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SYNTHESIS AND CHARACTERIZATION
OF A CRYSTALLINE ALKALIDE:
POTASSIUM-(HMHCY)-SODIUM

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Major professor

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SYNTHESIS AND CHARACTERIZATION OF A CRYSTALLINE ALKALIDE: POTASSIUM-(HMHCY)-SODIUM

By

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF A CRYSTALLINE ALKALIDE: POTASSIUM-(HMHCY)-SODIUM

By

Mark E. Kuchenmeister

A new crystalline alkalide [K^+(HMHCY)·Na^-] has been prepared from potassium, sodium, and hexamethylhexacyclen (HMHCY; a member of a new class of complexants).

The analysis shows that the new compound contains a 1:1:1 ratio of K, Na, HMHCY. Identification of the species present was made by optical transmission spectroscopy and MAS-NMR . These data indicate that the species is a sodide. The crystal structure was determined to be orthorhombic primitive $P2_12_12_1$ with $\underline{a}$ = 11.091, $\underline{b}$ = 11.172, $\underline{c}$ = 22.531 Å.

Calorimetric studies reveal that the compound is stable at room temperature under an inert atmosphere for short periods of time and melts at ~45°C, then decomplexes at ~55°C. The most noteworthy feature of this complexant is its extreme resistance to irreversible decomposition, which does not occur, even in the presence of Na-K, at temperatures below ~120°C. If the complexation constant could be increased it might be possible to prepare truly stable alkalides and electrides.

to my parents

ACKNOWLEGEMENTS

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I. Introduction

I. A. Background

Since 1864 when Weyl first reported the dissolution of sodium and potassium in ammonia, there has been much literature devoted to the nature of metal-ammonia solutions. Weyl's original assumption that ammoniums (NH_4) were being formed was later disproven and replaced by the notion of solvated electrons and alkali metal anions, given by the following equilibria.

$$2M(s) \rightleftharpoons M^+ + M^- \qquad 1$$

$$M^- \rightleftharpoons M + e^- \qquad 2$$

$$M \rightleftharpoons M^+ + e^- \qquad 3$$

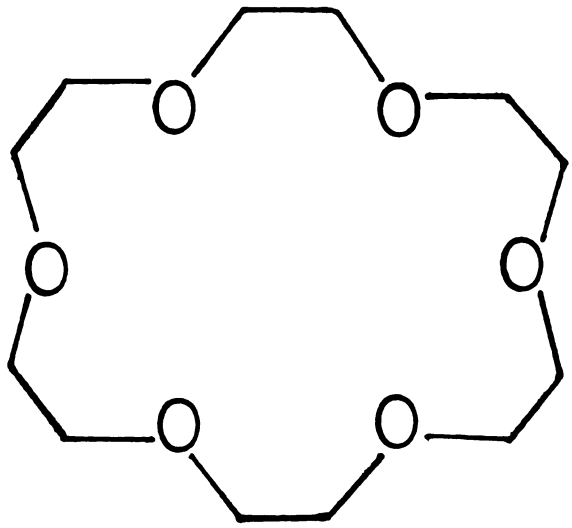
The study of the solvated electron was and still is an area of great interest in chemistry at both the fundamental and applied levels. However, the nature of the alkali metal anion was still a mystery and the study of its properties had been extremely difficult since equilibria 2 and 3 lie far to the right in ammonia solutions. In solvents other than ammonia, mixtures of M^- and e^-(solv) could be obtained;

however, the low solubilities of the metals as well as impurities in the solvent inhibited the study of the metal anions. In solvents capable of dissolving the alkali metals to an appreciable amount, the solutions would undergo irreversible decomposition as a result of the high reducing ability of the solvated electron.

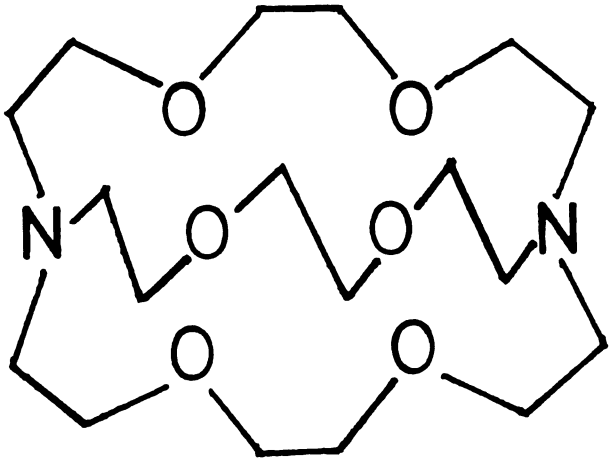
In 1970, Dye[1] discovered that the concentration of the alkali metals in solvents where they had previously been insoluble or only slightly soluble, could be increased by using organic complexing agents. The ligands, L, introduced a fourth equilibria:

$$M^+ + nL \rightleftharpoons M^+Ln \qquad 4$$

which drives equations (1) and (3) to the right. The two types of complexants used for this purpose have been crown ethers and cryptands, developed by Pederson[2] and Lehn and coworkers[3] respectively. Figure 1 gives examples of a crown ether, 18-crown-6 (18C6, or IUPAC: 1,4,7,10,13,16-hexaoxacyclooctadecane) and a cryptand C222 (IUPAC: 4,7,13,16,21,24-hexaoxa-1,10,diazabicyclo[8,8,8]hexacosane). It was found that these complexants also increase the stability of the solutions by partially shielding the cation from reductive attack by the electron. This development allowed one to choose a solvent in which equilibria (2) did not proceed strongly to the right so that the alkali metal



18-CROWN-6



2,2,2 CRYPTAND

Figure 1. 18-Crown-6 and Cryptand-2,2,2

anion would remain stable in solution long enough to study its properties at leisure with various techniques.

While working with concentrated solutions (~0.4 M) of sodium and C222 in ethylamine in 1974, Dye and coworkers[4] were able to form a solid gold-colored precipitate by cooling the solution to Dry Ice temperatures. Based on the stoichiometric analysis and its optical absorption band, the crystalline material was identified as having the stoichiometry $Na^+L \cdot Na^-$, where Na^+L refers to the complex formed by the sodium cation trapped inside of the "crypt". This identification was later verified by X-ray crystallography[5] giving the first structure of a salt of an alkali metal anion.

In 1979, DaGue et al.[6] reported that by decreasing the ratio of sodium to cryptand (R) in solution, the intensity of the optical absorption band of a dry film of the material would start decreasing at 15,400 cm^{-1} (the Na^- band) and begin growing at 7800 cm^{-1}. When R=1, the Na^- band nearly disappeared, leaving primarily the higher energy band. This band had been observed in a film of potassium and C222 from methylamine and assigned to the trapped electron[7]. Then in 1983, Ellaboudy and Dye[8] synthesized the first crystalline salt of the type $M^+L_2 \cdot e^-$ where all of the anionic sites are occupied by trapped electrons. Final conclusive evidence for this identification was provided by Dawes and

coworkers[9] who obtained the X-ray crystal structure of $Cs^{+}(18C6)_{2}\cdot e^{-}$.

The materials with the stoichiometry $M^{+}L_{n}\cdot N^{-}$, where M may be different from N, have been called alkalides (i.e., Na^{-} would be a sodide) and when the stoichiometry was $M^{+}L_{n}\cdot e^{-}$ they were called electrides. Since 1974, there have been 24 alkalides and 7 electrides synthesized and thoroughly classified in these laboratories (Table 1).

I. B. Properties of Alkalides and Electrides

These salts have been synthesized by using three different methods. The first and probably the easiest procedure has been to form a solution of metal and complexant, then evaporate the solvent rapidly to yield a film or a powder. This technique is the common method used to prepare thin films for optical spectroscopic studies. A disadvantage of this technique is that the crystals which form may or may not have the same stoichiometry as the solution from which they came. The second method also gives films for optical spectroscopy, but it involves vapor deposition of stoichiometric amounts of metal and complexant directly on the walls of an optical cell in vacuo. This procedure is more tedious than the first, but it can give a more uniform

Table 1. Alkalides and Electrides Synthesized to Date

$Na^+C211 \cdot Na^-$	Li12C4	$Cs^+(15C5)_2 \cdot e^-$
LiRbC211[a]	Na12C4	$Cs^+(15C5)_2 \cdot K^-$
$Na^+C221 \cdot Na^-$	$K^+12C4 \cdot Na^-$	$K^+18C6 \cdot Na^-$
$Na^+C222 \cdot Na^-$	Cs12C4	KRb18C6
$K^+C222 \cdot Na^-$	$K^+(15C5)_2 \cdot Na^-$	$Rb^+18C6 \cdot Na^-$
$K^+C222 \cdot e^-$	$K^+(15C5)_2 \cdot e^-$	$Rb^+18C6 \cdot Rb^-$
$K^+C222 \cdot K^-$	$K^+(15C5)_2 \cdot K^-$	Rb18C6
$K^+C222 \cdot Rb^-$	$Rb^+(15C5)_2 \cdot Na^-$	$Cs^+(18C6)_2 \cdot Na^-$
$Rb^+C222 \cdot Na^-$	$Rb^+(15C5)_2 \cdot e^-$	$Cs^+(18C6)_2 \cdot e^-$
$Rb^+C222 \cdot e^-$	$Rb^+(15C5)_2 \cdot Rb^-$	$Cs^+(18C6)_2 \cdot K^-$
$Rb^+C222 \cdot Rb^-$	KRb(15C5)	$Cs^+(18C6)_2 \cdot Rb^-$
$Cs^+C222 \cdot e^-$	$RbCs(15C5)_2$	$Cs^+(18C6)_2 \cdot Cs^-$
$Cs^+C322 \cdot Na^-$	$Cs^+(15C5)_2 \cdot Na^-$	$[K^+(HMHCY) \cdot Na^-]$[b]

a) Underlined compounds have not been fully characterised.
b) The compound in brackets is the subject of this Dissertation.

film, where as the previous method can leave gaps or clumps in the film. The final method is the one most commonly used to obtain large (~1 mmole) samples of the material for various studies. This procedure involves the gradual cooling of a saturated solution of the salt in an appropriate solvent (one in which it is not completely soluble) to cause precipitation of the crystals.

I. B. 1. Optical Properties

The optical spectra of alkalides and electrides have been obtained in the manner described above. Experience has shown that the best results are obtained when methylamine is used as the solvent. However, the actual absorption band for a given species is dependent on the nature of the complexing agent, the metals involved, the ratio of metal to ligand, and the solvent used. Table 2 gives the energies of the absorption maxima for various sodide films[10]. In general, the absorption bands occur at 13,000 - 16,000 cm^{-1} for Na^-, ~12,000 cm^{-1} for K^-, ~11,000 cm^{-1} for Rb^-, ~10,000 cm^{-1} for Cs^-, and 6000 - 9000 cm^{-1} for e^-(trapped). Typical absorption spectra of solvent free films of the alkali metal anions are given in Figure 2, and two examples of solvent free electride films are given in Figure 3.

Table 2. Position of the Absorption Maximum of Na^- in Various Sodide Films[a]

Film	Peak position ($cm^{-1} \times 10^{-3}$)
$Na^+C222 \cdot Na^-$	15.4
$Na^+18C6 \cdot Na^-$	16.9
$K^+18C6 \cdot Na^-$	14.0
$Rb^+18C6 \cdot Na^-$	13.8
$Cs^+C222 \cdot Na^-$	14.6
$K^+C222 \cdot Na^-$	15.1
$K^+(15C5)_2 \cdot Na^-$	14.3
$Rb^+(15C5)_2 Na^-$	13.9

a) ref. 10.

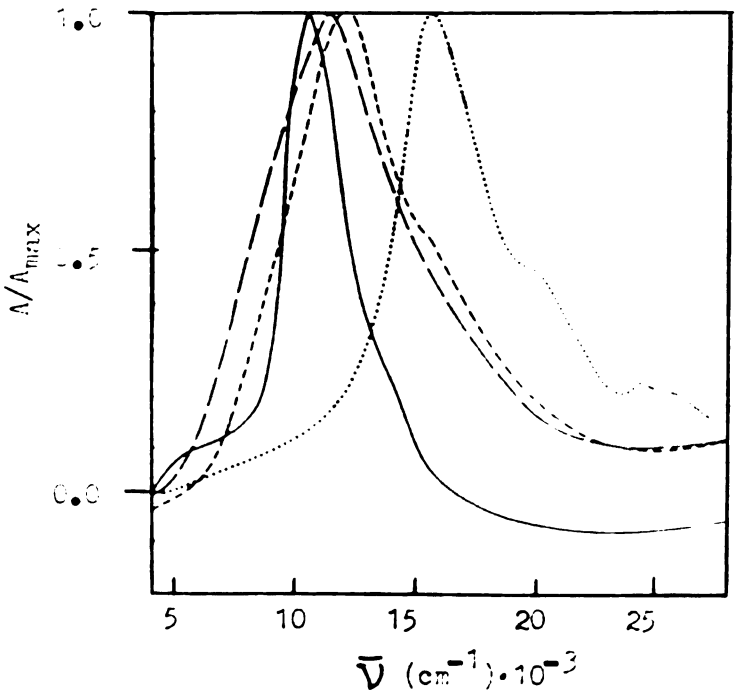


Figure 2. Spectra of solvent free films of $M^+C_{222}\cdot M^-$. Left to right; M = Na, K, Rb, Cs.

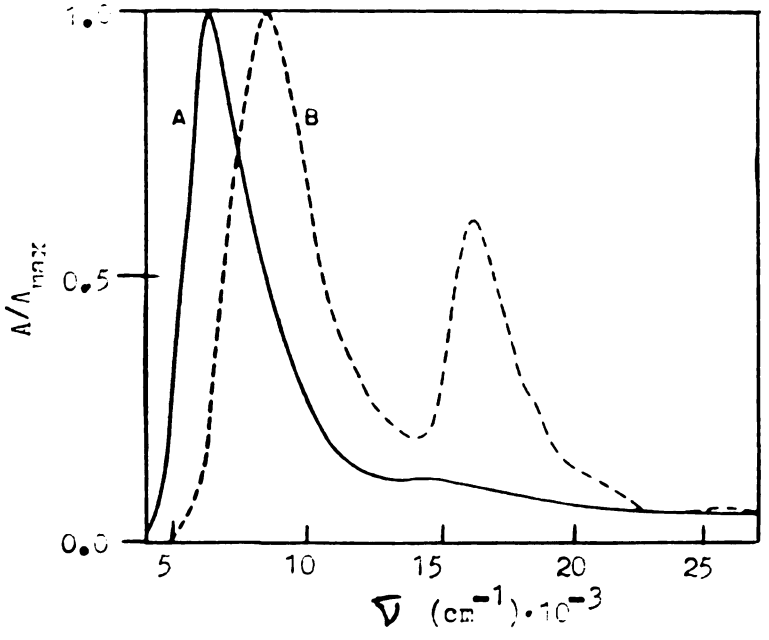


Figure 3. Spectra of solvent free electride films. A) Cs^- from methylamine. B) NaC_{222} from ammonia.

For the alkalides, the major absorption peak is believed to result from the ns to np transition of M^-. The shoulder which is quite distinct in the Na^- spectrum and slightly apparent in that of K^- could be a bound to continuum transition[11]. The electride spectra are in the near infrared as would be expected for a trapped electron. The observed spectra for electrides fall into one of two catagories, localized, or "metallic" behavior. Localized electrides, as in Figure 3, have absorption maxima that correspond to trap depths of 0.4 to 0.6 ev. These electrides tend to give broad absorption bands which may result from either electron-electron interactions, or a delocalized excited state. The "metallic" electrides give absorption spectra that remain high in the infrared out to at least 3000 cm^{-1}, similar to that of concentrated metal-ammonia solutions[10]. This would indicate either electron delocalization or shallow traps. Due to the extreme instability of these electrides, the "metallic" behavior has not been verified by D.C. conductivity measurements.

The position of the absorption maximum can thus be used as a tool in identifying the anionic species in the crystals; however, because of the dependence on enviroment, unequivocal identifications cannot always be made. For example, the absorption band for the compound RbNa18C6[12] lies between the band corresponding to that of Na^- in the

salt $Na^+C222 \cdot Na^-$ and the band corresponding to that of Rb^- in the salt $Rb^+C222 \cdot Rb^-$. This would lead one to conclude that either the Rb^- spectrum is red shifted by the different crystal, or the Na^- spectrum is blue shifted. Based solely on this information, one cannot tell which of these processes occurs. Also, the films are prepared by first dissolving the crystals in a solvent, then rapidly removing the solvent to produce the film. The optical spectra might reflect the species present in solution rather than those present in slowly grown crystals. Therefore, other techniques were needed that could determine the nature of the species present in crystalline alkalides and electrides.

I. B. 2. Nuclear Magnetic Resonance

Nuclear magnetic resonance spectroscopy (NMR) is a powerful technique for probing the electronic enviroment of the nucleus. In 1974, Ceraso and Dye[13] observed the sodium anion in nonaqueous solvents by using ^{23}Na NMR. Solutions of sodium and C222 in ethylamine and tetrahydrofuran each gave two resonances, a broad peak at ~-10 ppm and a narrow peak at ~-63 ppm, each diamagnetic with respect to saturated aqueous NaCl. On the basis of previous experience with salts of the complexed sodium cation[13],the broad peak

was assigned to Na^+L, so that the narrow upfield peak must have been due to Na^-. When trying to study solid crystalline sodides by using the same procedure at relatively low field strengths,line broadening obscured most of the information. Ellaboudy et al.[14] found that by using magic angle sample spinning (MAS) ^{23}Na NMR, both the dipolar and the second order quadrupolar broadening could be eliminated. This enabled them to detect both Na^+L and Na^- in solid crystalline sodides.

While the alkali metal anions, Rb^- and Cs^- were detected fairly readily in amine solutions[15] K^- remained undetected, presumably because of the equilibrium[16]:

$$K^- \rightleftharpoons K^+ + 2e^- \qquad 5$$

Recently, Tinkham[16] was able to obtain the K^- NMR spectrum by using a solvent of low donicity (Me_2O) to drive equation 5 to the left. By using MAS-NMR tuned to the appropriate nuclei, the anions of potassium[16], rubidium[17], and cesium[18] have all been detected in polycrystalline alkalides. Table 3 gives values of the chemical shifts of some of the alkalides and electrides, each referenced to the appropriate cation in aqueous solution at infinite dilution. The complexed cationic species that contain potassium

Table 3. MAS-NMR Peak Position of Various Alkalides and Electrides.

Compound	Calculated[a] Chemical Shift M^-(g), ppm	Calculated[b] Chemical Shift M^-(g), ppm	Observed[c] Chemical Shift M^-(g), ppm
(d)			
$Na^+C222 \cdot Na^-$	- 60.5 ± 1	- 63.1	- 61.3
$Na^+C222 \cdot Na^-$			- 23.7[h]
$K^+C222 \cdot Na^-$			- 23.7
$Cs^+(18C6)_2 \cdot Na^-$			- 62.9
$Rb^+(15C5)_2 \cdot Na^-$			- 61.3
(e)			
$K^+(15C5)_2 \cdot K^-$	- 101,1 ± .5	- 103.4	- 105.
$RbK(15C5)_2$			- 105.
$Cs^+(15C5)_2 \cdot K^-$			- 105.
$Cs^+(18C6)_2 \cdot K^-$			- 115.
(f)			
$Rb^+(15C5)_2 \cdot Rb^-$	- 211.6 ± 1	- 213.6	- 199.
$RbK(15C5)_2$			- 198.
$Cs^+(15C5)_2 \cdot Rb^-$			- 196.
$Rb^+(18C6)_2 \cdot Rb^-$			- 197.
(g)			
$Cs^+(18C6)_2 \cdot Cs^-$	- 344.3 ± .6	- 346.4	- 228.
$Cs^+(18C6)_2 \cdot Cs^-$			- 61.[i]
$Cs^+(18C6)_2 \cdot e^-$			+ 81[i]

a) ref. 42; b) ref. 43; c) shift from the appropriate M^+(aq.) at infinite dilution; d) ref. 14; f) ref. 17; g) ref. 18; h) due to Na^+C; i) due to Cs^+C.

and rubidium have not been detected in crystalline alkalides and electrides because of the large quadrupolar broadening.

These results show that MAS-NMR is a useful technique for identifying the anionic and, in most cases the cationic species in solid alkalides and electrides by the detection of (or absence of) the appropriate resonances. However, some salts with rubidium provide exceptions. The absence of the Rb^- peak cannot be used to prove conclusively that the Rb^- species is absent[17]. For example, XANES studies of Rb^-[19] have shown the presence of Rb^- in a salt of stoichiometry $Rb_2$18C6, while MAS-NMR studies did not detect Rb^- in this material.

The NMR results have also provided conclusive proof that the negatively charged species is a genuine anion rather than one of the several other proposed cation-based species[20,21]. Furthermore, the small shift in the peak position of Na^- from the calculated chemical shift of Na^- in the gas phase[22] indicates that this species is centrosymmetric with $3s^2$ character. The peak positions for K^- and Rb^- do shift somewhat from the calculated values[22] for the gaseous anions, indicating that the electron density can "spill out" to orbitals that have orbital angular momentum. There has been only one crystalline ceside synthesized to date, but small ceside peaks have been observed in other crystalline cesium systems[23] (and in solution) and the

chemical shift difference from the gaseous anion is even greater than those of potassium and rubidium. These results are expected, since there are low lying p and d orbitals available to potassium, rubidium, and cesium with decreasing energy gaps in this series, while the empty p and d orbitals of sodium lie well above the ground $3s^2$ state.

I. B. 3. Crystal Structures

The best proof of the existence of the alkalides and electrides is the determination of their crystal structures by X-ray crystallographic methods. The crystal structure of the first alkalide, $Na^+C222 \cdot Na^-$, was determined in 1974[5]. The crystals, prepared by slow cooling, were sealed in a glass capillary tube along with purified paraffin oil to hold them in place. Data needed to be collected on four different crystals (two crystals on a G. E. XRD-5 diffractometer and two crystals on a Picker FACS I diffractometer) since the work was done at ambient temperatures and the crystals decayed with time (sometimes as much as 35%). The crystal structure was described as closest-packing of NaC^+ and Na^- ions in a hexagonal unit cell. The cation-anion (Na^+ to Na^-) nearest neighbor distance is 7.06 Å.

Since that time, the techniques have been modified[24] and a Nicolet PF3 diffractometer has become available. A single crystal is selected from a polycrystalline sample under purified, cooled octane in an inert atmosphere, mounted on the tip of a glass capillary by using Celvacene grease, then transferred to the diffractometer while keeping the temperature of the crystal at or below -20°C. The crystal was maintained under a stream of cold nitrogen gas (~-65°C) while the data were being collected. This technique has been used to determine the crystal structures of five additional alkalides[25,26] and the first electride, $Cs^+(18C6)_2 \cdot e^-$[9]. With this improved technique, the greatest obstacle to structure determination is the difficulty in growing large enough single crystals.

I. B. 4. Calorimetry

Many of the alkalides (especially sodides) and a few electrides are stable up to their melting point, above which they decompose irreversibly and exothermally. The melting and decomposition temperatures of some alkalides and electrides were obtained by using differential scanning calorimetry (DSC). Some experiments were done by Dye[27] at A.T.&T. Bell Laboratories and others were carried out here with an instrument on loan from E.I. Dupont de Nemours Co.

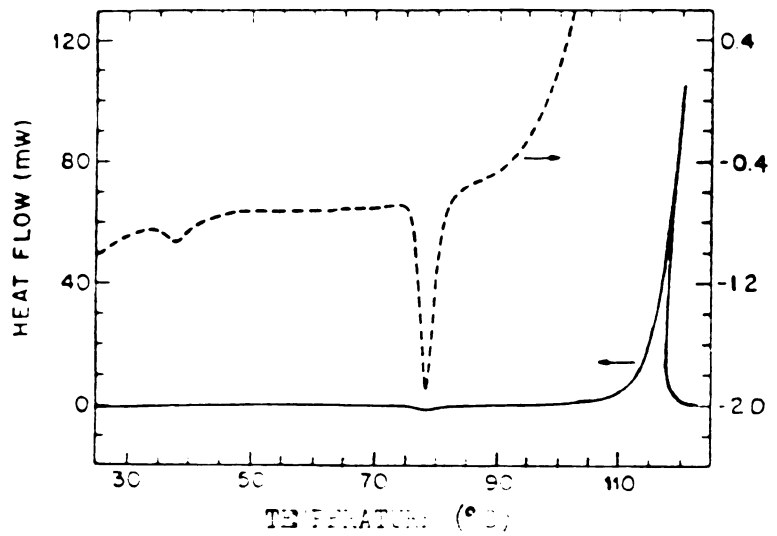


Figure 4. DSC trace for a 3.1 mg sample of $Rb^{+}(1806)\cdot Ia^{-}$ at a heating rate of 10 deg/min.

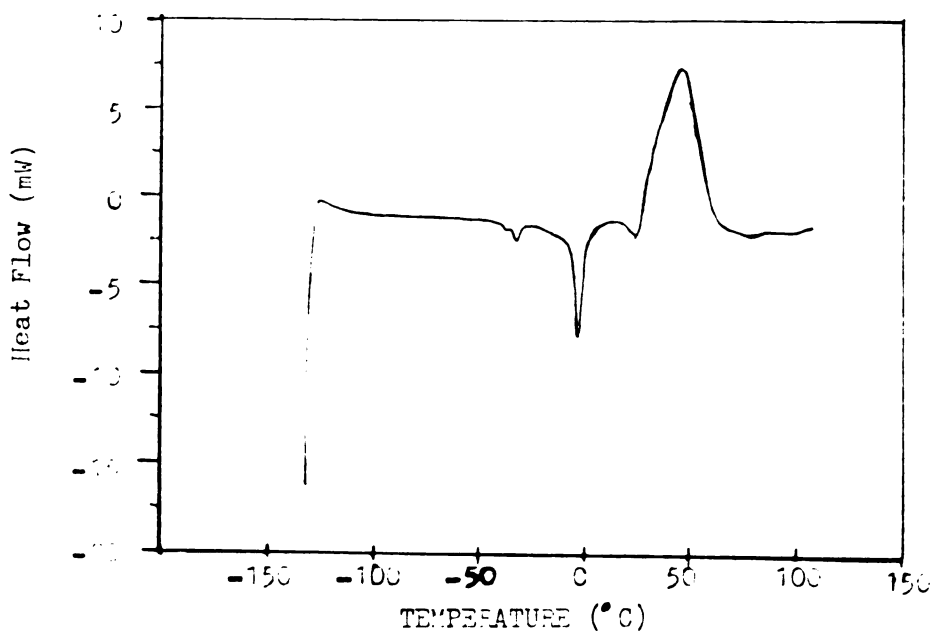


Figure 5. DSC trace for $Cs^{+}(1505)_2\cdot e^{-}$ at a heating rate of 10 deg/min.

A typical DSC trace is shown in Figure 4, where the dashed line is an expansion of the trace over the region shown. DSC measurements can also provide information about processes such as softening of the lattice. This can be seen, for example, by the endothermic peaks at ~-35° and -10° C in the DSC trace for $Cs^{+}(15C5)_2 \cdot e^{-}$ (Figure 5,[28]). This assignment is also based on visual observations and the temperature dependence of MAS-NMR studies. The melting point of this compound is ~25°C, and decomposition begins immediately above this temperature. Table 4 summarizes the DSC results.

I. B. 5. Summary

Prior to the present study, 38 compounds had been synthesized in this laboratory by many different investigators over a period of 12 years. Of these, 23 alkalides and 7 electrides were completely characterized by using the techniques described above together with analysis and other measurements. All of these compounds were synthesized by using one of the crown ethers (18C6, 15C5, or 12C4), or one of the cryptands (C211, C221, C222, or C322), (see Table 1). The study of these compounds has provided insight into the properties and enviroment of the negatively charged alkali metals and the solvent-free trapped electron. The potential applications of these compounds, for example as reducing

Table 4. DSC Results for Some Alkalides and Electrides

Compound	m.p.(°C)	Temperature of the decomposition peak (°C)
(a)		
$Na^+C222 \cdot Na^-$	73	105
$Rb^+C222 \cdot Na^-$	50	63
$K^+(15C5)_2 \cdot Na-$	45	108
$Rb^+(15C5)_2 \cdot Na^-$	75	121
$K^+18C6 \cdot Na^-$	38	86
$Rb^+18C6 \cdot Na^-$	66	92
$Cs^+(18C6)_2 Na^-$	38	103
$Cs^+(18C6)_2 \cdot e^-$	36	60
$Cs^+(18C6)_2 \cdot Cs^-$	60	95
(b)		
$Cs^+(15C5)_2 \cdot e^-$	25	45

a) ref. 10; b) ref 28.

agents in chemical synthesis[29] or as semiconductors[30], have not been pursued because of their high reactivity towards water and oxygen and their instability at room temperature and above. The high reactivity is an inherent property of these strong reducing agents, but the instability at room temperature results from the reactivity of the ligand. The aim of this research was to obtain an alkalide, and possibly an electride, which could be stable for longer periods of time at room temperature (or even above room temperature) by utilizing more robust complexants. Since the crown ethers tend to be more resistant to attack by the electron than do the cryptands[21], an attempt was made to use even larger crown ethers. Following this, the nitrogen analogs of the crown ethers were investigated. The results of this search for new complexants are described in this study.

II. Experimental

II. A. Glassware Cleaning

All glassware used to synthesize and handle solutions and crystals was cleaned by a general procedure as follows. The apparatus was first rinsed with an HF-cleaning solution [33% HNO_3 (16M), 5% HF (28M), 2% acid-stable detergent, and 60% deionized water by volume] then immediately rinsed several times with deionized water. The glassware was then filled with aqua regia (3 HCL:1 HNO_3) and left for at least six hours, followed by rinsing six times with deionized water and six times with conductance water (house deionized water which has been further deionized with a Fisher Scientific demineralizer system). The glassware was then dried in an oven at 232^{o}C for at least six hours and finally protected against further contamination by covering each opening with Parafilm-M.

II. B. Reagents

II. B. 1. Metals

Sodium, Potassium, and Rubidium. These metals (Alfa-Ventron Products, 99.95% purity) were obtained under argon in sealed glass ampoules with glass breakseals on one end. They were then distributed into smaller tubes following a procedure described elsewhere[31]. The required quantities of metal were obtained by premeasuring the inner diameter of the tube and isolating lengths to give the appropriate volumes.

Cesium. This metal (a gift from Dow Chemical Co.) was obtained in fifty gram ampoules and distributed into smaller breakseal tubes (Fig 6). The cesium was taken into the inert atmosphere box, heated to its melting point with a heat gun, and poured into the breakseal tubes through the Ace connector. The tubes were then capped with another Ace connector which had a Kontes valve and Fischer Porter opening, then removed from the dry box and evacuated to $\sim 2*10^{-5}$ torr. With the cesium immersed in liquid nitrogen, the ampoules were flame sealed under dynamic vacuum. This metal could then be treated following the same procedure as with the other metals.

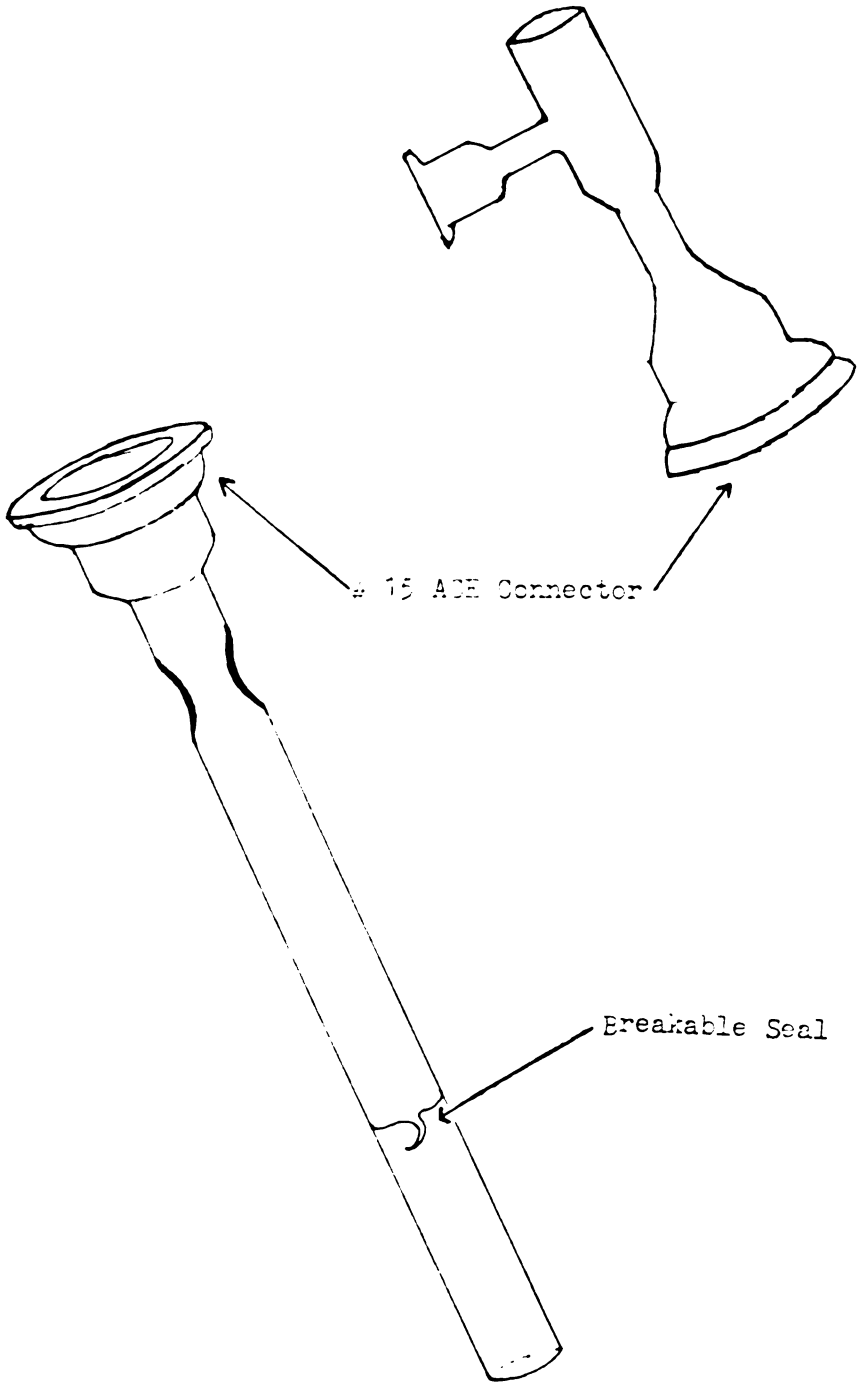


Figure 6. Apparatus used to distribute the 50 gram ampoules of cesium.

II. B. 2. Solvents

Methylamine ($MeNH_2$; Matheson, 98% pure) was stirred over calcium hydride at reduced temperatures (<-20°C) for several hours. It was then frozen in liquid nitrogen and pumped to ~$2*10^{-5}$ torr to remove residual gases. The stir-freeze-pump cycle was repeated until gas evolution was no longer observed during the stirring. This solvent was then transferred to bottles containing Na metal, frozen, pumped, and stored overnight. If the metal-methylamine solution remained blue (characteristic color of e^- solvated and Na^-), the dry methylamine was transferred to a stainless steel storage tank and subjected to freeze-pump-thaw cycles until the pressure over the frozen solvent was less than $1*10^{-4}$ torr. If the solution had not remained blue, it was transferred to another bottle containing Na metal and again left overnight before transferring it to the storage tank.

Dimethyl Ether (Me_2O; anhydrous, Matheson) was treated in the same manner as methylamine except that benzophenone was added to the Na as an indicator of dryness (Na is insoluble in dimethyl ether).

Trimethylamine (Me_3N; Matheson) was purified in the same manner as dimethyl ether. Final storage was in heavy-walled glass bottles.

Diethyl Ether and n-Pentane: The procedure for diethyl ether (Et_2O; ethyl ether, anhydrous, E.M. Science) and n-pentane (J.T. Baker Chemical Co.) was the same as for trimethylamine. Final storage was over Na-K alloy with no benzophenone.

II. B. 3. Complexing Agents

a. 21-Crown-7

21C7 Or I.U.P.A.C.: 1,4,7,10,13,16,19-Heptaoxacyclohene-icosane was prepared following a procedure by Greene[32]. First, it was neccessary to prepare triethylene glycol di-tosylate [3]. A solution of p-toluenesulphonylchloride (TsCl, 0.33 mol) in tetrahydrofuran (THF, 200 ml) was added drop-wise to a mixture containing triethylene glycol (0.15 mol), 100 ml sodium hydroxide (5.25 M), and THF (100 ml) under constant stirring at $0^{o}C$. The solution was kept at $0^{o}C$ with stirring for an additional two hours after all the TsCl had been added, then poured into aqueous hydrochloric acid (10%) at $0^{o}C$. The precipitated ditosylate was collected, washed with water, recrystalized in methanol, and

dried under vacuum. Yield was 67%; mp 81-83 C (lit[4] 80.5-81.5).

The triethylene glycol ditosylate (0.050 mol) in THF (280 ml), and potassium t-butoxide (0.55 mol) in THF (280 ml) were each added dropwise to a solution of tetraethylene glycol (0.055 mol) and potassium t-butoxide (0.055 mol) in THF (560 ml). The rate of addition of the ditosylate solution was twice the rate of addition of the potassium t-butoxide solution with the working flask kept at 35^{o}C under constant stirring. The final mixture was left stirring at 35^{o}C for an additional 18 hrs., filtered, and brought to dryness under vacuum. The crown was extracted from the solid by using diethyl ether in a soxhlet extractor assembly. The solvent was removed under vacuum, and the 21C7 was obtained by vacuum distillation of the residue at 100^{o}C and $2*10^{-5}$ torr (Fig. 7). The distillate was further purified by washing over a sodium metal film with Me_2O (Fig. 8). The reduced solids were filtered out by the glass frit, the solvent was removed, and the 21C7 was collected under inert atmosphere and then vacuum distilled again. The ^{1}H NMR spectrum in $CHCl_3$ showed a singlet at δ 3.5. The mass spectrum was comparable to that obtained by Lee et al.[35].

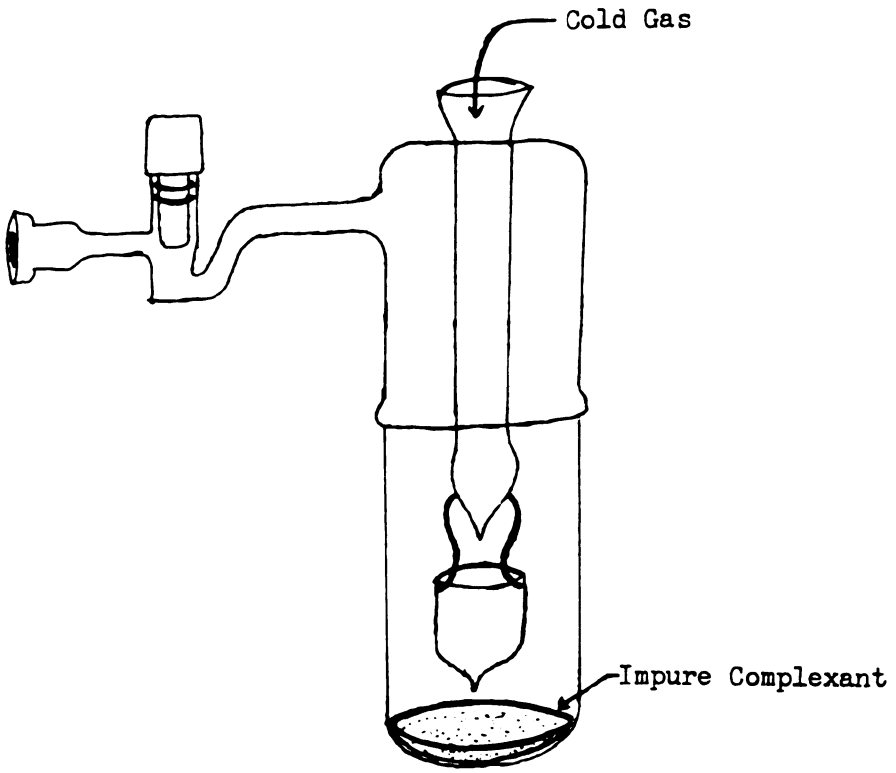


Figure 7. Vacuum Distillation Apparatus for Complexant Purification

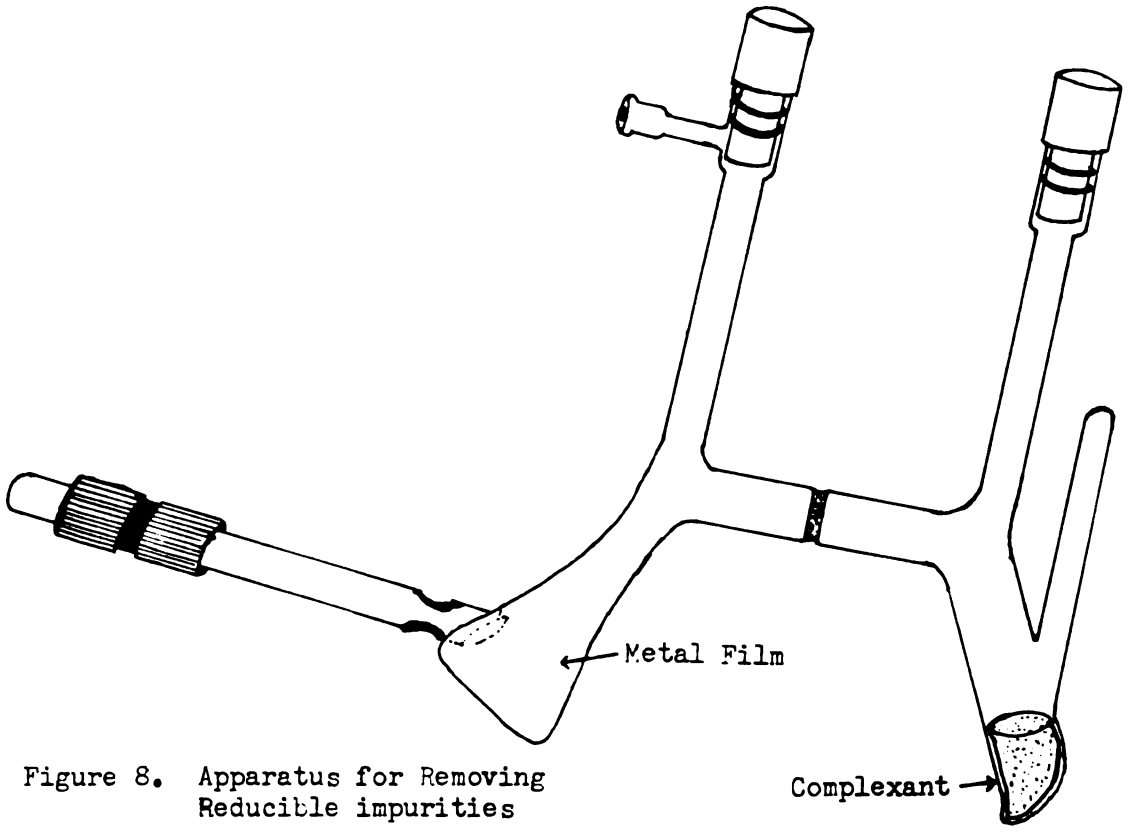


Figure 8. Apparatus for Removing Reducible impurities

b. Hexamethylhexacyclen

HMHCY or I.U.P.A.C.: 1,4,7,10,13,16-hexaaza-1,4,7,10,13,16-hexamethylcyclooctadecane was prepared following a procedure by Pez et al.[36]. Hexacyclen trisulfate (18.4 mmol, Aldrich Chemical Co.) was refluxed under constant stirring with 88% formic acid (60 ml) and 37% formaldehyde solution (33 ml) for 70 hrs. at 100°C. The mixture was brought to dryness under vacuum, cooled in an icewater bath, and made basic with 50% sodium hydroxide solution. The product was collected using THF in a liquid-solvent extractor (Fig 9). The solvent was then dried over sodium hydroxide pellets, decanted, and removed under vacuum. A yellow-orange liquid was obtained by vacuum distillation at 126-135°C and $2*10^{-5}$ torr. This was cleaned further by washing over Na-K alloy then vacuum distilling again. The ^{1}H NMR spectrum of the final product in $CDCl_3$ showed resonances at δ 2.20 (singlet, 18 H) and δ 2.40 (singlet, 24 H). The chemical ionization mass spectrum showed a molecular ion at m/e 341.

c. Tetramathylcyclam

TMCYL or I.U.P.A.C.: 1,4,8,11-tetraaza-1,4,8,11-tetramethylcyclotetradecane was prepared by following the same procedure as with HMHCY, but using 1,4,8,11-tetraazacyclotetradecane (cyclam, Aldrich Chamical Co.) as the starting

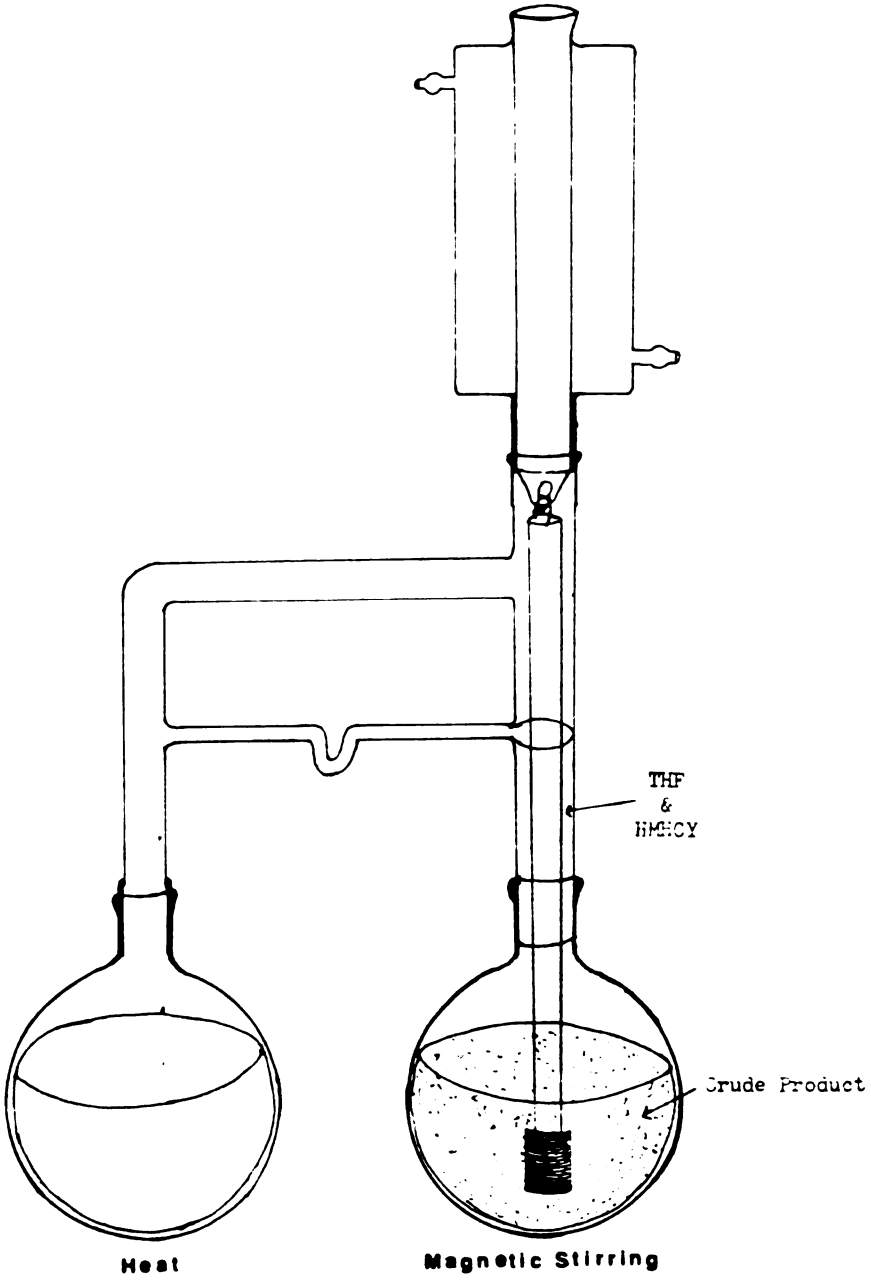


Figure 9. Liquid Solvent Extraction Assembly

material. White crystals (mp 38-42°C) were obtained. The ^{1}H NMR spectrum in $CDCl_3$ showed resonances at δ 1.63 (multiplet, 4 H), δ 2.18 (singlet, 12 H), and δ 2.42 (triplet, 16 H). The chemical ionization mass spectrum showed a molecular ion peak at m/e 255.

II. C. Sample Preparation

The crystals were prepared in an apparatus called an H-cell or a modified version such as that shown in Figure 10. The glass ampoules, which contained the measured amounts of the appropriate metals, were scribed with a glass knife, washed with acetone, and taken into the inert atmosphere box with the apparatus. The metal tubes were broken and dropped into sidearm A which was then capped with a Cajon Ultratorr coupling and a sealed glass tube. The stoichiometric amount of complexant was then added through sidearm B which was similarly capped. The entire apparatus was removed from the inert atmosphere box and evacuated to ~$2*10^{-5}$ torr. The Ultratorr caps were removed by seal off, the metal distilled into chamber M, and the sidearm A sealed off at the constriction. The complexant in Chamber C was cooled to ~-20°C in an isopropanol-Dry Ice bath, and either dimethyl ether or methylamine was added and mixed with the complexant. The

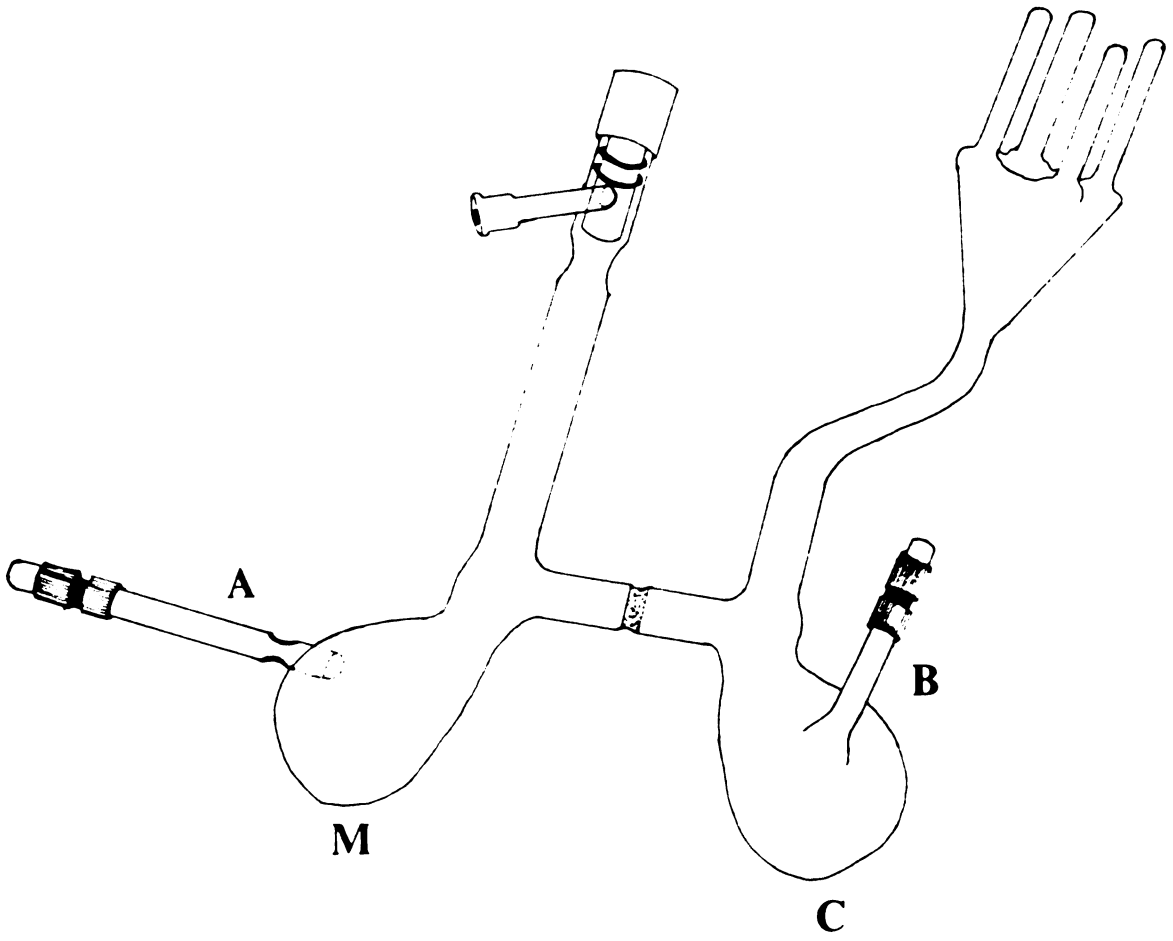


Figure 10. Synthesis Apparatus

apparatus was removed from the vacuum line, and the solution was poured through the frit onto the metal film while keeping both chambers below -20°C. The solvent was distilled back into chamber C and again poured onto the metal. This washing procedure was carried out several times to ensure that all the complexant had been transferred to the metal. The solution was shaken for several hours at ~-20°C until it appeared that all the metal had dissolved. The solution then was poured back into chamber C and most of the solvent was distilled into a waste bottle leaving a thick slurry. A cosolvent, either trimethylamine or diethyl ether, was introduced to make a concentrated solution of the slurry, then the solution was left for several hours at -78° C to allow crystals to precipitate. Then to increase the yield, most of the solvent was distilled into a waste bottle. The remaining solvent was poured off the crystals into chamber M, then also distilled into the waste bottle. A washing liquid, one in which the crystals were insoluble or only slighty soluble, was added to remove any nonreacted complexant from the crystals. After washing several times, all liquid was removed and the apparatus was evacuated to $2*10^{-5}$ torr to ensure complete dryness. The crystals were then poured into the fingers, immersed in liquid nitrogen, and sealed off for storage. When an unmodified H-cell was used, the complexant was added through a Kontes valve and

the crystals were removed through the same valve under inert atmosphere.

II. D. Analysis

The stoichiometry of the alkalide and electride systems was determined by using an analysis scheme developed by Dye and coworkers[31]. The metal content was determined by first reacting the crystals with water and measuring the amount of hydrogen evolved. This was followed by pH titration and metal analysis by flame emission on portions of the residue. The complexant content was determined by the pH titration data and also by quantitative ^1H NMR analysis of the residue.

II. D. 1. Hydrogen Evolution

A known mass of crystals was reacted with water according to the equation:

$$ML_x\ N + 2\ H_2O \text{ ---> } M^+ + N^+ + H_2 + xL + 2OH^- \qquad 6$$

M = metal 1 N = metal 2

x = 1 or 2 L = complexant

To protect the samples from thermal decomposition prior to the addition of water, they were kept in Dry Ice. The crystals were loaded under inert atmosphere into a glass vessel designed for this purpose, then capped off with a glass tube and Cajon Ultratorr coupling. If the sample was stable at room temperature for short periods of time, the crystals were weighed and transferred in the inert atmosphere box. For samples that would decompose if left at room temperature for an appreciable length of time, a preweighed tube that contained the sample was scribed, broken, and dropped into the apparatus under an inert atmosphere in a portable glove bag while being kept at liquid nitrogen temperature. The sample mass was determined later by subtracting the weight of the empty tube. For either case, the crystals were spread on the bottom of the apparatus to provide good thermal contact, placed in Dry Ice, attached to a vacuum system designed for hydrogen evolution[37], and the entire system evacuated to $5*10^{-5}$ torr. The conductance water used for decomposition, (previously degassed by repeated freeze-pump-thaw cycles), was allowed to distill into the vessel containing the crystals. After the reaction was complete, a manual Toepler pump was used to collect all the evolved hydrogen in an evacuated closed tube of known volume. The pressure was obtained by measuring the difference in the height of a mercury column open to the hydrogen on one end and to the

room on the other end. All of the hydrogen had been collected when ten successive pump cycles produced no further change in the pressure. The number of moles of H_2 was evaluated by using the ideal gas law. The residue (decomposed crystals plus water) was kept for further analysis.

II. D. 2. pH Titration

As shown by Equation (6), a pH titration of a portion of the residue from the H_2 evolution offers a second check on the amount of metal that was present in the sample. When the complexants are amines, which are also bases, a pH titration also offers information on the amount of complexant present. Using the information from the H_2 evolution to estimate the number of equivalents of base present, the residue was dissolved in a known amount of HCl and conductance water to give a solution of pH~3. This solution was then divided into five parts, one for flame analysis, one for ^1H NMR, and three for pH titration. A fresh solution of NaOH was standardized with potassium hydrogen phthalate, then used to titrate each portion of the residue designated for this purpose. A digital pH meter (ORIEN Research, Model 701A) and a Corning electrode were used to determine the endpoints for all titrations. To

prevent CO_2 absorption by the base, the titration was done with a buret enclosed in a glass tube that allowed dry nitrogen gas to flow over the NaOH solution.

II. D. 3. Flame Emission

The metal content of the solution was determined by using a Jarrell-Ash Atomic Absorption/Flame Emission Spectrophotometer. Only the flame emission feature was used in this work. The portion of the residue set aside for flame emission was divided and diluted to give solutions of ~30 ppm for each of the metals present. The wavelength was adjusted to give a maximum emittance for each metal and a calibration curve was obtained by using standard solutions in the 10-100 ppm range. The reading obtained with conductance water was noted between each standard in order to correct for baseline drift. The sample was determined at the beginning, end, and several times during the course of the standards and the results were averaged with proper weighting. A calibration curve of the output, given by a digital averager, vs the concentration of the metals was used to determine the concentration of the sample.

II. D.4. Proton NMR

The remaining portion of the residue was analyzed by proton NMR for the complexant content. This portion was first neutralized by adding an equimolar amount of NaOH as determined by the titration curve, then allowed to dry by slow evaporation. A weighed amount of sodium acetate was added to the remaining solid and diluted with deuterium oxide. The solution was analized on a Bruker 250 MHz Fourier Transform NMR instrument which provides a line fitting program that was used to fit the sodium acetate and complexant peaks to Lorentzian curves. This program gives the amplitute, full width at half height, and the standard deviation of the curve. The concentration of the complexant was determined by comparing the areas under the complexant peaks with that due to the acetate.

III. Synthesis

Introduction

The synthesis of alkalides and electrides has previously been accomplished by using cryptands or the crown ethers 12-crown-4,15-crown-5,and 18-crown-6. So far all crystals prepared have been unstable at room temperature and decomposed irreversibly upon standing. The main goal of this work was to investigate the preparation of new alkalides with different ligands in an effort to obtain a more stable crystal. First, a continuation of the crown ether sequence was investigated by attempting to form a complex with 21-crown-7. Next, after a report by Pez and coworkers[36] of obtaining blue solutions from a mixture of hexamethylhexacyclen (HMHCY) and Na-K alloy, complexes that used the nitrogen analogs of the crown ethers were employed.

III. A. Complexes of 21-Crown-7

The crown ethers show limited selectivity to complexation among the alkali metals as shown in Figure 11. However, the strongest complex forms when there is a good correlation between the cation size and the crown cavity. Table 5 gives the alkali metal cation diameters and the cavity size of the crown ether rings as determined by X-ray

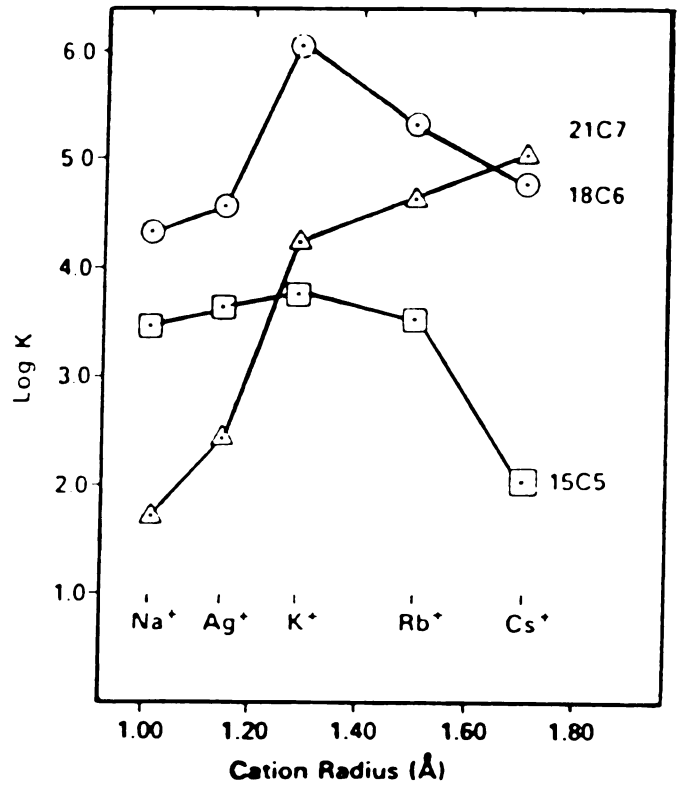


Figure 11. Log K vs. Cation Radius in Methanol at 25°C (ref. 44).

Table 5. Relative sizes of the Alkali Metal Cations and the Crown Ethers.

Cation	Diameter (Å)[a]	Crown Ether	Ring Size (Å)[b]
Li^+	1.48	12C4	1.2 - 1.5
Na^+	2.04	15C5	1.7 - 2.2
K^+	2.76	18C6	2.6 - 3.2
Rb^+	2.98	21C7	3.4 - 4.3
Cs^+	3.40		

a) ref. 45; b) ref. 38.

crystallographic data and from space filling models of the Corey-Pauling-Koltun type. Based on the selectivity of 21C7 and the relative sizes of the cations and crowns, one would expect 21C7 to form the most favorable complex with Cs^+. For the anion, previous experience has shown that the sodide is the easiest to crystallize and forms the most stable salts.

Several attempts were made to isolate crystals from an equimolar mixture of cesium, sodium, and 21-crown-7. The characteristic blue color of the solvated electron (or alkali metal anion) was immediately obtained upon mixing the complexant and the metal with dimethyl ether as the solvent. After several hours of stirring at $<-20^{o}C$, a significant amount of metal still had not dissolved. However, reddish-bronze films could be seen on the walls of the glassware. Therefore, an attempt was made to harvest any crystals which might be in solution whether as a sodide, electride, or a mixture of both. When diethyl ether was used as the cosolvent, the solution immediately began to decompose. This may have been caused by air getting into the system, or possibly by the more acidic β hydrogen. In all successive experiments, trimethylamine was used as the cosolvent with no indication of solution decomposition. Even with trimethylamine, all attempts to precipitate crystals were unsuccessfull. By removing all solvent, a black material could be obtained,but after washing, the material looked

like precipitated metal. In an effort to increase complexation, methylamine was tested as the initial solvent since the alkali metals are slightly soluble in pure methylamine. This proved to be a poor choice, as crystals still could not be precipitated, and the solution would decompose irreversibly if the temperature of the bath rose above -40°C.

To test the behavior of 21C7 with rubidium and potassium, in separate experiments, equimolar mixtures of cesium and rubidium with 21C7 and cesium and potassium with 21C7 were mixed using dimethyl ether as the solvent. In both cases, temperature dependent solutions were obtained. The rubidium solution appeared light blue at a temperature of -20°C and became increasingly darker as the solution was cooled. The potassium was clear at -20°C, but gradually became dark blue as it was cooled below -30°C. In both cases, the solutions would lighten if allowed to warm up and darken again if recooled.

One possible explanation of the temperature dependence is that the dilute solutions are decomposing at the higher temperature faster than the rate of complexation of the excess crown and metal. As the temperature is lowered, the rate of decomposition is decreased or stopped completely while complexation is still occurring. The discrepency in the temperature of the apparent decomposition of the solutions is due to the relative stability of each of the

anions to dissociation into the cation and solvated electron, where the order of stability is $Na^- > Rb^- > K^-$. The rubidide is slightly more stable than the potasside because of the higher solvation energy of the potassium cation.

A second explanation of the temperature dependence could be due to decomplexation of the cesium and the crown rather than decomposition at the higher temperatures. The equilibrium constant (K_1) for Reaction 7 was estimated by Dye[10] for the alkali metals in ethylenediamine. These values are shown below.

$$M^+ + N^- \underset{}{\overset{K_1}{\rightleftharpoons}} M^- + N^+ \qquad 7$$

Cs^+	Na^-	$K_1 \tilde{=} 10^{-6}$
	K^-	$K_1 \tilde{=} 10^{1}$
	Rb^-	$K_1 \tilde{=} 10^{-2}$

As the temperature increases, the reaction proceeds to the right with $K^- > Rb^- > Na^-$. These values are probably dependent on the solvent used, but they may explain the trend to the relative stabilities. At the higher temperatures, Equation 7 may proceed strongly to the right with potassium and to a lesser degree with rubidium. The crown would be less prone to complex the cations of potassium or

rubidium, the ceside would then oxidize and the cation would be reduced to give back the metals.

According to Pederson[2], the greater the number of oxygen atoms the complexant has, the more stable the complex will be, provided that the oxygens are coplanar and symmetrically distributed. With seven or more oxygens, the planar arranrement cannot be obtained; this might explain the difficulty in obtaining crystalline complexes with 21-crown-7. However, it may still be possible to synthesize crystals by utilizing different solvents, or possibly adding lithium to the solution as previously demonstrated for the 18-crown-6 systems by Issa and Dye[39].

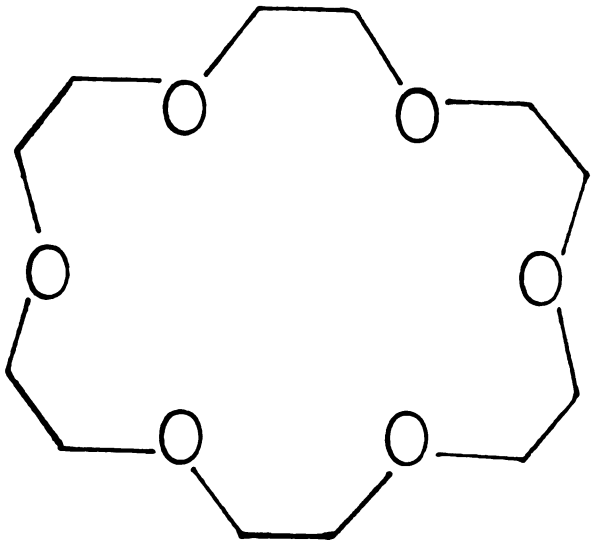
III. B. Complexes of Hexamethylhexacyclen

In 1984, Pez et al.[36] reported seeing blue solutions when adding HMHCY to a reaction in which there was some Na-K alloy. Due to this observation and the similarities between 18C6 and HMHCY (Fig. 12), it was believed that crystals of the stoichiometry potassium, sodium, HMHCY might be synthesized. Previous experience has shown that potassium forms a 1:1 complex with 18C6, a result that can be rationalized by comparing the cation and crown sizes in Table 5. With the similarities between the two complexants, it was assumed that HMHCY would also form a 1:1 complex with

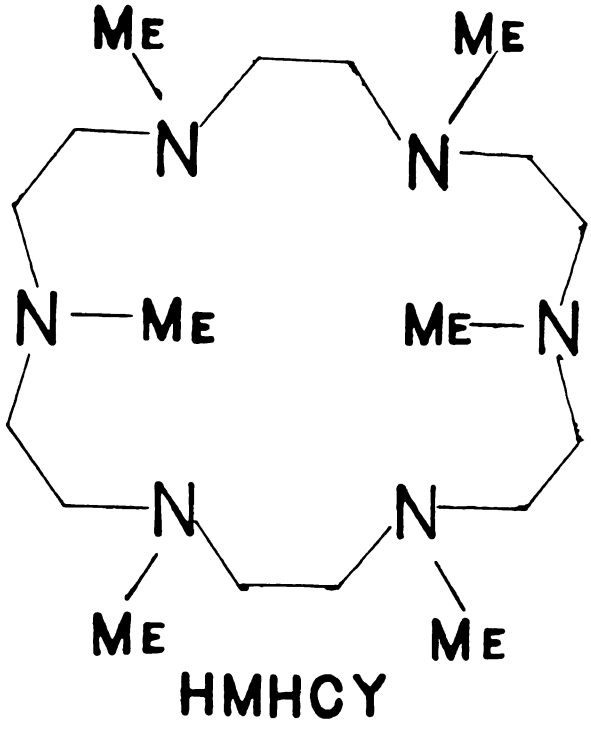
potassium. Using space filling models, the cavity size of HMHCY was estimated to be 3.0 - 3.25 A.

The complexant was dissolved in dimethyl ether and poured onto the metal to obtain a blue solution. After ~6 hrs. of mixing the solution at ~-20°C, red-bronze films formed easily on the sides of the vessel, but some metal remained undissolved and it appeared as if metal flakes were falling out of solution. At this point, the solution was poured away from the metal and most of the solvent was removed. Trimethylamine was added and the apparatus was packed in Dry Ice to allow crystals to precipitate. After standing for over 12 hrs., the solution still gave no sign of crystallization. All the solvent was then removed by slow evaporation to yield a dark mass of material. The washing solvents normally used, trimethylamine and diethyl ether, were inappropriate in this case due to the high solubility of this substance in these liquids. By using n-pentane to wash the material, shiny red-orange crystals were isolated. This procedure was repeated several times and gave the same results.

From the data in Table 5, the estimated size of the HMHCY, and the experience with 18C6, it also seemed likely that crystals could be synthesized with rubidium or cesium in place of potassium. Using the same procedure as with the potassium compound and a 1:1:1 ratio of rubidium, sodium, and HMHCY, dark red crystals were obtained. Due to a low



18-CROWN-6



HMHCY

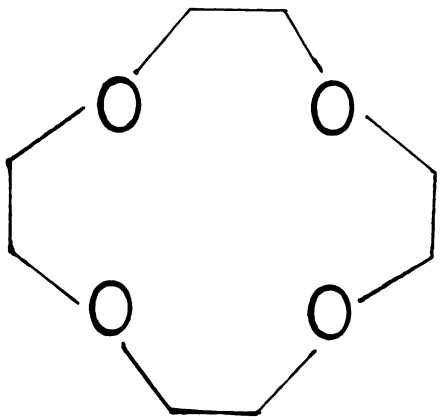
Figure 12. 18-Crown-6 and Hexamethylhexacyclen (HMHCY)

yield of these crystals and the fact that a large amount of metal was left undissolved, it was presumed that the crystals obtained were actually of the ratio 2:1 rubidium to HMHCY. However, complete analysis would be required to determine the stoichiometry of the crystals. With cesium, the large cation indicated that a sandwich complex would be necessary. A synthesis using cesium and HMHCY in a ratio of 1:2 was attempted in order to make a cesium electride. Using dimethyl ether as the solvent, the solution turned blue immediately upon mixing metal and complexant, and the cesium dissolved quickly. As the volume of Me_2O was being reduced, metal began precipitating out of solution. Adding either diethyl ether or trimethylamine as the cosolvent in separate experiments caused the solution to turn green and metal clumps to form.

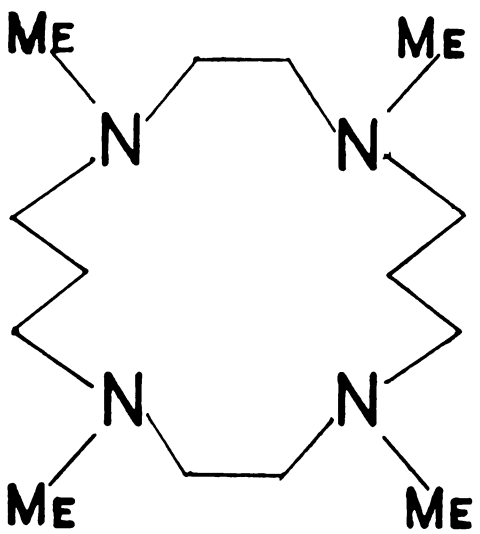
Looking at the space filling models,it can be seen that potassium and rubidium both fit within the ring cavity very well, whereas cesium is too large; as would be expected by the relative sizes. In trying to form a sandwich compound, the methyl groups on each of the HMHCY molecules would apparently cause too much sterric hinderence for two of the HMHCY molecules to fit around the cesium cation. Further attempts to form this sandwich compound were abandoned.

III. C. Complexes of Tetramethylcyclam

From successes in synthesizing alkalides using hexamethylhexacyclen, it was thought that tetramethylcyclam, (TMCYL, a similar compound to 12C4; Fig.13), would also form alkalides and possibly electrides. The space filling models indicated that cesium might form a solid sandwich complex with TMCYL. A synthesis involving cesium, sodium, and TMCYL in a ratio of 1:1:2 was attempted using dimethyl ether as the solvent. The complexant appeared to be insoluble in Me_2O (later it was shown to be slightly soluble), so this solvent was removed and methylamine was added. The solubility of TMCYL in $MeNH_2$ did not appear to be any better, but it was difficult to tell what was happening since the metal is slightly soluble in $MeNH_2$ and gives a blue solution. Using $MeNH_2$ to wash the metal onto the complexant also proved to be unsuccessfull. In a separate experiment, the metal film was first made, then the complexant was deposited directly on the metal. Dimethyl ether was added as the solvent in hope that complexation would increase the solubility of both the metal and the complexant. After stirring for ~1 hr. at ~-20^{o}C, there was no indication of complexation. The solution was cooled to Dry Ice temperatures without any improvement. In another experiment, the behavior of rubidium and potassium was examined by mixing



12-CROWN-4



TMCYL

Figure 13. 12-Crown-4 and
Tetramethylcyclam (TMCYL)

these metals with TMCYL in a ratio of 1:1:2 in an attempt to form a sandwich rubidium compound. Using Me_2O as the solvent gave the same results as with cesium and sodium. As a final test, the formation of lithium electride was attempted in a solution with $MeNH_2$. The results were the same as with the other alkali metals.

The absence of the blue solution in all of the trials indicates that TMCYL does not complex sufficiently with any of the alkali metals. This could result from decomposition, brought on by the acidic β hydrogen in the complexant. At any rate, further study of this complexant was abandoned.

IV. Characterization of K^+(HMHCY) Na^-

IV. A. Determination of Stoichiometry

The crystals that formed during the synthesis with the complexant HMHCY need not have the same stoichiometry as the solution from which they precipitated. An analysis scheme has been employed which offers three checks on the percent metal and two checks on the percent complexant in the sample. A general outline of the procedure has been reviewed in Chapter 2 of this dissertation. The samples were analysed according to Equation 6 by reacting the crystals with H_2O and measuring the volume of hydrogen evolved. The number of moles of hydrogen was calculated using the ideal gas law. The number of moles of hydroxide ion and HMHCY were determined by acidifying the residue with a known amount of hydrochloric acid and then back titrating with sodium hydroxide. The titration curve was analyzed by comparison with the curve obtained by acidifying pure HMHCY and titrating with sodium hydroxide (Fig. 14). It was observed that acidified HMHCY is a triprotic species with inflection points at pH ~4.50, pH ~6.75, and pH ~9.50. The number of moles of hydrochloric acid needed to raise the pH from the first point to the second corresponded to one equivalent of HMHCY, and to raise the pH from the second

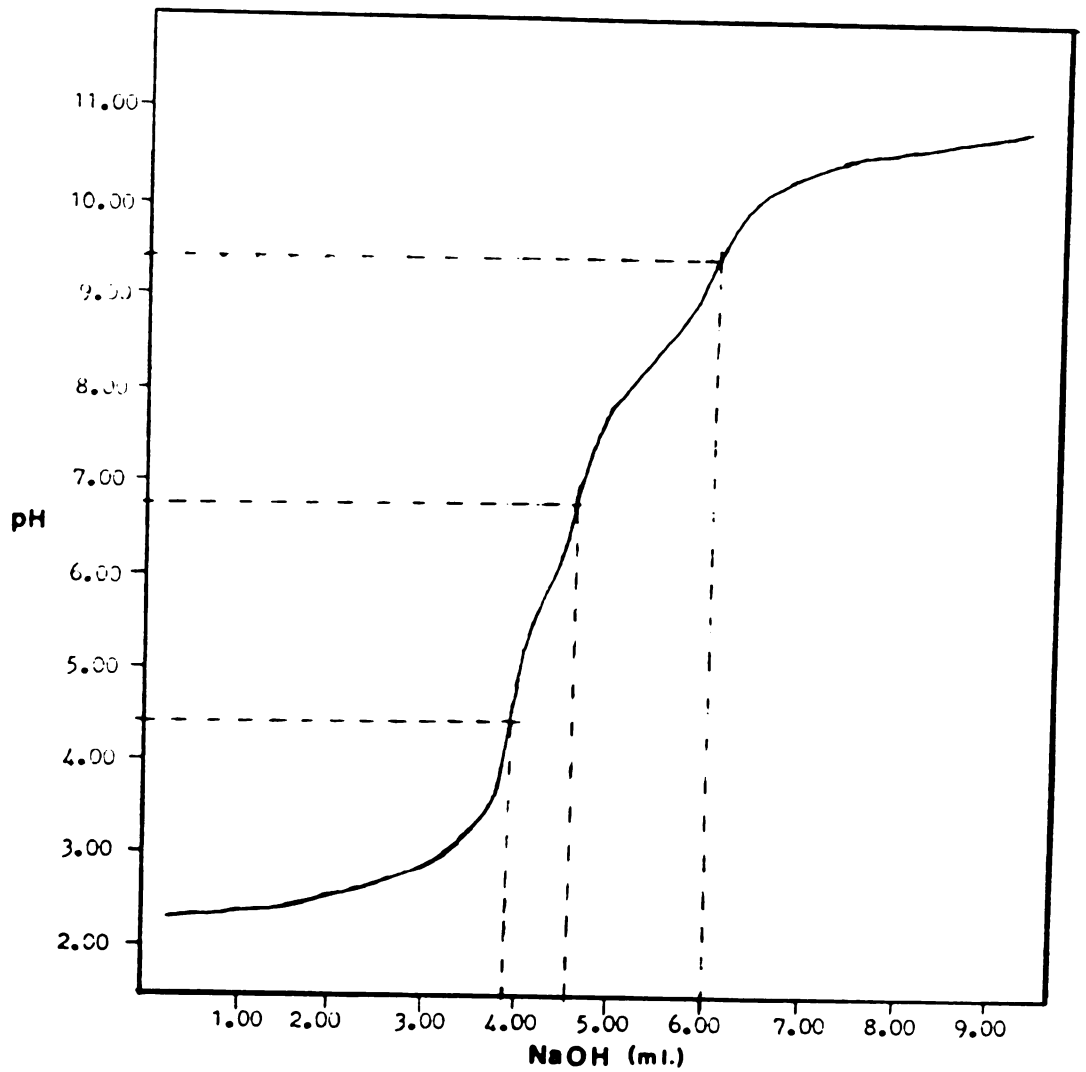


Figure 14. Titration Curve of Acidified HMHCY

point to the third corresponded to two equivalents of HMHCY. In the presence of the hydroxide ions from the decomposition reaction, the titration of the HMHCY is equivalent to that of the acidified complexant. However, it is shifted to the left by an amount proportional to the number of moles of hydroxide present. Flame emission analysis was performed to determine the number of moles of each metal present, and proton NMR analysis was performed as a second check on the number of moles of HMHCY present. The data for the crystals involving potassium, sodium, and HMHCY, are given in Table 6. The percentage deviation from the predicted stoichiometry based on the mass (or hydrogen evolution data when the mass was unknown) is also given in Table 6.

The hydrogen evolution data and the titration data agree with the expected stoichiometry quite well for all analyses. The flame emission data for analyses 3 and 4 agree with expected results while analyses 1 and 2 have a larger error with at least one metal. However, these errors could be a result of inaccuracies in dilution of the sample and/or deviations in the standardization curves. The proton NMR data were obtained only for analysis 3 and 4. Analysis 4 is consistant with the rest of the data while analysis 3 has a large negative error. Since the rest of the data for analysis 3 agrees with the expected stoichiometry, the NMR sample volume was probably in error. Overall, the four analyses show that the system has a 1:1:1 ratio of potassium, sodium, and HMHCY respectively.

Table 6. Results of the Stoichiometric Analyses of KNa(HMHCY)[a]

	Mass	Hydrogen Evolution	Titration		Flame Emission		NMR
			HMHCY	OH^-	K^+	Na^+	
1. KNa(HMHCY)	1.96	2.22[b] (8.2)	1.97 (0.5)	2.13 (8.7)	1.80 (-8.2)	1.60 (-18.4)	xxxx
2. KNa(HMHCY)	1.83	xxxx	1.88 (2.7)	2.00 (9.3)	2.15 (17.5)	1.87 (2.2)	xxxx
3. KNa(HMHCY)	xxxx	2.16[c] (xx)	2.21 (2.3)	2.34 (8.3)	2.11 (-2.3)	2.06 (-4.6)	1.68 (-22.2)
4. KNa(HMHCY)	1.75	1.81 (3.4)	1.84 (5.1)	1.61 (-8.0)	1.84 (5.7)	1.74 (-0.6)	1.80 (2.8)

a) x 10^{-3} moles; b) values in parentheses are percent error from expected stoichiometry; c) percent error calculated from hydrogen evolution data.

IV. B. Optical Spectra

The optical spectra of the KNa(HMHCY) system were obtained from dry films prepared by dissolving the crystals in methylamine and evaporating the solvent. A typical spectrum is shown in Figure 15. A sharp peak at 15,100 cm^{-1} (660 nm) and a shoulder at 18,900 cm^{-1} (530 nm) were observed. This spectrum is consistant with previously observed absorption spectra of some sodide compounds[9]. The high energy shoulder in the spectrum of KNa(HMHCY) may be due to the bound to continuum transition of the Na^- species as reported by Jaenicke and Dye[11] and presented in Chapter 1 of this dissertation. The main peak at the lower energy may also be attributed to the Na^- species and corresponds to the 3s to 3p transition. The sharpness of the peak suggests that only one species is responsible for the absorption. This rules out the possiblity of having a mixture of K^- and Na^- which would give a broad peak due to an overlapping of the K^- and Na^- absorption bands[40]. The possibility that this spectrum arises from the K^- species could not be completely ruled out. The excited states of the alkali metal anions may be perturbed by the complexing agent used and the counter ion in the crystal. As a result, the optical spectrum alone was not enough evidence to identify the anionic species.

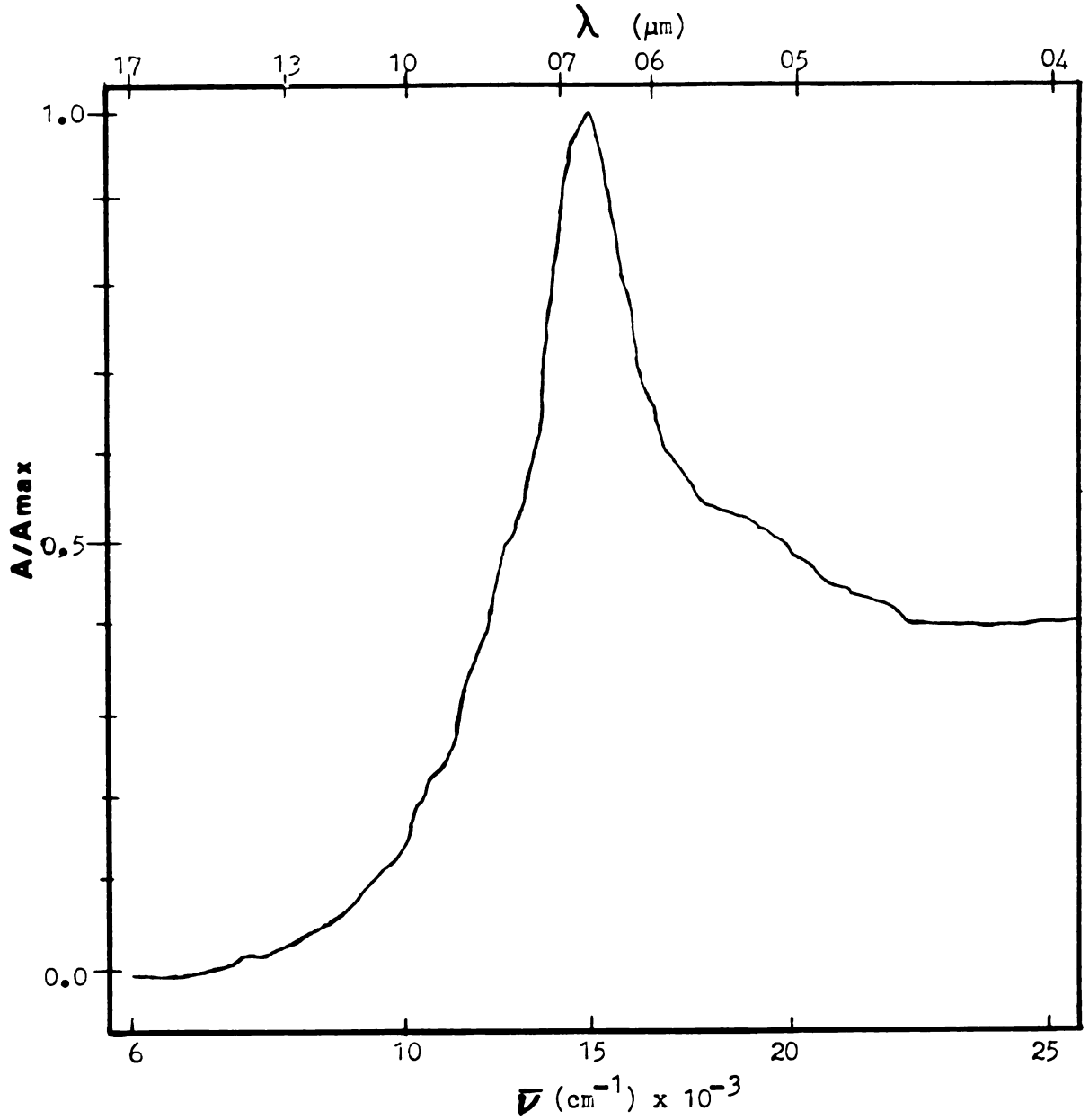


Figure 15. Spectra of a Solvent Free Film of K^+(HMHCY)•Na^- from Methylamine at - 78 C.

IV. C. Solid State NMR

Magic Angle Sample Spinning (MAS) NMR methods have been successful in detecting ^{23}Na in both the anionic and cationic states. However, the study of ^{39}K has been limited to seeing only the anionic species due to quadrupolar coupling present in the cationic species. The spectrum obtained by ^{23}Na MAS-NMR analysis of KNa(HMHCY), measured by L. Hill, contained only a strong absorption at -60.8 ppm, as compared to NaI at infinite dilution, and was assigned to Na^-. This assignment was based on the fact that all sodide salts have absorptions at a chemical shift of ~-61 ppm[13]. A spectrum of this material using ^{39}K MAS-NMR techniques was attempted by M. Tinkham, but resulted in the absence of any peaks, indicating that K^- is not present. On the basis of this result and the previous data, it would appear that Na^- is the sole anionic species in the crystal giving the stoichiometry $K^+(HMHCY)\cdot Na^-$.

IV. D. Melting Point

A sample of very finely divided crystalline $K^+(HMHCY)\cdot Na^-$ was sealed in a glass capillary tube to visually determine the melting point with a Thomas Hoover Capillary Melting Point Apparatus. As the sample was heated to ~45°C, the visible reflectance was replaced by a dark blue color. If the capillary was immersed in liquid nitrogen at this point, the reflective material could again be seen. This behavior was repeatable by successive heating and cooling, indicating a clear melting point. If, however, the heating was allowed to continue, at ~55°C the sample would appear to decomplex into a white liquid material (believed to be complexant) with a blue tint (which fades) and shiny flakes believed to be metal. This system did not appear to change with further heating until the temperature reached ~140°C at which point the metal flakes began forming small globules and the complexant began to turn yellow then brown indicating decomposition. Then at ~165°C, the material started to boil at which point the experiment was ended.

Using a differential scanning calorimeter (DSC on loan from E. I. Dupont de Nemours Co.) to monitor the endothermic and exothermic processes involved in heating the sample, the spectrum in Figure 16 was obtained. The endothermic peak starting at 50.4°C should be an overlapping of the melting

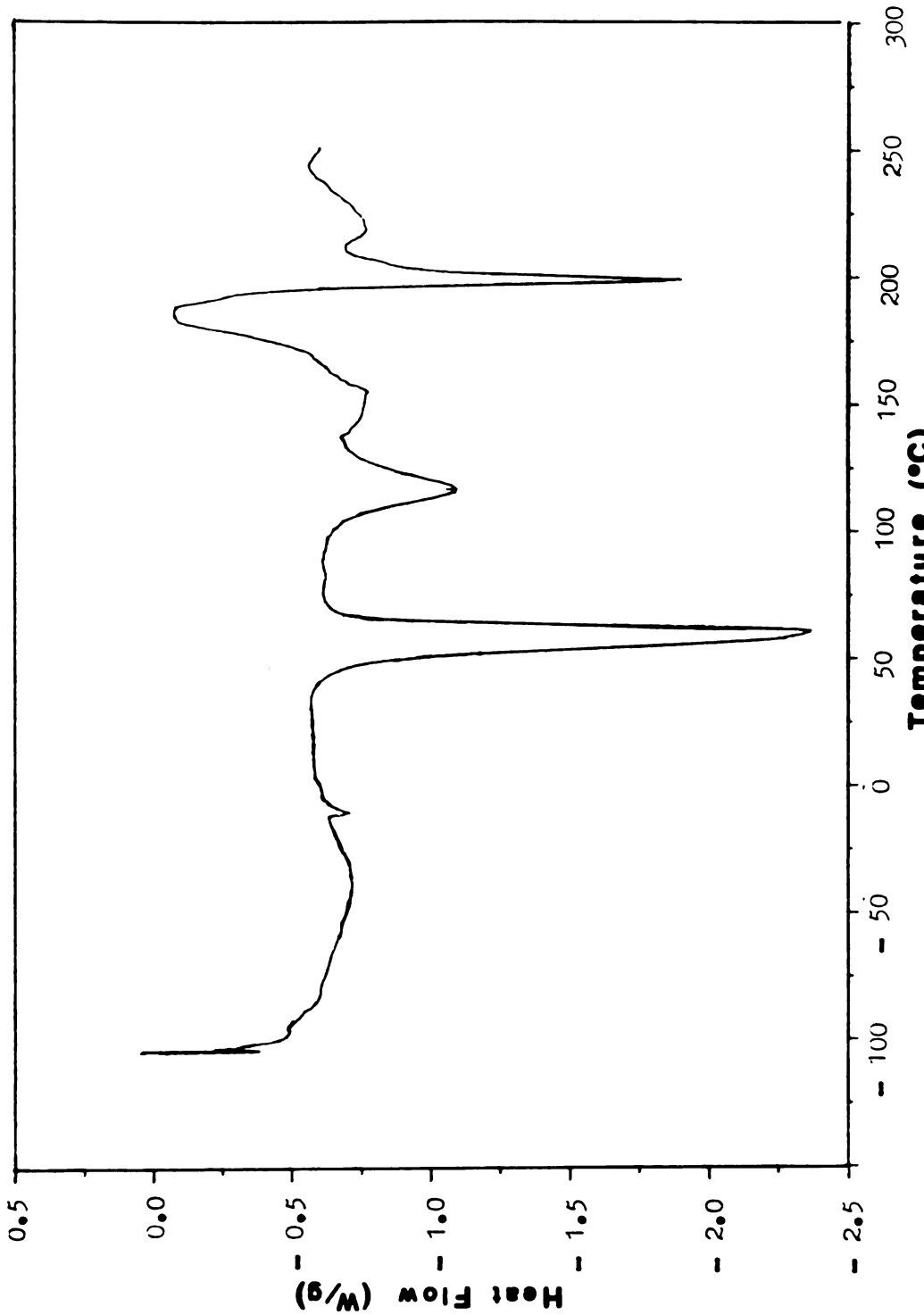


Figure 16. DSC Trace for a 3.3 mg Sample of K^{+}(HMHCY)•Na^{-} at a Heating Rate of 10 deg/min.

and decomplexation of the crystals. The region from ~150 - 200°C shows the onset of the decomposition of the complexant (exothermic peak) followed by evaporation (endothermic peak) of the resulting products. There is also a broad endothermic peak at 106.5°C in the DSC spectrum, although visual observations showed nothing occurring in this region. The best explaination at this point is that the HMHCY has some minor impurity which evaporates at this temperature. However, further investigation would be required to determine the exact nature of the transition. These data have shown that the system does undergo melting before it decomplexes. This might allow one to study the alkalides in the liquid state if proper temperature control were employed.

IV. E. Crystal Structure

The structure of $K^+(HMHCY)\cdot Na^-$ was determined on a Nicolet P3F diffractometer at ~-67°C by using theta-2 theta scanning techniques[14]. The space group was orthorhombic primitive $P2_12_12_1$ with $\underline{a}$ = 11.091, $\underline{b}$ = 11.172, and $\underline{c}$ = 22.531 Å. The refinement was initiated by using a Patterson map to locate the potassium ion positions. Least squares refinement was then used to position the sodium, nitrogen,

and carbon atoms. The hydrogens were added later and allowed to ride on their respective hosts. The agreement factors of R = 4.3 and R = 4.8 were obtained for 2092 observed unique reflections. The final structure still requires that the Na^- scattering factor be incorporated in the refinement, and that the hydrogen atoms be allowed to position themselves individually. However, this is not expected to change the structural data by a significant amount, but the added information should lower the agreement factors. The ORTEP packing diagram is shown in Figure 17.

The 1,4,7,10,13,16-hexaaza-1,4,7,10,13,16-hexamethylcyclooctadecane (HMHCY) ring is planar with respect to the 4,7,13,16-nitrogens $\pm$ .08 Å while the 1,10-nitrogens are tilted below the plane by 1.62 and 1.22 Å respectively. The corresponding 4,7,13,16-methyl groups are positioned on the same side of the plane as the potassium cation, while the 1,10-methyl groups are situated on the opposite side. The cation is 0.30 Å away from the plane with the anion an additional 4.28 Å away at an angle of ~2.48° from the normal.

In the unit cell, the molecules are ordered in a staggered arrangement,as shown in Figure 18, to give a roughly octahedral coordination between the potassium cations and the sodium anions. Also, the sodium anions are shielded from each other in all directions by the large cations

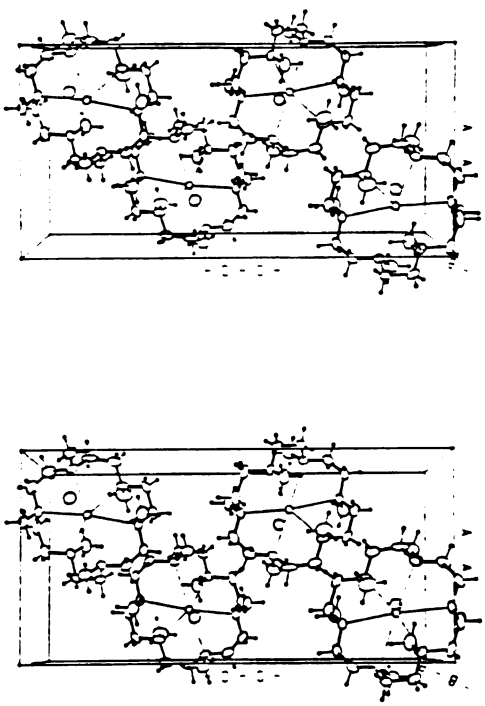
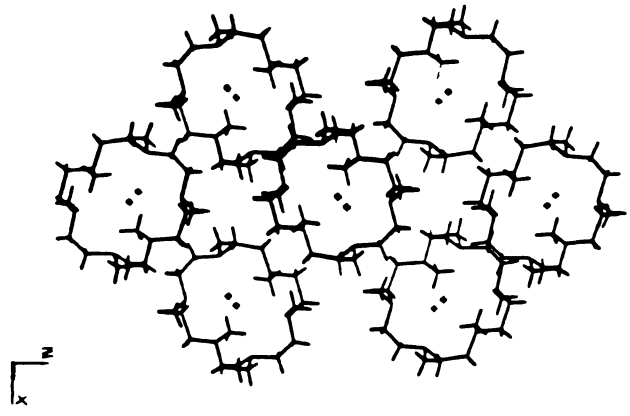
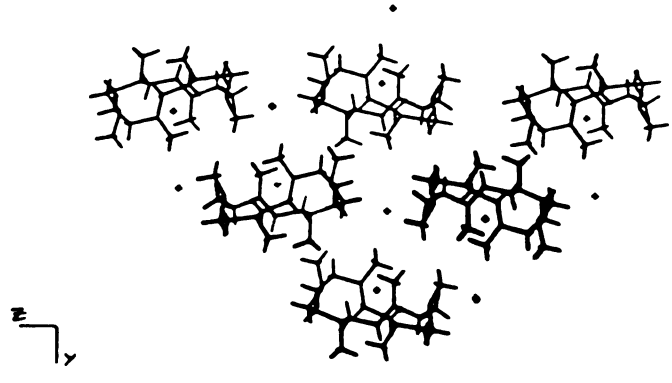


Figure 17. ORTEP Packing Diagram of $K^+(HMHCY)\cdot Na^-$



A

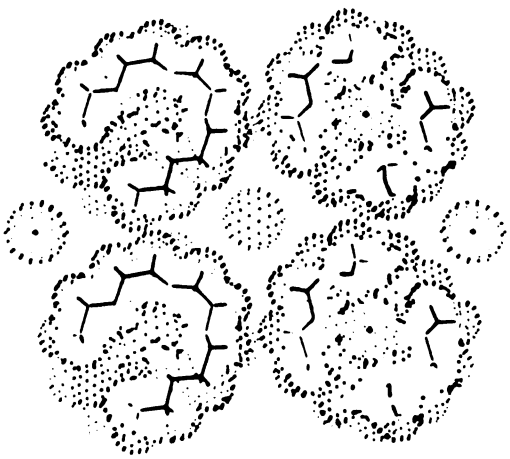


B

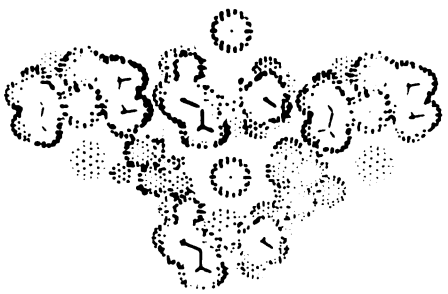
Figure 18. Molecular Packing Diagram
A. View down the Y - axis
B. View down the X - axis
(ref. 47)

K^+(HMHCY). This can be seen by observing a thin slice of the cavity for Na^- along the X,Y,and Z axis (Fig. 19).

The interatomic distances, positional parameters, and general temperature factor expressions, with there relative standard deviation, are given in Tables 7,8,and 9 respectively.



A



B

Figure 19. Views of the Sodide Cavity.[a]
A. Down the Y-Axis
B. Down the X-Axis

a) Sodide not drawn to scale.

Table 7. Interatomic Distances for the K^+(HMHCY)·Na^- Molecule.

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
K1	Na1	4.276(4)	C8	H8a	0.950(8)
K1	N1	2.910(7)	C8	H8b	0.950(10)
K1	N4	2.962(6)	C9	H9a	0.950(10)
K1	N7	2.912(6)	C9	H9b	0.950(11)
K1	N10	3.015(7)	C11	C12	1.487(15)
K1	N13	2.917(7)	C11	H11a	0.950(11)
K1	N16	2.902(6)	C11	H11b	0.950(10)
K1	C19	3.280(10)	C12	H12a	0.950(10)
N1	C2	1.437(10)	C12	H12b	0.950(8)
N1	C18	1.474(10)	C14	C15	1.334(15)
N1	C19	1.438(12)	C14	H14a	0.950(10)
N4	C3	1.449(11)	C14	H14b	0.950(14)
N4	C5	1.479(11)	C15	H15a	0.950(11)
N4	C20	1.441(11)	C15	H15b	0.950(14)
N7	C6	1.440(10)	C17	C18	1.506(15)
N7	C8	1.441(12)	C17	H17a	0.950(8)
N7	C21	1.477(12)	C17	H17b	0.950(10)
N10	C9	1.459(12)	C18	H18a	0.950(9)
N10	C11	1.442(11)	C18	H18b	0.950(9)
N10	C22	1.450(12)	C19	H19a	0.950(12)
N13	C12	1.494(13)	C19	H19b	0.950(9)
N13	C14	1.474(13)	C19	H19c	0.950(10)
N13	C23	1.449(13)	C20	H20a	0.950(10)
N16	C15	1.433(14)	C20	H20b	0.950(9)
N16	C17	1.470(13)	C20	H20c	0.950(9)
N16	C24	1.453(12)	C21	H21a	0.950(10)
C2	C3	1.531(13)	C21	H21b	0.950(9)
C2	H2a	0.950(9)	C21	H21c	0.950(12)
C2	H2b	0.950(10)	C22	H22a	0.950(12)
C3	H3a	0.950(9)	C22	H22b	0.950(12)
C3	H3b	0.950(8)	C22	H22c	0.950(11)
C5	C6	1.463(13)	C23	H23a	0.950(11)
C5	H5a	0.950(10)	C23	H23b	0.950(10)
C5	H5b	0.950(9)	C23	H23c	0.950(11)
C6	H6a	0.950(10)	C24	H24a	0.950(10)
C6	H6b	0.950(8)	C24	H24b	0.950(8)
C8	C9	1.530(15)	C24	H24c	0.950(10)

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

Table 8.

Table of Positional Parameters and
Their Estimated Standard Deviations for
[X88] K+ HMHCY·Na- Kuchenmeister, Dye & Ward

Atom	x	y	z	B(A2)
K1	0.2675(1)	-0.0748(2)	0.62911(7)	3.40(3)
Na1	0.2204(4)	-0.4523(3)	0.6082(2)	6.65(9)
N1	0.4506(6)	0.0829(6)	0.5796(3)	4.7(2)
N4	0.5215(6)	-0.1056(6)	0.6667(3)	4.5(2)
N7	0.3186(6)	-0.0791(7)	0.7559(3)	4.9(2)
N10	0.1097(6)	0.0701(7)	0.7110(3)	5.7(2)
N13	0.0282(6)	-0.0060(7)	0.5875(4)	6.6(2)
N16	0.2439(8)	-0.0062(7)	0.5054(3)	6.2(2)
C2	0.5737(7)	0.0584(9)	0.5954(4)	6.8(2)
C3	0.5869(8)	0.0052(9)	0.6577(4)	5.9(2)
C5	0.5241(9)	-0.1391(9)	0.7302(4)	6.7(3)
C6	0.4453(7)	-0.069(1)	0.7690(3)	6.0(2)
C8	0.253(1)	0.0088(9)	0.7895(4)	7.2(3)
C9	0.1207(9)	0.023(1)	0.7711(4)	7.8(3)
C11	-0.0128(8)	0.055(1)	0.6908(4)	7.5(3)
C12	-0.0343(7)	0.082(1)	0.6270(5)	8.5(3)
C14	0.0374(9)	0.044(1)	0.5272(4)	11.4(4)
C15	0.119(1)	0.003(1)	0.4889(4)	11.4(4)
C17	0.310(1)	0.1052(8)	0.4937(4)	7.9(3)
C18	0.4390(9)	0.1026(8)	0.5152(4)	7.3(3)
C19	0.404(1)	0.1833(9)	0.6124(4)	8.0(3)
C20	0.5712(8)	-0.2008(8)	0.6312(4)	7.4(3)
C21	0.274(1)	-0.2006(8)	0.7695(4)	8.4(3)
C22	0.143(1)	0.1955(9)	0.7094(6)	10.2(4)
C23	-0.0361(9)	-0.119(1)	0.5887(5)	8.8(3)
C24	0.3006(9)	-0.1075(9)	0.4761(4)	7.6(3)
H2a	0.607	0.002	0.568	5.0*
H2b	0.617	0.131	0.593	5.0*
H3a	0.554	0.062	0.684	5.0*
H3b	0.670	-0.006	0.666	5.0*
H5a	0.499	-0.220	0.733	5.0*
H5b	0.605	-0.132	0.744	5.0*
H6a	0.468	0.013	0.765	5.0*
H6b	0.458	-0.094	0.809	5.0*

Table 8. Continued

Table of Positional Parameters and Their Estimated Standard Deviations (contd.) in [X88] K+ HMHCY·Na- Kuchenmeister, Dye & Ward

Atom	x	y	z	B(A2)
H8a	0.257	-0.010	0.831	5.0*
H8b	0.290	0.084	0.782	5.0*
H9a	0.079	0.074	0.798	5.0*
H9b	0.086	-0.055	0.772	5.0*
H11a	-0.039	-0.024	0.699	5.0*
H11b	-0.060	0.111	0.713	5.0*
H12a	-0.003	0.159	0.618	5.0*
H12b	-0.118	0.080	0.619	5.0*
H14a	-0.040	0.035	0.509	5.0*
H14b	0.056	0.127	0.531	5.0*
H15a	0.115	0.050	0.454	5.0*
H15b	0.094	-0.076	0.481	5.0*
H17a	0.310	0.120	0.452	5.0*
H17b	0.270	0.169	0.514	5.0*
H18a	0.474	0.178	0.506	5.0*
H18b	0.481	0.041	0.495	5.0*
H19a	0.322	0.197	0.603	5.0*
H19b	0.411	0.168	0.654	5.0*
H19c	0.451	0.252	0.602	5.0*
H20a	0.568	-0.175	0.591	5.0*
H20b	0.652	-0.216	0.642	5.0*
H20c	0.525	-0.272	0.636	5.0*
H21a	0.317	-0.258	0.747	5.0*
H21b	0.283	-0.217	0.811	5.0*
H21c	0.191	-0.204	0.759	5.0*
H22a	0.225	0.202	0.721	5.0*
H22b	0.134	0.227	0.671	5.0*
H22c	0.094	0.239	0.736	5.0*
H23a	-0.039	-0.148	0.628	5.0*
H23b	-0.116	-0.110	0.574	5.0*
H23c	0.006	-0.174	0.564	5.0*
H24a	0.257	-0.179	0.483	5.0*
H24b	0.305	-0.092	0.435	5.0*
H24c	0.380	-0.115	0.492	5.0*

Starred atoms were refined isotropically.
Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as:

$(4/3) * [a^2*B(1,1) + b^2*B(2,2) + c^2*B(3,3)$
$+ ab(\cos \text{gamma})*B(1,2) + ac(\cos \text{beta})*B(1,3)$
$+ bc(\cos \text{alpha})*B(2,3)]$

Table 9.

Table of General Temperature Factor Expressions - B's
for [X88] K+ HMHCY·Na- Kuchenmeister, Dye & Ward

Name	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)	Beqv
K1	3.17(6)	3.70(6)	3.33(5)	0.11(8)	-0.23(7)	0.00(7)	3.40(3)
Na1	6.9(2)	5.5(2)	7.6(2)	-0.1(2)	-0.5(2)	-0.1(2)	6.65(9)
N1	5.5(3)	4.3(3)	4.3(3)	-0.5(4)	0.9(3)	-0.9(3)	4.7(2)
N4	3.7(3)	3.5(3)	6.3(4)	0.2(3)	0.2(3)	-0.3(3)	4.5(2)
N7	5.6(3)	5.5(3)	3.6(3)	-0.8(4)	-0.1(3)	-0.2(3)	4.9(2)
N10	3.4(3)	4.3(3)	9.4(4)	0.3(4)	0.7(3)	-1.7(4)	5.7(2)
N13	4.1(3)	8.2(5)	7.4(4)	-0.3(4)	-1.8(4)	2.2(4)	6.6(2)
N16	6.3(4)	8.8(4)	3.7(3)	0.5(4)	-0.7(4)	1.7(3)	6.2(2)
C2	5.5(4)	7.2(5)	7.6(5)	-2.9(5)	2.1(4)	-0.8(5)	6.8(2)
C3	3.6(4)	7.5(6)	6.8(5)	-0.1(5)	-0.4(4)	-0.7(5)	5.9(2)
C5	5.8(5)	6.9(5)	7.2(5)	0.2(5)	-2.2(4)	1.8(5)	6.7(3)
C6	7.0(5)	6.9(5)	4.0(4)	-0.2(6)	-0.8(4)	0.1(5)	6.0(2)
C8	8.4(6)	8.7(6)	4.7(4)	0.8(6)	1.1(5)	-1.5(4)	7.2(3)
C9	7.2(5)	10.8(7)	5.4(4)	1.2(6)	2.8(4)	-1.7(5)	7.8(3)
C11	4.9(5)	6.8(6)	10.9(7)	0.9(5)	1.1(5)	0.4(6)	7.5(3)
C12	2.4(3)	6.0(5)	17.0(8)	0.4(5)	0.2(5)	2.3(8)	8.5(3)
C14	6.0(6)	18(1)	10.1(7)	2.3(7)	-2.4(5)	4.2(7)	11.4(4)
C15	9.2(7)	19(1)	5.9(5)	5.8(7)	-2.7(5)	2.4(7)	11.4(4)
C17	13.6(9)	6.5(5)	3.5(4)	2.3(6)	-0.3(5)	1.1(4)	7.9(3)
C18	10.9(7)	6.4(5)	4.4(4)	-3.2(5)	1.9(5)	0.6(4)	7.3(3)
C19	11.4(8)	6.1(5)	6.5(5)	0.4(6)	0.4(6)	-0.9(5)	8.0(3)
C20	6.6(5)	5.3(4)	10.2(6)	1.8(4)	-1.0(6)	-1.4(5)	7.4(3)
C21	10.6(7)	6.9(5)	7.8(5)	-2.6(6)	-0.9(7)	1.7(5)	8.4(3)
C22	8.3(7)	6.6(6)	15.7(9)	0.5(7)	1.1(8)	-2.2(7)	10.2(4)
C23	6.5(5)	9.2(8)	10.8(8)	0.4(6)	-2.1(6)	-0.7(7)	8.8(3)
C24	9.7(7)	8.9(7)	4.2(4)	-1.3(6)	-0.1(5)	-0.1(5)	7.6(3)

The form of the anisotropic thermal parameter is:

$$\exp[-0.25\{h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)\}]$$

where a, b, and c are reciprocal lattice constants.

Conclusion and Suggestions for Future Work

A crystalline alkalide of potassium, sodium and a member of a new class of complexants hexamethylhexacyclen (HMHCY) has been isolated. The stoichiometric analysis revealed a 1:1:1 ratio of K, Na, HMHCY, and the optical spectrum, ^{23}Na MAS-NMR, and ^{39}K MAS-NMR all indicate that the anionic species in the system is Na^-. This assignment was verified by X-ray crystallography. The crystal structure was determined to be orthorhombic primitive with the potassium, sodium nearest neighbor distance of 4.28 Å.

The compound is stable at room temperature for as much as three days and has a melting point at approximately 45°C.

"Sandwich" complexes (2:1 ratio of complexant to metal) with HMHCY are not likely to be synthesized due to the probable sterric hinderance caused by the methyl groups. It may be possible to form "sandwich" compounds by using HMHCY along with some other complexant. For example, a compound of cesium, HMHCY, 12C4, and sodium in a ratio of 1:1:1:1 was attempted and did yield crystals. The exact stoichiometry was not explicitly determined, however the results did show promise. Also, the use of 1,4,7,10-tetraaza-1,4,7,10-tetramethylcyclododecane and 1,4,7,10,13-pentaaza-1,4,7,10,13-pentamethylcyclopentadecane (the methylated

nitrogen analogs of 12C4 and 15C5 respectively) should be explored as possible complexants for more stable alkalides or electrides. Also, one might try to add longer side-arms to selected positions in the ring, rather than methylating all nitrogens. This might increase the complexation constant, and protect the cation from reductive attack by the electron.

Another area which needs to be pursued more thoroughly is the determination of crystal structures by either single crystal or powder X-ray methods. The strange magnetic and electronic behavior of some of these systems may be understood if the enviroment of the anions is known and the paths by which the anions (especially the electrides) can communicate with each other is understood.

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46. Photos created using a PS300 FRODO-Molecular Graphics System in Professor Tulinsky's Laboratory.