end caps to the rotor was modified. The Kel-F bolt was drilled lengthwise into its center and the hollowed portion filled with a sample of methanol and sealed with epoxy. A schematic diagram of the sapphire rotor and bolt is shown in Figure 6.



Figure 6. A schematic diagram of the sapphire rotor and bolt.

This method allowed alternate 133Cs and <sup>1</sup>H measurements to be made without removing the sample rotor from the instrument. This provided a reliable and reproducible measurement of the sample temperature although the presence of temperature gradients within the sample holder could not be ruled out.

Static NMR measurements were also carried out at 52.5 MHz in a Varian VXR-400 spectrometer equipped with a 45 to 165 MHz broadband probe by using single pulses of width 0.5  $\mu$ sec and a delay time of 0.5 seconds. Cold nitrogen gas was used to control the temperature to within 0.3 K after a 3 to 10 minute equilibration time.

# Cs<sup>+</sup>(18C6)(15C5)X<sup>-</sup>

The MAS and static  $^{23}$ Na and  $^{133}$ Cs NMR spectra of the mixed complexant alkalides and electride were obtained at 47.6 MHz and 23.6 MHz respectively, with a Bruker WH 180 MHz (proton frequency) NMR spectrometer operating at a field of 4.2277 T with 3 to 5  $\mu$ sec pulse lengths and 1 to 2 second delay times. A variable temperature Doty dual-bearing MAS probe was used and samples were loaded into the precooled probe once the sample had been loaded into the rotor in a nitrogen filled glove bag at liquid nitrogen temperatures. The temperature was controlled by flowing the nitrogen spinning gas through a liquid nitrogen heat exchanger and then warming to the set temperature with an in-line heater. The temperature was monitored with a thermocouple placed in the gas stream at a point just ahead of where the gas entered the spinner.

# 3. Magnetic Susceptibility

Magnetic susceptibilities of  $Cs^+(15C5)_2e^-$ .samples were measured with an S.H.E. 800 Series SQUID magnetometer over a temperature range of 2 to 283 K in applied fields of 0.1 to 7 kG. The mixed crown ether alkalide and electride complexes were studied over a more limited temperature range of 2 to 220 K in applied fields of 0.25 to 7 kG for the electride and 5 kG for the alkalides. Samples were loaded into a Kel-F SQUID bucket in a nitrogen filled glove bag at liquid nitrogen temperature, then transported and loaded into the susceptometer at cryogenic temperatures while under inert atmosphere.

Once the susceptibility of the "live" sample had been measured, the background susceptibility was determined and subtracted from that of the live sample. The background susceptibility was obtained by allowing the sample to decompose to a diamagnetic product and rerunning the sample. This procedure allows one to obtain the electronic contribution to the susceptibility. Since the decomposed samples are diamagnetic and provide a direct measure of the atomic susceptibility, the electronic contribution results only from  $M^-$  or  $e^-$ .

### 4. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed with a DuPont 910 Differential Scanning Calorimeter. Samples were hermetically sealed in aluminum pans under nitrogen gas at cryogenic temperatures. The samples were transported and loaded into the DSC instrument under inert atmosphere at cryogenic temperatures.

## 5. Optical Absorption

Optical absorption spectra of thin solvent-free films of the electride  $Cs^+(15C5)_2e^-$  were measured from 700 to 2300 nm on a

Model 260 Guided Wave Spectrophotometer at temperatures from 164 to 273 K as recorded with a copper-constantan thermocouple. Thin films were made by preparing a solution of the compound in  $CH_3NH_2$ , pouring the solution over the quartz cell window and then rapidly evaporating the solvent.

### II.D. Results and Discussion

# $1. Cs^{+}(15C5)_{2}e^{-}$

The details of the crystal structure of this electride have been reported elsewhere.<sup>84</sup> It belongs to the triclinic space group P1 with one molecule per unit cell and cell parameters: a = 8.59(4), b =8.886(8), c = 9.94(1) Å;  $\alpha$  = 102.91(8),  $\beta$  = 90.06(6),  $\gamma$  = 9.4(6)°; V = 733.1(11)Å<sup>3</sup>,  $\rho = 1.30$  g cm<sup>-3</sup>. The structure was determined at a temperature of 215 ± 2 K. Below about 260 K powdered samples of the electride are polycrystalline and can be readily transferred from one container to another by pouring. As the temperature in increased, particularly above 266 K, the sample became "sticky" but remained solid. As shown in Figure 7, DSC reflects these changes in behavior. A pronounced endotherm at 266 K corresponds to  $\Delta H =$ 11.2  $\pm$  0.6 kJ mole<sup>-1</sup> and is reversible. When the sample that had been warmed to 283 K in the DSC was cooled to 230 K the same endothermic transition occurred during the second cycle. The position of the exothermic peak, due to irreversible decomposition, depends on the ramping rate. The temperature at which decomposition occurs increases with an increase in ramping rate. As



Figure 7. Differential Scanning Calorimetry (DSC) trace of Cs+(15C5)<sub>2</sub>e<sup>-</sup> at ramping rates of 2 K/min (lower trace) and 5 K/min (upper trace offset by one W/g).

the ramping rate is increased, an endothermic peak becomes visible at 295 K, immediately preceding irreversible decomposition. This peak is believed to be due to the melting of  $Cs^+(15C5)_2e^-$ . The endothermic melting transition is masked by the exothermic decomposition at slower ramping rates.

While the molar enthalpy change for the endothermic transition at 266 K can be measured as  $11.2 \pm 0.6$  kJ mole<sup>-1</sup> for all ramp rates, glass formation prevents the direct determination of the heat of fusion of 15C5. However, both 12C4 and 18C6 can be crystallized and have heats of fusion of 20  $\pm$  1 and 37  $\pm$  2 kJ mole<sup>-1</sup> respectively. The average, 28 kJ mole<sup>-1</sup> is assumed to be approximately the heat of fusion of 15C5. Thus, the observed transition of Cs<sup>+</sup>(15C5)<sub>2</sub>e<sup>-</sup> has a value of  $\Delta$ H that is about 20 percent of that expected for complete melting of two moles of 15C5. Enough energy is involved in the endothermic transition at 266 K for the compound to undergo structural changes, but these changes are smaller than those associated with melting.

The absorption spectra of thin films of  $Cs^+(15C5)_2e^-$  are more complex than those of other electrides which contain a single broad absorption in the near IR region at 1200 to 1600 nm.<sup>43,44,85,86</sup> Shown in Figure 8, the absorption spectra of thin films of  $Cs^+(15C5)_2e^-$  contain three peaks at 900 to 950 nm, approximately 1200 nm and 1600 to 1700 nm. At lower temperatures, the three absorption peaks are quite distinct. An increase in temperature appears to broaden each of these peaks. No change in the absorption spectra was observed at or above the phase transition at 266 K. However, once the temperature of the film had been taken above



Figure 8. The optical absorption spectrum of a thin film of  $Cs^+(15C5)_2e^-$  made from solvent evaporation of methylamine at temperatures of 188 K (diamonds) and 253 K (solid line).

that of the phase transition, the narrowing of the three distinct peaks was no longer reversible when the temperature was lowered. The appearance of three absorption peaks instead of a single broad absorption may be due to a degeneracy in the excited-state p orbitals; an s to p transition would then produce three distinct peaks as observed.

The magnetic susceptibility of  $Cs^+(15C5)_2e^-$  was studied over the temperature range 1.6 to 283 K and at field strengths from 0.1 to 7 kG.87 Samples that were quenched by sudden cooling to 5 K showed Curie-Weiss behavior from 5 to 260 K with only small deviations below 5 K. When a sample was "annealed" at a temperature of approximately 230 K for a few minutes, followed by slow cooling, a maximum in the susceptibility was observed at 4.5 K. The susceptibility data show that an antiferromagnetic transition occurs at about 4.5 K and that the anisotropy is relatively small. At temperatures well above the Neel temperature, the susceptibility followed the Curie-Weiss law. However, at about 260 to 265 K the slope of a plot of  $1/\chi$  vs. T changed in a direction that corresponds to less paramagnetism. This occurred just below the temperature of the endothermic transition seen in the DSC experiments. Whether an abrupt change in susceptibility accompanies the phase transition cannot be ascertained from the susceptibility data since the sample temperature in the SQUID susceptometer tends to overshoot before coming to equilibrium. In fact, high temperature susceptibility data needed to be corrected for partial decomposition of the sample due to the overshoot in temperatures in the instrument. Thus, partial

conversion to a less paramagnetic high temperature form could have occurred.

A large number of NMR experiments have been carried out on  $Cs^+(15C5)_2e^-$ . Both the early <sup>133</sup>Cs MAS measurements carried out by Steve Dawes that were hampered by difficulty in measuring the sample temperature, and later MAS measurements with more accurate temperature calibrations showed two peaks with chemical shifts of 490 and 290 ppm. Both peaks were present over the apparent temperature range 265 to 280 K, each at a constant value of the chemical shift as shown in Figure 9. These measurements had to be made rather rapidly to avoid decomposition, a process that could be monitored by the growth of a peak of the decomposition products at 61 ppm. Since the DSC results showed a reversible endothermic transition at 266 K, the phase transition may not have been complete in the NMR rotor at these temperatures during the measurement time and the actual sample temperature may have been at or near the transition temperature even though the temperature of the spinning gas continued to increase. The heat absorbed during the transition would tend to keep the temperature constant. That this was indeed the case was shown by studying the time-dependence of the static spectrum at 266 K. Over a 120 minute period the static peak with an isotropic chemical shift of 488 ppm decayed while that at 294 ppm grew in. Rapid cooling to 253 K caused reversal of the process over a period of 3 to 5 minutes. These results are in complete agreement with the DSC data and confirm the presence of a first-order phase transition at 266 K. In the temperature range of 280 to 290 K only one peak, corresponding to



Figure 9. 133Cs MAS NMR spectrum at a temperature of 276 K with two peaks at chemical shifts of 493 and 298 ppm obtained at a frequency of 23.6 MHz.

the new high temperature peak observed in the 265 to 280 K range, was present in both the MAS and static NMR data.

The static <sup>133</sup>Cs NMR spectra at 52.5 MHz were also obtained as a function of temperature. Typical gaussian-broadened powder patterns arising from chemical shift anisotropy (CSA) were obtained. The isotropic chemical shift ranged from 604 ppm at 183 K to 496 ppm at 258 K, in excellent agreement with that obtained from MAS-NMR measurements at 23.6 MHz. The anisotropy parameter,  $\eta_{CSA}$ , was temperature dependent, with values of  $0.30 \pm 0.05$  from 266 to The chemical shift anisotropy parameter increased with 243 K. decreasing temperature with a value of 0.60  $\pm$  0.05 at 213 K and  $0.65 \pm 0.05$  at 183 K. The required gaussian broadening corresponded to full widths at half maximum that ranged from  $3.3 \pm$ 0.2 KHz at 183 K to 1.45 ± 0.1 KHz at 243 K. Since the proton dipolar broadening as calculated from the crystal structure with the Van Vleck equation was 1.1 KHz<sup>88</sup>, much of the broadening can be attributed to incompletely relaxed electron-nucleus dipolar coupling. The rigid-lattice limit for such coupling was calculated to be 57.4 KHz. Electron spin-lattice relaxation averages out most, but not all of the strongly temperature dependent electron-nucleus coupling.

Below about 240 K, the chemical shift is linear in 1/T with an intercept of 180  $\pm$  10 ppm and has a slope of 7.9  $\pm$  0.5 x 10<sup>4</sup> ppm K. Figure 10 shows a plot of chemical shift vs 1/T for Cs<sup>+</sup>(15C5)<sub>2</sub>e<sup>-</sup> for both the MAS and static NMR data. This intercept is about 150 ppm higher than the chemical shift obtained for model salts that contain the Cs<sup>+</sup>(15C5)<sub>2</sub> cation.<sup>76</sup> The slope corresponds to a contact density at Cs<sup>+</sup> that has 0.063% atomic character, nearly twice that found for



Figure 10. Plot of chemical shift versus 1/T for Cs<sup>+</sup>(15C5)<sub>2</sub>e<sup>-</sup>; 180 MHz MAS NMR data (open squares); and 400 MHz static data with the isotropic chemical shift obtained from simulations of the experimental powder patterns (circles).

 $Cs+(18C6)_{2}e^{-76}$  The rather large anisotropy in the Cs<sup>+</sup> to e<sup>-</sup> distances suggests that the contribution to the contact density is different for different electrons.

The similarity in geometry and Cs-O distances in the electride complex when compared to the sodide and the small electron spin density at cesium strongly suggest that the excess electron density is centered in the anionic sites with probable extension of the wave function beyond the Van der Waals boundaries of the cavity.

The endothermic transition at 266 K, accompanied by a decrease in paramagnetism that is sluggish, made it impossible to distinguish between a discontinuity in the susceptibility and a change in the slope of  $1/\gamma$  vs. T as shown in Figure 11. One can conclude, however, that the electronic susceptibility 10 K above the transition is about 60 percent of the value 10 K below the transition. The chemical shift of the <sup>133</sup>Cs NMR signal decreases abruptly from 493 ppm below the transition temperature to 294 ppm above this temperature. The most likely cause of the change is the decrease in magnetic susceptibility since the chemical shift of a diamagnetic model salt is directly proportional to the susceptibility for a constant value of the unpaired spin density at Cs<sup>+</sup>. The decrease in the chemical shift at the transition, 57 percent, is very close to the 60 percent decrease in susceptibility, an indication that the transition to the higher temperature phase is accompanied by partial electron spin-pairing.

A remaining puzzle is the high value, 180 ppm, of the extrapolated chemical shift of the low temperature phase as well as the curvature of a plot of the shift vs. 1/T. This contrasts with the





chemical shift behavior of  $Cs^+(18C6)_2e^-$ , whose intercept at infinite temperature is the same as that of diamagnetic model compounds.<sup>76</sup> The high intercept in the present case may reflect a gradual increase in the contact density at Cs<sup>+</sup> that accompanies the increased motion of the crown ethers. Of particular interest in the study of this compound would be <sup>133</sup>Cs MAS NMR at temperatures of 180 K and below, especially at temperatures corresponding to the antiferromagnetic transition.

#### 2. Cs<sup>+</sup>(18C6)(15C5)Na<sup>-</sup> and Cs<sup>+</sup>(18C6)(15C5)Cs<sup>-</sup>

Although several methods have been used in attempts to grow single crystals of the compounds  $Cs^+(18C6)(15C5)e^-$  and  $Cs^+(18C6)(15C5)Na^-$ , a crystal of suitable quality for the collection of single crystal X-ray diffraction data could not be found. The first synthesis of a cesium mixed crown ether sodide system was characterized by 133Cs MAS NMR and contained multiple NMR peaks. A more careful synthesis yielded a single 133Cs MAS NMR peak at -11 ppm. In Table 2, the values of the 133Cs chemical shift in some pure  $Cs^+(15C5)_2$  and  $Cs^+(18C6)_2$  complexes are listed along with those of the  $Cs^+(18C6)(15C5)$  systems synthesized to date.

The chemical shift of approximately 90 ppm downfield of the  $Cs^+(15C5)_2$  salts from that of the  $Cs^+(18C6)_2$  salts suggests a stronger paramagnetic Ramsey interaction of the cesium cation with the oxygens of the crown ether 15C5 versus those in 18C6. In the structures of the  $Cs^+(15C5)_2$  and  $Cs^+(18C6)_2$  complexes, the mean Cs-O distance in the 18C6 sandwich is longer than that in the 15C5

Complex	<u>Chemical shift (ppm)</u> a
Cs+(18C6) <sub>2</sub> Na-	- 6 1
Cs+(18C6)(15C5)Na-	-8
Cs+(15C5) <sub>2</sub> Na-	+24
Cs <sup>+</sup> (18C6) <sub>2</sub> K <sup>-</sup>	- 5 8
Cs+(15C5) <sub>2</sub> K-	+24
Cs+(18C6) <sub>2</sub> Rb <sup>-</sup>	- 5 7
Cs+(15C5) <sub>2</sub> Rb-	+29
Cs+(18C6) <sub>2</sub> Cs <sup>-</sup>	- 4 1
Cs+(18C6)(15C5)Cs <sup>-</sup>	-11
Cs+(18C6)(15C5)e <sup>-</sup>	-6 to +31

Table 2.Characteristic 133Cs NMR Chemical shifts of the<br/>complexed cation.76.

<sup>a</sup>Chemical shifts are referenced to  $M^+(aq)$  at infinite dilution.

complex.<sup>40,78,84</sup> This reduction in bond length could result in a greater overlap of the cesium cation with the lone pair electrons on oxygen. If one were to predict that the chemical shift of the mixed crown ether system were to fall half way between the chemical shifts of the pure complexes, one would obtain a chemical shift value of approximately -16 ppm.

The experimental value of -11 ppm is quite close to the predicted value. This chemical shift was reproducible on several different samples. The sodide chemical shift in the mixed crown ether complex occurs at -61 ppm, unshifted from the value calculated for gaseous Na<sup>-,89</sup> There is no Na<sup>+</sup> NMR peak observed, an indication of the formation of a true cesium sodide compound. Upon decomposition of the sodide, two cesium cation peaks occur at 21 and 13 ppm, paramagnetically shifted from the <sup>133</sup>Cs peak in the live sample. The change in chemical shift could be due to the shortening of the Cs-O bonds since the decomposed sample is a very viscous liquid and the Cs-O distances may change once the ordered crystalline solid is no longer present.

In order to confirm the presence of a single phase, the DSC pattern of  $Cs^+(18C6)(15C5)Na^-$  was measured and the decomposition temperatures of this compound were compared to those obtained at the same ramping rates for  $Cs^+(18C6)_2Na^-$  and  $Cs^+(15C5)_2Na^-$ . For example, at a ramping rate of 2 K/min,  $Cs^+(18C6)_2Na^-$  decomposes at 367 K with a  $\Delta H$  value of -208 kJ/mole, while that of  $Cs^+(15C5)_2Na^$ decomposes at 340 K with a  $\Delta H$  value of -141 kJ/mole. The mixed sodide at the same ramping rate decomposes at 343 K with a  $\Delta H$ value of -215 kJ/mole and an irreversible endothermic transition at 260 K with a  $\Delta H$  value of 7.2 kJ/mole. Preceding the decomposition exotherm, there is a small peak visible at slower ramping rates that may be due to a small portion of the sample on the outer edges or in another area in the sample pan so that the decomposition does not take place homogeneously.

Originally, one of the reasons for pursuing the mixed complexant systems was that, in molecular models, the "fit" of the cesium cation was better for a  $Cs^+(18C6)(15C5)$  system than for either of the pure sandwich compounds. The cavity for  $Cs^+$  in the 18C6 sandwich complex appeared to be slightly too large while that of the 15C5 sandwich complex was slightly too small. Pedersen and Izatt have shown that the cation radius and cavity size of the crown are the most important factors in the determination of the cationcrown complex stability.<sup>24,90,91</sup> Although no study has been done on the stability of the complex, the DSC data on the sodide indicate that there has been no significant increase in the stability of the alkalides towards thermal decomposition through the mixing of two different crown ethers in the formation of the sodide.

The other mixed crown ether alkalide that was prepared was the compound  $Cs^+(18C6)(15C5)Cs^-$ . A single 133Cs MAS NMR peak was observed at -8 ppm. The slight paramagnetic shift of the 133CsNMR peak for this mixed crown ether ceside as compared to that of the sodide may be due to the slight shortening of the Cs-O bond distances to cause a greater overlap between the cesium cation and the unpaired electrons on the oxygens. For example, the chemical shift of the cesium cation in the analogous compound  $Cs^+(18C6)_2Cs^$ is more paramagnetic than that of  $Cs^+(18C6)_2$  in the sodide, rubidide



Figure 12. The <sup>133</sup>Cs MAS NMR spectrum of the mixed crown ether complex, Cs<sup>+</sup>(18C6)(15C5)Cs<sup>-</sup>, obtained at 245 K and a frequency of 23.6 MHz. and potasside.<sup>76</sup> Figure 12 shows the <sup>133</sup>Cs MAS NMR spectrum of Cs<sup>+</sup>(18C6)(15C5)Cs<sup>-</sup>.

The peak for the cesium anion, however, was not observed. In the compound  $Cs^+(C222)Cs^-$ , two  $Cs^+$  peaks in the <sup>133</sup>Cs NMR can be observed for the  $Cs^+(C222)$ , presumably due to the inclusive and exclusive complexes, respectively; however, none of the samples showed the NMR signal of  $Cs^-.76$  Similarly samples known to contain Rb<sup>-</sup> have also shown no <sup>87</sup>Rb signal.<sup>58</sup> The anion peaks in these compounds may be broadened by strong interactions between adjacent alkali metal anions to such an extent that the signal is no longer detectable. This may be the case for the compound  $Cs^+(18C6)(15C5)Cs^-$ , however, the  $Cs^-$  to  $Cs^-$  distances are not known since no crystal structure for this compound has been obtained.

The magnetic susceptibility of this compound was obtained and, as for the sodide with a dopant level of approximately 1 percent, displays a slightly paramagnetic behavior with an electron dopant level of approximately 3 percent. The 133Cs NMR of these alkalides demonstrates the potential of mixed crown ether complexes to allow one to fine tune the characteristics of a compound.

## <u>3. Cs+(18C6)(15C5)e</u>-

Several preparations of the mixed electride, Cs<sup>+</sup>(18C6)(15C5)e<sup>-</sup>, have been synthesized and studied. The first synthesis yielded a compound that, when studied by magnetic susceptibility, contained only approximately 3% unpaired electrons and had two <sup>133</sup>Cs NMR peaks at 220 and 132 ppm respectively. Synthesis and handling

techniques for these compounds were improved and a set of more reproducible results was obtained.

133Cs MAS NMR spectra were obtained from the mixed crown ether electride with some interesting results. In one sample, a single peak at 36 ppm was observed, and this peak did not appear to shift with temperature. The chemical shift of the decomposed sample appears at 15 ppm. However, for the most recent sample of the compound, 133Cs MAS NMR data were obtained in the 180 MHz Bruker instrument. The sample has both a temperature and time dependent chemical shift. The chemical shift of the 133Cs peak became more paramagnetic with increasing temperature from approximately 6 ppm at 180 K to 31 ppm at 300 K. Upon recooling the sample to 180 K, the chemical shift was no longer at 6 ppm, but 9.5 ppm. When the sample was placed in the instrument at a set temperature and data were collected as a function of time, the 133Cs

The 133Cs chemical shift is very sensitive to the environment of the cesium cation, so that only small changes need to occur within the compound to cause these changes in the chemical shift. The increase in the paramagnetic chemical shift may be due to a shortening of the Cs-O bond distances as one increases the temperature. The data, however, will have to be reproduced on another synthesis of the sample.

The magnetic susceptibility of the compound, as shown in Figure 13, follows the Curie-Weiss law. The Weiss constants for two different data sets are rather large and negative,  $\Theta = -45$  and -72, an indication of the presence of antiferromagnetic interactions and



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synthesis-dependent properties. The data were fit at temperatures of 40 K and above, since the Curie-Weiss equation is a high temperature approximation and deviations are expected to occur at low temperatures. Annealing the sample did not appear to have an effect on the susceptibility, nor did there appear to be any significant field dependence. The smaller values of  $1/\chi_m$  at every temperature for the 0.25 kG data are probably due to residual field effects, which are more important at lower fields. The average percent of unpaired spins was 60  $\pm$  1 percent for the two different sample data sets when only temperatures greater than or equal to 40 K were used to fit the data. The deviation of the percentage in unpaired spins from 100% may be due to partial decomposition of the compound when the sample was loaded into the instrument or contamination of the electride by ceside, a diamagnetic compound.

The DSC trace of  $Cs^+(18C6)(15C5)e^-$  showed that the enthalpy of decomposition is intermediate to those of the two "parent" electrides. At a ramping rate of 2 K/min,  $Cs^+(18C6)_2e^-$  decomposes at 315 K with a  $\Delta$ H value of -71 kJ/mole and  $Cs^+(15C5)_2e^$ decomposes at 299 K with a  $\Delta$ H value of -103 kJ/mole while the compound  $Cs^+(18C6)(15C5)e^-$  falls intermediate between the two with a decomposition temperature of 308 K and a  $\Delta$ H value of -98 kJ/mole. As with  $Cs^+(15C5)_2e^-$ , the mixed crown ether electride undergoes a transition at 284 K with a  $\Delta$ H value of 7 kJ/mole before decomposition. The transition, however, is not reversible. A DSC trace of the mixed crown ether electride is shown in Figure 14.

While this and other mixed crown ether alkalides and electrides offer great potential in the study of how structure affects



Figure 14. DSC trace of the mixed crown ether electride, Cs+(18C6)(15C5)e<sup>-</sup>, at a ramping rate of 5 K/min.

the properties of these compounds, the main difficulty in these systems is the synthesis of pure bulk materials for characterization. This is especially true in the case of electrides where a small contamination level may cause large changes in the bulk properties. The synthesis techniques for these compounds need to be improved and the work presented on the electride reproduced in other syntheses. Synthesis techniques should be developed to improve the methods for the transfer of the crown ethers so that complexant is not lost during the interval between weighing the complexant and the addition of solvent to the synthesis apparatus. The X-ray structure should be obtained for these compounds; that of the electride would be of particular interest.

#### III. AZA COMPOUNDS

#### III.A. Introduction

Alkalides and electrides are two unique classes of compounds with unusual properties. Unfortunately, due to their extreme sensitivity, these compounds must be handled under inert atmosphere at cryogenic temperatures. Since the compounds undergo irreversible decomposition du to their thermal instability, the utility of alkalides and electrides, such as in reduction processes<sup>92,93</sup> has been limited.

To date, most of the alkalides and electrides synthesized have utilized two classes of complexing agents, crown ethers or cryptands. In the pursuit of more robust alkalides and electrides, the use of the fully methylated aza analogs of crown ethers was pursued.<sup>72</sup> Pez and co-workers began to work with solutions of the complexant hexamethylhexacyclen (HMHCY), the fully methylated aza analog of 18C6, in the search for more chemically resistant cation-complexing agents in organic syntheses.<sup>92</sup> While benzene solutions of the cryptand C222 in the presence of Na/K alloy rapidly degrade at room temperature, HMHCY develops a deep blue color which persists for approximately 30 minutes at room temperature. When used in the selective hydrogen reduction of benzene to cyclohexane, these reactions were always accompanied by extensive degradation of the HMHCY complexant.
Based on the potential for more thermally stable alkalides and electrides, HMHCY was used in the synthesis of several sodides. When monitored by DSC, the thermal properties indicate that the compounds Cs<sup>+</sup>(HMHCY)Na<sup>-</sup> and K<sup>+</sup>(HMHCY)Na<sup>-</sup> melt at 281 K and 315 K respectively, but without thermal decomposition. However, an overall increase in stability of the alkalides is not achieved since decomplexation is observed at 310 K and 347 K respectively. Further heating yields no sign of decomposition of the complexant at temperatures up to 393 K.

The use of these more robust aza complexants has potential for an increase in the thermal stability of alkalides and electrides, but the substitution of nitrogens for ether oxygens in a ring reduces the affinity of the ligand for the alkali metal ion.<sup>94</sup> This factor may be part of the reason that  $Cs^+(HMHCY)Na^-$  undergoes decomplexation. Attempts to synthesize  $Cs^+(HMHCY)e^-$  were unsuccessful. In the pursuit of 133Cs NMR data for the cesium cation in the compound  $Cs^+(HMHCY)Na^-$ , an investigation of electron doping in this compound was undertaken to determine how several properties such as magnetic susceptibility and NMR spectra, are affected by the dopant level.

Further studies have been done on the use of other aza-crown ethers as complexants in the synthesis of alkalides and electrides. Preliminary work has been done on compounds synthesized with the fully methylated aza analog of 15C5, pentamethylpentacyclen (PMPCY). For the first time in the use of aza complexants an electride was formed, Li<sup>+</sup>(PMPCY)e<sup>-</sup>, although the crystal structure of this compound is not known.<sup>74</sup> Unlike the compound Cs<sup>+</sup>(HMHCY)Na<sup>-</sup>, this electride does not decomplex before it undergoes irreversible decomposition at 353 K when monitored by DSC at a ramping rate of 5 K/min. The magnetic susceptibility measurements indicate that antiferromagnetic interactions are present in Li<sup>+</sup>(PMPCY)e<sup>-</sup>, making the properties of this compound and the crystal structure of particular interest.

The trimethyltricyclen (TMTCY) complex with lithium has been studied, but the resulting compound had not been not fully characterized.<sup>74</sup> A mixture of the complexants trimethyltricyclen and dimethyltricyclen (DMTCY), however, produced a compound that contained a mixed unit of Li<sup>+</sup>(TMTCY) and Li<sup>+</sup>(DMTCY<sup>-</sup>)·CH<sub>3</sub>NH<sub>2</sub> with a sodide anion to yield the overall stoichiometry of Li<sup>+</sup>(TMTCY)[Li<sup>+</sup>(DMTCY<sup>-</sup>)·CH<sub>3</sub>NH<sub>2</sub>]Na<sup>-.95</sup> The lithium sodide synthesized with the pure TMTCY complexant was characterized by several methods and the crystal structure was obtained once problems with complexant purity were overcome. Once again, however a mixed system, Li<sup>+</sup><sub>2</sub>(TMTCY)<sub>2</sub>Na<sup>-</sup>·CH<sub>3</sub>NH<sup>-</sup> was formed.

While fully methylated aza analogs of the crown ethers have been previously studied, no work had been done with the analogs of cryptands. Since three dimensional cryptands form considerably more stable metal complexes than the corresponding two dimensional crown ethers, alkalides and electrides synthesized from the fully methylated aza analogs of cryptands might be more stable to decomplexation than the crown ether analogs.96,97,98 These complexants offer the additional advantages of the ability to selectively encapsulate small ions, as well as pre-orientation of the ligand to yield relatively low entropies of formation for the

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complexes.<sup>99</sup> The use of 5,12,17-trimethyl-1,5,9,12,17-pentaazabicyclo[7.5.5]nonadecane (TMPAND) shown in Figure 15



Figure 15. 5,12,17-trimethyl-1,5,9,12,17-penta-aza bicyclo[7.5.5]nonadecane (TMPAND).

in the synthesis of a lithium sodide and electride has shown promising results.

#### III.B. Theory

# 1. Decomposition Studies

In the search for more thermally stable alkalides and electrides, the ability to more quantitatively determine the relative thermal stability of a compound was needed. Until now only qualitative determinations of the thermal stability of a compound were made, either through Differential Scanning Calorimetry (DSC) data collected at a single ramp rate or visible observations.<sup>74</sup> The first quantitative determination of the activation energy of the decomposition of the electrides, K<sup>+</sup>(C222)e<sup>-</sup> and Li<sup>+</sup>(PMPCY)e<sup>-</sup>, was undertaken with DSC methods.<sup>100</sup>

It has been found that the peak temperature of a DSC trace increases with an increase in the rate of heating or ramp rate.<sup>68</sup> This observation can be used to determine decomposition parameters with the methods derived by Kissinger<sup>70</sup> and Ozawa.<sup>69,70</sup> For the Kissinger method, it has been shown by Murray and White that first order chemical reactions follow the equation:<sup>101</sup>

$$\operatorname{Aexp}^{-E/RT}_{m} = \frac{E}{RT_{m}^{2}} \frac{dT}{dt} \quad (3.1)$$

where R is the gas constant, T the absolute temperature, dT/dt the heating rate,  $T_m$  the peak temperature, E the activation energy for decomposition and A the pre-exponential factor. Equation (3.1) can be written as:

$$\ln\left(\frac{\Phi}{T_{m}^{2}}\right) = \ln\left(\frac{RA}{E}\right) - \frac{E}{RT_{m}} \quad (3.2)$$

where  $\phi = dT/dt$  and all other terms are as previously defined. In plots of  $\ln(\phi/T_m^2)$  versus  $1/T_m$  for a number of materials, Kissinger obtained straight lines from which activation energies were calculated.<sup>70</sup> In a subsequent paper, it was shown that this equation applies to nth as well as first order reactions.<sup>102</sup> Analysis shows that for a generalized chemical reaction,  $1/T_m$  varies linearly with  $ln(\phi)$  with the slope of the line equal to (0.4567\*E)/R in the Ozawa method.<sup>69</sup> Activation energies determined by each method are in good agreement.<sup>68,100</sup> If a reaction monitored possesses an activation energy, the position of the peak will vary with the ramp rate. Since all alkalides and electrides studied to date possess an activation energy, decomposition temperatures obtained at a single ramp rate for a compound do not a provide a quantitative basis for a comparison of relative stability.

#### 2. Quadrupole Coupling Constants

An electric quadrupole moment can be described as a series of mutipoles of the form:

$$\sum_{i} \varepsilon_{i} r_{i}^{2} \qquad (3.3)$$

where r is the distance to the charge  $\varepsilon_i$  from the electrical center of gravity. A quadrupole does not interact with a homogeneous electric field, however, there is an energy of interaction of a quadrupole with an inhomogeneous electric field, an electric field gradient. Nuclei with spin quantum numbers greater then 1/2 possess electric quadrupole moments usually expressed in terms of eQ, where e is the charge on the proton and Q is the quantity referred to as the

electric quadrupole moment of the nucleus. Since there are two types of distributions of charge, roughly cigar-shape (+) or disc-shape (-), nuclear quadrupole moments also possess signs.

If a nucleus has a quadrupole moment or is magnetically coupled to another nucleus with a quadrupole moment in a magnetic field, the quadrupolar nucleus has two energy terms that need to be considered, Zeeman and quadrupole terms where Q is the nuclear quadrupole moment and q is the strength of the field-gradient. In the high field case the Zeeman term predominates and the energy levels are essentially those of the Zeeman term perturbed by quadrupole effects. Therefore, the effect of  $\mathcal{H}_Q$  is usually treated by perturbation theory and to first order each level  $E_m^0$  is shifted by an amount  $E_m^{1}$ :

$$E_{m}^{1} = \frac{A}{2} [3\cos^{2}\Theta - 1] [3m^{2} - I(I+1)] \quad (3.4)$$

where  $\Theta$  is the angle between the principal axis of the field gradient tensor and the direction of the magnetic field H<sub>0</sub> for the case in which the asymmetry parameter is equal to zero and A is defined as  $e^2Qq/(4I(2I-1))$ . Since the shift depends on m with  $\Delta m = \pm 1$ , the original line is split into 2I lines corresponding to different values of m, as shown in equation (3.5).

$$v_{m \to m+1} = v_{m}^{0} + \frac{3A}{h}(m+1/2)(3\cos^{2}\Theta - 1)$$
 (3.5)

To first order, the central line (m =  $-1/2 \longrightarrow m = 1/2$ ) is unshifted for nuclei with half-integral spin. The second order shift of the central line is given in equation (1.4).

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For a polycrystalline sample, the effect of quadrupole coupling is averaged over all orientations. Figure 16 illustrates the idealized line-shapes expected for I=3/2 when the asymmetry parameter,  $\eta_Q$ , is zero. The distance between the two satellite peaks is equal to  $v_q$ .

$$v_{q} = \frac{3e^{2}qQ}{(h2I(2I-1))}$$
 (3.6)

$$v_{q} = \frac{e^{2}qQ}{2h}$$
 For I=3/2 (3.7)

From equations 3.6 and 3.7, the quadrupole coupling constant for I=3/2 can be calculated as  $2v_q = e^2 qQ/h = Quadrupole$  Coupling Constant (QCC). The value of QCC reflects different values of the field gradient for the same nucleus in different compounds. Examples of the value of QCC for several ion pairs of lithium halides in the gas phase are given in Table 3. Since the splitting by quadrupole effects is symmetric about the unperturbed resonance line, the position of

Figure 16. The idealized line-shape for a polycrystalline sample with quadrupolar coupling for I=3/2 when the asymmetry parameter is zero.

the quadrupole satellites does not reveal the sign of the coupling constant.

Table 3.	<sup>7</sup> Li Quadrupole Coupling Constants (QCC) of lithium halides for the gas phase ion-pairs. <sup>103</sup>			
<u>Species</u>	OCC			
LiCl	0.192 MHz			
LiBr	0.184 MHz			
LiI	0.172 MHz			

#### III.C. Experimental

#### 1. Complexant Purification

The fully methylated aza analogs of the crown ethers were obtained from Dr. Farnum at Michigan State University. The complexant HMHCY was placed over Na<sup>O</sup> and evacuated to  $2 \times 10^{-5}$ Torr to remove water and volatile solvents. The complexant HMHCY was then further purified by vacuum distillation at 398 K. The purified HMHCY is a viscous clear liquid. The complexant TMTCY was purified by vacuum distillation at 298 K to yield a clear liquid. Contamination of this aza complexant with dimethyltricyclen (DMTCY) resulted in the need for several distillation cycles of the complexant over Li<sup>O</sup> to remove the impurity.

The complexant TMPAND was obtained from Dr. M. Micheloni at the University of Florence, Italy. The complexant was obtained as the hydrochloride salt which was stirred in 1 N NaOH for 1 hour, then extracted into an organic solvent and dried over MgSO<sub>4</sub>. Following removal of the drying agent and evaporation of the solvent, the freebase of the complexant was purified by vacuum sublimation at 423 K at a pressure of  $2 \times 10^{-5}$  Torr or below. The free base was obtained from the hydrochloride salt by Dr. Evelyn Jackson. A white crystalline compound with a trace of yellow tinges was obtained after several days of sublimation. Due to the extremely long times needed for sublimation, the second time the complexant was purified by simply placing the complexant under vacuum at  $2 \times 10^{-5}$  Torr for a 48 hour period while being gently heated. Syntheses done with complexant purified in this manner were not visibly different from those done with complexant purified by vacuum sublimation, yet the loss of complexant due to the purification process was minimized.

#### 2. Synthesis

## a. Cs<sup>+</sup>(HMHCY)Na<sup>-</sup>

The general synthesis of alkalides and electrides has been described in detail elsewhere.<sup>29,34</sup> The synthesis of Cs<sup>+</sup>(HMHCY)Na<sup>-</sup> was performed under two different set of conditions, (P) and (E). For the first synthesis (P), a 60 percent excess of sodium metal was added to the complexant HMHCY and cesium metal. Extra care was taken to maximize the amount of sodium dissolved through the use of relatively warm synthesis temperatures and longer times allowed to dissolve the metal. For the second synthesis (E), a 2:1 ratio of the alkali metals cesium:sodium was used and no extra care was taken to allow all of the sodium metal to dissolve.

When the synthesis of  $Cs^+(HMHCY)e^-$  was attempted, light blue solutions were visible in dimethylether. No deep blue solutions formed. Attempts to dissolve additional metal by distillation of the solvent onto the metal mirror lead to decomplexation, since cesium metal could be observed on both sides of the frit in the synthesis apparatus. Removal of the solvent led to the starting materials.

# b. $Li^{+}_{2}(TMTCY)_{2}Na^{-}CH_{3}NH^{-}$ and $Li^{+}_{2}(TMTCY)_{2}e^{-}CH_{3}NH^{-}$

Since lithium metal is relatively insoluble in dimethylether, methylamine was added in order to dissolve the alkali metal(s) in the synthesis of these compounds. Once the metal(s) had dissolved, all of the solvent was removed and the cell was pumped on the line overnight to remove any residual solvent. Dimethylether was then added to wash the compound through a frit, away from any excess lithium metal. Crystals formed after slow evaporation of the solvent and were then washed with n-pentane. During the attempts to synthesize the electride, no solid was observed until n-pentane was added. If all of the dimethylether was removed before the npentane was added, then a viscous deep blue solution formed and lithium metal began to collect on the bottom of the synthesis cell as decomplexation occurred. Once the crystals were washed, solvent was removed and the cell was evacuated to  $2 \times 10^{-5}$  Torr before the crystals were harvested.

# c. Li<sup>+</sup>(TMPAND)Na<sup>-</sup> and Li<sup>+</sup>(TMPAND)e<sup>-</sup>

The attempted synthesis of the compound Na<sup>+</sup>(TMPAND)Na<sup>-</sup> failed. A blue solution, an indication of the presence of e<sup>-</sup> and/or Na<sup>-</sup> in solution, was not visible even after 16 hours with the sodium metal and complexant in a solution of dimethylether. Once all of the solvent had been removed from the failed synthesis, the cell was pumped out and placed in the dry box to introduce another metal. The complexant remained a pale yellow color throughout this process.

Lithium metal was placed in the synthesis apparatus and methylamine was added to dissolve the sodium and lithium alkali metals. The solution bubbled as the metals dissolved and a deep blue solution resulted. The solution was packed in dry ice overnight to allow the lithium time to complex. After approximately 12 hours the methylamine solution was deep purple in color with bronze films that formed if the solution was swirled on the sides of the glass synthesis apparatus. All of the methylamine was removed, since methylamine will complex alkali metals by itself, and the excess metal present in the cell became apparent as the cell took on an overall grey color. There were copper colored crystals present in the bulk metal.

Dimethylether was added to the synthesis bulb and a deep blue solution was observed. Since dimethylether will not dissolve sodium or lithium metal, this solution was poured through a frit to another glass bulb on the synthesis apparatus to separate the complexed cation from any excess metal present. Deep bronze films were observed on the sides of the bulb. Trimethylamine was then added to the solution as a cosolvent to induce crystallization. Bronze colored crystals could be observed on the bottom of the bulb and no metal was apparent. Once the dimethylether/trimethylamine solvent mixture was removed, pure trimethylamine was added to wash the compound and remove any excess complexant. The yield of the compound was relatively large, although the need to keep the sample cold did not permit an actual weight to be obtained. Throughout the entire synthesis the solution was kept below 248 K in dry ice/isopropanol baths or dry ice alone.

The electride Li<sup>+</sup>(TMPAND)e<sup>-</sup> was prepared in the same manner in a quartz synthesis apparatus. A solution of lithium metal, complexant, and methylamine was made to dissolve the metal and aid complexation. Methylamine was then removed and dimethylether added to wash the complex from the excess metal. Trimethylamine was added to the dimethylether to crystallize the electride. Finally pure trimethylamine was added to solvent-free crystals to wash the compound. The synthesis was done at a temperature of 228 K or below with good yield.

#### 3. Methylamine Test

When the crystal structure of the compound Li<sup>+</sup>(TMTCY)[Li<sup>+</sup>(DMTCY<sup>-</sup>)·CH<sub>3</sub>NH<sub>2</sub>]Na<sup>-</sup> was solved, methylamine was found to be present in the structure.<sup>95</sup> This was the first time that solvent had been observed in the crystal structure of an alkalide or electride. All other analyses done on this compound and that of  $Li^{+}_{2}(TMTCY)_{2}Na^{-}CH_{3}NH^{-}$  gave no indication that methylamine was present, therefore a simple method was designed to test for the solvent.

To test for methylamine, harvested crystals of the compound to be tested were cooled to liquid nitrogen temperatures in a glove bag. Approximately 10 to 25 mg of sample was then placed in a beaker that had been cooled to the same temperature. The beaker was removed from the cooling source, then placed on the bottom of the glove bag. While still cold, approximately 1 ml of  $D_2O$  was pipetted over the sample.

The  $D_2O$  immediately froze and then was allowed to slowly warm to room temperature. Since the volatile methylamine is soluble in  $D_2O$ , upon decomposition of the sample the solvent was dissolved in  $D_2O$  rather than escaping into the glove bag. Proton NMR spectra were then obtained for the decomposed sample as well as the same decomposed sample with methylamine added. If one of the peaks present in the decomposed sample grows upon addition of methylamine, then solvent is present in the sample. Integration of the peak heights yields the relative ratios of complexant to methylamine. This test gives no indication of whether the methylamine is present as  $CH_3NH_2$  or  $CH_3NH^-$  in the crystals. Attempts were made to decompose the sample directly in the

synthesis apparatus and use this solution for the test in order to avoid decomposition of additional sample. This should be avoided since residual  $CH_3NH_2$  present in the synthesis apparatus will give a  $CH_3NH_2$  peak in the proton NMR spectrum, although the solvent may not be a integral part of the crystal structure.

#### 4. NMR

#### a. Cs<sup>+</sup>(HMHCY)Na<sup>-</sup>

Variable temperature 133Cs and 23Na MAS NMR spectra were obtained at 23.6 and 47.6 MHz respectively on a Bruker WH 180 MHz (proton frequency) NMR spectrometer operating at a field strength of 4.2277 T, with 4 µsec pulse lengths and 0.5 to 1 second delay times. The temperature was controlled by the flow of nitrogen spinning gas through a liquid nitrogen heat exchanger followed by increasing the gas temperature with an in-line heater. After the samples had been loaded into the rotor in a nitrogen filled glove bag at liquid nitrogen temperatures, the sapphire rotor that contained the sample was loaded into a precooled NMR probe. The sample temperature was monitored with a thermocouple placed in the gas stream at a point just ahead of where the gas entered the spinner.

The variable temperature static and MAS <sup>7</sup>Li and <sup>23</sup>Na NMR spectra were obtained at 69.95 and 47.6 MHz respectively on a Bruker WH 180 MHz (proton frequency) NMR spectrometer operating at a field strength of 4.2277 T, with 4  $\mu$ sec pulse lengths and 2 second delay times. Sample preparation and temperature control of the Bruker instrument were as described above. Variable temperature solution <sup>7</sup>Li and <sup>23</sup>Na NMR spectra were obtained at 69.95 and 47.6 MHz respectively on a Bruker WH 180 MHz (proton frequency) NMR spectrometer, as the solid samples were. Samples were prepared in a nitrogen filled glove bag. Crystalline samples of  $\text{Li}_2(\text{TMTCY})_2\text{Na}$ -CH<sub>3</sub>NH<sup>-</sup> were loaded into a cooled quartz NMR tube. The tube was then temporarily sealed with a stop-cock and placed on a vacuum line and evacuated until a pressure of 2 x 10<sup>-5</sup> Torr was obtained. To dissolve the sample, dimethylether was distilled into the quartz NMR tube until a level of 2 to 4 cm was reached. The solution was then frozen and a quartz seal-off done to permanently seal the tube. Samples were kept at temperatures below 193 K until placed in the NMR instrument.

c. Li<sup>+</sup>(TMPAND)Na<sup>-</sup> and Li<sup>+</sup>(TMPAND)e<sup>-</sup>

Variable temperature MAS <sup>7</sup>Li NMR spectra for Li<sup>+</sup>(TMPAND)e<sup>-</sup> were obtained at 69.95 MHz on a Bruker WH 180 MHz (proton frequency) NMR spectrometer operating at a field strength of 4.2277 T, with 4  $\mu$ sec pulse lengths and 1 second delay times. Sample preparation and temperature control of the Bruker instrument were as described above.

<sup>7</sup>Li and <sup>23</sup>Na static NMR measurements were carried out for Li<sup>+</sup>(TMPAND)Na<sup>-</sup> at 155.454 and 105.8 MHz respectively on a Varian VXR-400 spectrometer equipped with a 45 to 165 MHz broadband probe by using single pulses of width 2  $\mu$ sec and a delay of 1 second. Cold nitrogen gas was used to control the temperature to within 0.3 K after 3 to 10 minutes equilibration time.

# 5. Magnetic Susceptibility

Magnetic susceptibilities were measured with an S.H.E. 800 Series SQUID magnetometer. Samples were loaded into a Kel-F SQUID bucket in a nitrogen filled glove bag at liquid nitrogen temperature, then transported and loaded into the susceptometer at cryogenic temperatures while under inert atmosphere. The samples were loaded into the instrument by either zero field cooling the sample or cooling the sample to 5 K in an applied field. Table 4 contains the specific conditions for each set of data.

Once the susceptibility of the "live" sample had been measured, the background susceptibility was determined and subtracted from that of the live sample. The background susceptibility was obtained by allowing the live sample to decompose to a diamagnetic product and rerunning the sample. This procedure allows one to obtain the electronic contribution to the susceptibility. Since the decomposed samples are diamagnetic and provide a direct measure of the atomic susceptibility, the electronic contribution results only from  $M^-$  or  $e^-$ .

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TMTCY, and TMPAND.					
<u>Species</u>	<u>Temperature</u>	Field			
Cs <sup>+</sup> (HMHCY)Na <sup>-</sup> (P)	1.8 to 180 K	1 and 5 kG Zero field cooled			
Cs <sup>+</sup> (HMHCY)Na <sup>-</sup> (P)	1.8 to 204 K	5 kG Quenched			
Cs <sup>+</sup> (HMHCY)Na <sup>-</sup> (E)	1.8 to 223 K	5 kG Quenched			
Li <sup>+</sup> 2(TMTCY)2 <sup>e</sup> CH3NH-	1.8 to 193 K	1 and 5 kG Quenched			
Li <sup>+</sup> (TMPAND)e <sup>-</sup>	1.8 to 220 K	3, 5 and 7 kG Zero field cooled			
Li <sup>+</sup> (TMPAND)e <sup>-</sup>	2.5 to 200 K	0.5, 5 and 7 kG Zero field cooled			

Table 4. Magnetic Susceptibility conditions for the data sets of compounds that were made with the complexants HMHCY, TMTCY, and TMPAND.

#### 6. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed with a DuPont 910 Differential Scanning Calorimeter. Samples were hermetically sealed in aluminum pans under nitrogen atmosphere at cryogenic temperatures. The samples were transported and loaded into the DSC instrument under inert atmosphere at cryogenic temperatures.

## 7. Optical Absorption

Optical absorption spectra of thin solvent-free films of the sodide were measured from 300 to 1500 nm on a Model 260 Guided Wave Spectrophotometer at temperatures from 262 to 283 K as recorded with a copper-constantan thermocouple. Thin films were made by first preparing a solution of the compound in dimethylether, then pouring the solution over the quartz cell window and then rapidly evaporating the solvent.

#### 8. Conductivity Methods

A 2-probe conductivity cell for d.c. measurements was designed by M. R. Yemen and J. L. Dye.<sup>104</sup> The 5 to 15 mg sample to be studied was placed in a 4 mm glass tube which fit tightly over the bottom stainless steel electrode. The top electrode was spring loaded to ensure proper contact against the bottom electrode. To shield the cell, the bottom electrode was electrically insulated from the body of the cell by a teflon spacer and the cell body was connected to the shield of the coaxial leads used in conductivity measurement.<sup>100</sup>

All d.c. conductivity experiments were performed with a Keithley 617 Programmable Electrometer used as both a voltage source and an ammeter. Variable temperature data were collected with a computer controlled Keithley 617 electrometer to record sample measurements and a Keithley 580 micro-ohmmeter to record resistance data from a four-probe carbon glass thermometer. Rectangular voltage pulses 10 seconds in length and 100 mV in

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amplitude of alternate polarity were applied to the sample to eliminate polarization effects. Temperature data were collected immediately following each electrical measurement.

#### 9. Electron Paramagnetic Resonance

Samples for electron paramagnetic resonance (EPR) measurements were prepared in a nitrogen filled glove bag. A quartz EPR tube was filled to a length of approximately 1 cm with sample while the tube and sample were kept at liquid nitrogen temperatures. The stopcock attached to the EPR tube was closed and then the EPR tube was removed from the glove bag and placed on a vacuum line. When the EPR tube had been evacuated to  $2 \times 10^{-5}$ Torr, a quartz sealoff was done to permanently seal the sample tube. Samples were kept at temperatures below 193 K until EPR measurements were made.

EPR measurements were performed with an X-band ER200D Series Bruker Spectrometer by Dr. Michael Atamian. The spectrometer is controlled by a Nicolet 1180 data system and a slow cryogenic system was used for low temperature work.

#### 10. X-ray Crystallography

The single crystal X-ray diffraction study of this compound was done in collaboration with Dr. Rui Huang. Single crystals of  $Li^{+}_{2}(TMTCY)_{2}Na^{-}CH_{3}NH^{-}$  were obtained by slow solvent evaporation from a solution of dimethylether at 193 K. Once grown, single crystals of the compound were placed under a microscope on a microscope slide at approximately 223 K under a layer of octane. The crystal selected for the study had the approximate dimensions  $0.3 \times 0.3 \times 0.7 \text{ mm}^3$ . The handling and mounting procedures have been described in detail elsewhere.105 The diffractometer was a Nicolet P3F that used graphite monochromatized Mo K $\alpha$  radiation with a locally modified Nicolet LT-1 low-temperature system. Unit cell parameters were determined by least squares from the setting angles of 19 reflections in the range  $15^{\circ} < 2\Theta < 20^{\circ}$ . Intensity data were collected with  $\omega$  scans at 2 deg/min to  $\sin \Theta / \lambda < 0.595 \text{ Å}^{-1}$ ; reflection indices:  $0 \le h \le 10$ ,  $0 \le k \le 19$ , and  $0 \le l \le 24$ . A linear decay correction was based on the intensities of three monitored reflections measured every 93 reflections. A numerical absorption correction was obtained from the program DIFABS with a maximum correction of 1.191; minimum of 0.258 and average of 0.818. Taking a data cut-off of  $I > 3\sigma(I)$ , there are 996 observed and 2114 unobserved data. The structure was solved by direct methods with the SHELXS-86 program. Full least squares refinement was on F with all atoms except protons refined anisotropically. H atoms were constrained to ride on their bonded C-atoms with fixed isotropic thermal parameters. There were 263 total parameters, W = 1.78, and the function minimized was  $\sum w(|F_0| - |F_c|)^2$ . The maximum shift error ratio ( $\delta/\sigma$ ) was equal to 0.08, with R = 0.073 and wR = 0.067. R is defined as  $\Sigma |F_0| - |F_c|/\Sigma |F_0|$ . The final difference map peak heights ranged from -0.17 to 0.19  $e/Å^3$ . Scattering factors were obtained from Cromer and Waber<sup>106</sup> and f' and f' from Cromer<sup>107</sup> except that of the sodium anion which was obtained from Dr. David

A. Liberman.<sup>40</sup> All computations were carried out on a VAX11/750 computer.

The cell parameters for the compound were: A = 8.896, B = 16.704 and C = 21.051 Å with  $\alpha = \beta = \gamma = 90^{\circ}$ . The cell volume is equal to 3092.99 with 4 molecules per unit cell. The crystal belongs to the Orthorhombic 222 space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>.

#### **III.D.** Results and Discussion

#### 1. Cs+(HMHCY)Na-

Although the crystal structure of Cs<sup>+</sup>(HMHCY)Na<sup>-</sup> is known and the compound has been well characterized, previous attempts to obtain <sup>133</sup>Cs NMR spectra on the compound have failed.<sup>72</sup> The separation of the cation-anion Van der Waals surfaces is between -0.13 and +0.07 Å if the effective radius of the cesium cation is taken to be 1.69 Å and that of the sodium anion to be between 2.50 and 2.70 Å. This is the first evidence for the presence of contact ion pairs in alkalides. It was believed that the absence of the 133Cs NMR signal may have been due to a strong perturbation of the p electrons in Cs<sup>+</sup> as a result of their close proximity to Na<sup>-</sup>. There is evidence, however, that the cesium cation signal also is sensitive to the level of electron doping in the compound. The solutions from which crystals of alkalides are grown contain solvated electrons as well as alkali metal anions that cause defect electrons in alkalide salts.<sup>108</sup> Work was carried out in collaboration with Sylvie Doueff on samples that contained two different electron dopant levels, those that were

relatively pure with approximately 2 percent or less electron doping (P) and one that had a relatively large level of electron doping (E).

In the Cs<sup>+</sup>(HMHCY)Na<sup>-</sup> samples with minimal electron doping, a <sup>133</sup>Cs NMR signal was observed at 249  $\pm$  15 ppm for two different samples. Reasonable signal to noise ratios were obtained with approximately 3000 scans. The electron dopant level measured by magnetic susceptibility on one of these samples was approximately 2 percent. The NMR lines were relatively narrow, with a full width at half height ( $\Delta v_{1/2}$ ) value of 722 Hz. When the temperature was slowly raised to approximately 300 K, the <sup>133</sup>Cs signal disappeared. Since the compound decomplexes at 310 K, the loss of signal was probably due to the decomplexation of Cs<sup>+</sup>(HMHCY)Na<sup>-</sup>. No signal could be observed in the Bruker 180 MHz NMR instrument for Cs<sup>o</sup> or the CsNa alloy. The sodide signal was observed before the variable temperature <sup>133</sup>Cs data were collected. The <sup>23</sup>Na peak with a  $\Delta v_{1/2}$  value of 233 Hz, occurred at -59 ppm a chemical shift characteristic of all sodide salts.<sup>47,55</sup>

The EPR spectrum of  $Cs^+(HMHCY)Na^-(P)$  indicates that there is a clear hyperfine coupling to the cesium metal cation, I=7/2. While it is clear that electrons are trapped in the crystal, the nature of the trapping site is still under investigation.<sup>109</sup> When no attempt was made to minimize the electron dopant level in the compound, the EPR signal contains the same hyperfine interactions with the cesium cation overlayed on a broad single featureless peak. The intensity of this line was not as large as one would expect for an alkalide so heavily doped with electrons. The loss in intensity may be due in

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part to a poorly packed sample and/or partial decomposition or decomplexation of the sample.

While the sodide peak in the  $^{23}$ Na MAS NMR spectra could be observed at -61 ppm (E), the value of  $\Delta v_{1/2}$  was relatively large, 2250 Hz. The line width in the heavily doped sample was approximately 10 times broader than in the minimally doped sample. This may be due in part to an increase in dipolar broadening from the dipole interactions between Na<sup>-</sup> and e<sup>-</sup>. The  $^{133}$ Cs MAS NMR spectra of the heavily doped sample changed as well. A very poor signal with a signal to noise ratio of approximately 2 was present after 17,000 scans at 186 ppm. No signal was observed if a smaller number of scans was used. Therefore, this signal may have been due to noise in the probe, but even if it is not, the need to obtain 17,000 scans to observe the signal indicates that it was not from a major fraction of the  $^{133}$ Cs nuclei in the sample.

The electron dopant level in this sample was determined to be  $33 \pm 1$  percent. The sample followed the Curie-Weiss law with a Weiss constant of  $-27 \pm 4$  K, an indication of antiferromagnetic interactions. The magnetic susceptibility data for the heavily doped sample are shown in Figure 17. With  $33 \pm 1$  percent of the sodium anions replaced by electrons, the dipolar and quadrupolar broadening would be extremely large and could cause the loss of the 133Cs cation NMR signal.

Although a change in the NMR, EPR and magnetic susceptibility data occurred when the electron dopant level was increased, the transition temperature for melting and decomplexation in the DSC trace of the compound did not change. The DSC trace for a lightly



Figure 17. Magnetic susceptibility plot of  $1/\chi_e^m$  versus T for the heavily doped sodide, Cs<sup>+</sup>(HMHCY)Na<sup>-</sup>, quenched and run in a field of 5 kG.

doped and heavily doped compound are shown in Figure 18. The same transition temperatures for melting and decomplexation were observed in both the samples (P) and (E), although the  $\Delta H$  value of the transitions had changed. The melting transition at 281 K for (P) and (E) had  $\Delta H$  values of 12.9  $\pm$  1.0 and 38  $\pm$  15 kJ/mole respectively. One possible reason for the increase in the  $\Delta H$  value of the heavily doped sample in this transition is that the melting of the sample may have initiated decomplexation. The electron may have been able to recombine with the cesium cation more easily than the sodium anion was able to. This would also explain the broad featureless decomplexation peak in the heavily doped sample, since partial decomplexation would already have occurred. This was an indication that major structural changes have not occurred, since one would expect a change in the transition temperatures if radical structural changes had occurred.

The compound  $Cs^+(HMHCY)Na^-$  is the most heavily doped alkalide synthesized to date. This is unusual in that the electride of this compound could not be synthesized. Perhaps it is the inability of the compound to undergo phase separation that allows such large dopant levels to be obtained. It has been shown that it is possible to obtain 133Cs NMR data for this compound in a minimally doped sample. The large paramagnetic shift of the cation was not unexpected since the chemical shift of the cesium cation increases with an increase in polarizability of the anion<sup>87</sup> as well as with overlap of the cesium cation with the unpaired electrons on the nitrogen.



Figure 18. The DSC traces of Cs<sup>+</sup>(HMHCY)Na<sup>-</sup> for the heavily doped sample (bottom line) and the minimally doped sample (top line offset by 1 W/g) obtained at a ramping rate of 5 K/min.

A study of the electron dopant levels in the intermediate range of 5 to 15 percent would be of interest to study the transition from minimal dopant levels to maximum dopant levels. This study has also shown the need for care in the synthesis of alkalides and electrides, since the dopant level of unpaired electrons can change the properties of a compound under study.

# 2. $Li^+_2(TMTCY)_2Na^-CH_3NH^$ and $Li^+_2(TMTCY)_2e^-CH_3NH^-$

In the original attempts to synthesize  $Li^+(TMTCY)_2Na^-$ , the complexant was contaminated with DMTCY. The crystal structure obtained with the mixture of complexants contained DMTCY<sup>-</sup>, TMTCY and CH<sub>3</sub>NH<sub>2</sub> as integral parts of the crystal structure.<sup>95</sup> In order to overcome this problem, the complexant was purified extensively to obtain pure TMTCY.

The molecular structure of the compound synthesized with pure TMTCY is shown in Figure 19. A sandwich compound in which the lithium cation is complexed between two molecules of the complexant was expected, however, methylamine is also present in the crystal structure as an anion. Both lithium cations have coordination numbers of four. Each nitrogen is coordinated by the three nitrogens on the TMTCY molecule and by the N<sup>-</sup> of the CH<sub>3</sub>NH<sup>-</sup> anion. The N<sup>-</sup> of the CH<sub>3</sub>NH<sup>-</sup> forms a bridge between the two lithium cations and the bond distances between N<sup>-</sup> and the two lithium cations are shorter than the six Li<sup>+</sup>-N bonds. Table 5 lists selected bond distances. The refined atomic coordinates and isotropic



B



Figure 19. A) The molecular structure and numbering of atoms in Li<sup>+</sup><sub>2</sub>(TMTCY)<sub>2</sub>Na<sup>-</sup>·CH<sub>3</sub>NH<sup>-</sup>; and B) Stereographic packing diagram of Li<sup>+</sup><sub>2</sub>(TMTCY)<sub>2</sub>Na<sup>-</sup>·CH<sub>3</sub>NH<sup>-</sup>.

temperature factors as well as bond distances and bond angles are presented in Appendix A.

The N-Li<sup>+</sup>-N bond angles for nitrogens on the TMTCY molecule range from 83.8° to 88.8°. The lithium cation, while four coordinate, is not in a tetrahedral coordination site. The small bond angles indicate that the lithium cation is well above the plane of the three nitrogen atoms of the complexant. Although molecular models indicate that Li<sup>+</sup> would fit well between two TMTCY molecules, this does not appear to be the case. The reason that a sandwich compound does not form may be due to the lithium cation not fitting well in the cavity of the complexant and the plane of the nitrogens or the preference of lithium for a four coordinate environment.<sup>110</sup>

Table 5.	Selected	bond	distances	for	the	compound

Bond	Length (Å)
Li1 - N	2.135, 2.091, 2.074
Li1 - N-	1.903
Li2 - N	2.116, 2.088, 2.055
Li2 - N <sup>-</sup>	1.928
C - N	1.444 to 1.521
C-C	1.369 to 1.457

This was only the second crystal structure where methylamine is observed and incorporated as a stoichiometric part of the structure. In order to more easily determine if this solvent is present in crystals without the determination of a crystal structure, a test was developed to determine the presence of methylamine. Figure 20 shows the proton NMR spectra from the test for this solvent when performed on  $\text{Li}^+_2(\text{TMTCY})_2\text{Na}^-\text{CH}_3\text{NH}^-$ . The ratio of methyl protons:  $\text{CH}_3\text{NH}_2/\text{TMTCY}$  is approximately 7:1, close to the 6:1 ratio expected for one methylamine molecule to two TMTCY molecules, the ratio in the compound. <sup>7</sup>Li and <sup>23</sup>Na MAS and static NMR spectra were performed on this compound as well as several other analysis techniques, but no other methods except the X-Ray diffraction data and the test specifically for  $\text{CH}_3\text{NH}_2$  indicated the presence of the solvent.

<sup>7</sup>Li Static NMR data were recorded and a single rather broad line was recorded at approximately 0.1 ppm with  $\Delta v_{1/2} = 5036$  Hz. The chemical shift value is reasonable for a lithium cation coordinated by four nitrogen atoms in a sodide.<sup>65</sup> The dipolar broadening for the <sup>7</sup>Li cation was calculated with the Van Vleck equation<sup>88</sup> from the coordinates obtained from the crystal structure. The calculated value of 5691 Hz is in good agreement with that of the actual sample. Variable temperature <sup>7</sup>Li MAS NMR spectra indicated the linewidth narrowed so that  $\Delta v_{1/2} = 3700$  Hz at 220 K, however, the chemical shift does not change. All attempts to perform <sup>7</sup>Li and <sup>23</sup>Na solution NMR failed.



Figure 20. Methylamine Test A) Li<sup>+</sup><sub>2</sub>(TMTCY)<sub>2</sub>Na<sup>-</sup>·CH<sub>3</sub>NH<sup>-</sup> quenched in D<sub>2</sub>O at cryogenic temperatures; and B) Li<sup>+</sup><sub>2</sub>(TMTCY)<sub>2</sub>Na<sup>-</sup>·CH<sub>3</sub>NH<sup>-</sup> quenched in D<sub>2</sub>O at cryogenic temperatures to which a solution of CH<sub>3</sub>NH<sub>2</sub> in D<sub>2</sub>O has been added.

The  $^{23}$ Na NMR peak for the solid compound occurred at -59 ppm, the chemical shift characteristic of all sodide salts, even though the crystals contained both Na<sup>-</sup> and CH<sub>3</sub>NH<sup>-</sup>. The optical absorption spectrum with a single peak at 700 nm obtained by M. Kuchenmeister for the sodide also gave no indication that the crystals studied were not those of a pure sodide.<sup>74</sup> Magnetic susceptibility studies of this compound indicate a diamagnetic sample as expected, with less than a 0.1 percent electron dopant level.

The DSC trace of the compound was originally done by M. Kuchenmeister, however, these data were obtained before the complexant was properly purified. A decomposition temperature of 353 K at a ramp rate of 5 K/min was obtained by M. Kuchenmeister.<sup>74</sup> In contrast, a decomposition temperature of 330 K with a  $\Delta$ H value of -41.9 kJ/mole was obtained when the experiments were repeated at a ramp rate of 5.5 K/min. Figure 21 shows the DSC trace of the more recently obtained data. A low temperature transition was observed in some of the samples; however, it was not reproducible in all of the samples. Not all of the samples loaded in the DSC sample pans had reproducible thermal behavior. The samples, which contain a lithium cation, may have been extremely sensitive to storage in a liquid nitrogen filled dewar or have reacted with the aluminum sample pans.<sup>100</sup>

Several attempts were made to synthesize an electride with the TMTCY complexant. Although deep blue solutions form, severe decomplexation problems occurred when solvent was removed. Attempts to collect magnetic susceptibility data on the compound failed. <sup>7</sup>Li MAS NMR spectra of the compound, however, had a peak



Figure 21. DSC trace of the sodide, Li<sup>+</sup><sub>2</sub>(TMTCY)<sub>2</sub>Na<sup>-</sup>·CH<sub>3</sub>NH<sup>-</sup>, obtained at a ramping rate of 5.5 K/min.

at approximately 36 ppm at a temperature of 180 K when data were collected on the Bruker 180 MHz instrument. As the temperature of the sample was raised, no change occurred in the spectra until 220 K. At this temperature the peak at 36 ppm disappeared and a peak appeared at approximately 1 ppm, the region where one would expect the chemical shift value of the decomposed sample to occur.<sup>111</sup> When the sample temperature was lowered to 180 K, the peak at 36 ppm did not return.

If an electride forms with the TMTCY complexant it appears to be very unstable. Good crystalline material of this compound has not yet been obtained due to the severe decomplexation problems in the synthesis of the compound. Problems with decomplexation may be due to the volatile nature of the complexant. As one pumps off the solvent, the complexant is removed as well which leads to the formation of lithium metal particles.

Although the crystal structures of compounds formed with TMTCY as a complexant are of interest, there are several drawbacks to the use of TMTCY in the synthesis of alkalides and electrides; the incorporation of solvent molecules in the crystal structure and the inability to synthesize a crystalline electride for characterization. There is evidence that the pure TMTCY sodide may, in fact, have another crystal structure with the same molecular structure but another packing arrangement.<sup>112</sup> One possible solution to the problems with the TMTCY complexant may be the alteration of the complexant through the use of propyl instead of ethyl linkages between the nitrogens to open up the complexant ring so that the lithium cation may more easily sit in the plane of the nitrogen atoms.

#### 3. Li<sup>+</sup>(TMPAND)Na<sup>-</sup> and Li<sup>+</sup>(TMPAND)e<sup>-</sup>

The first fully methylated aza analog of a cryptand was used in the synthesis of a lithium sodide and electride. The crystal structure of the TMPAND compounds has not been determined; however, the methylamine test was performed on harvested crystals of the sodide. No peak associated with methylamine was observed in the proton NMR of this sample, a strong indication that this solvent is not an integral part of the crystal structure as it is in the TMTCY compound.

Optical absorption spectra of this compound were obtained at several temperatures. Figure 22 shows the optical absorption spectra of Li<sup>+</sup>(TMPAND)Na<sup>-</sup> at two different temperatures, 183 and 262 K, with the maximum at 698 and 717 nm (14330 and 13950 cm<sup>-1</sup>) respectively. The major peak at approximately 700 nm in the spectra of these thin films produced by solvent evaporation is attributed to the 3s<sup>2</sup> to 3s3p transition of the anion, Na<sup>-</sup>.<sup>31</sup> The transition was slightly temperature dependent with a red shift at higher temperatures. No sharp break at any temperature occurred but a gradual change with dv/dt of approximately -5 cm<sup>-1</sup>K<sup>-1</sup>. The peak also became broader at higher temperatures. Both of these properties are observed in Na<sup>+</sup>(C222)Na<sup>-</sup> films.<sup>42</sup>

Although no sharp break occurs in the optical absorption spectra, a phase transition occurs at low temperatures in  $Li^+(TMPAND)Na^-$ . At an onset temperature of 200 ± 2 K with a  $\Delta H$


Figure 22. Optical absorption spectra of Li<sup>+</sup>(TMPAND)Na<sup>-</sup> obtained at 262 K (top line offset by +0.2 on the Relative Absorption scale) and 183 K.

value of  $3.3 \pm 1$  kJ/mole, the compound undergoes a solid to solid transition. The phase transition could not be observed visibly since the crystals neither change color not appear to soften. The kinetics of decomposition for Li<sup>+</sup>(TMPAND)Na<sup>-</sup> were studied by DSC methods with variable ramp rates. Figure 23 illustrates that the decomposition temperature of the compound is dependent on the ramp rate and shows the DSC trace of Li<sup>+</sup>(TMPAND)Na<sup>-</sup> at two different ramp rates. Specific data for the decomposition temperature at different ramp rates are given in Table 6. The  $\Delta$ H value for decomposition was determined to be  $-52 \pm 17$  kJ/mole.

With the Kissinger method<sup>70</sup>, the activation energy for the decomposition of Li<sup>+</sup>(TMPAND)Na<sup>-</sup> was determined. The graph of  $ln(\phi/T_m^2)$  versus  $1/T_m$  used to determine the activation energy is shown in Figure 24. At 101  $\pm$  5 kJ/mole, the activation energy of the sodide Li<sup>+</sup>(TMPAND)Na<sup>-</sup> is greater than the two electrides studied with this method. Li<sup>+</sup>(PMPCY)e<sup>-</sup> and K<sup>+</sup>(C222)e<sup>-</sup> have activation energies of 87 kJ/mole and 66 kJ/mole respectively.<sup>100</sup> Although there is not a large basis for comparison, the compound Li<sup>+</sup>(TMPAND)Na<sup>-</sup> appears to be relatively stable to thermal decomposition. Activation energies, however, have not been determined for any other alkalides.



Figure 23. The DSC trace of Li<sup>+</sup>(TMPAND)Na<sup>-</sup> obtained at a ramp rate of 12 K/min (top line offset by 2 W/g) and 7 K/min.



Figure 24. Plot of  $\ln(\phi/T_m^2)$  versus 1/T for Li<sup>+</sup>(TMPAND)Na<sup>-</sup> used to determine the activation energy for decomposition.

Decomposition Temperature (K)	Ramp Rate (K/min)
349.5	1
357.8	2
369.7	7
371.5	10
376.1	12
378.3	15

Table 6. Table of thermal decomposition temperatures for Li<sup>+</sup>(TMPAND)Na<sup>-</sup> and the ramp rate at which they were obtained.

The d.c. conductivity of the sodide was measured by K. Moeggenborg.<sup>100</sup> Figure 25 shows a plot of the the d.c. conductivity results for this compound. At temperatures below the solid-solid phase transition the sample resistance was beyond the measurement range of the instrument. The sample behaves as a semiconductor with a band gap of approximately 1.2 eV above a point with corresponds to the temperature of the phase transition. The possibility of ionic conductivity in Li<sup>+</sup>(TMPAND)Na<sup>-</sup> was tested through the use of a sodium electrode. The Ohm's law plot for the cell was symmetrical and passed through the origin of the I-V plane. This fact, along with the lack of electrochemical cell behavior, suggests that ionic conductivity is not present. Therefore



Figure 25. The variable temperature d.c. conductivity data for Li<sup>+</sup>(TMPAND)Na<sup>-</sup> obtained in a 2-probe conductivity apparatus.100

Li<sup>+</sup>(TMPAND)Na<sup>-</sup>, an insulator below the phase transition, is a semiconductor with a band gap of 1.2 eV above approximately 200 K.

The high temperature static <sup>23</sup>Na NMR peak of Li<sup>+</sup>(TMPAND)Na<sup>-</sup> occurs at a chemical shift value of -60.7 ppm with a  $\Delta v_{1/2}$  value of approximately 1500 Hz. The chemical shift value, very characteristic of sodides, indicates that the sodium anion is in a highly symmetric environment with minimal overlap of its p orbitals with the surroundings.<sup>31</sup> When the temperature of the sample was lowered below the temperature of the phase transition, a second peak could be observed. Figure 26 shows the <sup>23</sup>Na static NMR spectra above and below the phase transition. The second rather broad peak occurred at approximately -10 ppm, a paramagnetic shift from the typical sodide peak at -60.7 ppm. If the temperature was raised above the phase transition, the second <sup>23</sup>Na peak at -10 ppm disappeared. It appears that only a portion of the sodium in the compound is involved in the process in the compound that causes the -10 ppm peak to occur since the peak at -60.7 ppm remains. To date, no transition of this type has been observed in any other sodide studied.

A possible explanation of the peak at -10 ppm is that the p orbitals in the sodium anion may interact with the lithium cation or are deformed by the crystal packing below the phase transition. Perhaps there are two different sodide sites in the lattice, the reason only some of the sodide anions have a paramagnetic shift.

The <sup>7</sup>Li static NMR spectra of Li<sup>+</sup>(TMPAND)Na<sup>-</sup> have a central transition at approximately -9 ppm. Unlike the sodide, the chemical shift is not temperature dependent; however, the value of the full



Figure 26. <sup>23</sup>Na static NMR spectra of Li<sup>+</sup>(TMPAND)Na<sup>-</sup> obtained at A) 189 K and B) 213 K.

width at half height  $(\Delta v_{1/2})$  does depend on temperature. Due to the absence of nuclear motion in crystalline solids, quadrupolar interactions, dipolar interactions and chemical shift anisotropy are not averaged and cause line broadening. Therefore, it is not totally unexpected that an increase in temperature would cause line narrowing due to an increase in molecular motion. At the phase transition, there was also a sharp break in the plot of the value of  $\Delta v_{1/2}$  versus temperature as shown in Figure 27. The sharp change in the value of  $\Delta v_{1/2}$  may be due in part to an large increase in molecular motion above the transition.

Although the crystal structure of Li<sup>+</sup>(TMPAND)Na<sup>-</sup> is not known, that of an analogous crystal Li<sup>+</sup>(TMPAND)BPh<sub>4</sub><sup>-</sup> has been determined.<sup>113</sup> The dipolar interaction was calculated with the Van Vleck equation with the lithium-nitrogen and lithium-proton distances obtained from the crystal structure of the model salt.<sup>88</sup> A calculated value of 8200 Hz was obtained. This compares quite well with the experimental value of 7700 Hz for Li<sup>+</sup>(TMPAND)Na<sup>-</sup> obtained at 173 K where molecular motion is minimized in the sodide.

Not only could the central transition of the <sup>7</sup>Li static NMR spectra be observed, but also the satellite transitions. When the asymmetry parameter,  $\eta_Q$ , is assumed to be zero, the distance between the satellite transitions can be used to calculate the quadrupolar coupling constant for this compound. In Figure 28, the central transition observed in <sup>7</sup>Li static NMR as well as the satellite transitions are shown. The quadrupolar coupling constant (QCC) simply reflects different values of the electric field-gradient for the



Figure 27. Plot of the full width at half height versus temperature for the <sup>7</sup>Li static NMR spectra obtained for Li<sup>+</sup>(TMPAND)Na<sup>-</sup>. The solid-solid phase transition occurs at the temperature of the observed discontinuity in the curve.



Figure 28. <sup>7</sup>Li static NMR spectrum of Li<sup>+</sup>(TMPAND)Na<sup>-</sup> obtained at 203 K.

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<sup>7</sup>Li nucleus in different compounds. The value for QCC of .188 MHz at 173 K for Li<sup>+</sup>(TMPAND)Na<sup>-</sup> is quite close to the value obtained for LiCl of .192 MHz. This value of QCC for LiCl in the gas phase is for a contact ion pair.<sup>103</sup> This may also be the interaction that occurs between the lithium cation and sodium anion in Li<sup>+</sup>(TMPAND)Na<sup>-</sup>. The value of QCC was temperature dependent and the plot of the value of QCC versus temperatures is shown in Figure 29. The plot has a distinct break at the phase transition, however, the calculated contribution to the value of  $\Delta v_{1/2}$  due to quadrupolar interactions is much less than 80 Hz.<sup>114</sup>

Through a combination of <sup>7</sup>Li and <sup>23</sup>Na static NMR spectral data, a possible explanation of the observed behavior can be proposed. At temperatures below the phase transition, the crystal structure of the compound may be locked in a conformation that increases the interaction between the lithium cation and sodium anion, perhaps through the formation of a contact ion pair. This would explain the large QCC value obtained from the <sup>7</sup>Li NMR data as well as the second paramagnetic chemical shift in the <sup>23</sup>Na NMR at low temperatures. According to this model, once the temperature of the compound was increased above the temperature of the phase transition, an increase in molecular motion or a conformational change in the crystal would cause the interactions between the cation and anion to decrease. This would be reflected in a sharp decrease in the value of QCC and the disappearance of the second more paramagnetic chemical shift in the <sup>23</sup>Na static NMR spectra. Single crystal X-ray data, especially if performed at temperatures both



Figure 29. Plot of the Quadrupolar Coupling Constant (QCC) calculated from <sup>7</sup>Li static NMR spectra of Li<sup>+</sup>(TMPAND)Na<sup>-</sup> versus the temperature of the sample. The solid-solid phase transition occurs at the temperature of the observed discontinuity in the curve.

above and below the phase transition, would be required to substantiate this explanation.

The lithium electride was also synthesized with the complexant TMPAND. When the sample was tested for methylamine, however, solvent was detected in the crystals. It is not known whether the methylamine is a regular part of the crystal lattice or simply due to residual solvent. Since solvent was present in the crystals, some of the general properties reported here, may or may not change when a pure electride is synthesized and characterized.

Although DSC data were collected, no reproducible exothermic peak could be observed, therefore the decomposition temperature is not known. The magnetic susceptibility of the electride was recorded for two different syntheses. The plots of  $1/\chi_e^{m}$  (emu/mole) versus temperature are shown in Figure 30. The samples follow the Curie-Weiss law. The more paramagnetic sample contained 29  $\pm$  1 percent unpaired electrons with a Weiss constant of  $-24 \pm 9$  K for data above 40 K. The less paramagnetic sample shown by the plus symbols in Figure 30, contained only 12  $\pm$  0.3 percent unpaired electrons with a Weiss constant of  $-18 \pm 5$  K when determined for data obtained above 40 K. The samples did not appear to be field dependent and the Weiss constants indicate the presence of antiferromagnetic interactions.

Since 100 percent unpaired electrons are expected for a pure electride, the Li<sup>+</sup>(TMPAND)e<sup>-</sup> may contain  $CH_3NH^-$  as an anion as with the lithium sodide synthesized with the TMTCY complexant. Part of the difficulty in the use of TMPAND as a complexant is the



Figure 30. Magnetic susceptibility plot of  $1/\chi_e^m$  versus T for Li<sup>+</sup>(TMPAND)e<sup>-</sup> obtained for two different syntheses. The squares represent the sample with 29 percent unpaired electrons run at 3, 5 and 7 kG. The plus symbols represent the sample with 12 percent unpaired electrons run at 5 and 7 kG.

extremely slow rate at which this complexant is able to complex the lithium cation, even at room temperature.<sup>113</sup>

<sup>7</sup>Li MAS NMR data obtained on the more paramagnetic electride sample contained two NMR peaks at 46 and 33 ppm with a rather rolling baseline when originally placed in the Bruker WH instrument at 180 K. When the sample was warmed to 220 K, only two peaks were observed, one at 36 ppm due to the compound Li<sup>+</sup>(TMPAND)e<sup>-</sup> and one at 260 ppm the observed chemical shift of lithium metal. The rather large paramagnetic shift of the sample indicates the presence of unpaired electrons. Other than the lithium metal peak, only one peak was observed for the sample. Therefore, any other lithium species present must have been broadened into the baseline, since DSC and magnetic susceptibility results indicated that this was not a homogeneous sample.

Data collected for both compounds are promising, and the Li<sup>+</sup>(TMPAND)Na<sup>-</sup> compound exhibits some interesting properties. Since the value of QCC for <sup>7</sup>Li has been determined, <sup>6</sup>Li static NMR spectra could yield the ratios of the quadrupole moment for <sup>7</sup>Li/<sup>6</sup>Li. The determination of spin-lattice relaxation times for <sup>7</sup>Li would allow the correlation of relaxation time and the value of the QCC for the compound Li<sup>+</sup>(TMPAND)Na<sup>-</sup>. In order to synthesize a pure electride, the kinetics of the complexation of the lithium cation by TMPAND at low temperatures in methylamine should be investigated. Properties of other fully methylated aza analogs of cryptand should be pursued, not only for their unique properties, but also in the attempt to form more thermally stable alkalides and electrides.

### **IV. ETHYLAMINE SOLUTIONS**

### IV.A. Introduction

It has been observed that addition of lithium metal to a solution of starting materials in methylamine inhibited the decomposition process in the synthesis of other alkalides and electrides. These Li/methylamine solutions appeared to be more stable than equivalent solutions that did not contain lithium metal. $^{86,115}$  M. Faber also observed that methylamine enhances the solubility of lithium in certain solvents. $^{19}$  For example, lithium is insoluble in 2-aminopropane but a solution of Li<sup>+</sup>(CH<sub>3</sub>NH<sub>2</sub>)<sub>4</sub> is soluble in this solvent. Li/methylamine solutions also appeared to increase the solubility of other alkali metals in solution.

In the absence of complexing agents, sodium metal is only slightly soluble in methylamine.<sup>19</sup> However, concentrated solutions of sodium metal form in the presence of  $\text{Li}^+(\text{CH}_3\text{NH}_2)_4$ . Similar results were found when sodium was replaced by rubidium. It was presumed that the concentrated solutions had the stoichiometry  $\text{Li}^+(\text{CH}_3\text{NH}_2)_4\text{M}^-$ , where M<sup>-</sup> is Na<sup>-</sup> or Rb<sup>-</sup>. Optical absorption spectra of thin films of Li/CH<sub>3</sub>NH<sub>2</sub>/Na solutions contained a peak at 660 nm as expected for a sodide. However, attempts by O. Fussa to isolate the compound Li<sup>+</sup>(CH<sub>3</sub>NH<sub>2</sub>)<sub>4</sub>Na<sup>-</sup> were unsuccessful.<sup>116</sup>

L. E. H. McMills extended the methylamine assisted solubilization of O. Fussa and M. Faber to other solvents.<sup>19</sup> The studies of the Li/methylamine systems were extended to include a more extensive study of the magnetic properties of these systems,

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specifically <sup>7</sup>Li and <sup>23</sup>Na solution NMR spectra. The Li<sup>+</sup>(amine)<sub>x</sub>Nasystems were studied from x = 4 to 16 by J. Kim and L. E. H. McMills. Table 7 contains the lithium chemical shifts for x = 4 at several temperatures in methylamine and ethylamine.<sup>65</sup> The value in ethylamine is consistent with that expected for a diamagnetic compound that contained lithium as a cation while the temperaturedependent shift in methylamine suggests the presence of some paramagnetic species. Table 8 gives the lithium chemical shifts at different temperatures for the known compound Li(NH<sub>3</sub>)<sub>4</sub>.<sup>18,65</sup>

Table 7. <sup>7</sup>Li NMR chemical shift values obtained for Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Na<sup>-</sup> and Li<sup>+</sup>(CH<sub>3</sub>NH<sub>2</sub>)<sub>4</sub>Na<sup>-.65</sup>

Compound	<u>Temperature (K)</u>	<u>Chemical Shift (ppm)</u>
Li <sup>+</sup> (CH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> ) <sub>4</sub> Na <sup>-</sup>	253	2.1
	233	2.1
	213	2.0
Li <sup>+</sup> (CH <sub>3</sub> NH <sub>2</sub> ) <sub>4</sub> Na <sup>-</sup>	253	9.0
	233	7.4
	213	5.6

The  $Li(NH_3)_4$  system is of particular interest since the liquid phase of this compound is a nearly free electron metal and the solid is a highly correlated metal below 80 K.<sup>18</sup> When ammonia is replaced by methylamine, the liquid is metallic but never reaches the nearly free electron behavior found in concentrated lithium/ammonia systems.<sup>18</sup>, <sup>117</sup> The behavior of  $Li(CH_3NH_2)_4$  remains that of a highly correlated metal.

Table 8. <sup>7</sup>Li NMR chemical shift values obtained for  $Li(NH_3)_4$ .<sup>65</sup>

<u>Temperature(K)</u>	<u>Chemical Shift (ppm)</u>	<u>Δν<sub>1/2</sub> (ppm)</u>
200	19.9	1.4
213	20.3	1.4
233	20.8	1.5
203	20.0	1.7

While the lithium sodide systems studied with the solvent ethylamine are diamagnetic compounds, the systems  $Li^+(CH_3CH_2NH_2)_4K^-$  and  $Li^+(CH_3CH_2NH_2)_4Cs^-$  studied in collaboration with M. DeBacker display some unexpected properties. These compounds may lie on the border of the metal to non-metal transition.

#### IV.B. Theory

In his view of the transition between metallic and insulating states, Mott considered an array of hydrogen atoms.<sup>118</sup> At high densities, the electron gas screens the positive ions and the electrons are itinerant. As the density decreases, the electrons are captured by the ionic cores and the material becomes nonconducting. The Mott criterion predicts whether a metallic or nonmetallic state exists and is given in equation 4.1.

$$n_c^{1/3}a^* = 0.26$$
 (4.1)

where  $n_c$  is the critical carrier concentration and  $a^*$  is the value of the effective Bohr radius.<sup>118</sup> Classical percolation, in which small metallic regions permeate an insulating medium and provide conducting paths, as well as non-interacting scaling theory suggested by Abrahams are other models proposed to explain the metal to insulator transition.<sup>119,120</sup>

In the metallic state, itinerant electrons produce the electrical, magnetic and optical properties associated with metals. The transition from metallic to insulating behavior is accompanied by a marked change in electrical conductivity. In a semiconductor or insulator, the electrical conductivity increases with temperature while it decreases with temperature in a normal metal.

The itinerant electrons in a metal also exhibit a reflectance spectrum that has a sharp cutoff at the plasma frequency.<sup>121</sup> It is this reflectance that is responsible for the metallic glitter of metals. However, this single observation cannot be used to unambiguously judge metallic character.

The magnetic properties of localized unpaired electrons are also significantly different from itinerant electrons in a metal. In contrast to the Curie law behavior of localized, non-interacting electrons, the Pauli susceptibility of itinerant electrons is essentially independent of temperature. Itinerant electrons are not spatially localized, nor do they respond independently to the magnetic field. The Pauli susceptibility is considerably smaller than the corresponding Curie value, even at room temperature.

# IV.C. Experimental

## 1. Sample Preparation

Samples of the compounds studied were prepared in the quartz SQUID cell shown in Figure 31. Since the solutions are quite volatile, a Kel-F squid bucket could not be used since loss of sample would occur upon loading and during decomposition of the sample. Therefore, a cell was designed that allowed the sample to be manipulated on a vacuum line during preparation while permitting one to permanently seal the sample for magnetic susceptibility measurements. Before the specific amount of metal to be used was calculated, the amount of solvent was determined. A small glass solvent bottle or break seal ampule was weighed, then approximately 0.2 ml of purified ethylamine was distilled into the container. The difference in weight between the full and empty container was used to determine the weight of ethylamine.



Figure 31. Schematic diagram of the quartz SQUID cell.

Once the amount of ethylamine had been determined, the amount of alkali metal necessary to obtain the correct stoichiometry in the solutions, Li:4  $CH_3CH_2NH_2$ :X where X = Na, K, and Cs, was calculated. After the quartz SQUID cell was evacuated to a pressure of 2 x 10<sup>-5</sup> Torr, the cell was placed in a helium glove box and the calculated amount of alkali metal was added to the cell. Due to the "sticky" nature of alkali metals and the necessity to have exact stoichiometric amounts, the metals were chilled for several minutes before they were placed in the SQUID cell. Cooling the metals seemed to keep them from sticking to the sides of the cell and the loss of small amounts of metal was minimized. Once the metal had been added, the SQUID cell was sealed with a stop-cock and removed from the dry box. The metals were kept under helium atmosphere until evacuated to a pressure of 2 x 10<sup>-5</sup> Torr. The metals were then frozen at 77 K as the cooled ethylamine was slowly distilled over the metals. Care must be taken in the distillation since these solutions are extremely sensitive and tend to "bump". If the lithium metal "bumped" above the line of the seal-off, the quartz SQUID cell cracked when the lithium metal was heated during the seal-off. Once all of the solvent had been distilled over the metal, then a quartz seal-off was made approximately 2 cm from the bottom of the hook on the SQUID cell. The sample was kept at cryogenic temperatures until loaded in the NMR instrument or SQUID susceptometer.

#### 2. NMR

The NMR spectra and the magnetic susceptibility data for each compound were obtained on the same sample. In order to obtain NMR spectra on the sample contained in the SQUID cell, a 10 mm NMR tube was used. Kimwipes were packed in the bottom of the cooled NMR tube in order to place the sample on the same level as the NMR coil in the Bruker 180 MHz instrument. A small amount of Kimwipe was also packed on top of the SQUID cell to prevent sample movement in the cooled NMR tube that might cause breakage when the sample was loaded in the instrument.

Variable temperature <sup>7</sup>Li and <sup>133</sup>Cs solution NMR spectra were obtained at 69.95 and 23.6 MHz respectively on a Bruker WH 180 MHz (proton frequency) NMR spectrometer operating at a field strength of 4.2277 T, with 4  $\mu$ sec pulse lengths and 0.25 to 1 second delay times. The temperature was controlled by the flow of nitrogen spinning gas through a liquid nitrogen heat exchanger and then warming the gas with an in-line heater. After the samples had been loaded into the NMR tube as described above, the sample was loaded into a precooled NMR probe. The sample temperature was monitored with a thermocouple placed in the gas stream at a point just ahead of where the gas entered the spinner.

# 3. Magnetic Susceptibility

Magnetic susceptibilities were measured with an S.H.E. 800 Series SQUID magnetometer. Samples were loaded into a quartz SQUID cell as described in the sample preparation, then transported and loaded at cryogenic temperatures into the susceptometer by a string tied to the hook on the SQUID cell. The samples were loaded into the instrument by zero field cooling the sample then applying a field of 3 kG. A field study was obtained at 3 and 7 kG over the temperature range 2 to 220 K. The sample was then placed in a constant temperature bath at approximately 223 K for several days. Data were then obtained at the same fields with the same loading procedure to determine if "aging" of the sample changed magnetic properties. The NMR data obtained by L. E. H. McMills for the compound  $Li^+(CH_3CH_2NH_2)_4Na^-$  were dependent on the "age" of some samples.<sup>65</sup>

Once the susceptibility of the "live" sample had been measured, the background susceptibility was determined and subtracted from that of the live sample. The background susceptibility was obtained by allowing the live sample to decompose to a diamagnetic product and rerunning the sample. Since the decomposed samples are diamagnetic and provide a direct measure of the atomic susceptibility, this procedure allows one to obtain the electronic contribution to the susceptibility. Since volatile gases are generated upon decomposition and contained in the volume of the small sealedoff SQUID cell, care must be taken in handling the decomposed sample. The sample was decomposed and loaded into the SQUID susceptometer behind a blast shield. The SQUID cell of the decomposed sample was also destroyed behind a shield.

## IV.D. Results and Discussion

Although the NMR chemical shifts for the <sup>7</sup>Li and <sup>23</sup>Na nuclei in Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Na<sup>-</sup> have been investigated extensively,<sup>65</sup> the magnetic susceptibility of this sodide was not studied. The <sup>7</sup>Li NMR chemical shift at 2 ppm indicates the lithium cation is well-shielded by the ethylamine molecules.<sup>65</sup> The chemical shift of the sodium anion at -59 ppm is consistent with the value obtained for other sodides.<sup>47,55</sup>

The magnetic susceptibility data for the compound  $Li^+(CH_3CH_2NH_2)_4Na^-$  are shown in Figure 32. The diamagnetic susceptibility of an atom is proportional to the ionic radius. The halide anions were used to predict the value of the diamagnetic susceptibility of the sodide anion. The known ratios of the ionic radii squared and the corresponding diamagnetic susceptibilities of the halide ions were compared. When this comparison is extended to the sodide anion with a radius of 2.5 Å,<sup>72</sup> a value of approximately -8 x 10<sup>-5</sup> emu/mole is obtained for the diamagnetic susceptibility of Na<sup>-</sup> based on the Languin formula.<sup>122</sup> This value is very close to the





Figure 32. Magnetic susceptibility plot of  $\chi_e^m$  versus T for Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Na<sup>-</sup> obtained at two different fields (3 and 7 kG) and two different times, the initial data collection and the data collection after the sample had "aged".

experimental value obtained for the sodide anion in Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Na<sup>-</sup> of  $-9 \pm 1.5 \times 10^{-5}$  emu/mole. This compares well with the value obtained by D. Issa of  $-10.5 \times 10^{-5}$  emu/mole for Na<sup>-</sup> in Cs<sup>+</sup>(18C6)<sub>2</sub>Na<sup>-</sup>.<sup>123</sup>

One of the problems with the magnetic susceptibility data for the sample is the unexpected field dependence of the magnetic susceptibility. The residual field in the SQUID magnometer would have to be on the order of 500 G to obtain the magnitude of field dependence observed in the sample. In order to determine the origin of the field dependence, the quartz tube of the SQUID cell was run separately. Although field dependence was observed, this could be attributed to a residual field of 50 G. It is therefore unlikely that the field dependence of the sample is due to the SOUID cell or residual field. M. Kuchenmeister obtained field dependent data for a sample of pure lithium metal. The residual field in the SQUID magnometer would have to be on the order of 600 G to obtain the magnitude of field dependence observed for the lithium metal sample.<sup>124</sup> Therefore, the field dependence of the  $Li^+(CH_3CH_2NH_2)_4Na^-$  sample appears to be due to a field dependent impurity in the lithium metal. The impurity does not contribute to the magnetic susceptibility of the decomposed sample or it would be subtracted out with the diamagnetic background of the decomposed sample. The impurity might be destroyed during the decomposition of the sample. The field dependence is likely to be the result of a small amount of ferromagnetic material such as iron.

In contrast to the diamagnetism of the sodide, the compounds  $Li^+(CH_3CH_2NH_2)_4K^-$  and  $Li^+(CH_3CH_2NH_2)_4Cs^-$  are paramagnetic.

Their magnetic susceptibility is similar to the susceptibility data of liquid Li(NH<sub>3</sub>)<sub>4</sub> which has a temperature independent value of  $60 \times 10^{-6}$  emu/mole, consistent with a Pauli metal.<sup>18</sup> Figure 33 shows a plot of  $\chi_{molar}$  versus temperature obtained at two different fields. The data taken at a field of 7 kG at low temperatures appear temperature independent and paramagnetic. The value of the molar susceptibility, approximately  $65 \times 10^{-6}$  emu/mole, is quite close to the value of the known metal Li(NH<sub>3</sub>)<sub>4</sub>.<sup>18</sup> For the data obtained at a field of 7 kG, the sample became more paramagnetic above a temperature of 140 K. A small amount of K<sup>-</sup> might dissociate to form potassium metal and electrons at high temperatures. This is one possible explanation of the increase in paramagnetic behavior in the sample.

Unlike the Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Na<sup>-</sup> sample, the field dependence in the Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>K<sup>-</sup> sample cannot be attributed completely to a paramagnetic contaminant. A residual field on the order of 1.6 kG would be necessary to account for the field dependence of the susceptibility for the sample at 3 and 7 kG in the "aged" sample. The potassium metal used to synthesize the compound was never tested for field dependent behavior, therefore, a new source of field dependent contamination may be due to the potassium metal as well as the lithium metal. If the sample is field dependent, the NMR chemical shift may also be field dependent. Variable field NMR data for the <sup>7</sup>Li chemical shift would be of interest to determine if the sample is field dependent or the field dependence is due to the impurity.



Figure 33. Magnetic susceptibility plot of  $\chi_e^m$  versus T for Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>K<sup>-</sup> obtained at two different fields (3 and 7 kG) and two different times, the initial data collection and the data collection after the sample had "aged".

The temperature dependent increase in susceptibility at higher temperatures is reflected in the chemical shift value of the <sup>7</sup>Li peak for Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>K<sup>-</sup>. As with the susceptibility, the chemical shift value of the <sup>7</sup>Li peak increases at higher temperatures with a value of approximately 18 ppm at 210 K. This value is more paramagnetic than the chemical shift value of 2 ppm for the diamagnetic compound Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Na<sup>-</sup> in the same temperature region.<sup>65</sup> The value of the <sup>7</sup>Li chemical shift of the known metallic compound Li(NH<sub>3</sub>)<sub>4</sub> of 20.3 ppm at 213 K is quite close to the value obtained for Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>K<sup>-</sup>. A plot of the

chemical shift value of  $Li^+(CH_3CH_2NH_2)_4K^-$  versus temperatures is shown in Figure 34. In the temperature range of 253 to 193 K for very concentrated Cs/ammonia solutions, the variation in chemical shift versus temperature is linear.<sup>80</sup> In these Cs/ammonia solutions, the electrons are delocalized and the solution has metallic character.<sup>125</sup>

The same temperature dependence is also observed in the <sup>7</sup>Li chemical shift of the compound Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Cs<sup>-</sup> and is shown in Figure 35. The <sup>7</sup>Li NMR data for this compound were obtained in a temperature region where the magnetic susceptibility of the compound became more paramagnetic with increasing temperature. The <sup>7</sup>Li peak was sharp and relatively narrow, with a value of  $\Delta v_{1/2}$  of less than 350 Hz. <sup>133</sup>Cs NMR data for Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Cs<sup>-</sup> consisted of a broad rolling baseline with no distinguishable peak for data collected over 15,000 scans.

The magnetic susceptibility data for the "aged" sample have a temperature independent value of approximately  $105 \times 10^{-6}$ 



Figure 34. Plot of the <sup>7</sup>Li NMR chemical shift value for the compound Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>K<sup>-</sup> versus temperature.



Figure 35. Plot of the <sup>7</sup>Li NMR chemical shift value for the compound Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Cs<sup>-</sup> versus temperature.

emu/mole below 120 K at a field of 7 kG. Between 120 K and 140 K, the magnetic susceptibility contains a discontinuity as shown in Figure 36 for the 7 kG data. This change in susceptibility might be due to a phase change in the compound, however no DSC data have been obtained for these compounds. At higher temperatures (180 K and above for the 7 kG as well as the 3 kG data that are shown in Figure 37) the susceptibility becomes more paramagnetic with increasing temperature. As with the compound  $Li^+(CH_3CH_2NH_2)_4K^-$ , this increase towards more paramagnetic behavior may be due to Cs<sup>-</sup> dissociating to cesium metal and e<sup>-</sup>. The Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Cs<sup>-</sup> magnetic susceptibility data in Figure 37 for the 3 kG field study show two different curves at low temperatures. The top curve in both the initial data collected and the data obtained for the "aged" sample had a more paramagnetic susceptibility for the sample when it was rapidly cooled to 5 K at zero field followed by the application of a field and data collection. The lower more diamagnetic curve in each of the data sets shown was obtained by slowly cooling the sample in a field of 3 kG; this effect disappeared at higher fields. The field dependence of the susceptibility data for  $Li^+(CH_3CH_2NH_2)_4Cs^$ was of the same magnitude as that of the lithium metal. The effect of the lithium impurity might be eliminated by purification of the metal and should be investigated.

If the individual atoms are sufficiently large or their density is sufficiently high, the valence electrons which had been bound to their respective atoms or ions are set free via mutual polarization and the solid becomes metallic.<sup>126</sup> K. F. Herzfeld recognized this link between atomic properties, density and the metallic state.<sup>127</sup> The



Figure 36. Plot of  $\chi_e^m$  versus T for Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Cs<sup>-</sup> obtained at 7 kG for two different time periods, the initial data collection and the data collection after the sample had "aged".



Figure 37. Plot of  $\chi_e^{m}$  versus T for Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Cs<sup>-</sup> obtained at 3 kG for two different time periods, the initial data collection and the data collection after the sample had "aged".

two properties that are of importance are the force that holds an ionizable electron in place versus the density of valence electrons in the solid. The gaseous alkali metal atoms have positive electron affinities that range from 0.62 eV for lithium to 0.47 eV for cesium.<sup>128</sup> Therefore if the density of the ethylamine solutions presented here are equivalent, the force that hold the ionizable electron decreases from sodium to cesium. This decrease in force could cause a non-metal to metal transition in these ethylamine systems as one progresses from sodium metal to cesium metal.

Although the data that have been presented are very preliminary, the Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>K<sup>-</sup> and Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Cs<sup>-</sup> systems do not have the diamagnetic susceptibility nor the <sup>7</sup>Li chemical shifts expected for an alkalide. As with the Li(NH<sub>3</sub>)<sub>4</sub> systems, the behavior of these new systems appears more metallic in nature.<sup>18</sup> For example, the Fermi temperature of the compound Li(NH<sub>3</sub>)<sub>4</sub> is 6,300 K while the Fermi temperature of the compounds Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>K<sup>-</sup> and Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Cs<sup>-</sup> are 5,800 K and 3,600 K respectively.<sup>18</sup> The Fermi temperature is related to the energy per electron in the ground state and a simple way to compare the Pauli paramagnetism of a metallic compound to the Curie law form is to find the temperature through the equation  $\chi = C/T$ . For comparison, the Fermi temperature of sodium metal is 37,700 K and decreases to 18,400 K for cesium metal.<sup>129</sup>

The data from the studies presented here must be reproduced on other samples. The nature of the difference in magnetic susceptibility data collected from "fresh" and "aged" sample must be investigated. Conductivity measurements could determine if these
compounds exhibit metallic behavior, but the conductivity for the compounds would be very difficult to obtain. If the ethylamine solvent were to partially evaporate or "bump", the lithium and cesium or potassium metal that was deposited would have metallic behavior. This would make it difficult to differentiate the conductivity of the ethylamine compounds from that of deposited metal. The optical absorption spectra of these systems could be obtained to look for the existence of a plasma edge.

The difficulty with these samples is the extreme sensitivity of the ethylamine solutions to temperature gradients that cause the solvent to "bump", which destroys the stoichiometry of the solution. Another difficulty is that metal precipitation cannot be easily detected. The intriguing properties of these systems suggest that the further characterization might verify a new class of "metallic" compounds.

## **V SPIN-ECHO NMR STUDIES**

## V.A. Introduction

Solid state NMR has been used extensively as a probe of the alkali metal environment in alkalides. Alkali metal NMR of the alkali metal anions has been observed for all of the anions synthesized, Na<sup>-</sup>, K<sup>-</sup>, Rb<sup>-</sup>, and Cs<sup>-</sup> in crystalline alkalides.<sup>47,57,58,59,60</sup> As shown in Chapters 2 and 4, both the cesium and lithium cation have also been studied extensively with single pulse solid state NMR techniques.

Due to the low sensitivity of the <sup>39</sup>K nucleus, single pulse techniques could not be used to obtain the NMR spectra of the potassium cation in solids. An added problem with this nuclei is the low magnetogyric ratio that leads to probe "ringing" and either distortion or severe broadening of the line. Oldfield et. al. reported the use of a two-pulse spin-echo sequence with appropriate phase cycling to obtain relatively undistorted second order powder pattern spectra of the nuclei <sup>39</sup>K in solids.<sup>64</sup> A study was undertaken to obtain <sup>39</sup>K and <sup>87</sup>Rb NMR spectra for alkalides or electrides that contain the complexed cations Rb<sup>+</sup> and K<sup>+</sup>. Rubidium nuclei were included in the study since previous attempts to obtain NMR spectra for the rubidium cation in solid state NMR experiments had been unsuccessful due to the large quadrupole moment of this nucleus.

A collaboration with L. E. H. McMills, J. Kim, and A. Ellaboudy to obtain data on both the potassium and rubidium cations was

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successful.<sup>65,66</sup> However, the lineshapes of the rubidium spectra were extremely difficult to phase. The reason for this difficulty in phasing the spectra appeared to be due to the extremely broad linewidths of the rubidium spectra. An NMR instrument with a fast digitizer and therefore a larger sweepwidth was used to repeat the data collection on the alkalides and electrides that contain rubidium cations. This work has been continued at the new NMR facility at Michigan State University in collaboration with J. Kim.

#### V.B. Theory

## 1. Quadrupole Coupling

As with the <sup>7</sup>Li nucleus with a spin I=3/2, the <sup>87</sup>Rb nucleus posseses a quadrupole moment. Nuclei with spins greater than 1/2 have quadrupole moments that can interact with electric field gradients and cause the 2I + 1 nuclear energy levels to shift and broaden. The Hamiltonian can be written as the sum of the Zeeman Hamiltonian,  $\mathcal{H}_{Z}$ , and the quadrupole Hamiltonian,  $\mathcal{H}_Q$ .

$$\mathcal{H} = \mathcal{H}_{Z} + \mathcal{H}_{Q} \quad (5.1)$$

The effect of  $\mathfrak{H}_Q$  is usually treated as a perturbation on the Zeeman terms. The quadrupolar Hamiltonian is given by:

$$\Re_{Q} = \frac{e^{2}qQ}{4I(2I-1)} \left[ 3I_{z}^{2} - I(I+1) + 1/2\eta (I_{+}^{2} + I_{-}^{2}) \right]$$
(5.2)

The axes X, Y, and Z are the principle axes of the tensor that describes the electric field gradient. The case  $\eta_Q = 0$  corresponds to axial symmetry of the electric field gradient of the nuclei when  $V_{XX} = V_{yy}$ . The asymmetry parameter,  $\eta_Q$ , is a measure of the deviation from axial symmetry and defined by:

$$\eta_{Q} = \frac{(V_{xxx} - V_{yy})}{V_{zz}} \qquad 0 \le \eta_{Q} \le 1 \quad (5.3)$$

There is no first order shift for the central transition for  $^{87}$ Rb, a half-integer spin. The second order effects are inversely proportional to the external magnetic field as defined by equation 1.4. In order to interpret the environment of the rubidium cation in the compounds studied by the spin-echo NMR technique it is necessary to determine the values of the asymmetry parameters and the quadrupole coupling constants (QCC) =  $e^2qQ/h$ .

## 2. Nuclear Relaxation

Nuclear spins that have been excited to higher energy levels return to lower energy states through the transfer of energy. This process is called relaxation. When the transfer of energy is to the surroundings of a particular nucleus, the variation of the population difference between the energy levels as a function of time follows an exponential decay curve with a time constant  $T_1$ , the spin-lattice relaxation time. The value of the spin-lattice relaxation time can be obtained from the following equation:

$$M_{+} = M_{0} [1 - \exp(-t/T_{1})]$$
 (5.4)

where  $M_0$  is the magnetization at infinite time and  $M_t$  is the magnetization or intensity of the signal at time t.

Nuclei exchange their magnetic energy with their surroundings indirectly through magnetic dipolar or electric quadrupole interactions. There are several principal types of magnetic interactions that contribute to spin-lattice relaxation in quadrupolar nuclei. For quadrupolar nuclei, there is an effective coupling of the nuclei to the surroundings. The non-spherical nuclear charge distribution can interact strongly with electric field gradients. Induced fluctuations in the electric field gradient at a particular quadrupolar nucleus due to lattice vibrations give rise to quadrupole relaxation.

Dipole-dipole interactions contribute to spin-lattice relaxation and occur when the nucleus experiences a fluctuating field due to motion of neighboring dipoles. In non-quadrupolar nuclei, this is an important magnetic interaction that contributes to spin-lattice relaxation. Another type of interaction is chemical shift anisotropy that arises due to chemical shielding of the nucleus and depends on the orientation of the molecule with respect to the magnetic field. Fluctuations in the weak magnetic secondary field due to the electrons surrounding the nucleus precessing in the magnetic field occur due to movement in the molecule. In contrast to spin-lattice relaxation, spin-spin relaxation is the decay of the transverse magnetization or spin coherence. Mechanisms of spin-lattice relaxation are also mechanisms of spin-spin relaxation.

## V.C. Experimental

## 1. Synthesis

The synthesis of alkalides and electrides has been described in detail<sup>29,34</sup>, and these techniques were used in the synthesis of the compounds used in this study. The methods used to synthesize the model salts used in the study, as well as the methods to grow single crystals of models salts have also been described in detail elsewhere.<sup>66</sup>

## 2. NMR

Static  $^{87}$ Rb spectra were obtained at 130.9 MHz on a Varian VXR-400 spectrometer equipped with a 45 to 165 MHz broad band probe. A solution of RbCl was used to determine the 90 degree solution pulse for this nucleus and half of this value, 1.7  $\mu$ sec, was used for the 90 degree solid pulse in experiments. The spin-echo pulse sequence is shown in Figure 38. Phase cycling was used to cause destructive interference of the free induction decay tails, but coaddition of the spin-echo signals.<sup>64</sup> The program for the spin-echo pulse sequence is given in Appexdix B. The spin-echo sequence allowed both pulses,  $P_1$  and  $P_2$ , and tau values, as well as the delay

time to be varied independently. With constant tau values and delay times, the pulse lengths were varied to determine the relative signal



Figure 38. The spin-echo pulse sequence.

to noise ratios for several combinations of pulse lengths. As shown in Figure 39 for the compound Rb<sup>+</sup>(18C6)Cl<sup>-</sup>, the largest signal to noise ratio was obtained for the 90° - 90° or 1.7 - 1.7  $\mu$ sec spin-echo pulse sequence. Optimum tau values were determined through the systematic variation of the tau values until the probe "ringing" was absent without significant loss of signal due to the decay of the FID. The optimized tau values determined by this method were tau1 = 50  $\mu$ sec and tau2 = 44  $\mu$ sec. The delay time, D<sub>1</sub>, between each pulse sequence was varied from 0.3 to 2.0 seconds, with most spectra obtained with a delay time of 0.5 seconds. The spectra of model salts were obtained at ambient temperature. The spectra of alkalides and electrides were obtained at 223 K. For low temperature data collection, cold nitrogen gas was used to control the temperature to within 0.3 K after 3 to 10 minutes equilibration time.

Single crystal NMR spectra were obtained with the spin-echo pulse sequence for  $Rb^+(C222)Cl^-$  on a home built single crystal NMR



Figure 39. The 87Rb NMR spectra obtained for Rb<sup>+</sup>(18C6)Cl<sup>-</sup> at different pulse lengths to determine the optimum pulse lengths for the spin-echo pulse sequence.

probe tuned for  $^{87}$ Rb. The experiments were performed on a Varian VXR-400 instrument at 130.9 MHz at ambient temperature. The angle of the sample in the single crystal probe was controlled by a one dimensional goniometer that can be rotated through 180 degrees. The single crystal of Rb<sup>+</sup>(C222)Cl<sup>-</sup> used in these experiments was mounted in a cubic box and data were collected along the a or b crystalline axes; these axes are equivalent.

The spin-spin relaxation time of the model salt was determined at four different orientations of the crystal with the pulse sequence shown in Figure 40. Tau values were varied from 20 to 230  $\mu$ sec with a delay time, D<sub>1</sub>, of 0.5 or 1 second for this experiment.



Figure 40. The pulse sequence used to determine the spin-spin relaxation time of Rb<sup>+</sup>(C222)Cl<sup>-</sup> at four different orientations of the crystal.

Data were fit with a simple exponential with KINFIT, a nonlinear curve fitting program.<sup>130</sup> The spin-lattice relaxation times were determined at the same four orientations used to determine the spin-spin relaxation time. The variable delay of the pulse sequence shown in Figure 41 was incremented from 0.005 to 1.0 seconds and the data fit with an exponential by KINFIT.



Figure 41. The pulse sequence used to determine the spin-lattice relaxation time of Rb<sup>+</sup>(C222)Cl<sup>-</sup> at four different orientations of the crystal.

V.D. Results and Discussion

## 1. 15C5 Complexes

The peak for the rubidium cation was observed in both  $Rb^+(15C5)_2Rb^-$  and  $Rb^+(15C5)_2e^-$ . The lineshape for the compounds was simulated with VMASS, a program written by J. Kim.<sup>66</sup> This program can be used to simulate either static or spinning NMR spectra lineshapes and accounts for chemical shift anisotropy, dipolar and quadrupolar interactions. For the rubidium NMR spectra simulations in this study, the chemical shift anisotropy interactions were assumed to be negligible.

The dominant feature in the NMR spectra of  $Rb^+(15C5)_2Rb^-$  is the narrow rubidium anion peak at -195 ppm. The quadrupolar interaction of the anion is estimated to be less than 2 MHz. From the small quadrupolar interaction observed and the chemical shift value of the rubidium anion, one can infer that the spherical symmetry of the 5s orbital for the anion is nearly unperturbed by surrounding charges and dipoles. When the spectra of  $Rb^+(15C5)_2Rb^-$  were expanded along the vertical axis, an underlying peak was observed and is believed to be due to the complexed rubidium cation,  $Rb^+(15C5)_2$ . The estimated value of the quadrupolar coupling constant (QCC) of the cation in  $Rb^+(15C5)_2Rb^-$  is 11 to 12 MHz, however; even after 23,000 scans the signal to noise ratio was poor and the asymmetry parameter could not be determined. The spectra of  $Rb^+(15C5)_2Rb^-$  and  $Rb^+(15C5)_2e^-$  are shown in Figure 42.

An NMR peak at a chemical shift value of -193 ppm in the compound  $Rb^+(15C5)_2e^-$ , shows that there was a small amount of  $Rb^+(15C5)_2Rb^-$  in the electride. The signal to noise ratio in this spectrum was poor, even after 43,000 scans. The value of the QCC for this compound was determined to be approximately 8 MHz. The difference in the values of the QCC constant indicates that the environment of the complexed rubidium cation in  $Rb^+(15C5)_2Rb^-$  is different from that of the rubidium cation in  $Rb^+(15C5)_2Rb^-$  is different from that of the electride is not known and therefore no direct comparison can be made. Although relatively narrow with a linewidth of approximately 650 ppm, the NMR peak for the rubidium cation in  $Rb^+(15C5)_2Na^-$  had an extremely poor signal to noise ratio, even after 24,000 scans. No simulations of this spectrum were performed.

Although the rubidium anion has been observed in single pulse and in spin-echo experiments, the rubidium cation could be observed in the spin-echo experiments in the 15C5 complexes only after several thousand scans and even then only with a poor signal to noise ratio. The poor signal obtained for these complexed cations



Figure 42. 87Rb NMR spectra of A) Rb+(15C5)<sub>2</sub>Rb<sup>-</sup> and B) Rb+(15C5)<sub>2</sub>e<sup>-</sup> obtained with the spin-echo pulse sequence.

might be due to an extremely short relaxation time for the cation, therefore most of the FID could have decayed before acquisition. When the tau values in the pulse sequence are shortened in attempts to correct this problem, baseline distortion becomes a problem. If the temperature at which the spectra were obtained were lowered, the spin-lattice relaxation time would increase and a better signal to noise ratio might be obtained for the complexed cation in these compounds.

## 2. 18C6 Complexes

NMR spectra were obtained for the alkalides  $Rb^+(18C6)Rb^-$  and  $Rb^+(18C6)Na^-$  with the spin-echo pulse sequence and the spectra are shown in Figure 43. Although fewer transients were observed, the relative signal to noise ratios for these compounds are better than the three 15C5 complexes studied. One possible explanation is that the relaxation time of the complexed cation has increased.

In contrast to the rubidium anion in  $Rb^+(15C5)_2Rb^-$ , the anion in  $Rb^+(18C6)Rb^-$  has a non-axially symmetric powder pattern. The rubidium anions in  $Rb^+(18C6)Rb^-$  form chains throughout the structure as shown in Figure 44 and the rubidium cation is in contact with the anion.<sup>131</sup> The non-axially symmetric lineshapes and second order quadrupolar broadened NMR spectra for the rubidium anion with a QCC value of 5 MHz are consistent with the highly anisotropic crystal structure. The large paramagnetic shift of the rubidium anion of approximately 70 ppm also suggests that there is



Figure 43. <sup>87</sup>Rb NMR spectra of A) Rb<sup>+</sup>(18C6)Na<sup>-</sup> and B) Rb<sup>+</sup>(18C6)Rb<sup>-</sup> obtained with the spin-echo pulse sequence. The solid lines are the observed spectra and the dotted lines the simulated spectra.



Figure 44. A cross section of the crystal structure of Rb+(18C6)Rbshowing the rubidium anion chains that are present.<sup>131</sup>

significant overlap of the p and d orbitals on the anion with its surroundings.

The rubidium cation in  $Rb^+(18C6)Rb^-$  has an  $\eta$  value of 0.16, therefore, neither the cation nor anion is in an axially symmetric environment. This is consistent with the crystal structure and the NMR data observed for the rubidium anion. The QCC value for the rubidium cation, asymmetry parameter, and chemical shift value in  $Rb^+(18C6)Rb^-$  of 11.2 MHz, 0.16 and 105 ppm respectively are quite similar to the values determined for  $Rb^+(18C6)Na^-$  of 10.8 MHz, 0.15 and 110 ppm respectively. Although the crystal structure of  $Rb^+(18C6)Na^-$  is not known, the similarities in the NMR data obtained for the rubidium cation in these two compounds suggest that the crystal structure of  $Rb^+(18C6)Na^-$  is similar to the crystal structure of  $Rb^+(18C6)Rb^-$ .

## 3. HMHCY Complex

The crystal structure of Rb<sup>+</sup>(HMHCY)Na<sup>-</sup> is known.<sup>74</sup> The separation between the Van der Waals surfaces of the cation and anion is between 0.02 and 0.22 Å. The asymmetry parameter of 0.8 as well as the large QCC value of 13 MHz reflects the nonsymmetric environment of the rubidium cation in the crystal structure. The spectra of the compound and the simulation are shown in Figure 45. This was the first time that the rubidium cation had been observed in a fully methylated aza analog of a crown ether by solution or solid state NMR techniques.



Figure 45. 87Rb NMR spectra of Rb<sup>+</sup>(HMHCY)Na<sup>-</sup> obtained with the spin-echo pulse sequence. The solid line is the observed spectrum and the dotted line is the simulated spectrum.

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## 4. C222 Complexes

The spin-echo NMR technique was used to obtain NMR spectra for several model salts and the alkalide Rb<sup>+</sup>(C222)Rb<sup>-</sup>. Table 9 CONtains the values of the QCC, asymmetry parameter and chemical shift values obtained for these compounds as well as the values obtained for the other compounds discussed in this chapter for COMParison. The rubidium cation in Rb<sup>+</sup>(C222)I<sup>-</sup> and Rb<sup>+</sup>(C222)SCN<sup>-</sup> model salts is not in an axially symmetric environment since both COMPounds have rather large asymmetry parameters determined from lineshape simulations of the powder patterns. The spectra of these two compounds are shown in Figure 46.

In contrast, the rubidium cation in the compounds  $Rb^+(C222)Cl^$ and  $Rb^+(C222)Rb^-$  is in an axially symmetric environment. The Spectrum of  $Rb^+(C222)Rb^-$  is shown in Figure 47. These differences in axial symmetry may be due to changes in the crystal packing in these compounds that are dependent on the anion. All of the rubidium cations complexed by the cryptand C222 have large Quadrupole coupling constants. The large electric field gradients Present in these compounds could be due to the close proximity of the unpaired electrons on the oxygens to the rubidium cation in the Cryptand. The average  $Rb^+$ -O bond distance in the compound  $Rb^+(C222)Rb^-$  is 2.96(6) Å.<sup>131</sup>

The rubidium anion in  $Rb^+(C222)Rb^-$  is in an axially symmetric environment; however, the line is broadened due to quadrupolar interactions. The crystal structure of this compound indicates that the rubidium anions form dimers.<sup>131</sup> This is similar to the anion

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Compound	OCC(MHz)	n	<u>δ(ppm)</u>
<b>Rb</b> +(15C5)2Rb- <b>*</b>	~11 to 12	?	~200
Rb+(15C5)2 <b>Rb</b> -+	< 2	?	-195
<b>Rb</b> +(15C5)2e <sup>-</sup> *	~8	?	~0
<b>Rb+</b> (18C6)Na <sup>-</sup>	10.8	0.15	110
Rb+(18C6) <b>Rb-*</b>	~5	>0	~70
<b>Rb+</b> (18C6)Rb <sup>-</sup>	11.2	0.16	105
Rb+(HMHCY)Na <sup>-</sup>	13.0	0.8	80
<b>Rb</b> +(C222)Cl <sup>-</sup>	16.4	0	70
<b>Rb+</b> (C222)I <sup>-</sup>	18.2	0.82	
<b>Rb</b> +(C222)SCN-	17.8	0.7	
Rb+(C222) <b>Rb</b> -	6.25	0	27
<b>Rb+</b> (C222)Rb <sup>-</sup>	16.6	0	70

Table 9.NMR parameters determined from the simulation of<br/>powder patterns from 87Rb NMR spectra.

QCC = quadrupole coupling constant  $\eta$  = asymmetry parameter  $\delta$  = chemical shift \* = estimated values

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Figure 46. <sup>87</sup>Rb NMR spectra of the model salts A) Rb<sup>+</sup>(C222)SCNand Rb<sup>+</sup>(C222)I<sup>-</sup> obtained with the spin-echo pulse sequence.



Figure 47. 87Rb NMR spectrum of Rb+(C222)Rb- obtained with the spin-echo pulse sequence. The solid line is the observed spectrum and the dotted lines are the simulated spectra.

chains in the compound Rb+(18C6)Rb<sup>-</sup>. Both compounds have relatively large QCC values for the rubidium anion combined with a paramagnetic chemical shift from the expected value for a rubidium anion in a spherically symmetric 5s orbital. The NMR lineshape of the rubidium anion is quite sensitive to the environment of the anion in the crystal structure.

## 5. Single Crystal NMR

Although the lineshapes of the experimental data could be simulated, the relative intensities of the powder pattern of the simulated spectra did not always correspond to the experimental The transmitter offset was changed to center it on different data. portions of the powder pattern but this did not correct the difficulty with relative intensities in the powder pattern. Therefore the problem does not appear to be the inability of the pulse to excite the entire linewidth of the powder pattern. Single crystal NMR data for the model salt  $Rb^+(C222)Cl^-$  were obtained by J. Kim to determine the reason for the loss of relative intensity in some of the powder patterns. The single crystal NMR orientation plot for Rb<sup>+</sup>(C222)Cl<sup>-</sup> is shown in Figure 48. The single crystal data were simulated with KINFIT and XTAL, a program obtained by J. Kim for the simulation of single crystal NMR data.66

The spin-lattice and spin-spin relaxation times were determined at four different orientation of the single crystal. As shown in Figure 49, the spin-lattice relaxation time does not appear to change significantly at the different orientations studied.



Figure 48. The single crystal 87Rb NMR orientation plot for the compound Rb+(C222)Cl<sup>-</sup>.



Figure 49. A) The <sup>87</sup>Rb NMR spectrum of Rb<sup>+</sup>(C222)Cl<sup>-</sup> obtained with the spin-echo pulse sequence for a powdered sample and B) Plot of the relaxation time (T<sub>1</sub> spin-lattice and T<sub>2</sub> spin-spin) versus chemical shift of the rubidium cation for four orientations of the single crystal Rb<sup>+</sup>(C222)Cl<sup>-</sup>.

However, the spin-spin relaxation time decreased from 154  $\mu$ sec at a chemical shift value of 800 ppm to 63  $\mu$ sec at a chemical shift value of -600 ppm for a different orientation of the single crystal.

This indicates that loss of spin coherence in the transverse axis for certain crystal orientations may be the cause of the relative intensity loss in portions of the powder pattern. Although the shape of the powder pattern can be simulated to determine the value of QCC and  $\eta$ , the relative intensities of the powder pattern between simulated and experimental data cannot be compared directly.

This study has shown that the spin-echo technique with phase cycling is a powerful tool in the determination of the environment of rubidium in alkalides and electrides. The fast digitizer on the Varian 400 MHz instrument at Michigan State University has allowed the observation of rubidium cation linewidths of over 2,000 ppm. The pulse program and optimal delay times that have been determined will allow routine determination of rubidium NMR spectra for new alkalides or electrides. The further study of spin-lattice and spin-spin relaxation time in these compounds would be of interest. This study may also be extended to  $^{85}$ Rb for the comparison of the value of the QCC for the observed powder patterns obtained by NMR methods as well as the comparison of the relative relaxation times of  $^{87}$ Rb/ $^{85}$ Rb in alkalides and electrides.

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## VI. CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

The chemical shift of the cesium cation is extremelý sensitive to the unpaired electron density at the nucleus. 133Cs NMR has proven to be a useful tool in the study of the electrides Cs<sup>+</sup>(15C5)<sub>2</sub>e<sup>-</sup> and Cs<sup>+</sup>(18C6)<sub>2</sub>e<sup>-.76</sup> The fractional atomic s character of the electron in these compounds is quite small, an indication that the electrons have only weak overlap with the complexed cation. This is further evidence that the electron density in electrides is centered in the empty anionic cavities present in the crystals. If a high-quality single crystal X-ray study of an electride could be done in which the background noise is below the electron density of the trapped electron, the unpaired electron in the cavities might be observed. This would offer further proof of the location of the electron in electrides.

The study of  $Cs^+(15C5)(18C6)Na^-$ , a mixed crown ether system, has shown the potential to "fine-tune" the characteristics of alkalides and electrides based on the appropriate choice of crown ethers and alkali metal cations. The problem with these systems arises from the difficulty in obtaining pure compounds for the study of bulk properties. However, the synthesis of a pure compound  $Cs^+(15C5)(18C6)e^-$  would allow the study of a system intermediate between the two electrides  $Cs^+(15C5)_2e^-$  and  $Cs^+(18C6)_2e^-$ , and should yield information about how structure affects properties. Therefore, the X-ray structures and the further characterization of the properties should be pursued for these compounds.

The study of alkalides and electrides that contain fully methylated aza analogs of crown ethers and cryptands has resulted in the synthesis of several new and reasonably stable compounds. Studies of the compound Cs<sup>+</sup>(HMHCY)Na<sup>-</sup> have demonstrated that defect electrons can cause significant changes in the properties observed. The electron dopant level in this compound was 33 percent, but attempts to dope Rb<sup>+</sup>(HMHCY)Na<sup>-</sup> or K<sup>+</sup>(HMHCY)Na<sup>-</sup> to large levels have not been made. Because trapped electrons can affect the properties and may be present at high levels, the electron dopant levels in alkalides should be more systematically studied when a compound is synthesized. This could be achieved by EPR or magnetic susceptibility measurements. A study to determine to what levels these systems can be doped would be of interest as well as the effect of dopant level on the physical properties. The ability to achieve extremely high dopant levels in Cs<sup>+</sup>(HMHCY)Na<sup>-</sup> may be due to a slow rate of decomplexation. The electride could not be synthesized as the system decomplexed upon solvent removal. Other systems such as Rb<sup>+</sup>(18C6)Rb<sup>-</sup> and Rb<sup>+</sup>(C222)Rb<sup>-</sup>, for which the pure electride is not known to exist, should also be doped with excess electrons and the resultant dopant levels and properties studied.

The compounds synthesized with TMTCY have allowed the observation of solvent in the crystal structure of alkalides for the first time. The sodide anion is not the only anion present in these systems (as an amide ion was also present) and a pure electride could not be synthesized. However, if a better "fit" were achieved between the cation and complexant such as in the case of tetramethyltetracyclen, an electride and pure sodide might be synthesized. The work done in the TMTCY system has also demonstrated the need, especially for lithium compounds to test for the presence of solvent in the crystals and to isolate crystals that have not been subject to high vacuum.

In contrast, the TMPAND complexant forms a pure sodide with no methylamine contamination. The use of DSC techniques in the investigation of the decomposition kinetics of Li<sup>+</sup>(TMPAND)Na<sup>-</sup> has shown the usefulness of these methods in the determination of the activation energy of decomposition. Further research on the decomposition kinetics and mechanisms would provide information that might be useful in the choice of complexants for the synthesis of more thermally stable alkalides and electrides. The OCC measured in Li<sup>+</sup>(TMPAND)Na<sup>-</sup> for <sup>7</sup>Li is the first time the value of OCC has been obtained for the complexed lithium cation in an alkalide or electride. Further studies of this type would allow the correlation of quadrupole coupling constants with <sup>7</sup>Li relaxation times. It would also permit comparison of the ratio of the values of QCC for  $^{6}Li/^{7}Li$ . The crystal structure of this compound should be obtained if possible, both above and below the phase transition. Once the kinetics of the complexation of the lithium cation by TMPAND at low temperatures in methylamine have been determined, the electride should be synthesized and its properties studied. The fully methylated aza analogs of cryptands show great potential as complexing agents and similar complexants should be used to synthesize additional alkalides and electrides.

The simplest amine systems presented,  $Li^+(CH_3CH_2NH_2)_4Na^-$ ,  $Li^+(CH_3CH_2NH_2)_4K^-$ , and  $Li^+(CH_3CH_2NH_2)_4Cs^-$ , showed a progression from the sodide, a diamagnetic material to the potasside and ceside which are paramagnetic. The characterization of these systems by magnetic susceptibility, EPR, NMR, and optical absorption should be pursued since further study may verify the supposition that these form a new class of "metallic" compounds. The electride  $Li(CH_3CH_2NH_2)_4$ , as well as the rubidide,  $Li^+(CH_3CH_2NH_2)_4Rb^-$ , should also be studied to complete the series. The characterization of more dilute solutions may also yield some insight into the properties of the more concentrated solutions presented in this study.

The  $^{87}$ Rb NMR data collected with the spin-echo pulse sequence have proven useful in the characterization of alkalides and electrides that contain a complexed rubidium cation. This technique can now be used in the routine study of new compounds. It could also be used to obtain the  $^{87}$ Rb NMR spectra for Li<sup>+</sup>(CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub>)<sub>4</sub>Rb<sup>-</sup>. Single crystal NMR data should be obtained for alkalides and electrides for comparison with the data already obtained for the model salt Rb<sup>+</sup>(C222)Cl<sup>-</sup>. The spin-lattice and spinspin relaxation times might also be determined for the complexed rubidium cation. The mechanisms of relaxation could then be correlated with the values obtained for QCC from the simulation of the experimental NMR lineshape and/or the variation of these parameters with crystal orientation. To make the best use of such data, the crystal structures must be determined by X-ray diffraction. **APPENDICES** 

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APPENDIX A

# APPENDIX A

Atom	x	У	Z	B(A2)
Na	0.0010(7)	0.6646(3)	0.8155(3)	8.9(1)
N1	0.052(1)	0.4876(5)	0.5756(4)	6.3(2)
N4	-0.248(1)	0.4447(5)	0.5452(4)	5.9(2)
N7	-0.006(1)	0.3834(5)	0.4700(4)	6.5(3)
N13	0.062(1)	0.5943(6)	0.2772(4)	6.5(3)
N16	0.014(1)	0.7461(5)	0.3347(5)	7.5(3)
N19	0.269(1)	0.6468(6)	0.3748(4)	7.7(3)
N101	-0.100(1)	0.5884(5)	0.4354(4)	7.0(3)
C2	-0.048(2)	0.4636(9)	0.6244(6)	9.9(5)
C3	-0.205(2)	0.454(1)	0.6111(6)	10.3(5)
C5	-0.245(1)	.3615(9)	0.5293(8)	12.0(5)
C6	-0.144(2)	0.3359(8)	0.4833(7)	11.6(5)
C8	0.115(2)	0.3675(8)	0.5137(6)	10.9(5)
C9	0.155(2)	0.4226(8)	0.5588(8)	11.1(5)
C10	0.145(2)	0.5590(7)	0.5941(6)	9.8(4)
<b>C</b> 11	0.032(2)	0.3746(7)	0.4028(5)	8.1(4)
C12	-0.397(1)	0.4810(9)	0.5345(7)	10.1(5)

Table of Positional Parameters and Their Estimated Standard Deviations

(4)
(4)
l <b>(6)</b>
l <b>(5)</b>
(4)
(4)
ł(6)
)(7)*
3(5)
l <b>(7)</b>
(5)
<b>i(5)</b>
F 3 1 5(

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: (4/3) \* [a2\*B(1,1) + b2\*B(2,2) + c2\*B(3,3) + ab(cos gamma)\*B(1,2)+ ac(cos beta)\*B(1,3) + bc(cos alpha)\*B(2,3)]

# Table of Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
N1	C2	1.41(2)	N16	C17	1.47(2)
N1	C9	1.46(2)	N16	C23	1.43(2)
N1	C10	1.49(2)	N16	Li	2.09(2)

<b>N74</b>	T :0	157	2710	<b>C</b> 10	
NI	L12	2.12(2)	N19	C18	1.51(2)
N4	C3	1.44(2)	N19	C20	1.42(2)
N4	C5	1.43(2)	N19	C24	1.45(2)
N4	C12	1.46(2)	N19	Li	2.07(3)
N4	Li2	2.09(2)	N101	C102	1.34(2)
N7	C6	1.48(2)	N101	Li	1.90(2)
N7	C8	1.43(2)	N101	Li2	1.93(2)
N7	C11	1.47(1)	C2	വ	1.41(2)
N7	Li2	2.06(2)	C5	<b>C</b> 6	1.38(2)
N13	C14	1.48(2)	C8	<b>C</b> 9	1.37(2)
N13	C21	1.52(2)	C14	C15	1.43(2)
N13	C22	1.46(2)	C17	C18	1.46(2)
N13	Li	2.14(2)	C20	C21	1.46(2)
N16	C15	1.47(2)	C102	Li2	2.58(3)

Numbers in parentheses are estimated standard deviations in the least significant digits.

# Table of Bond Angles in Degrees

Atom 1	Atom 2	Atom 3	Angle
C2	N1	С9	111.(1)
C21	N13	C22	13.(1)
C2	N1	C10	112(1)
<b>C2</b> 1	N13	Li	104.1(9)
C2	N1	Li2	107.4(9)
C22	N13	Li	116(1)

C9	)	N1	C10	108.9(9)
C1	5	N16	C17	111.(1)
C9	)	N1	Li2	101(1)
Cl	5	N16	C23	112.(1)
Cl	0	N1	Li2	116.5(9)
C1	5	N16	Li	,107.7(9)
C3		N4	C5	110.(1)
C1	7	N16	C23	109.(1)
C3	)	N4	C12	110(1)
C1	7	N16	Li	100(1)
C3		N4	Li2	106.9(9)
C2	3	N16	Li	116.(1)
C5	í	N4	C12	112(1)
C1	8	N19	C20	116.(1)
C5	5	N4	Li2	105.8(9)
C1	8	N19	C24	112.(1)
C1	2	N4	Li2	112.8(9)
C1	8	N19	Li	103.(1)
C6	)	N7	C8	113(1)
C2	0	N19	C24	108.(1)
C6	)	N7	C11	109(1)
C2	O	N19	Li	102.2(9)
C6	)	N7	Li2	102.1(9)
C2	4	N19	Li	116.(1)
C8		N7	C11	116.(1)
C1	02	N101	Li	111.(1)
C8		N7	Li2	104.9(9)
C1	02	N101	Li2	103.(1)
C1	1	N7	Li2	111.8(9)
Li		N101	Li2	131.(1)
C1	4	N13	C21	111.(1)
N1		C2	C3	120.(1)
C1	4	N13	C22	111.(1)
N4	l i i i i i i i i i i i i i i i i i i i	C3	C2	118.(1)
C1	4	N13	Li	102.1(9)
N4	ļ	C5	C6	118.(1)
N7	1	C6	C5	120.(1)
N1	6	Li	N19	88.8(9)
N7	7	C8	<b>C9</b>	121.(1)
NI	.6	Li	N101	124.(1)
NI		C9	C8	121.(1)
NI	.9	Li	N101	131.(1)
NI	13	C14	C15	115.(1)

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		-	
N1	Li2	N4	83.9(8)
N16	C15	<b>C14</b>	115.(1)
N1	Li2	N7	87.0(8)
N16	C17	<b>C18</b>	117.(1)
N1	Li2	N101	129.(1)
N19	<b>C18</b>	<b>C17</b>	116.(1)
N1	Li2	C102	108.8(9)
N19	C20	<b>C21</b>	118.(1)
N4	Li2	N7	86.7(8)
N13	C21	C20	113.(1)
N4	Li2	N101	126.(1)
N101	C102	Li2	46.9(8)
N4	Li2	C102	107.3(9)
N13	Li	N16	84.5(8)
N7	Li2	N101	129.(1)
N13	Li	N19	86.4(9)
N7	Li2	C102	160.(1)
N13	Li	N101	128.(1)
N101	Li2	C102	30.4(6)

Numbers in parentheses are estimated standard deviations in the least significant digits.
APPENDIX B

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## **APPENDIX B**

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#endif								
/* ssecho - solid state echo sequence modified Varian program								
d 1 1	p180 *****	d 2	p1-x *****	tau l	pw-y *****	tau2	acquire	
***** ******** ************************								
parameters:								
1	p180:	optional 180 pulse for t1 studies. if $p180 = 0$ , the delay d2 is ignored						
1	p1:	first	pulse, shou	ld be 90	degrees	h	A	
1	pw:	final then	final pulse, usually 90 degrees but sometimes less then 90 for spin i>3/2 nuclei					
•	compul:	if y, each 90 pulse is replaced by the composite pulse $135(x) - 90(-x) - 45(x)$ if n, conventional pulses are used						
Modification history								
110188 potentially negative delays removed -ehw 010389 Rx gating modified for 2.1 -ehw								
*/								
#include <standard.h></standard.h>								
pulsesequence ()								
L .	double	taul, tau2,	•					
/*	char initialize p taul = get tau2 = get	p180 comp parame val("ta val("ta	; ul[MAXSTH eters */ uu1") uu2")	<b>{</b> ];				

```
getstr("compul", compul);
p180 = getval("p180"0;
if (p1 == 0.0)
     p1 = pw
                       /* insure a value for p1 pulse */
if (p180 == 0.0)
     d2 = 0.0:
                      /* don't do d2 delay if no 180 pulse*/
status(A);
delay(d1);
status(B);
rgpulse(p180, zero, rof1, 0.0);
if (p180 > 0.0) /*if we have inversion-recovery */
ł
if (d2<= rof1) /* and d2 is smaller than amp turnon time*/
Ł
     rcvroff();
     delay(d2);
      }
     else
                 /* when d2 is long */
      Ł
     delay(d2 - rof1);
     rcvroff();
     delay(rof1);
      }
}
else
                 /* no inversion-recovery */
{
     rcvroff();
     delay(rof1);
}
if (compul[0] == 'y')
                 /* composite pulse experiment */
     fprintf(stdout, "ssecho - Using composite pulses/n")'
     hlv(ct, v1);
                       /* v1=0 0 1 1 2 2 3 3 4 4 5 5 6 6 7 7 */
                       /* v1=0 0 0 0 1 1 1 1 2 2 2 2 3 3 3 3 */
     hlv(v1,v1);
     dbl(v1,v3)l
                       /* v3=0 0 0 0 2 2 2 2 4 4 4 4 6 6 6 6 */
     add(one,oph,v2); /* v2=1 2 3 4 1 2 3 4 1 2 3 4 1 2 3 4 */
     add(v1,v2,v2); /* v2=1 2 3 4 2 3 4 5 3 4 5 6 4 5 6 7 */
     mod4(v2,v2);
                       /* v2=1 2 3 0 2 3 0 1 3 0 1 2 0 1 2 3 */
     add(oph,v3,v1); /* v1=0 1 2 3 2 3 4 5 4 5 6 7 6 7 8 9 */
     mod4(v1.v1);
                       /* v1=0 1 2 3 2 3 0 1 0 1 2 3 0 3 0 1 */
     add(two,v2,v3); /* v3=3 4 5 2 4 5 2 3 5 2 3 4 2 3 4 5.*/
     mod4(v3,v3);
                     /* v3=3 0 1 2 0 1 2 3 1 2 3 0 2 3 0 1 */
```

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           add(two,v1,v4); /* v4=2 3 4 5 4 5 2 3 2 3 4 5 4 5 2 3 */
           mod4(v4,v4); /* v4=2 3 0 1 0 1 2 3 2 3 0 1 0 1 2 3 */
           rgpulse(1.5 * p1, v4, rof1, 0.0);
                                                         È
           rgpulse(p1, v1, 0.0, 0.0);
           rgpulse(0.5 * p1, v4, 0.0, 0.0);
           rgpulse(1.5 * pw, v3, tau1, 0.0);
           rgpulse(pw, v2, 0.0, 0.0);
           rgpulse(0.5 * pw, v3, 0.0, rof2);
                            /* new for 2.1 */
           rcvron():
     delay (tau2 - rof2 + 1.25 * pw);
                                        /* 1.25 corrects for pulse*/
                                        /*widths*/
}
else
{
     fprintf(stdout, "ssecho - Using single pulses/n");
                      /* v1=0 0 1 1 2 2 3 3 4 4 5 5 6 6 7 7 */
     hlv(ct,v1);
                      /* v1=0 0 0 0 1 1 1 1 2 2 2 2 3 3 3 3 */
     hlv(v1,v1);
                      /* v3=0 0 0 0 2 2 2 2 4 4 4 4 6 6 6 6 */
     dbl(v1,v3);
     add(one,oph,v2); /* v2=1 2 3 4 1 2 3 4 1 2 3 4 1 2 3 4 */
     add(v1,v2,v2); /* v2=1 2 3 4 2 3 4 5 3 4 5 6 4 5 6 7 */
     mod4(v2,v2);
                      /* v2=1 2 3 0 2 3 0 1 3 0 1 2 0 1 2 3*/
     add(oph,v2,v1); /* v1=0 1 2 3 2 3 4 5 4 5 6.7 6 7 8 9*/
                      /* v1=0 1 2 3 2 3 0 1 0 1 2 3 2 3 0 1*/
     mod4(v1,v1);
     rgpulse(p1, v1, rof1, 0.0);
     rgpulse(pw, v2, tau1, rof2);
     rcvron();
      delay(tau2 - rof2 + pw);
      }
status(C):
                           /* wait out group delay */
delay(1.0 / (beta * fb));
                            /* acquire data */
acquire(np, 1.0 / sw);
}
```

LIST OF REFERENCES

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## REFERENCES

- 1. W. Weyl, Ann. Physik. <u>121</u>, 601 (1863).
- 2. C. A. Kraus, J. Am. Chem. Soc. <u>36</u>, 864 (1914).
- 3. J. Jortner, J. Chem. Phys. <u>30</u>, 839 (1959).
- 4. J. Jortner, S. A. Rice and E. G. Wilson, "Metal-Ammonia Solutions", (G. Lepoutre and M. J. Sienko, eds.), Benjamin, New York, 1964.
- 5. J. C. Thompson, "Electrons in Liquid Ammonia", Clarendon Press, Oxford, 1976.
- 6. J. R. Buntaine, M. J. Sienko and P. P. Edwards, J. Phys. Chem. <u>84</u>, 1230 (1980).
- 7. M. H. Cohen and J. Jortner, J. Phys. Chem. 79, 2900 (1975).
- 8. U. Even and J. Jortner, "Electrons in Fluids", (J. Jortner and N. R. Kestner, eds.), Springer-Verlag, Berlin, 1973.
- 9. R. Hensel, "Electrons in Fluids", (J. Jortner and N. R. Kestner, eds.), Springer-Verlag, Berlin, 1973.
- 10. F. Hensel and E. V. Franck, *Ber. Bunsenges. Phys. Chem.* <u>70</u>, 1154 (1966).
- 11. F. Hensel, Ber. Bunsenges. Phys. Chem. 75, 619 (1971).
- 12. T. V. Ramakrishnan, "The Metallic and the Non-Metallic States of Matter", (P. P. Edwards and C. N. R. Rao, eds.), Taylor and Francis, London, 1985.
- 13. N. Mammano and L. V. Coulter, J. Chem. Phys. <u>47</u>, 1564 (1967).
- 14. A. M. Stacy and M. J. Sienko, Inorg. Chem. 21, 2294 (1982).

- 15. N. Mammano and M. J. Sienko, J. Am. Chem. Soc. <u>90</u>, 6322 (1968).
- 16. A. M. Stacy, D. C. Johnson and M. J. Sienko, J. Chem Phys. <u>76</u>, 4248 (1982).
- 17. P. P. Edwards, A. R. Lusis and M. J. Sienko, J. Chem. Phys. <u>72</u>, 3103 (1980).
- 18. A. M. Stacy, P. P. Edwards and M. J. Sienko, J. Solid State Chem. 45, 63 (1982).
- M. K. Faber, O. Fussa'-Rydel, J. B. Skowyra, L. E. H. McMills and J. L. Dye, J. Am. Chem. Soc. <u>111</u>, 5957 (1989).
- 20. J. L. Dye, M. G. DeBacker and V. A. Nicely, J. Am. Chem. Soc. <u>92</u>, 5226 (1970).
- J. L. Dye, M. T. Lok, F. J. Tehan, R. B. Coolen, N. Papadakis, J. M. Ceraso and M. G. DeBacker, Ber. Bunsenges. Phys. Chem. <u>75</u>, 659 (1971).
- 22. M. T. Lok, F. J. Tehan and J. L. Dye, J. Phys. Chem. <u>76</u>, 2975 (1972).
- 23. J. L. Dye, "Electrons in Fluids", (J. Jortner and N. R. Kestner, eds.), Springer-Verlag, Berlin-Heidelberg-NewYork, 1973.
- 24. C. J. Pederson, J. Am. Chem. Soc. <u>89</u>, 7017 (1967).
- 25. B. Dietrich, J. M. Lehn and J. P. Sauvage, Tetrahedron Lett. 34, 2885 (1969).
- 26. G. P. Pez, I. L. Mador, J. E. Galla, R. K. Crissey and C. E. Forbes, J. Am. Chem. Soc. <u>107</u>, 4098 (1985).
- 27. J. L. Dye. C. W. Andrews and S. E. Mathews, J. Phys. Chem. <u>79</u>, 3065 (1975).
- 28. J. L. Dye, J. Phys. Chem. <u>84</u>, 1084 (1980).
- 29. J. L. Dye, J. Phys. Chem. 88, 3842 (1984).

- 30. A. L. Wayda and J. L. Dye, J. Chem. Educ. <u>62</u>, 356 (1985).
- 31. J. L. Dye and M. G. DeBacker, Ann. Rev. Phys. Chem. <u>38</u>, 271 (1987).
- 32. J. L. Dye, J. M. Ceraso, M. T. Lok, B. L. Barnett and F. J. Tehan, J. Am. Chem. Soc. <u>96</u>, 608 (1974).
- 33. F. J. Tehan, B. L. Barnett and J. L. Dye, J. Am. Chem. Soc. <u>96</u>, 7203 (1974).
- 34. B. VanEck, L. D. Le, D. Issa and J. L. Dye, Inorg. Chem. 21, 1966 (1982).
- 35. A. W. Weiss, Phys. Rev. <u>166</u>, 70 (1968).
- 36. W. H. E. Schwarz, Chem. Phys. Lett. 10, 478 (1971).
- 37. J. L. Dye and J. Papaioannou, Rev. Sci. Instrum. <u>59</u>, 496 (1988).
- 38. D. Issa, A. Ellaboudy, R. Janakiraman and J. L. Dye, J. Phys. Chem. <u>88</u>, 3847 (1984).
- 39. S. B. Dawes, D. L. Ward, R. H. Huang and J. L. Dye, J. Am. Chem. Soc. <u>108</u>, 3534 (1986).
- 40. R. H. Huang, D. L. Ward, M. E. Kuchenmeister and J. L. Dye, J. Am. Chem. Soc. <u>109</u>, 5561 (1987).
- 41. R. H. Huang, M. K. Faber, K. J. Moeggenborg, D. L. Ward and J. L. Dye, *Nature* <u>331</u>, 599 (1988).
- 42. J. L. Dye, M. R. Yemen, M. G. DaGue and J. M. Lehn, J. Chem. Phys. <u>68</u>, 1665 (1978).
- 43. M. G. DaGue, J. S. Landers, H. L. Lewis and J. L. Dye, Chem. Phys. Lett. <u>66</u>, 169 (1979).
- 44. J. L. Dye, M. G. DaGue, M. R. Yemen, J. S. Landers and H. L. Lewis, J. Phys. Chem. <u>84</u>, 1096 (1980).

- 45. L. D. Le, D. Issa, B. VanEck and J. L. Dye, J. Phys. Chem. <u>86</u>, 7 (1982).
- 46. R. R. Dewald and J. L. Dye, J. Phys. Chem. <u>68</u>, 121 (1964).
- 47. A. Ellaboudy, M. L. Tinkham, B. VanEck, J. L. Dye and P. B. Smith, J. Phys. Chem. <u>88</u>, 3852 (1984).
- 48. N. F. Ramsey, Phys. Rev. <u>77</u>, 567 (1950).
- 49. E. R. Andrew, A. Bradbury and R. G. Eades, *Nature (London)* <u>183</u>, 1802 (1959).
- 50. E. R. Andrew, Arch. Sci. (Geneva) 12, 103 (1959).
- 51. I. J. Lowe, Phys. Rev. Lett. 2, 285 (1959).
- 52. D. Ikenberry and T. P. Das, Phys. Rev. A 138, 822 (1965).
- 53. C. Deverell, Progr. Nucl. Magn. Reson. Spectrosc. 4, 278 (1969).
- 54. H. J. Behrens and B Schnabel, *Physica B* <u>114</u>, 185 (1984).
- 55. A. Ellaboudy and J. L. Dye, J. Mag. Res. <u>66</u>, 491 (1986).
- 56. R. Concepcion and J. L. Dye, J. Am. Chem. Soc. <u>109</u>, 7203 (1987).
- 57. M. L. Tinkham and J. L. Dye, J. Am. Chem. Soc. <u>107</u>, 6129 (1985).
- 58. M. L. Tinkham, A. Ellaboudy, J. L. Dye and P. B. Smith, J. Phys. Chem. <u>90</u>, 14 (1986).
- 59. A. Ellaboudy, J. L. Dye and P. B. Smith, J. Am. Chem. Soc. <u>105</u>, 6490 (1983).
- 60. J. L. Dye and A. Ellaboudy, Chem. Br. 20, 210 (1984).
- 61. J. L. Dye, C. W. Andrews and J. M. Ceraso, J. Phys. Chem. <u>79</u>, 3076 (1975).

- 62. D. M. Holton, P. P. Edwards, D. C. Johnson, C. J. Page, W. McFarlane and B. Woods, J. Chem. Soc., Chem. Commun., 740 (1984).
- 63. O. Fussa', S. M. Kauzlarich, J. L. Dye and B. K. Teo, J. Am. Chem. Soc. <u>107</u>, 3727 (1985).
- 64. A. C. Kunwar, G. L. Turner and E. Oldfield, J. Mag. Res. <u>69</u>, 124 (1986).
- 65. L. E. H. McMills, Ph.D. Dissertation, Michigan State University, 1989.
- 66. J. Kim, Ph.D. Dissertation, Michigan State University, 1989.
- 67. K. J. Moeggenborg, J. L. Eglin and J. L. Dye, unpublished results.
- 68. R. G. Patel and M. M. Caudhri, *Thermochimica Acta* 25, 247 (1978).
- 69. T. Ozawa, Bull. Chem. Soc. Jpn. <u>38</u>, 1881 (1965).
- 70. H. E. Kissinger, J. Res. Nat. Bur. Stand. <u>57</u>, 217 (1956).
- 71. A. Maercker, Angew. Chem. Int. Ed. Engl. 26, 972 (1987).
- 72. M. E. Kuchenmeister and J. L. Dye, J. Am. Chem. Soc <u>111</u>, 935 (1989).
- 73. H. K. Frensdorff, J. Am. Chem. Soc. <u>93</u>, 600 (1971).
- 74. M. E. Kuchenmeister, Ph.D. Dissertation, Michigan State University, 1989.
- 75. R. Huang, J. L. Eglin, D. Ward and J. L. Dye, unpublished results.
- 76. S. B. Dawes, A. S. Ellaboudy and J. L. Dye, J. Am. Chem. Soc. <u>109</u>, 3508 (1987).
- 77. S. B. Dawes, A. Ellaboudy and J. L. Dye, unpublished results.
- 78. S. B. Dawes, D. L. Ward, O. Fussa'-Rydel, R. Huang and J. L. Dye, Inorg. Chem. <u>28</u>, 2232 (1989).

- 79. P. P. Edwards, Adv. Inorg. Chem. Radiochem. <u>25</u>, 135 (1982).
- 80. J. P. Lelieur and P. J. Rigny, J. Chem. Phys. 59, 1148 (1973).
- 81. W. D. Knight, Phys. Rev. <u>76</u>, 1259 (1944).
- 82. O. Yamamotot and M. Yanagisawa, Anal. Chem. <u>42.</u> 1463 (1970).
- 83. A. VanGeet, Anal. Chem. <u>42</u>, 679 (1970).
- 84. D. L. Ward, Rui H. Huang, M. E. Kuchenmeister and J. L. Dye, unpublished results.
- 85. J. S. Landers, J. L. Dye, A. Stacy and M. J. Sienko, J. Phys. Chem. 85, 1096 (1981).
- 86. D. Issa and J. L. Dye, J. Am. Chem. Soc. 104, 3781 (1982).
- 87. S. B. Dawes, Ph.D. Dissertation, Michigan State University, 1986.
- 88. J. H. Van Vleck, Phys. Rev. 74, 1168 (1948).
- 89. A Beckmann, K. D. Boken and D. Elke, Z. Phys. <u>270</u>, 173 (1974).
- 90. C. J. Pederson, J. Am. Chem. Soc. <u>90</u>, 3299 (1968).
- 91. J. D. Lamb, R. M. Izatt, C. S. Swain and J. J. Christensen, J. Am. Chem. Soc. <u>102</u>, 475 (1980).
- 92. G. P. Pez, I. L. Mador, J. E. Galle, R. K. Crissey, and C. E. Forbes, J. Am. Chem. Soc. <u>107</u>, 4098 (1985).
- A. G. Barrett, C. R. Godfrey, D. M. Hollinshead, P. A. Prokopiou, D. H. Barton, R. B. Boar, L. Joukhadar, J. F. McGhie and S. C. Misra, *JCS. Perkin I*, 1501 (1981).
- 94. R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb, J. J. Christensen and D. Sen, Chem. Rev. <u>85</u>, 271 (1985).
- 95. R. H. Huang, D. Ward, and J. L. Dye, unpublished results.

- 95. R. H. Huang, D. Ward, and J. L. Dye, unpublished results.
- J. D. Lamb, R. M. Izatt, J. J. Christensen and D. J. Eatough, "Coordination Chemistry of Macrocyclic Compounds", (G. A. Melson, ed.), Plenum Press, New York, 1979.
- 97. J. J. Christensen, D. J. Eatough and R. M. Izatt, Chem. Rev. <u>74</u>, 351 (1974).
- 98. J. M. Lehn and J. P. Sauvage, J. Am. Chem. Soc. 97, 6700 (1975).
- 99. M. Micheloni, J. Coord. Chem. 18, 3 (1988).
- 100. K. J. Moeggenborg, Ph.D. Dissertation, Michigan State University, 1990.
- 101. P. Murray and J. White, J. Trans. Br. Ceram. Soc. 54, 204 (1955).
- 102. H. E. Kissinger, Anal. Chem. 29, 217 (1957).
- 103. R. A. Logan, R. E. Cote and P. Kusch, Phys. Rev. <u>85</u>, 280 (1952).
- 104. M. R. Yemen, Ph.D. Dissertation, Michigan State University, 1982.
- 105. D. L. Ward, R. H. Huang and J. L. Dye, Acta Cryst. <u>C44</u>, 1374 (1988).
- 106. D. T. Cromer and J. T. Waber, "International Tables for X-Ray Crystallography", Vol. IV, Table 2.2B, Kluwer Academic Publisher, Dordrecht, 1974.
- D. T. Cromer, "International Tables for X-Ray Crystallography", Vol. IV, Table 2.3.1, Kluwer Academic Publisher, Dordrecht, 1974.
- 108. J. L. Dye, "Valency and Charge Distribution in Alkalide and Electride Salts", The Robert A. Welch Foundation Conference on Chemical Research, VALENCY XXXII, 1988.
- 109. M. Kuchenmeister, A. Ellaboudy, C. Bender, J. Babcock, J. Kim, Dae-Ho Shin and J. L. Dye, unpublished results.

- 110. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry A Comprehensive Text", 4th Edition, John Wiley and Sons, New York, 1980.
- 111. L. E. H. McMills and J. L. Dye, unpublished results.
- 112. R. H. Huang, D. Ward and J. L. Dye, unpublished results.
- 113. A. Bencini, A. Bianchi, A. Borselli, M. Ciampolini, E. Garcia-Espana, P. Dapporto, M. Micheloni, P. Paoli, J. Ramirez, and B. Valtancoli, *Inorg. Chem.* 28, 4279 (1989).
- 114. D. Freude, T. A. Carpenter, J. Haase, J. Klinhowski and G. Ronikier, Chem. Phys. Lett. <u>119</u>, 365 (1985).
- 115. J. L. Dye, Prog. in Inorg. Chem. <u>32</u>, 327 (1984).
- 116. O. Fussa', Ph.D. Dissertation, Michigan State University, 1986.
- 117. C. N. R. Rao and P. P. Edwards, Proc. Indian Acad. Sci. <u>96</u>, 473 (1986).
- 118. N. F. Mott, "Metal-Insulator Transitions", Taylor & Francis, London, 1974.
- 119. I. Weberman, J. Jortner and M. H. Cohen, *Phys. Rev. B*. <u>11</u>, 2885 (1975).
- 120. E. Abrahams, P. W. Anderson, D. C. Licciardell and T. V. Ramakrishman, *Phys. Rev. Lett.* <u>42</u>, 673 (1979).
- 121. C. Kittel, "Introdution to Solid State Physics", 2nd Edition, Wiley, New York, 1963.
- 122. D. H. Martin, "Magnetism in Solids", The M.I.T. Press, Cambridge, 1967.
- 123. D. Issa, Ph.D. Dissertation, Michigan State University, 1982.
- 124. M. Kuchenmeister and J. L. Dye, unpublished results.

- 126. P. P. Edwards and M. J. Sienko, J. Chem. Ed. <u>60</u>, 691 (1983).
- 127. K. F. Herzfeld, Phys. Rev. 29, 701 (1927).
- 128. T. A. Patterson, H. Hotop, A. Kasdan, D. W. Norcross and W. C. Lineberger, *Phys. Rev. Lett.* <u>32</u>, 189 (1974).
- 129. N. Aschcroft and N. Mermin, "Solid State Physics", Holt, Rinehart and Winston, New York, 1976.

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- 130. J. L. Dye and V. A. Nicely, J. Chem. Ed. 48, 443 (1971).
- 131. R. H. Huang, D. L. Ward and J. L. Dye, J. Am. Chem. Soc. <u>111</u>, 5707 (1989).

