Li+(TMPAND)Na−: The First Alkalide Prepared from an Azacage Complexant[#]

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Abstract. The new lithium-selective complexant 5,12,17-trimethyl-1,5,9,12,17-pentaazabicyclo[7.5.5]nonadecane (TMPAND) was used to synthesize Li+(TMPAND)Na−, the first alkalide prepared from an azacage complexant. This sodide was characterized by a variety of methods. Differential scanning calorimetry experiments showed a reversible, endothermic, solid-solid phase transition at an onset temperature of $-75 \pm 3°C$ and with $\Delta H = 3.3 \pm 1$ kJ/mol. ^{23}Na NMR spectra showed a peak at -61 ppm, characteristic of a sodium anion, and a second minor peak at -10 ppm, probably due to the interaction of Na− with trapped electrons. The quadrupole coupling constant of the complexed lithium cation was found to be 0.19 MHz at $-100°C$, and ^{7}Li NMR spectra showed a discontinuity in the line width of the ^{7}Li NMR peak and in the quadrupole coupling constant at the phase transition.

Key words. Alkalide, electride, azacage, cryptand, sodium NMR, lithium NMR.

1. Introduction

Alkalides and electrides [1] are two unique classes of compounds with unusual properties that result from the presence of weakly bound electrons. Solubilization of an alkali metal by coordination with a crown ether [2], a discovery that grew out of the work of Pedersen *et al.* [3], led to the use of [2.2.2]cryptand [4] (C222) for the preparation of the first sodide, Na+(C222)Na− [5]. This alkalide is a stable crystalline salt with a sodium anion. More recently, crystalline electrides, analogous salts with electrons serving as anions, have been synthesized [6].

Since these initial discoveries, crystal structures have been obtained for 30 alkalides and four electrides. These compounds have been characterized and studied by a variety of techniques, including pressed powder d.c. conductivity, EPR spectroscopy, magnetic susceptibility, X-ray crystallography, powder X-ray diffraction, optical absorption spectroscopy of thin films, and magic angle spinning (MAS) and static NMR spectroscopy [7]. Such studies have yielded a great deal of insight into the nature of the trapped electron and the alkali metal anion [1d].

Alkalides and electrides are extremely sensitive to air, moisture and elevated temperature. They must be handled *in vacuo* or under an inert atmosphere, and at

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[#] This paper is dedicated to the memory of the late Dr C. J. Pedersen.
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temperatures below about $-40°C$. These materials undergo irreversible decomposition due to their thermal instability, although the exact nature of the decomposition process (or products) is as yet unknown. The propensity to thermally decompose has limited the routine use of presynthesized alkalides and electrides as reagents in synthesis, in spite of their strong reducing ability. (The solvated electron is thermodynamically the most powerful reducing agent in a given solvent.) However, they can be used in crystalline form [8] or prepared *in situ* for use in reduction processes [9].

In pursuit of more thermally stable alkalides and electrides, the use of fully methylated aza analogs of crown ethers as complexing agents was investigated. These complexants [10] included hexamethylhexacyclen (HMHCY), pentamethylpentacyclen (PMPCY), and trimethyltricyclen [11] (TMTCY). They were expected to be more robust toward the highly reducing environment imposed by electron counterions and alkali metal anions [7f, 9a, 9b].
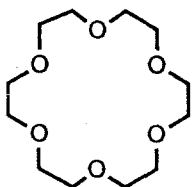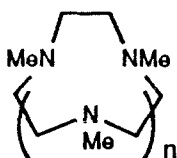
**18crown6**   n=4 **HMHCY**

n=3 **PMPCY**

n=1 **TMTCY**

Several sodides were successfully prepared using HMHCY, and their relative stabilities were compared with the stabilities of the corresponding crown ethers. It was found by differential scanning calorimetry (DSC) that $Cs^+(HMHCY)Na^-$ and $K^+(HMHCY)Na^-$ melted without thermal decomposition at 8°C and 42°C, respectively; but on further temperature increase they underwent decomplexation at 37°C and 74°C, respectively [7f]. However, irreversible decomposition of the organic ligand did not occur below $\sim 150°C$. Under similar conditions in the DSC, alkalides that contain crown ethers or cryptands undergo irreversible thermal decomposition below $\sim 90°C$ [12]. It is tempting to conclude from these data that alkalides made with HMHCY are stable at room temperature, when in fact they have a limited shelf-life (on the order of days) because of the thermodynamically favored decomplexation [7f].

These results indicated that the thermal instability of alkalides and electrides was complicated by competition between decomposition and *decomplexation*. With crown ether and cryptand complexants, irreversible decomposition generally occurs before the compound has an opportunity to decomplex. But when the aza crown ether HMHCY was used, decomplexation occurred before decomposition and at a lower temperature than was found for the oxa compounds. This decomplexation is not surprising since, in general, aza complexing agents have lower binding constants

than their oxa counterparts [13]. Thus a *useful* increase in stability was not achieved with HMHCY.

In order to stabilize alkalides and electrides towards decomplexation without sacrificing chemical stability, aza complexants of increased binding strength were sought. The azacage complexant 5,12,17-trimethyl-1,5,9,12,17-pentaazabicyclo[7.5.5]nonadecane (TMPAND) selectively encapsulates a lithium cation in aqueous solution to form a stable 1:1 complex [14]. This fully methylated aza analog of [1.1.1]cryptand [15] (with two ethyl linkages replaced by *n*-propyl groups) was subsequently used to synthesize a sodide, $Li^+(TMPAND)Na^-$. The properties of this compound are described in this paper.
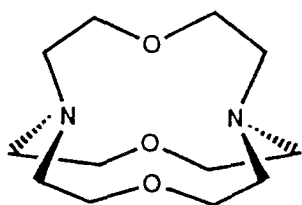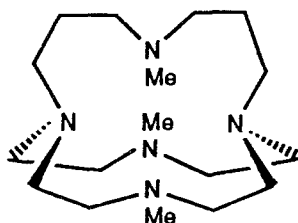
[1.1.1]cryptand   **TMPAND**

2. Experimental

The synthesis of $Li^+(TMPAND)Na^-$ followed procedures that have been described in detail elsewhere [12]. In a helium-filled dry box, excess lithium and sodium were added to ~300 mg TMPAND in a modified, Kontes Airless-Ware® double tube ('H-cell'). After evacuation to ~10^{-5} torr, purified methylamine was distilled onto the metals and complexant at −40°C to −50°C. The alkali metals dissolved to form a deep blue solution. The solution was packed in dry ice for at least 12 h, after which time it was deep purple in color, and bronze films formed on the sides of the glass apparatus when the solution was swirled. The methylamine was evaporated to dryness, followed by addition of dimethyl ether (Me_2O) to form a deep blue solution. This was poured through a frit to another glass bulb in order to separate the products from excess metal. After addition of trimethylamine (Me_3N) to induce crystallization, bronze-colored crystals formed. The Me_2O/Me_3N solvent mixture was evaporated, and pure Me_3N was added. The liquid was decanted through the frit and redistilled onto the compound to remove excess complexant. After several washes of this type, the Me_3N was removed by distillation and the compound was dried *in vacuo*. The polycrystalline powder was harvested in a nitrogen glove bag while the sample was kept cold on an aluminum support immersed in liquid nitrogen. Samples were stored in Cryotubes® under liquid nitrogen.

Optical absorption spectra of thin, solvent-free films of $Li^+(TMPAND)Na^-$ were measured from 300 to 1500 nm with a Model 260 Guided Wave Spectrophotometer at temperatures from −90°C to −10°C as recorded with a copper–constan-

tan thermocouple. Thin films were made by first preparing a solution of the compound in Me_2O, then pouring the solution over the quartz cell window and rapidly evaporating the solvent.

Differential scanning calorimetry (DSC) was performed with a du Pont 910 Differential Scanning Calorimeter. Cold samples that had been at liquid nitrogen temperatures were quickly sealed hermetically in aluminum pans under a nitrogen atmosphere, and the samples were transported at liquid nitrogen temperature. They were loaded into the pre-cooled DSC instrument under an inert atmosphere.

Variable temperature ^{7}Li and ^{23}Na static NMR measurements were carried out for $Li^+(TMPAND)Na^-$ at 155.5 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 μs and a delay of 1 s. The NMR sample tube was loaded into the precooled probe and cold nitrogen gas was used to control the temperature to within 0.3°C after 3 to 10 minutes equilibration time. Chemical shifts are relative to aqueous Li^+ and Na^+ at infinite dilution.

The d.c. conductivity of packed powders was measured as a function of temperature with a computer-controlled Keithley 617 Programmable Electrometer. The temperature was measured with a computer-controlled Keithley 580 micro-ohmmeter and a four-probe carbon glass thermometer. Rectangular voltage pulses of alternate polarity 10 s in length and 100 mV in amplitude were applied to the sample to minimize polarization effects. To check for deviations from Ohm's law due to electrode effects, the electrodes were coated with sodium metal [16].

3. Results

3.1. OPTICAL SPECTRA

The optical absorption spectrum of $Li^+(TMPAND)Na^-$ shown in Figure 1 has a major peak at ~ 700 nm. The transition is slightly temperature dependent, with a gradual and reversible red shift ($d\nu/dT \approx -5$ cm^{-1} deg^{-1}). The peak also became broader at higher temperatures. A red shift of -1.6 cm^{-1} deg^{-1} and line broadening of about 1.1 cm^{-1} deg^{-1} with increasing temperature had previously been observed with $Na^+(C222)Na^-$ films [17].

3.2. THERMAL BEHAVIOR

Differential scanning calorimetry (DSC) studies of $Li^+(TMPAND)Na^-$ show a reversible, endothermic, solid-solid phase transition with an onset temperature of -75 ± 3°C and a ΔH value of 3.3 ± 1 kJ/mol. Figure 2 shows this transition in addition to the exothermic decomposition peak ($\Delta H = -50 \pm 20$ kJ/mol) at ~ 95°C. By measuring the decomposition temperature at six ramp rates, an activation energy of 101 ± 5 kJ/mol was determined by the Kissinger method [18]. Extrapolation of these results to lower temperature may not be valid because other factors such as autocatalytic processes may control the rate of decomposition. Direct extrapolation of the high temperature data yields half-lives of about 70 h at 25°C and 2800 h at 0°C.
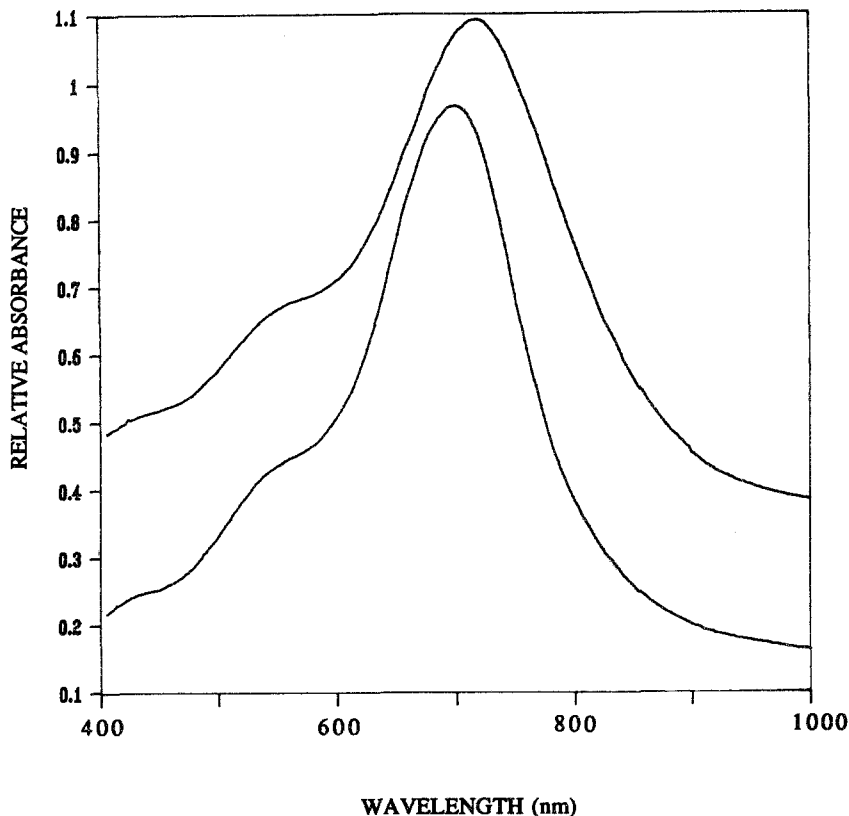
Fig. 1. Optical absorption spectra of thin films of $Li^+(TMPAND)Na^-$ obtained at $-10°C$ (*top line;* offset by $+0.2$ on the Relative Absorbance scale) and $-90°C$.

3.3. ^{23}Na AND ^{7}Li NMR SPECTRA

The major static ^{23}Na NMR peak of $Li^+(TMPAND)Na^-$ occurs at a chemical shift of -61 ppm with a width at half-height $(\Delta v_{1/2})$ of ~ 1500 Hz. This chemical shift is characteristic of sodides and indicates that the sodium anion is in a highly symmetric environment with minimal overlap of its filled p orbitals with the surroundings [19]. When the temperature of the sample was below the temperature of the phase transition, the ^{23}Na NMR peak at -61 ppm saturated readily and a second, rather broad peak of low intensity was observed at ~ -10 ppm $(\Delta v_{1/2} \approx 9500$ Hz). This is a substantial paramagnetic shift from the typical sodide peak at -61 ppm. Figure 3 shows the ^{23}Na static NMR spectra above and below the phase transition. When the temperature was raised above that of the phase transition, the ^{23}Na peak at -10 ppm was obscured by the intense peak at -61 ppm. Evidently, the T_1 relaxation time of the major Na^- species decreases dramatically as the temperature is increased through the phase transition temperature.

The ^{7}Li static NMR spectrum of $Li^+(TMPAND)Na^-$ has a central $(-1/2 \rightarrow 1/2)$ transition at ~ -9 ppm independent of temperature. The line width, $\Delta v_{1/2}$,
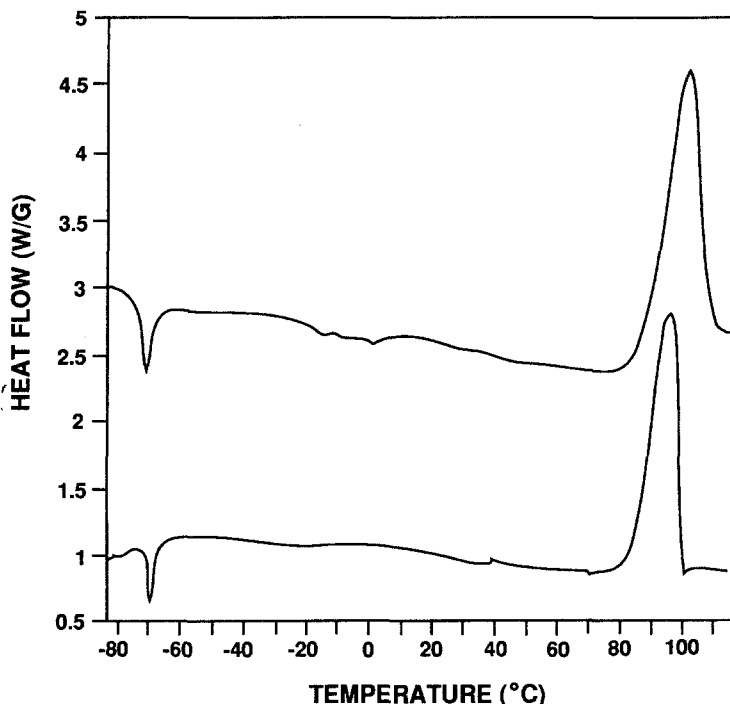
Fig. 2. DSC traces of $Li^+(TMPAND)Na^-$ obtained at ramp rates of 12°C/min (*top line;* offset by 2 W/g) and 7°C/min. (Note that the area under a peak is inversely proportional to the ramp rate.)

decreases with increasing temperature from 7.7 kHz at $-100°C$ to 6.5 kHz at a transition temperature of $-75°C$, and shows a discontinuity to 3.2 kHz at the transition temperature. Above the transition temperature, the line width continues to decrease, leveling off at 2.3 kHz above $-60°C$.

Although the crystal structure of $Li^+(TMPAND)Na^-$ is not known,[1] that of $Li^+(TMPAND)BPh_4^-$, a model salt with the same cation, has been determined [14b]. A linewidth contribution of 8.2 kHz from the dipolar interaction was calculated with the Van Vleck equation [20] by using the lithium–nitrogen and lithium–proton distances obtained from the crystal structure of the model salt. This calculated linewidth is close to the experimental value of 7.7 kHz for $Li^+(TMPAND)Na^-$ obtained at $-100°C$ where molecular motion is minimized. The quadrupolar contribution to the linewidth is less than 80 Hz [21] and can be neglected.

In addition to the central transition, the ^7Li static NMR spectrum (Figure 4) shows the satellite transitions, whose separation gives the quadrupole coupling constant (QCC), assuming axial or nearly axial symmetry. The QCC for the ^7Li nucleus in different compounds reflects different values of the electric field gradient. The value of the QCC, 0.19 MHz, for $Li^+(TMPAND)Na^-$ at $-100°C$ is close to the value of 0.192 MHz obtained for the gas phase LiCl molecule [22]. The ^7Li QCC of the sodide depends on temperature as shown in Figure 5. The plot has a
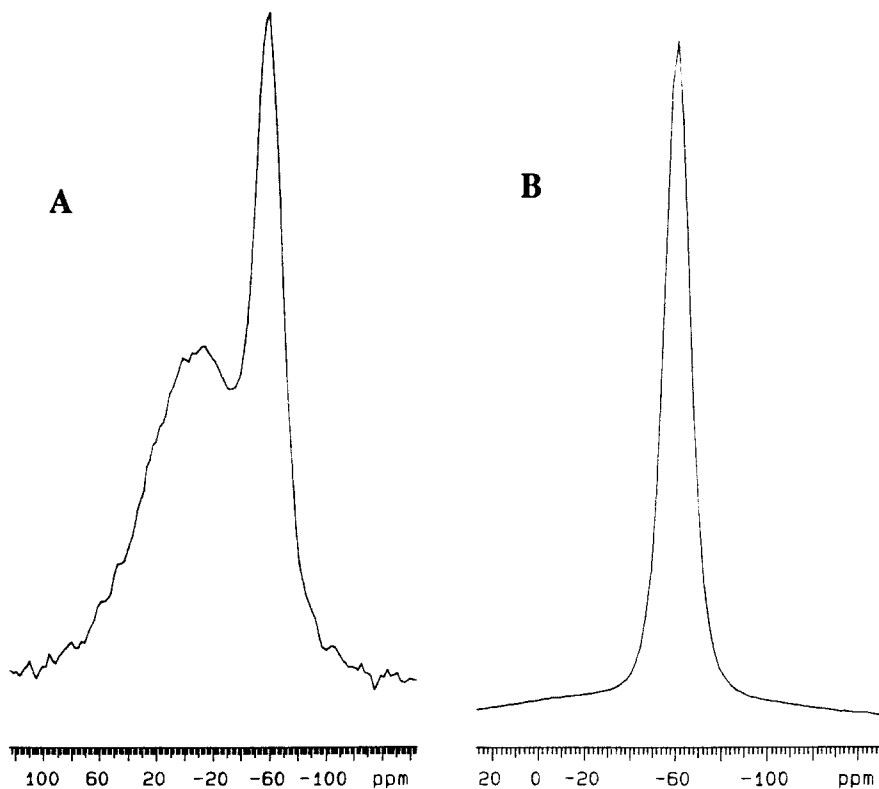
Fig. 3. ^{23}Na static NMR spectra of Li$^+$(TMPAND)Na$^-$ obtained at (A) $-84°$C and (B) $-60°$C. The peak at -61 ppm in A has greatly reduced intensity because of partial saturation.

distinct break at the temperature of the phase transition ($\sim -75°$C) and continues to decrease as the temperature is raised.

3.4. ELECTRICAL CONDUCTIVITY

The d.c. powder conductivity of Li$^+$(TMPAND)Na$^-$ was studied as a function of temperature. Below the solid–solid phase transition temperature the sample resistance was beyond the measurement range of the instrument, thus providing no information about the conductivity of this phase, except that it is low ($<10^{-12}$ ohm^{-1} cm^{-1}). Above the transition temperature the sample behaved as a semiconductor with an apparent band gap of ~ 1.2 eV. A test for electrode effects was made by using a single sodium electrode and a steel counter-electrode [16]. Ohm's law was obeyed and there was no electrochemical cell behavior, suggesting that ionic conductivity is not important and that electrode effects are minimal.

4. Discussion

This work shows that the compound formed from lithium, sodium, and TMPAND is a sodide. The major peak at ~ 700 nm in the optical absorption spectrum is
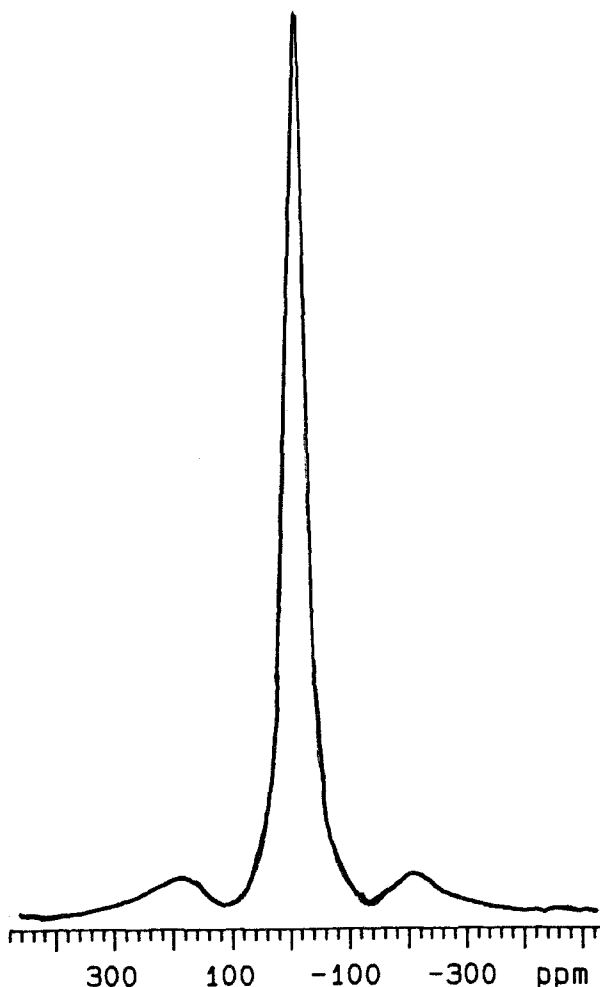
Fig. 4. ^{7}Li static NMR spectra of Li$^+$(TMPAND)Na$^-$ obtained at $-70°C$.

typical of sodides, and it is attributed to a $3s^2 \rightarrow 3s3p$ transition of Na$^-$ [1d, 1f]. No change was observed at or around the phase transition at $-75°C$, indicating that either Na$^-$ is still present in the low temperature phase, or that this phase does not form in the thin films used.

Both the ^{7}Li and ^{23}Na NMR spectra are dramatically affected by the phase transition. The chemical shift range of ^{7}Li is small in diamagnetic compounds, so the constancy of the lithium chemical shift is not surprising, but does suggest the absence of *large* concentrations of unpaired electrons both above and below the phase transition.

Positive chemical shifts (paramagnetic direction) of ^{23}Na can have several origins: (1) overlap of electron pairs from surrounding molecules with the unoccupied $3p$ orbitals of sodium and mixing of the $2p$ and $3p$ states (Ramsey shift [23]); (2) interaction with paramagnetic species such as trapped electrons; (3) rapid exchange
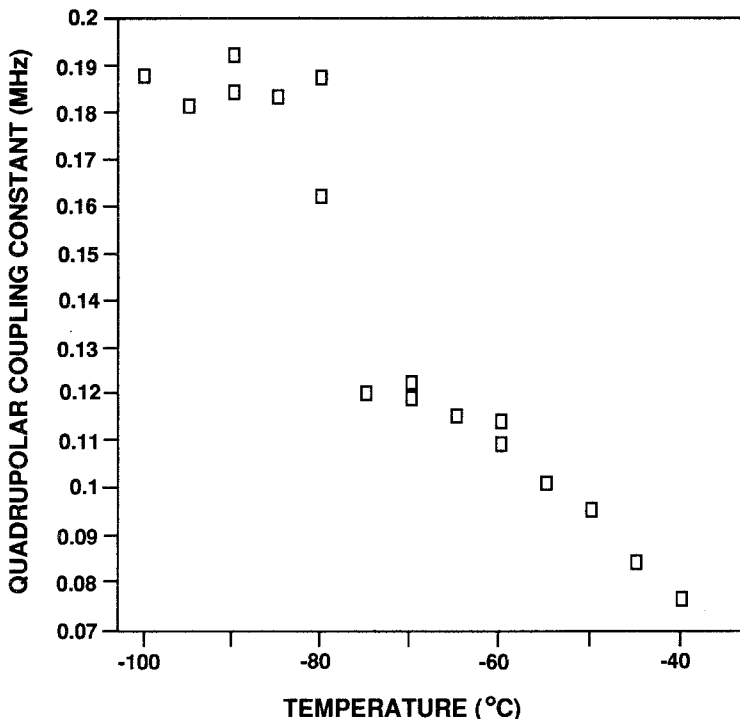
Fig. 5. Temperature dependence of the quadrupole coupling constant (QCC) calculated from the ^{7}Li static NMR spectrum of $Li^{+}(TMPAND)Na^{-}$.

with species such as Na atoms that exhibit large chemical shifts. Because Na^{-} is a very large anion (radius 2.6 Å [7c]) with two electrons in the $3s$ orbital that effectively screen the $2p$ electrons, the chemical shift of -61 ppm is essentially the same as that of Na^{-} in the gas phase and tends to be insensitive to the environment [19]. The chemical shift of the second ^{23}Na NMR peak is substantially more paramagnetic than the confirmed chemical shift of the sodium anion in any environment encountered to date. If the signal is from Na^{-} in a diamagnetic environment, the large chemical shift implies strong interaction of the p orbitals of Na^{-} with Li^{+} or with atoms of the complexant. EPR studies [24] show no change in the concentration of trapped electrons at the transition temperature, the optical spectrum is not altered, and the ^{7}Li chemical shift does not change. All of these observations make it unlikely that there is a significant difference in the trapped electron concentration above and below the phase transition. The most likely explanation for the shifted Na^{-} peak is the interaction between a small fraction of the sodium anions and nearby trapped electrons.

It appears that, below the phase transition temperature, $Li^{+}(TMPAND)Na^{-}$ is locked in a conformation that increases the T_1 relaxation time of Na^{-} and gives the static value of the ^{7}Li linewidth and quadrupole coupling constant. Enough trapped electrons are present to yield a substantial paramagnetic shift of some of the sodium anions. According to this model, at the temperature of the phase

transition a change occurs that results in substantially greater motion of the complexant. This could yield a sharp decrease in the value of the ^7Li QCC and its linewidth, coincident with a decrease in the longitudinal relaxation time of the major Na^- species.

The linewidth of the ^7Li NMR peak of the low temperature phase agrees with that calculated from a rigid lattice model and is primarily due to proton–lithium dipolar interactions. The abrupt decrease in width at the transition, and the continuing decrease as the temperature is raised, results from motion of the hydrogens of the complexant. Such motion, which reflects increased conformational freedom of the $-CH_2-$ groups, is commonly encountered in alkalides and electrides as indicated by both NMR line widths [1d] and powder X-ray diffraction studies [25].

In addition to preparing the alkalide, attempts were made to synthesize the corresponding lithium electride, $Li^+(TMPAND)e^-$. Paramagnetic solids were obtained, but the samples were not pure and included excess solvent. A potential difficulty with the use of azacage complexants is the slow rate of encapsulation of Li^+ into the cage. A similar problem was noted in the synthesis of the electride $Li^+(C211)e^-$ when methylamine was used [26]. It was necessary to let the solution stand for several hours at $-40°C$ to allow formation of the inclusive complex. Recent work [26b] used several dissolutions in Me_2O and subsequent evaporations to remove traces of methylamine. The current difficulty in preparing pure $Li^+(TMPAND)e^-$ may be the formation of mixtures that contain both inclusive and exclusive complexes [27].

Unlike compounds synthesized with HMHCY [7f], decomplexation was not observed for $Li^+(TMPAND)Na^-$, and irreversible decomposition did not occur below 65°C in the DSC experiments. Both of these results point to good thermal stability. The high affinity of TMPAND for Li^+ results in an increased binding constant, which overcomes the propensity to decomplex, while retaining the resistance to decomposition. This chemical stability is not surprising, since fully methylated aza crown ethers were shown to be more stable to decomposition than their oxa analogs [7f, 9a, 9b], and we expect similar trends in the azacage/cryptand series. The mechanism of decomposition is not known, but a likely initial step is deprotonation of the methylene groups, a step that would be favored by the more acidic hydrogens of the oxa complexants. Other fully methylated azacage complexants become attractive candidates for the synthesis of more thermally stable alkalides and electrides.

Since thermal decomposition of electrides at temperatures higher than about $-40°C$ is a continuing barrier to the study of their properties, the prospect of electrides that are stable to both decomposition and decomplexation at room temperature is an attractive one that warrants further study of the azacage systems.

Acknowledgements

Note

[1] A recent structure determination (R. H. Huang and J. L. Dye, unpublished results) shows the incorporation of one molecule of methylamine for every two $Li^+(TMPAND)Na^-$ units. In the present work, most or all of the methylamine may have been removed by the prolonged evacuation of the powdered sample.

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