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SYNTHESIS AND CHARACTERIZATION OF A CRYSTALLINE ALKALIDE: POTASSIUM-(12-CROWN-4)-SODIUM

By

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF A CRYSTALLINE ALKALIDE: POTASSIUM-(12-CROWN-4)-SODIUM

By

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A new crystalline alkalide $[K^+(12C4)_2 \cdot Na^-]$ has been prepared from potassium, sodium and the macrocyclic polyether complexant 12-crown-4. The alkalide was obtained by precipitation from an amine solvent that contained dissolved metals and the complexing agent.

The analysis shows that the new compound contains a 1:1:2 ratio of Na, K and 12C4, although in some samples the content of sodium and crown deviates slightly from this stoichiometry. The identification of the species present was made by optical transmission spectroscopy and ^{23}Na "magic-angle sample spinning" (MASS)-NMR. The optical spectra of dry thin films prepared by rapid solvent evaporation show a major band at 13,000 cm^{-1} and a minor one at 17,100 cm^{-1}. The ^{23}Na MASS-NMR spectrum has a strong absorption at -61.1 ppm. This indicates that the compound is a sodide. D.C electrical conductivity measurements show that the compound is a semiconductor with an apparent band gap of 2.20 eV. The extrapolated conductivity at infinite temperature is 2.03×10^{13} ohm^{-1} cm^{-1}, which suggests that in addition to the electronic conduction, ionic conduction may be important. The crystalline alkalide is

diamagnetic, as indicated by the molar susceptiblities measured from 1.5 K to 200 K. Decomposed samples are less diamagnetic and may contain some trapped electrons and/or some organic radicals.

Melting point studies reveal that the compound is stable at room temperature under inert atmosphere or vacuum. The crystals melt around +60°C and decompose at about +80°C.

The thermodynamic stabilities of several series of sandwich-type alkalides have also been estimated by means of a modified Born-Haber cycle.

I can Do all things
through him (God, my Lord) who
strengthens me.

Phillipians 4:13

To my Husband Honoré

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CHAPTER I

INTRODUCTION

A. Metal-Ammonia Solutions

It is well known that the alkali metals dissolve in liquid ammonia. These solutions exhibit a characteristic blue color when dilute and are metallic bronze when concentrated. Saturation occurs around 20 mole percent metal (MPM) for Li, 16 MPM for Na, K and Rb, while Cs reaches higher concentration [1]. In fact Cs at its melting point is completely miscible with ammonia.

In dilute solutions (i.e. $c \lesssim 10^{-3}$ M), it is universally agreed that the major species present are the solvated electron (e^-_{solv}) and the metal cation (M^+_{solv}) which form according to the equation:

$$M(s) \xrightarrow{NH_3} M^+_{solv} + e^-_{solv} \; . \qquad (1)$$

The properties observed in this concentration range have been attributed to the solvated electron. Optical transmission studies show a strong absorption in the near infrared with a peak maximum at 1470 nm (6800 cm^{-1}) [2-5]. The absorption is asymmetric with a high energy tail in the visible region, which is responsible for the blue color. The spectrum is temperature and pressure dependent and is red shifted with increasing temperature, but blue shifted with increasing pressure. However, the spectral shape and the peak position are independent of the metal and are similar to those produced by pulse radiolysis of the pure solvent; i.e., in the absence of metal [6,7]. EPR spectra display a single narrow line (linewidth = 0.5 G) near the free electron g-value ($g = 2.0012$) [8]. This indicates that the electron does not interact with the cation or the solvent. Moreover, conductance measurements show an electrolytic behavior of the dilute solution with the electrons as the negative charges (or ions) carrying most of the current [9]. As the metal concentration increases, the properties of the solutions change gradually from electrolytic behavior to metallic around 8 MPM.

The paramagnetic shift (Knight shift) of the resonance position observed in the alkali metal NMR spectra show that there is interaction between the cation and the electron as concentration increases [10,11]. Proof of electron spin interactions to form diamagnetic states has been obtained by static magnetic susceptibility [12,13] and EPR spin susceptibility [8,14] studies. Many species such as ion pairs, triples and even higher aggregates of M^+ and e^- have been proposed to account for the interactions. Conductance [15] and transference [16] measurements also show a decrease in the cation conductance with increasing concentration resulting from electron-cation interactions. The absorption maximum of the solvated electron shifts to lower energies as the metal concentration increases and spectra obtained by reflectance techniques indicate that it disappears between 5.3 and 6.2 MPM. At the same time, an absorption edge (plasma edge) due to conduction electrons builds with an increase in concentration [17]. At $c > 8$ MPM, the solutions have very high conductivities [18]. The most agreed upon model for the solvated electron is that of an electron trapped inside a cavity. It was first proposed by Ogg [19] and quantitatively refined by Jortner [20]. The electron is stabilized by short range interaction with the solvent dipoles and by long-range polarization effects. Although metal-ammonia solutions have been studied for over a century, the nature of the species is still not completely understood. However, results from metal-amine and ether solutions have revealed the presence of at most two types of species in these solutions: the solvated electrons and the metal anions.

B. Metal Anions in Solution

The investigation of solvated metals in amine and ether solvents has its origin in the study of metal-NH_3 solutions. Many attempts have been made to understand the properties of these solutions, but progress has been hampered mainly by the low solubility of the metals due to the low dielectric constants of the solvents. In 1970, Dye et al. described the use of metal complexants to increase the solubility of metals in these solvents [21] and this process not only extended the number of solvents used but permitted extensive investigations of these solutions from very dilute to saturated.

The solutions exhibit a metal-independent absorption band in the infrared region as well as one or two additional bands in the visible [2,22,23]. The infrared band is attributed to the solvated electron; this assignment results from the similarity of the band location with those of dilute M-NH_3 solutions and from pulse radiolysis [6,7] and flash photolysis [24] studies. However, the nature of the higher energy bands was originally a matter of considerable controversy. Covalent dimers such as K_2, Rb_2, and Cs_2 have been proposed to account for the corresponding 850, 920, and 1030 nm bands in ethylenediamine [25,26]. Moreover, various theories such as doubly trapped electrons $(e_2^{2-})^{2+}$, ionic covalent dimers (e.g. $K_2^+.e^-$) [25] and monomers K, Rb, Cs [26] have been proposed to account for an absorption around 660 nm. In 1968 Hurley et al. demonstrated that this third band is merely due to traces of sodium contamination from the Pyrex glass apparatus used to prepare the solutions [28]. Therefore, at most two bands are observed in metal amine and ether solutions, the second being assigned to the metal anionic species M^-. For example, Figure 1 shows spectra of Na^-, K^-, Rb^-, Cs^- and e^-_{solv} in ethylenediamine (EDA) [29]. As one clearly sees, there is doubt about the existence of Li^- in solution. The spectrum produced by dissolving this metal is that of e^-_{solv}. K, Cs and Rb spectra show infrared shoulders attributed to the solvated electron. The ratio of this absorbance to that of the anions was found to be strongly dependent on the concentration of metal. On the other hand, the sodium solution does not contain e^-_{solv} which suggests that in this solution, Na^- is so stable that reaction (2) is largely favorable.

$$Na^+ + 2e^-_{solv} \longrightarrow Na^- \qquad (2)$$

Many observations give conclusive proof that the species responsible for the higher energy bands are metal anions with two electrons in the ns orbitals:

-The d.c electrolysis of a solution of crystals of stoichiometry Na_2C222 in methylamine deposited sodium metal at the anode as expected for the oxidation of Na^- to Na(s) [30].

-Matalon, Golden and Ottolenghi [31], applying the Stein and Treinin relation for the charge-transfer-to-solvent (ctts) transition [32], showed that the spectroscopic behavior of the species responsible for the visible

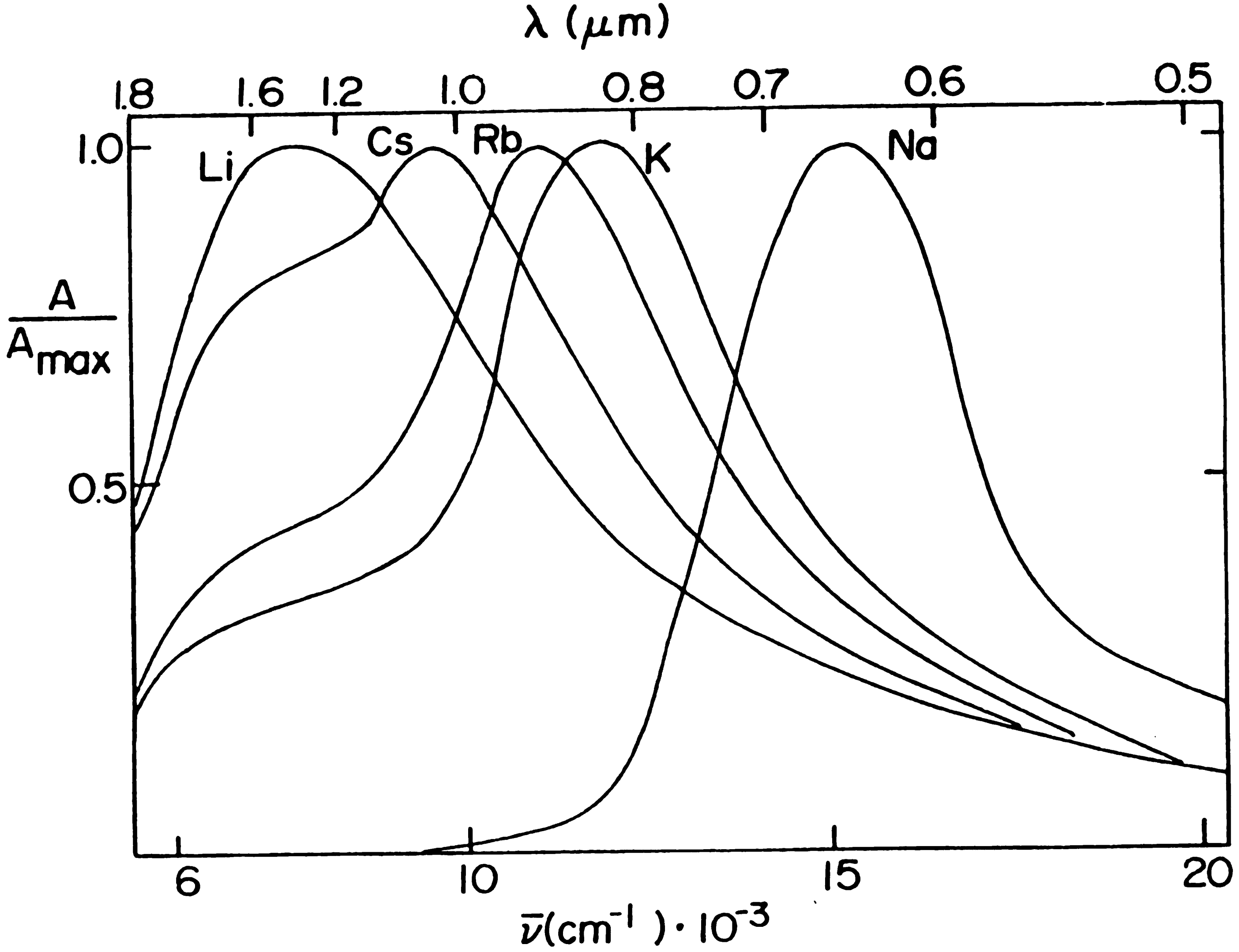

Fig. 1 Optical spectra of alkali metal-ethylene diamine solutions.

band is consistent with the principal requirements of a spectrum of a negative ion. This was further strengthened by the work of Dye <u>et</u> <u>al</u>. using more concentrated solutions [33].

-The oscillator strength of 1.9 ± 0.2 from DeBacker <u>et</u> <u>al</u>. is consistent with a metal anion model [34].

-Pulse radiolysis studies [7] show that when sodium salts are added to solutions of e^-_{solv} in EDA, the rate of decay of the absorbance of e^-_{solv} and the growth of that of Na^- are both second order with respect to the concentration in solvated electrons as one might expect for the reaction

$$2e^-_{solv} + Na^+ \longrightarrow Na^- \ .$$

Dye has proposed that the interaction of the species in the solutions can be described by the equilibria:

$$2M(s) \rightleftharpoons M^+_{solv} + M^-_{(solv)} \qquad (3)$$

$$M^-_{(solv)} - \rightleftharpoons M_{(solv)} + e^-_{solv} \qquad (4)$$

$$M_{solv} \rightleftharpoons M^+_{solv} + e^-_{solv} \qquad (5)$$

in which $M_{(solv)}$ is a monomer and is present in low concentration. The addition of a metal complexant L to the solution introduces a new equilibrium

$$M^+ + L \rightleftharpoons M^+L \qquad (6)$$

that shifts reactions (3) and (5) to the right. This process paved the way for the preparation of crystalline compounds from metal-methylamine and metal-ether solutions.

C. Alkalides and Electrides

1. Definitions

An alkalide is a salt of stoichiometry $M^+L_n.N^-(s)$ that contains a complexed alkali metal cation M^+L_n and an alkali metal anion N^- where M may or may not be the same metal as N. The formation reaction of a salt of this kind may be written as:

$$M(s) + nL(s \text{ or liq}) + N(s) \longrightarrow M^+L_n.N^-(s)\ . \qquad (7)$$

M and N denote the alkali metals, and L is a metal complexer. Likewise, an electride $M^+L_n.e^-$ is also a salt containing a complexed alkali metal cation, but the positive charge is balanced by a solvent-free trapped electron ($e^-{}_t$). It is formed from the reaction:

$$M(s) + nL \longrightarrow M^+L_n.e^-(s) \qquad (8)$$

where M and L have the same meaning as above.

The synthesis of these compounds has been made possible through the discovery that concentrated solutions of alkali metals in amines and ethers can be formed by the addition of an appropriate metal complexant. The first compound was synthesized in 1974 from Na and the cryptand C222 in ethylamine [35]. A 2:1 ratio of metal and complexant was used and the resulting salt was called sodium-C222-sodide ($Na^{+}C222.Na^{-}$). Since that time, over thirty compounds have been isolated from different macrocyclic polyethers, macrobicyclic cryptands and all the alkali metals. Their stoichiometries have been elucidated and many of their properties are known [36].

2. Nature and the role of ligands

As cryptands and crown ethers are essential for the formation of these salts, their nature and role need to be specified. The commonly used complexants to date are the cryptands C211 (or IUPAC: 4,7,13,18-tetraoxa-1,10-diazabicyclo-[8.5.5]eicosane), C221, C222, C322 (these three others also have very lengthy names as for C211) and the crown ethers 12C4, 15C5 and 18C6 (18-crown-6 or IUPAC: 1,4,7,10,13,16-hexaoxacyclo-octadecane; similar nomenclature applies to the first two crown ethers). The cryptands were first synthesized by Lehn *et al.* in 1969 [37]. These complexants are composed of three strands of oxygen and carbon atoms linked by two nitroten atoms. The numbers in the abbreviated names of these compounds refer to the number of oxygen atoms in each strand. The arrangement of the strands in each ligand yields a three dimensional cavity which encloses the metal cation upon complexation. This leads to very strong complexes. X-ray crystallography studies on Rb^+ and Cs^+ complexes with C222 have shown that the cation is located at the center of the cavity and that the oxygen and nitrogen atoms participate in the bonding to the cation [38]. Numerous studies have been reported on the thermodynamics of complexation of cations by cryptands in aqueous and nonaqueous solvents as well as on rates of complex formation and dissocation [39-42]. Stability constants of 10^8 and higher were found. A characteristic feature of these ligands is that they show high selectivity among the alkali cations: Li^+, Na^+, K^+, Cs^+ for C211, C221, C222 and C322 respectively. E. Kauffmann _et_ _al_. have demonstrated that the high stability of the macrobicyclic complexes as compared to the macromonocyclic ones, or cryptate effect, is of enthalpic origin [42]. Many authors have argued that the selectivity among the cations depends on a match between the size of the cation and that of the cavity of the cryptand [39]. Where there is a good fit of these parameters, strong 1:1 complexes result which are called inclusive complexes. For cations smaller than the cavity of a cryptand, complexation can still occur because of the flexibility of the complexants. They adopt the conformation that best fits the cation. On the other hand, exclusive complexes result when the cation is too large for the cavity [43].

Pedersen, in 1967, demonstrated the use of macrocyclic crown ethers in complex formation with metal cations [44]. Crown ethers are rings of oxygen and carbon atoms and take a planar arrangement upon complexation with a cation that fits the cavity well. The axial positions of the complexes remain open, which allows interaction of the complexed cation with the solvent and the counterions in solution. No dramatic selectivity was found for the crown ethers among the alkali metal cations as in the case of the cryptands. This is shown in Figure 2 where we notice no selectivity at all for 15C5 with Na^+, K^+ and Rb^+. Table 1 gives cation sizes and crown ether ring sizes as determined by x-ray crystallographic data and from space filling models of the Corey-Pauling-Koltun type. According to these values and the complexation constants observed from the curves, 12C4, 18C6 and 21C7 should form strong 1:1 complexes with Li^+, K^+ and Cs^+ respectively. For the crown ethers, studies have revealed that sandwich-type complexes are mostly formed when the polyether is not the optimal one for the cation. In such complexes, the cation is enclosed within two crowns with all the oxygen atoms taking part in the bonding with the cation. The formation of sandwich complexes has been detected by Popov *et al*. using multinuclear NMR techniques [45-47]. This has been demonstrated for Li^+ with 12C4, K^+

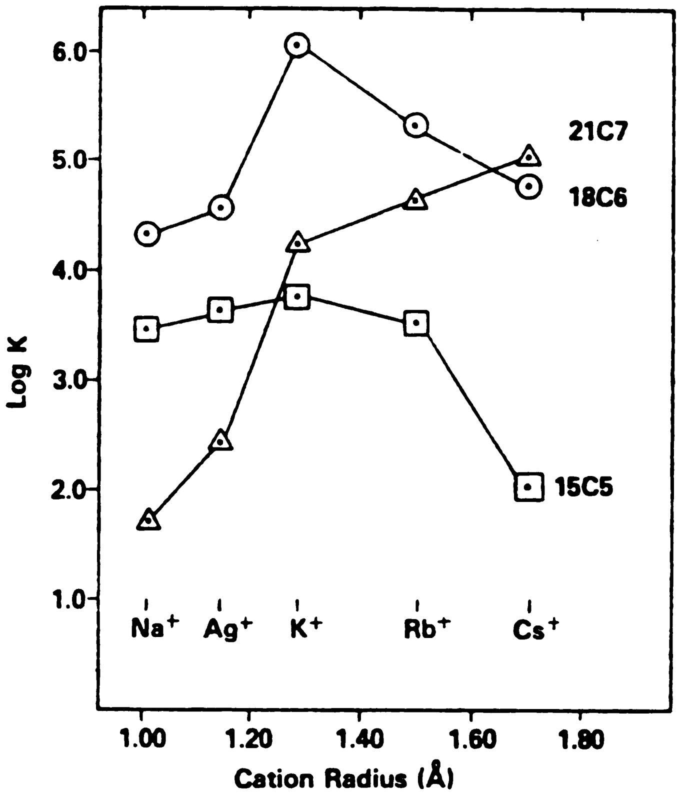

Fig. 2 Log K vs. cation radius in methanol at 25°C (from R.M. Izatt *et al.*, J. Am. Chem. Soc. 102, 47 (1980)).

Table 1 Alkali Cation and Macrocyclic Polyether Ring Diameters.

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

[a] From R.D. Shannon and C.T. Prewitt, Acta Crystallogr. Sect. B25, 925 (1969).

[b] From C.J. Pedersen, J. Am. Chem. Soc. 92, 386 (1970).

and Na^+ with 15C5 and Cs^+ with 18C6 in many nonaqueous solvents of low donicity. Moreover, the work of J.S. Shih on K^+ with 12C4 in methanol does not rule out the formation of a sandwich compound between these species [48]. In general, in solutions where sandwich complex formation takes place these authors found that the chemical shifts (paramagnetic or diamagnetic) of the alkali metal nuclei vary linearly with the mole ratio of crown to metal until a 1:1 ratio is reached, but further addition of the crown causes a reversal in the direction of the shift. This behavior indicates a two-step complexation: formation of a 1:1 complex followed by the addition of another ligand to yield the sandwich compound.

The role of the complexants in the synthesis of the alkalides and electrides is three-fold. The major role is to form strong complexes with the metal cations, thus enhancing the solubility of the metal in the amine or ether solvent. This permits the formation of very concentrated solutions. The rate of release of the cation from a complexant cavity is very slow for cryptands and moderate for crown ethers. This inclusion of the cation prevents its direct recombination with N^- and/or e^- to form the metal in solution and in the crytals. Finally, the complexants provide an easy control of the stoichiometry of the metal/solutions.

3. Properties of alkalides and electrides

These salts can be prepared by three different procedures. The first method, which is the simplest, consists of a rapid evaporation of the solvent from a solution of known stoichiometry of metal and complexant to yield films or powders. An alkalide or an electride may form depending on the relative ratio of the starting reagents. This technique is commonly used to produce thin films for optical spectroscopic studies. The second method is direct vapor deposition of stoichiometric amounts of metal and complexant as a film on the walls of an optical cell [49]. The last technique is the most frequently used [50]. It consists of gradually cooling a saturated solution of an appropriate solvent and metal to cause the precipitation of crystals which may or may not be of the same stoichiometry as the solution.

The optical spectra of the metal anions show dependence on the nature of the complexing agent, the metal, the solvent and the ratio of metal to ligand. In general the absorption bands occur at 13000-16000 cm^{-1} for Na^-, 12,000 cm^{-1} for K^-, ~11,000 cm^{-1} for Rb^-, ~10,000 cm^{-1} for Cs^-, and 6,000-9,000 cm^{-1} for e_t^-. Films of stoichiometry M^+C222M^- with M = Na, K, Rb and Cs from methylamine are gold-bronze in color by reflected light and blue by transmission [51]. $Na^+C222.Na^-$ films have a major peak at 15,400 cm^{-1}, a pronounced shoulder at

18,900 cm^{-1} and a small peak at 24,500 cm^{-1}. The major peak may be assigned to a $3s \rightarrow 3p$ bound-bound transition of Na^- whereas the shoulder may result from a bound-continuum transition. The origin of the absorption at 24,500 cm^{-1} is uncertain. Measurements carried out with $K^+C222Na^-$ films show a peak of Na^- red-shifted by ~300 cm^{-1} from that of $Na^+C222.Na^-$. The shoulder and high energy peaks of $Na^+C222Na^-$ are absent. Other films containing Rb^-, K^-, and Cs^- have maxima at 11,900, 11,600 and 10,500 cm^{-1} respectively which may correspond to $ns \rightarrow np$ transitions for these anions. These films are unstable compared to Na^- films; irreversible decomposition occurs at about 0°C. The absorptions of Na^-, K^-, Rb^- and Cs^- compare well with those previously observed in ethylenediamine. Equimolar potassium and C222 in methylamine yields solutions of K^+C222_{solv} and e^-_{solv}. Films from these solutions are blue both by reflected and transmitted light. They have a strong absorption band at 7400 cm^{-1} assigned to e^-_t. This absorption decreases in intensity when more metal is present relative to a growing K^- band. Some films from 18C6 and the alkali metals in methylamine (MA) and ammonia have been reported [52]. Although most of their spectra indicate the presence of metal anions, some films from MA show infrared shoulders as in the case of ethylenediamine where no complexant was used. For instance, films of K and Rb with 18C6 in a 2:1 ratio have peaks at 12,200 and 12,000 cm^{-1} respectively and corresponding shoulders at

9000 and 9100 cm^{-1} due to K^-, Rb^- and e_t^-. This gives evidence that in solution the stability of the alkali metal anion and the solvated electron compete. If a cooling process were used, both types of crytals might precipitate. Cs solutions with ratios of metal/complexant 2, 1, 0.5 also yield films with maximum absorption at 6400-6700 cm^{-1} assigned to e_t^-. $K^+18C6Na^-$ in methylamine has a peak at 13,300 cm^{-1} and a shoulder at 9000 cm^{-1} according to Dheeb Issa [53]. The large red shift of the main absorption made ambiguous the identification of the compound, but further analysis by M.L. Tinkham [54] gives evidence of assignement of the peak to Na^-.

The electrical conductivities of many alkali compounds have been measured. Although $Na^+C222.Na^-$ has a metallic appearance, the data show that it is an intrinsic semiconductor with a band gap of 2.4 eV [55]. M.R. Yemen carried out an extensive study on the conductivity of many compounds [56]. He reports that samples of the sodide $K^+C222.Na^-$ have band gaps of 0.87 eV and 0.98 eV. These lower values may be due to conductivity by impurities such as e_t^-. $Rb^+C222.Na^-$ presents band gaps of 1.20 and 2.05 eV. $Cs^+18C6.Na^-$, $K^+18C6.Na^-$ and $Rb^+18C6.Na^-$ have average band gaps of 1.7, 0.98 and 0.89 eV respectively. Yemen also reported that the electrides $Li^+C211.e^-$ and $Cs^+(18C6)_2.e^-$ show band gaps of 0.99 to 1.28 and 0.90 eV respectively. A gap of 0.8 eV has been measured for

$Cs^+(18C6)_2Cs^-$ samples [57]. The conductivities at infinite temperature extrapolated from the log R vs. 1/T curves range from ~1 ohm^{-1} cm^{-1} to $>10^6$ ohm^{-1} cm^{-1}, and suggest that all these compounds behave as semiconductors.

EPR and static magnetic susceptibilities give evidence that the alkalides are diamagnetic. This was expected from their ns^2 configuration in which the two electrons in the ns orbitals have opposite spins. Crystals of $Na^+C222.Na^-$ have no appreciable EPR absorption, while samples of $K^+18C6.Na^-$ and $Rb^+18C6.Na^-$ have weak EPR signals with hyperfine structure caused by the interaction of electrons trapped at anionic defect sites with the nuclei [54]. In most of the cases, a single narrow line is observed near the free electron g-value due to delocalization of the electrons. Some electrides such as some samples of $Li^+C211.e^-$ that show plasma absorption have less than 1% unpaired spins while those that have localized electron absorption have from 30 to 100% unpaired spins. Films of $K^+C222.e^-$ show also metallic character whereas those of $Na^+C222.e^-$, $Rb^+C222.e^-$ and $Cs^+C3222.e^-$ have localized electron absorptions. Samples of $Cs^-(18C6)_2.e^-$ are strongly paramagnetic with an asymmetric intense EPR line characteristic of high microwave conductivity [57].

NMR studies of $^{87}Rb^-$ in ethylamine (EA) and tetrahydrofuran (THF), and $^{133}Cs^-$ in THF and $^{23}Na^-$ in EA, THF and MA have been made [58]. The chemical shift of Na^- is independent of the solvent and is nearly the same as that calculated for gaseous Na^- (~-2 ppm relative to $Na_{(g)}$). Therefore, the 2p electrons of the Na^- are well shielded from interaction with the solvent by the two 3s electrons. Rb^- and Cs^- gave narrow lines which are diamagnetically shifted from the corresponding cations.

Precise identification of the alkalides and electrides is possible through solid state NMR [59]. At least eight crystalline sodides which use C222, 18C6 and 15C5 have been positively identified by ^{23}Na, and ^{133}Cs magic angle spinning NMR. $Na^+C222.Na^-$ has two separate peaks at $\delta = -23.7$ ppm and $\delta = -61.3$ ppm for Na^+C222 and Na^- respectively. Heteronuclear sodium alkalides show single peaks at $\delta = -55.9$ to -61.3 ppm which indicates that they are true sodides. A compound of stoichiometry Cs:18C6 = 1:1 has two peaks in its ^{133}Cs NMR spectra which appear at -61 ppm for Cs^+ and -228 ppm for Cs^-. Notice here the large diamagnetic shift of Cs^- with respect to Cs^+.

The structures of most of the alkalides and electrides are not yet known. Only for $Na^+C222.Na^-$, has the structure been fully determined by x-ray crystallography [60]. It consists of alternate layers of Na^- anions and cryptate Na^+C222 cations in a closest packing arrangement. Structures of some compounds which contain Rb^+ and Rb^- are under study by EXAFS. This work is the study of properties of a new alkalide of stoichiometry $NaK(12C4)_2$.

D. Thermochemistry

There is ample evidence for the stability of sodium, potassium, rubidium and cesium anions both in solution and in the crystalline states. Many of the isolated compounds are solvent-free and stable at room temperature for hours to days; examples are $K^+(15C5)_2.Na^-$, $Rb^+(15C5)_2.Na^-$, $Cs^+(18C6)_2.e^-$, $Cs^+(18C6)_2K^-$ and $Na^+C222.Na^-$. Key factors to the stability are the choice of an appropriate complexant for the desired cation, the right co-solvent and starting reagents of high purity.

Dye and coworkers have measured the e.m.f. of the cell $Pt|Na(s)|Na^+\beta\text{-alumina}|Na^+C222.Na^+(sat)|Pt$ as a function of temperature in various solvents [61]. Both $Na^+C222.Na^-$ and C222 were maintained saturated and the net cell reaction can be written as

$$2Na(s) + C222(s) \rightleftharpoons Na^+C222.Na^-(s) \ .$$

The measurements yielded:

$$\Delta G^\circ = -2FE^\circ = -1.7 \pm 0.3 \text{ Kcal mole}^{-1} \text{ at } 298 \text{ K.}$$

$$\Delta H^\circ = -8.1 \pm 1.0 \text{ Kcal.mole}^{-1} \ .$$

$$\Delta S^\circ = -22 \pm 4 \text{ cal mole}^{-1} \text{ deg}^{-1} \ .$$

These results predict a stability up to approximately 90-120°C. $\Delta G^\circ < 0$ indicates that $Na^+C222.Na^-$ is relatively stable with respect to dissociation into Na(s) and C222(s) at 25°C. The compound decomposes at 83°C. The e.m.f. was not affected by any change in solvent.

In addition to this experimental evidence of the stability of $Na^+C222.Na^-$, theoretical estimates have been made for many other compounds by means of a Born-Haber cycle. Such calculations have shown that the hypothetical ionic salts $M^+.M^-(s)$ formed from the reaction:

$$2M(s) \longrightarrow M^+.M^-(s)$$

where M is an alkali metal, have enthalpies of formation that range from 11.2 Kcal $mole^{-1}$ for Li to 15.8 Kcal $mole^{-1}$ for Rb [62]. Enthalpies as small as these are due to the positive electron affinities and the relatively low lattice energies and ionization potentials of the metals. The lattice enthalpies of the hypothetical ionic crystal $M^+.M^-(s)$ are estimated by assuming that the interionic distance is the same as the interatomic distance in the metal lattice. These calculations show that the anion of any alkali metal should form under favorable circumstances such as the stabilization of M^+ inside a cavity of a metal complexant.

Estimates of the stabilities of the alkalides and electrides that use the cryptands as metal complexers have been previously made by Van Eck [63]; they indicate that all these compounds are moderately stable at 25°C. An effort has been made in the present work to extend these stability estimates to the crown ether sandwich type alkalides. The results of these calculations are presented in Chapter IV.

CHAPTER II

EXPERIMENTAL

The delicate stability of the alkalide and electride salts in solution as well as in crystalline form requires that glassware and reagents used be free of all reducible impurities. The synthesis and analysis methods have also been carefully designed to prevent the decomposition of the solutions and crystals by contact with air, moisture, heat and light.

A. Glassware Cleaning

The following procedure was applied to all glassware used in the synthesis and handling of the solutions and crystals of these compounds.

First, the glassware was rinsed with an HF-cleaning solution (33% HNO_3, 5% HF, 2% acid soluble detergent, 60% water by volume) for several minutes, followed by five to six rinses with distilled water.

The vessels were then filled with aqua regia (3:1, hydrochloric acid 12 M/nitric acid 16 M) and allowed to stand for several hours. They were afterwards rinsed at least six times with distilled water and six times with conductance water.

Finally, they were dried overnight in an oven at 125°C. After oven-drying, they were protected against further contamination from dust and other impurities by carefully covering any opening with Parafilm-M.

B. Reagents

1. Solvents

The solvents were treated with appropriate drying agents and stored in vacuum storage bottles.

a. Methylamine (MA):

Methylamine (98% pure, Matheson) was stirred over calcium hydride for several hours at reduced temperatures (-20°C). It was then frozen by immersing the bottle in liquid nitrogen and pumped to 1×10^{-5} torr to remove residual gases. If any gas evolution was observed after a freeze-pump-thaw cycle, this procedure was repeated. The solvent was then transferred by distillation onto a NaK_3 alloy where it was freeze-pumped again. This process was repeated until the metal-methylamine solution remained blue (characteristic color of e^-_{solv} and Na^-) for at least 24 hours. The dry MA was then transferred to a heavy-walled storage bottle.

b. Trimethylamine (TMA):

Trimethylamine (Matheson) was treated in the same manner as methylamine.

c. Dimethyl ether (DME):

Dimethyl ether (anhydrous, Mallinkrodt, Inc.) was purified in the same way as MA, but with benzophenone added to the Na/K alloy as an indicator of dryness. The final storage was over Na/K with no benzophenone. The Na/K alloy is insoluble in dimethyl ether.

2. Complexing agent

12-Crown-4 (12C4 or IUPAC: 1,4,7,10-tetraoxacyclodecane) was purchased from PCR, Inc. This complexing agent is a liquid and, as with other liquid crown ethers, is sufficiently volatile that is should be handled with great care; skin contact and breathing of vapors should be avoided. Therefore the impure crown was transferred to a sublimation apparatus (Figure 3) via pipette and gloves in an exhaust hood. The purification was carried out under dynamic vacuum by heating the impure crown with an oil bath at 65-70°C and maintaining the cold finger of the apparatus cool enough with cold N_2 gas. The N_2 gas was cooled with a water-ice bath. It is very important that liquid N_2 not be used in place of the water-ice bath because it lowers the temperature of the finger such that many impurities (e.g., H_2O) codistill with the crown and

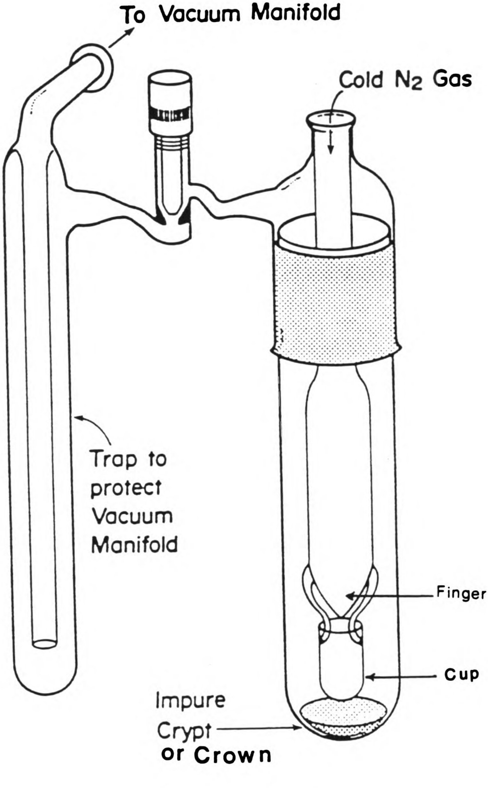

Fig. 3 Liquid cryptand and crown purification apparatus.

freeze also on the finger where the pure crown is to be collected during the sublimation. Purification made at moderate temperatures below the boiling point of the crown ether (at reduced pressures) with a water-ice bath minimized the codistillation of water.

When all the crown was distilled, the finger was kept cold for at least an hour to insure that all the vapor was condensed and dropped into the cup. The entire apparatus was then allowed to warm to room temperature under static vacuum and brought into a dry box where the crown was transferred into a storage bottle. Storage and transfer of the purified crown into any other apparatus was done under an inert atmosphere to avoid contamination by impurities.

3. Metals

a. Sodium and potassium

These metals (Alpha Ventron, 99.95% purity) were received under argon in sealed glass ampoules with break-seals. They were transferred by vacuum distillation into Pyrex tubes of 2-8 mm OD following a procedure described elsewhere [50]. When a sample of particular mass is needed, a tube of appropriate diameter and length is isolated and sealed off.

C. Sample Preparation

Two different sorts of apparatus were used for the syntheses. As the contamination of Na from Pyrex glass does not affect the compound stoichiometry, the apparatuses were made from Pyrex. Each apparatus had two different chambers appropriate for complexant (main chamber) and metal (second chamber) loading. The method of preparation of the crystals involves many steps which were carefully followed for any alkalide or electride and will be described for utilization of one type of apparatus (called the "cow") (shown in Fig. 4). The use of the second apparatus differs slightly from the first only in the last step, the storage of the crystals.

The vessel was cleaned as previously described and was ready for reagent loading. Two glass ampoules that contained measured amounts of K and Na were cleaned and dried with acetone, scribed with a glass knife and put into the metal sidearm of the apparatus. A length of heat shrinkable tubing which had one end sealed to a glass tubing (as shown) was connected to the sidearm. The entire apparatus was then evacuated to 1×10^{-5} torr. The metal tubes were broken at the scribe inside the heat-shrinkable tubing and shaken down the sidearm. The tubing was immediately removed by flame seal-off at the sidearm. At this point the apparatus was removed from the vacuum line and brought into a dry box where a weighed amount of 12C4 was loaded in the main chamber

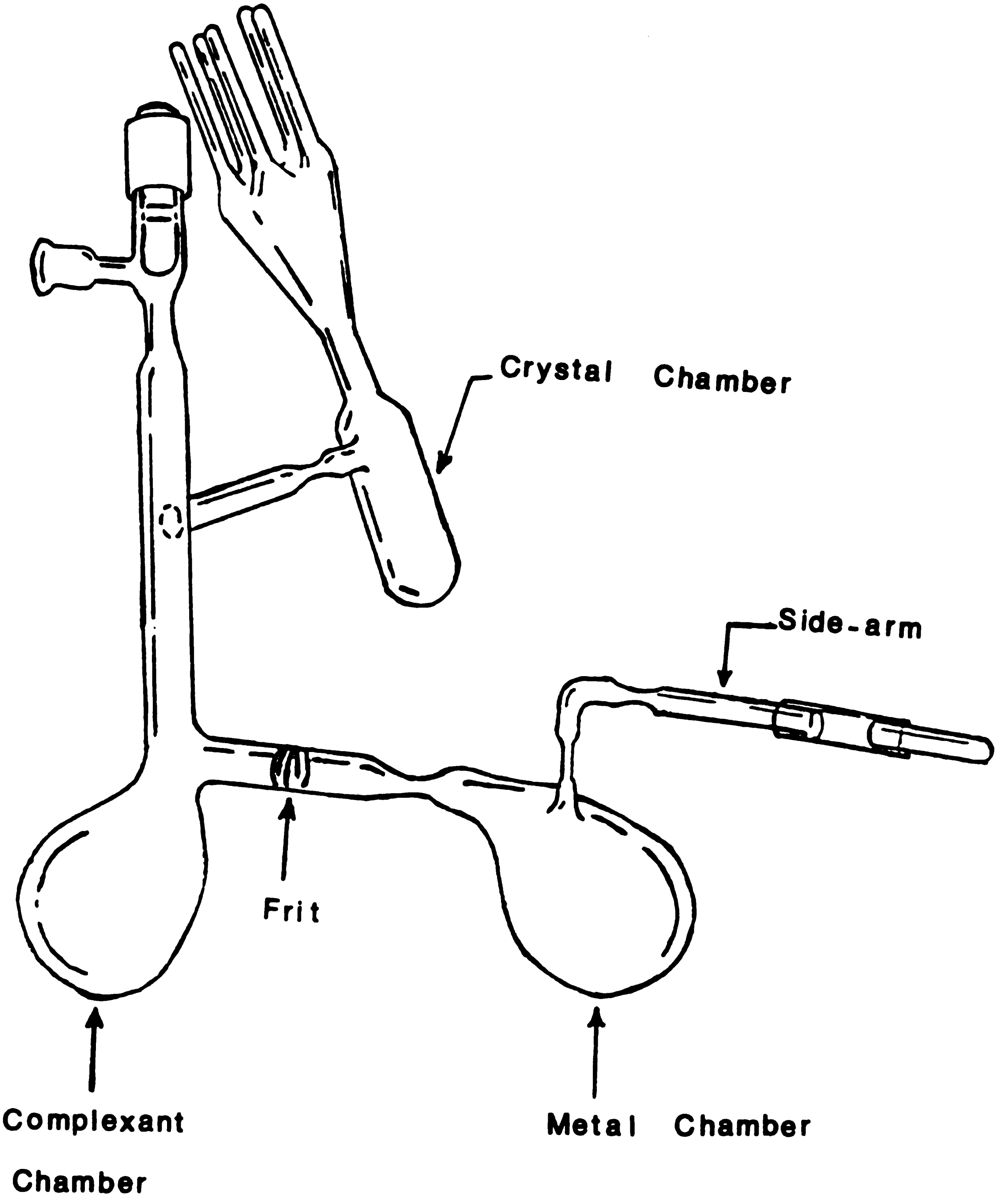

Fig. 4 Apparatus for the preparation of crystalline alkalides and electrides.

through the Fisher-Porter joint. The valve was then closed, and the apparatus was again connected to the vacuum line and pumped down to 1×10^{-5} torr while the crown was cooled with an isopropanol bath cooled with dry ice to -10°C to prevent contamination of the line by the liquid crown. After evacuation, the metals were distilled into the metal chamber and the sidearm was removed by flame seal-off at the constriction. Either methylamine or dimethyl ether was vacuum distilled into the main chamber (cooled to -10°C) and shaken to make a homogeneous mixture of crown and solvent. All the parts of the apparatus that would be in contact with the metal solution were cooled to -40°C with an isopropanol-dry ice bath, and the mixture of solvent-complexant was poured onto the metal through the frit. A blue solution formed immediately. It was poured back and forth between the two chambers to insure that all the complexant was collected. The second step in the synthesis consists of precipitating crystals from the metal solution. Therefore, after the metal dissolution had stopped (about 10 hours), the solution was collected in the main chamber and the methylamine or dimethyl ether was distilled into a waste bottle, leaving about a third of the solvent. Then, trimethylamine was added at -50°C, and very few crystals precipitated. The solution was further cooled to -78°C and a lot of crystals precipitated. It was left overnight at -78°C. After the formation of crystals had stopped, the mother liquor was poured into the metal chamber and frozen with liquid nitrogen. The metal chamber was then removed by flame seal-off at the constriction near the frit. Trimethylamine was again condensed onto the crystals as a washing solvent and the slurry was transferred to the upper chamber. The crystals were rinsed many times by distilling the solvent onto the crystals, stirring and pouring the liquid back down into the crown chamber. Since the complexation of K by 12C4 is relatively weak, care was taken at this point to decant as much solvent as possible onto the crystals and to stir well to remove all non-reacted crown. When the crystals were apparently free of any blue solution, the solvent was frozen in liquid nitrogen while the upper chamber was kept in dry ice. The apparatus was again evacuated to 1×10^{-5} torr and pumped down for half an hour to insure that all the solvent was removed; during this period the crystals were shaken from time to time. The crystal chamber was then removed by seal-off. Finally, the fingers attached to this crystal chamber were placed in liquid nitrogen and the crystals were transferred into the fingers by inverting the chamber. Very nice red copper colored crystals that grew as very fine square flakes were gathered. When the H-cell was used crystals were transferred into similar tubes under dry nitrogen atmosphere.

D. Analysis

1. Elemental analysis

The analytical scheme used to determine the stoichiometry of the alkalide and electride salts was designed by Dye and coworkers [50]. The metal content was checked by reacting the crystals with water and measuring the amount of hydrogen evolved, followed by a pH titration and alkali metal flame emission analysis of the residue. The complexant content was further obtained by quantitative ^{1}H NMR analysis of the residue.

a. Hydrogen evolution

The alkalide and electride compounds are strong reducing agents so that their reaction with water provides the amount of reductant present. The aim is to react a known mass of crystals according to the equation:

$$K\text{-}(12C4)_2\text{-}Na + 2H_2O \rightarrow K^+ + Na^+ + H_2 + 2OH^- + 2(12C4) \ . \qquad (9)$$

The apparatus used to measure the hydrogen evolved had several components: a calibrated pipette where the H_2 is collected, a mercury Toepler pump with leveling bulb to provide manual pumping of the hydrogen into the pipette, a sample compartment, a water bulb and a double liquid nitrogen trap to prevent the contamination of the vacuum line by H_2O. This apparatus is described in detail by Van Eck [63]. Extreme care was taken to avoid thermal decomposition of the sample prior to analysis. A scribed sample tube that was kept cold in an isopropanol-dry ice bath at -78°C was broken in an inert atmosphere bag and the crystals were immediately transferred to a glass vessel designed for this purpose. The vessel was previously cleaned and evacuated to 1×10^{-5} torr and kept cold in the bag by using liquid nitrogen. The crystals were spread on the bottom of the apparatus to provide good contact with the liquid nitrogen bath. The apparatus was then tightly capped with a glass tube and Cajon ultratorr coupling and connected to the hydrogen evolution assembly while it was retained in dry ice. After a second evacuation, the crystals were reacted with cold deuterium oxide which had been previously degassed by repeated freeze-pump-thaw cycles. When the reaction was complete, the deuterium evolved was pumped with manual Toepler pump into the calibrated pipette and the pressure was obtained by measuring the height of the mercury column. The number of moles of D_2 was evaluated with the ideal gas law. During the pumping, the residue (decomposed crystals plus D_2O) was kept frozen in liquid nitrogen for future use.

b. pH titration

According to Equation (9), a pH titration of a portion of the residue from the H_2 evolution permits a second check of the amount of reductant that was in the sample. This step is also important because it helps test whether or not the sample decomposed prior to analysis. The residue was transferred to a 10 ml volumetric flask and the vessel was rinsed many times with D_2O. The resulting solution was diluted with more D_2O to the mark on the flask. A known volume of that preparation was taken and treated with a known volume of HCl and conductance water to make a solution of pH $\simeq 3$. The solution was titrated with freshly standarized NaOH solution for which a potassium hydrogen phtalate solution had been used as an acidic standard. A digital pH meter (ORIEN Research, model 701 A) and a Corning electrode were used for the titration. The end point was determined from the titration curve, from which only the number of moles of OH^- present was obtained.

c. Flame emission

Flame absorption/emission spectroscopy is a useful tool for the analytical determination of the metal content of a sample and therefore was used here for the analysis of K and Na content of $K^+(12C4)_2Na^-$. A second portion of the solution from the residue of H_2 evolution was diluted with conductance water to make a solution of concentrations in K^+ and Na^+ between 30 and 50 ppm. This analysis should not make use of the solution from the pH titration because of the interference of K^+ from the calomel electrode and also of Na^+ from the alkaline solution. The freshly prepared solution was therefore analyzed by using a Jarrell-Ash atomic absorption/flame emission spectrophotometer. The wavelengths for maximum absorption/emission for K^+ and Na^+ were successively chosen and standard solutions of each metal (10-100 ppm) were run with the sample. The emission values of these standards, given by a digital averager, were plotted against the concentrations for each metal and the resulting working curves were used to determine the concentrations in the sample. All emission values were baseline-corrected by running conductance water between each determination.

d. Proton NMR analysis of crown

The rest of the preparation from the residue was analyzed for crown content. This "left over" was divided into two parts and two separate weighed amounts of sodium acetate were added to serve as internal standards. These solutions were analyzed with a Bruker 250 MHz Fourier transform NMR instrument which provides a line fitting program that was used to fit the sodium acetate and crown peaks to Lorentzian curves. It immediately gives the standard deviation, the amplitude and the full width at half-height of the curves. These last two data were used to calculate the area under each curve and from these areas the ratios of sodium acetate to crown were obtained. From these ratios and the amount of sodium acetate added, the number of moles of crown was known.

2. Characterization methods: instrumental techniques

a. Optical spectra

The transmission spectra of K-$(12C4)_2$-Na were obtained from dry films made following direct dissolution of the crystals in methylamine. The apparatus used to prepare the films had two compartments: a quartz cell where films were made and a side vessel for solution storage. Except for the cell, it was made entirely from Pyrex. The apparatus was evacuated to $\sim 1 \times 10^{-5}$ torr and the crystals were transferred from a sample tube into the cell under a dry nitrogen atmosphere. They were maintained cold by using liquid N_2 kept in another vessel. The apparatus was again evacuated to remove all the residual gases from the crystals, and afterwards methylamine was vacuum distilled over the crystals. A homogeneous dark blue solution formed. The vessel was then submerged in a dry ice-isopropanol bath at ~-40°C. The films were prepared by pouring the solution into the other compartment, leaving about a quarter of it in the cell. This compartment was kept in liquid N_2 while the cell was in the ice bath, and the apparatus was vigorously skaken to spread the solution over the windows of the cell. A film of uniform thickness is generally difficult to prepare, but one can be reasonably obtained by repeatedly thawing the solution in the side vessel and distilling some solvent over the film. The spectra were measured with a Beckman DK-2 recording spectrophotometer equipped with an insulated cell compartment through which cold N_2 gas was circulated. The temperature in the vicinity of the cell was measured with a copper-Constantan thermocouple. Spectra were recorded at different temperatures from -100 to +10°C and from the infrared to the visible region. The reference beam passed through air. The spectra were finally baseline-corrected by subtracting the spectrum of the empty cell and they were normalized by scaling the lowest absorbance to zero and the highest to 1.

b. Pressed powder conductivity

The powder conductivity of the crystals of $K_-(12C4)_2$-Na as well as their band gap were investigated by the voltmeter-ammeter method using an apparatus designed by Dye and Yemen [56]. This apparatus, called the "cold jacket cell (c.j.c.)" was composed of a heavy-walled fused silica 2 mm I.D tube inside which the sample was loaded and of two stainless steel electrodes which were inserted into both sides of the tube to compress the powder. Pressure was generated by means of a spring of measured force constant connected to one of the electrodes. Prior to sample loading, the crystals were ground to produce very small ones because in general the crystals grow as fine flasks and would leave gaps between them which would prevent the passage of the current. The sample loading and the assemblage of the c.j.c. for current measurement was done under a dry N_2 atmosphere to prevent the decomposition of the crystals by contact with air. The cell was then inserted in a cooling jacket which was maintained cold by liquid N_2 boil-off. The N_2 flow and temperature were regulated by a Varian V-4540 variable temperature controller and the temperature was measured by placing a thermocouple near the powder tube. The powder was cooled from -20°C to -65°C while applying a constant voltage between the two electrodes and the current was read at about two degree intervals. The temperature was raised back to -20°C at the same voltage and current measurements were made again. Then the cell was disassembled to check if the powder retained its red shiny color. If so, the cell was reassembled and at constant temperature (~-20°C), Ohm's law was checked by measuring the current as a function of the voltage. Afterwards, the temperature was lowered again and the current was measured for another run. At the end, the height of the powder in the tube was measured and used to calculate the specific resistivity of the crystals.

c. Magnetic susceptibility

The measurements of the static susceptibilities of the samples were done with an S.H.E. SQUID (superconducting Quantum Interference Device) susceptometer. This instrument is equipped with a sample cooling system that permits measurements down to 1.5 K. The technique of sample loading and instrument operation are described in detail by Issa [53]. The crystals were first loaded into a small Delrin plastic bucket which was introduced into the SQUID.

CHAPTER III

CHARACTERIZATION OF POTASSIUM-(12-CROWN-4)-SODIUM

Before this work, the crown ethers utilized as ligands for the preparation of the crystalline alkalide and electride systems were 18-crown-6 and 15-crown-5. Therefore, the main purpose of this thesis was to investigate the preparation of the same types of compounds with the ligand 12-crown-4. After numerous attempts, a compound was isolated from a mixture of potassium, sodium and 12-crown-4 (12C4) in trimethylamine. The method of preparation of the compound has already been described in the preceding chapter. Several different syntheses were analyzed to determine the stoichiometry. The optical spectra were taken and attempts were made to study the electrical and magnetic properties. The techniques involved in these studies have also been outlined in the experimental section (Chapter II). The results are discussed in the present section.

A. Determination of the Stoichiometry of the System

The different samples reported here were prepared with the same experimental conditions. A 1:1:2 ratio of metals to ligands was used and crystals of similar appearance were obtained in every synthesis. It was extremely difficult to dissolve all the metal even though long periods of time were allocated to this process. This may be due to the weak interaction of 12C4 with K^+ as already outlined elsewhere [48]. The samples were analyzed according to Equation (1), by reacting the crystals with D_2O and measuring the hydrogen evolved. The number of moles of this gas was calculated from the ideal gas law. In some cases in which the hydrogen evolution was not made, a known mass of sample was reacted with cold D_2O in a dry nitrogen atmosphere. The mass of the sample as well as the number of moles of hydrogen evolved may be used as reference for the number of moles of K-(12-crown-4)$_2$-Na present. The results of the stoichiometric analysis are summarized in Table 2, along with the percentage deviation from the predicted stoichiometry. It is observed that the deviation depends on the amount of sample used and is relatively large for large samples. The first analysis of synthesis I where only about 1 mmol of sample was used, yielded a 1:1 stoichiometry of K and Na. A second analysis of this preparation was done to determine the crown content. In this analysis and that of synthesis II, the number of moles of OH^- deviates slightly from the predicted stoichiometry. It is likely that the compound partially decomposed during handling of the crystals, but it was also realized

Table 2 Results of the Stoichiometric Analysis of $K-(12C4)_2Na$.[a]

Synthesis	Mass of Sample (g)	Moles $H_2 \times 10^4$	Moles $OH^- \times 10^4$	Moles $K^+ \times 10^4$	Moles $Na^+ \times 10^4$	Moles 12C4 $\times 10^4$
I	—	0.947	1.856 (-2.0)	0.961 (+1.5)	0.914 (-3.5)	—
	—	2.044	4.520 (+10.6)	2.075 (+1.5)	2.200 (+7.6)	4.195 (+2.6)
II	0.0676 (1.631×10^{-4} mol)	—	2.980 (-8.6)	1.608 (-1.4)	1.626 (+0.3)	3.207 (-1.7)
III	0.12595 (3.039×10^{-4} mol)	—	5.990 (-1.4)	3.091 (+1.7)	3.230 (+6.3)	6.870 (+13.0)

[a] The number of mmoles of H_2 evolved or the mass of the sample used is taken as reference to calculate the percent deviation from the predicted stoichiometry given in parentheses.

that the exact end points were difficult to determine from the pH titration curves. The results of these two analyses are nevertheless in good agreement with a stoichiometry of 1:2:1 of potassium, 12-crown-4 and sodium respectively. The third sample shows a relatively high content of 12C4. Probably, the crystals were not washed enough to separate the uncomplexed crown. Another possible reason may be that the preparation contained a small amount of electride $Na^+(12C4)_2.e^-$, as indicated by the observed high sodium content of this sample.

Some systematic errors caused by the instruments used should also be taken into account in the estimation of the overall errors. In any event, the analysis of the three preparations show that the system has a 1:2:1 ratio of K, 12C4 and Na respectively, within an estimated error of ±5%.

The crystals were also tested for the presence of solvent of crystallization. The ^1H NMR spectra of the two last syntheses showed only peaks attributed to 12C4 and sodium acetate, the latter being added as an internal standard. No peak corresponding to trimethylamine was found. However, sample 1 showed a small but distinct solvent peak in addition to those observed with the other samples. The area under this peak was compared to that of the internal standard and indicated the presence of 3 mole percent solvent.

B. Optical Spectra

The optical spectra of the $K(12C4)_2Na$ system were recorded from dry films prepared by directly dissolving the crystals in methylamine and evaporating the solvent.

A typical spectrum is shown in Figure 5. A sharp absorption at 13,100 cm^{-1} (760 nm) and a second peak at 17,000 cm^{-1} (580 nm) were observed. The peak at 13,100 cm^{-1} is red shifted from previously observed absorptions of some sodide compounds that occurred around 15,000 cm^{-1}. The peak at 17,000 cm^{-1} is also slightly shifted to the red with respect to a shoulder observed for dry films of $Na^+C222.Na^-$. But this absorption occurs at the same wavelength as that of maximum fluorescence of single crystals of $Na^+C222.Na^-$ determined by Jaenicke [64]. The maximum absorption of dry films of that compound occurs at 15,400 cm^{-1}. The observation just made suggests that the high-energy peak in the spectrum of $K\text{-}(12C4)_2\text{-}Na$ is due to the species Na^- and may be assigned to a bound-continuum transistion, as was done for $Na^+C222.Na^-$. The sharpness of the main peak suggests that one kind of species is responsible for the absorption. This contrasts with the broad peak observed for some samples of $K^+18C6.Na^-$ which had a center at 13,000 cm^{-1} but was probably overlapping absorptions of K^- and Na^- [53]. The excited states of the alkali metal anions may be perturbed by their surroundings (complexing agents and counterions) so that a strong dependence of the absorption locations on the host

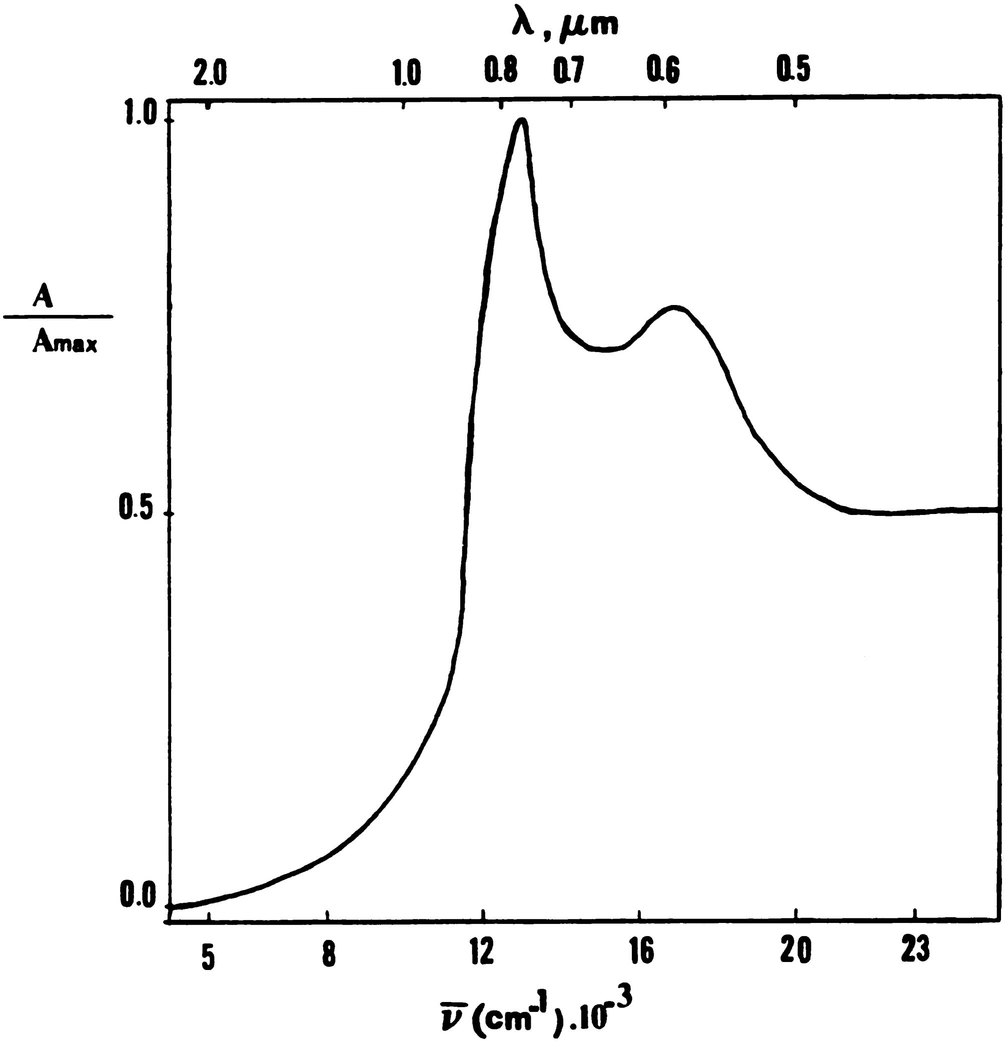

Fig. 5 Optical spectra of dry thin film of $K-(12C4)_2-Na$ in methylamine.

lattice results as was found for many alkalide and electride salts. Therefore, the peak at 13,100 cm^{-1} may also be attributed to the species Na^- and may correspond to a 3s → 3p transition. The possibility that this absorption arises from K^- could not be completely ruled out, because dry films prepared by solvent evaporation may not have the same stoichiometry as the solution or the crystals formed by a slow cooling. Because of these reasons, the identification of a species in a given salt on the basis of the optical spectra alone is weak. Further experiments were performed to determine the anionic species in the $K-(12C4)_2-Na$ systems.

C. Solid State NMR Studies

Since the crystals obtained by slow cooling of a saturated metal complexant system in an amine or ether solvent may be of a stoichiometry different from that of the dry films prepared from the same solution, it is important that species identification be made directly with the crystals. The magic angle sample spinning (MASS)-NMR method was successfully used for this purpose.

In solids, the broadening of the NMR line arises from many factors: anisotropy in the chemical shift, magnetic dipolar interactions of the nuclei, indirect electron-coupled and electric quadrupolar interactions of the nuclei. It has been shown that high-speed rotation of the sample about an axis which forms the "magic" angle $\Theta = 54°44'$ with the direction of the magnetic field, removes to first order all the anisotropic sources of line broadening. Moreover, the $-\frac{1}{2}$ to $+\frac{1}{2}$ transition is also narrowed for nuclei with half integer spin. The application of ^{23}Na MASS-NMR and that of ^{133}Cs has helped to identify numerous heteronuclear alkalides that contain these nuclei. A detailed review of the theory as well as the applications to alkalides and electrides has been made by A. Ellaboudy [65]. A spectrum obtained by ^{23}Na MASS-NMR technique for $K(12C4)_2Na$ is shown in Figure 6. This spectrum, measured by A. Ellaboudy, M. Tinkham, and S. Dawes, contains a strong absorption at -61.1 ppm assigned to Na^- and a very small peak around -11 ppm that could be due to some Na^+ complexed by the ligand or could be formed by decomposition of Na^-. The assignment of the main peak to Na^- is based on the fact that many other sodide salts such as $K^+(15C5)_2.Na^-$, $Rb^+(15C5)_2.Na^-$, $Na^+C222.Na^-$ have absorptions at the same chemical shift. The narrowness of the line attests to the spherical symmetry of the species and indicates that the anionic species in this system is the genuine alkali metal anion, Na^-.

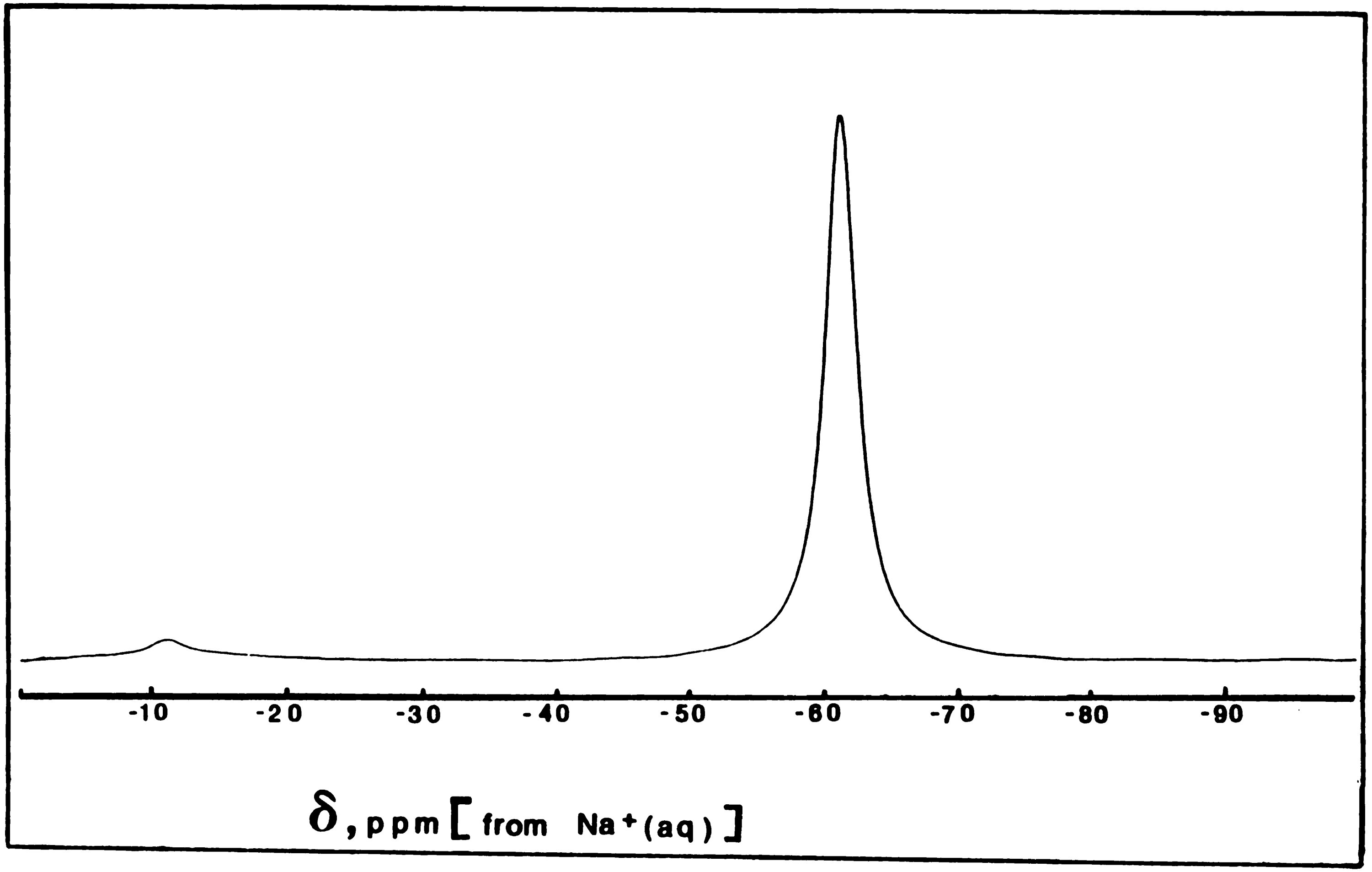

Figure 6 ^{23}Na MASS-NMR spectra of crystalline K-(12C4)$_2$.Na$^-$.

D. D.C Conductivity

The pressed powder conductivity of the compound was also studied. The temperature-dependent electrical conductivity was that expected for a semiconductor.

Semiconductors are substances that show electrical conductivity as the temperature is increased from absolute zero, but this conductivity tends to zero as the temperature is lowered. The dependence on T is expressed by the relation:

$$\sigma = \sigma_\infty \exp\left(-\frac{E_g}{2k_B T}\right) \tag{10}$$

where k_B is the Boltzmann constant, E_g is the energy difference between the conduction band and the valence band and σ_∞ is the extrapolated conductivity at infinite temperature.

This behavior of semiconductors constrasts with that of metals whose conductivity decreases with increasing temperature, due to an increase in lattice vibrations. At room temperature, the resistivities of semiconductors are between 10^{-3} and 10^{9} ohm-cm, intermediate between insulators (10^{14} to 10^{22} ohm-cm) and metals (10^{-3} to 10^{-6} ohm-cm). Semiconductors owe their conductivities to:

-thermal excitation of electrons from a valence band into a conduction band.

-impurities which may be of various types: atoms of a foreign element, stoichiometric excess of one constituent, electrons trapped at points where negative ions are missing (F-centers).

-lattice defects (mainly encountered in crystals). One distinguishes two types of semiconductors. In an extrinsic semiconductor, the impurities contribute a significant fraction of the conduction band electrons or the valence band holes. Intrinsic semiconductivity is found with pure substances. In this case, the electrons are thermally excited from the valence band into the conduction band. Both the electrons and the holes left behind can contribute to the conductivity. Most alkalides behave as extrinsic semiconductors in which the impurities are trapped electrons and with conductivities at infinite temperature of 10^{-2} to 10 $\text{ohm}^{-1}\ \text{cm}^{-1}$. For $K(12C4)_2Na$, the D.C conductivity measurements were performed on pressed powdered samples by first checking the adherence to Ohm's law (made by measuring the current as a function of the applied voltage), followed by the measurement of the current as a function of the temperature at a fixed voltage. The data plotted in Figure 7 were fit by the equation:

$$\log R = \log R_\infty + \frac{E_g}{4.6\ k_B T} \tag{11}$$

in which R and R_∞ denote the resistance of the sample at temperature T and at infinite temperature respectively. The

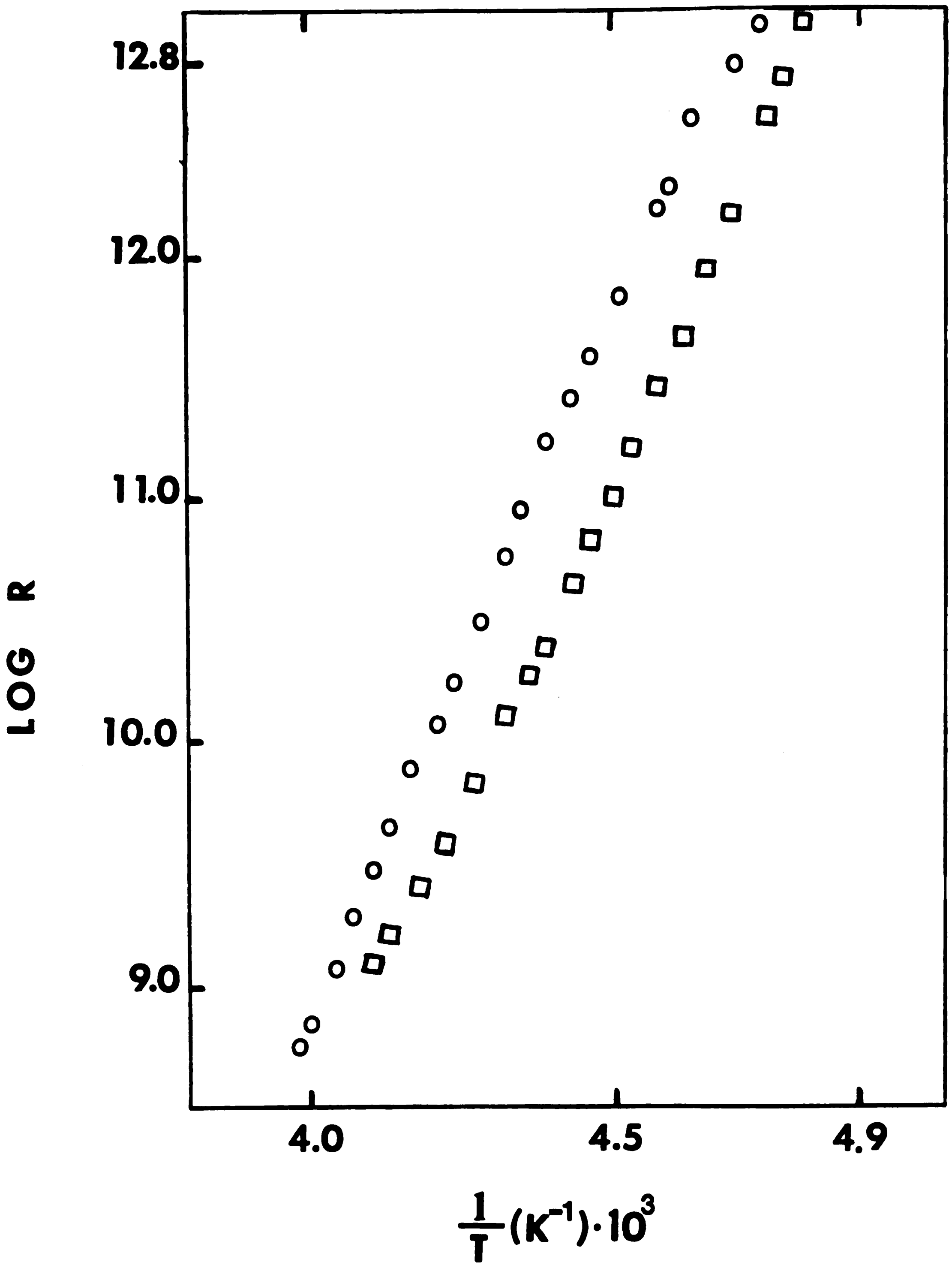

Fig. 7 Plot of log resistance vs. reciprocal temperature for polycrystalline K-$(12C4)_2$-Na. ○ represents log R obtained when raising the temperature and □ represents log R when lowering the temperature.

nonlinear least squares program KINFIT was used in this fitting. An average band gap of 2.17 ± 0.03 eV and a conductivity at infinite temperature of 2.03×10^{13} ohm^{-1} cm^{-1} were obtained. This value of the limiting conductivity is too large for either an intrinsic or an extrinsic semiconductor but a similar behavior was observed in one case with the compound $\mathrm{Na}^{+}\mathrm{C222.Na}^{-}$ [56]. In the case of $\mathrm{K}^{+}(12\mathrm{C}4)_{2}.\mathrm{Na}^{-}$, the plot of current vs. voltage was also not completely ohmic (Figure 8). This indicates that one has not only an electronic contribution to the conductivity, but that polarization effects are also present. It is likely that an ionic conduction occurs simultaneously which may be caused by motion of lattice defects. The results indicate that $\mathrm{K}^{+}(12\mathrm{C}4)_{2}\mathrm{Na}^{-}$ may be an intrinsic semiconductor with a band gap of 2.20 eV, but that other conduction mechanisms are also important.

E. Magnetic Susceptibility

The magnetic susceptibility of the alkalide was measured in the temperature range of 1.5 K to 200 K. Figure 9 shows the magnetic behavior vs. temperature for the fresh and the decomposed samples. The magnetic behavior of the fresh sample is that expected for a system in which nearly all the ground state electrons are paired. The data were fit to Equation (12) by using the nonlinear least square program KINFIT.

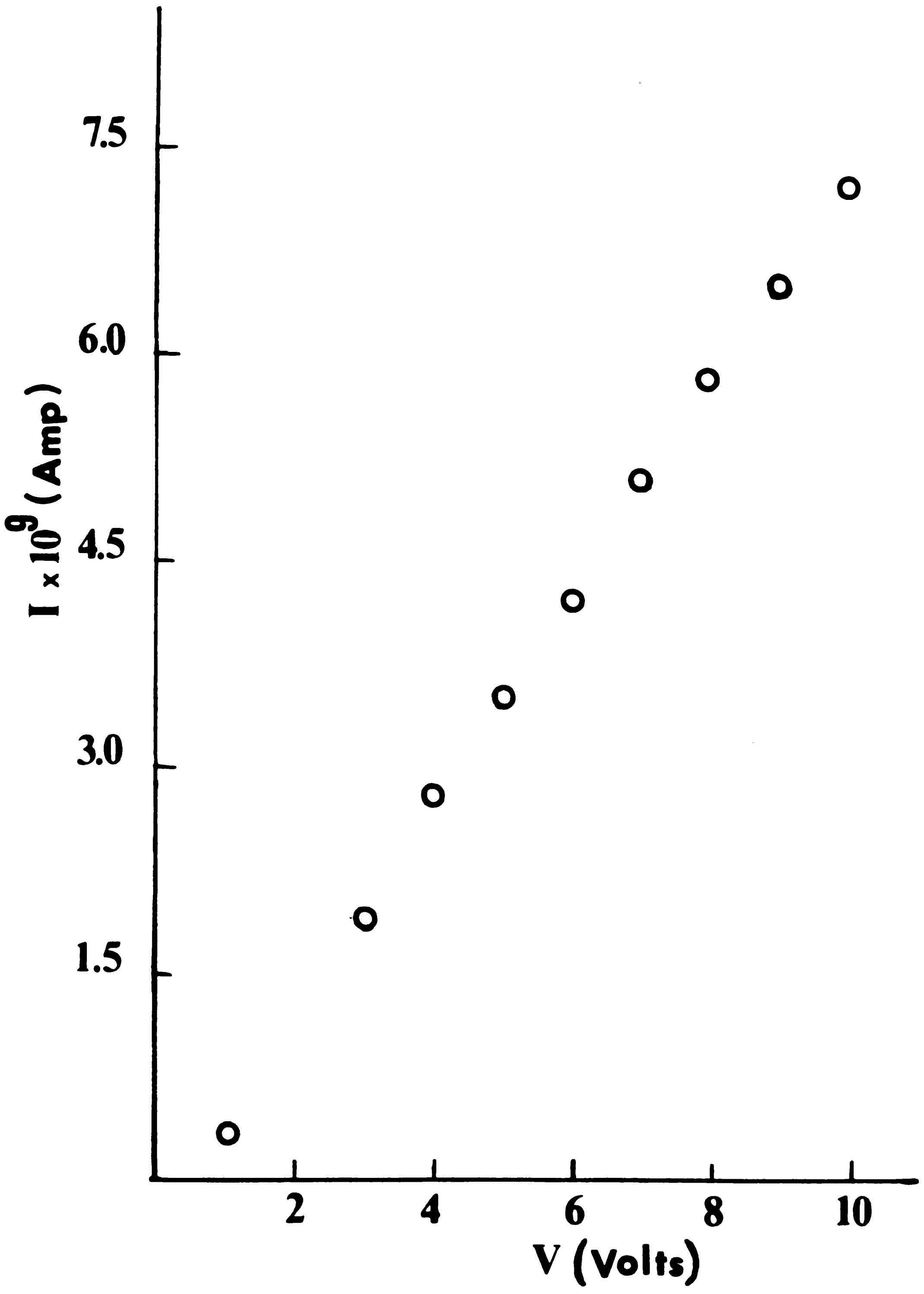

Fig. 8 Current vs. voltage for K-(12C4)$_2$-Na powders.

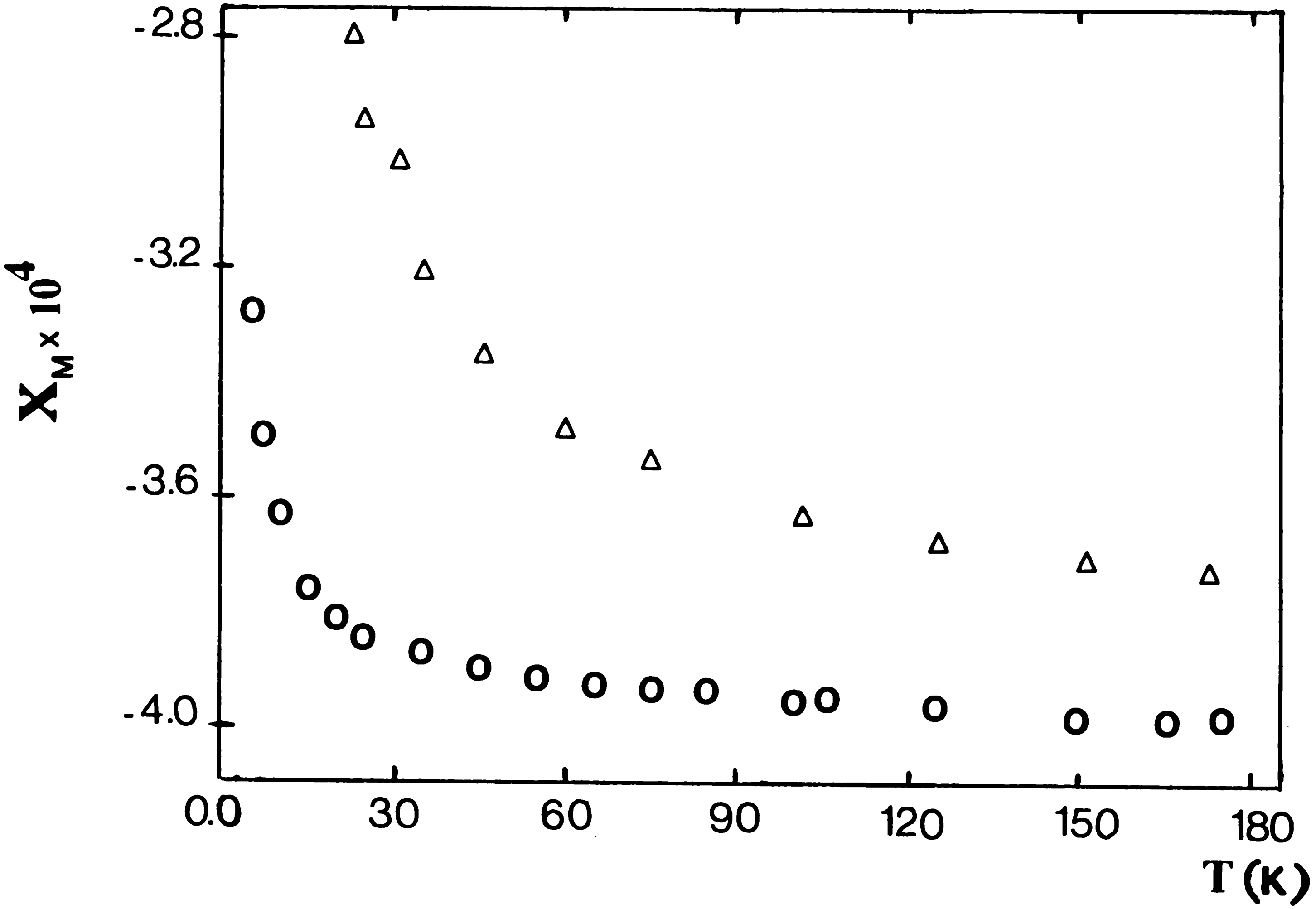

Fig. 9 Molar susceptibilities for fresh and decomposed samples of crystalline K-$(12C4)_2$-Na. (Δ = decomposed sample, O = fresh sample.)

$$\chi_M = \chi^{elect} + \chi^{diam} \tag{12a}$$

or

$$\chi_M = \frac{FC}{T-\Theta} + B \ . \tag{12b}$$

χ^{elect} is the electronic contribution to the susceptibility and χ^{diam} is the diamagnetic term. The paramagnetic term χ^{elec} was directly fit to the Curie-Weiss law: $\chi^{elec} = FC/T-\Theta$ in which F is the fraction of unpaired spins, C is the Curie constant (= 0.37604 cm^3 K mol^{-1}, and Θ is a temperature characteristic of the system generally called the Weiss constant. The results indicate that the fresh sample contained 0.1% free spins while the decomposed sample had about 0.7% unpaired spins. This suggests that some organic radicals or trapped electrons are likely formed by thermal decomposition of the alkalide. The observed diamagnetic susceptibility is -4.0×10^{-4} e.m.u./mole. This value is in the same range as the calculated value of -3.0×10^{-4}, estimated by means of Pascal's constants for diamagnetic susceptibility of the constituents of the alkalide [66].

F. Melting Point

Attempts were also made to study the melting point of the compound. At dry ice temperature, freshly prepared crystals are very well defined, shiny, square flakes of red-copper color by reflected light. Kept under vacuum at a pressure of ~1 × 10^{-5} torr, they remain shiny at room temperature. The study was carried out by progressively heating some crystals enclosed in a sample tube. As the temperature was increased from room temperature up to +50°C, no apparent change in the crystal shape and color occurred. They darkened around +55°C and formed a blue liquid at +60°C that likely contained the metal cations, the complexant and either solvated electrons or alkali metal anions. This liquid retained its dark blue color up to +80°C where decomposition to a white residue took place. This study attests that the compound is thermodynamically stable at room temperature. Its stability is comparable to that of the well-characterized sodide, $Na^+C222.Na^-$, that decomposed at +83°C [61].

CHAPTER IV

THERMODYNAMICS OF FORMATION OF SOME ALKALIDE SALTS OF THE CROWN-ETHERS

The isolated alkalide salts of stoichiometry $M^+L.N^-(s)$, where L is a molecule of the crown ether or cryptand classes, exhibit remarkable stabilities and important properties. This has prompted an investigation to predict whether similar salts of stoichiometry $M^+L_2.N^-(s)$, in which L is a crown-ether, could be made with all the alkali metals.

An approach that can be successful in this area is that of thermodynamic arguments pioneered by Golden, Guttman and Tuttle on the presence of the alkali metal anions in metal-ammonia solutions [67].

The compounds of stoichiometry $M^+L_2.N^-(s)$ will be thermodynamically stable if the Gibbs free energy change is negative for the following process:

$$M(s) + 2L_{(s\ \mathrm{or}\ \mathrm{liq})} + N(s) \longrightarrow M^+L_2.N^-(s)\ . \qquad (13)$$

In fact, the thermodynamic stability of a chemical species at a temperature T may be defined as its ability to resist dissociation into the starting reagents and can be quantitatively expressed by all of the standard Gibbs free energies of formation at that temperature. This latter may be considered as the change in G when a mole of the substance at 1 atm pressure is formed from its elements each at the same temperature. (We will use the term "formation" somewhat loosely to refer to the formation of an alkalide or electride from the metals and the complexant rather than from all the elements.) The Gibbs free energy of complexation at $T = 298$ K has been evaluated for numerous chemical species including complexes of the crown ethers with the alkali metal cations, based on the determination of the formation constants according to the equation:

$$\Delta G_f^\circ = -RT \ln K_f \ . \tag{14}$$

The formation constants are generally obtained for reactions in the gas phase or in solution by many methods including calorimetric, potentiometric, polarographic and spectroscopic techniques. ΔG_f° is also related to other important thermodynamic parameters, that is, the enthalpy and entropy change of the system by the equation:

$$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ \ . \tag{15}$$

The enthalpy of formation may be obtained directly by calorimetric measurements at a given temperature, or by measuring the formation constant as a function of temperature, in which case ΔS_f° is also obtained from the plot of $\ln K$ vs. $1/T$.

The Gibbs free energy and enthalpy of formation of the salt $Na^+C222.Na^-$ have already been determined by an electrochemical technique and agree reasonably well with the calculations performed for this compound [61]. Furthermore, good agreement between the observed stabilities and the calculated thermodynamic quantities was found for various cryptate alkalides and electrides [63]. In this section, similar theoretical estimates of the thermodynamic quantities are performed for many sandwich alkalides by means of a modified Born-Haber cycle (Figure 10) where the reaction is written as a process involving several steps. Reasonable estimates of the thermodynamic parameters are obtained from this method, as available experimental quantities can be conveniently used for many steps of the cycle.

A. Evaluation of the Energy Terms in Aqueous Solutions at 298 K

The energies of formation have been calculated for each of the following reaction steps of the modified Born-Haber cycle.

$$M(s) \longrightarrow M(g) \tag{16}$$

$$N(s) \longrightarrow N(g) \tag{17}$$

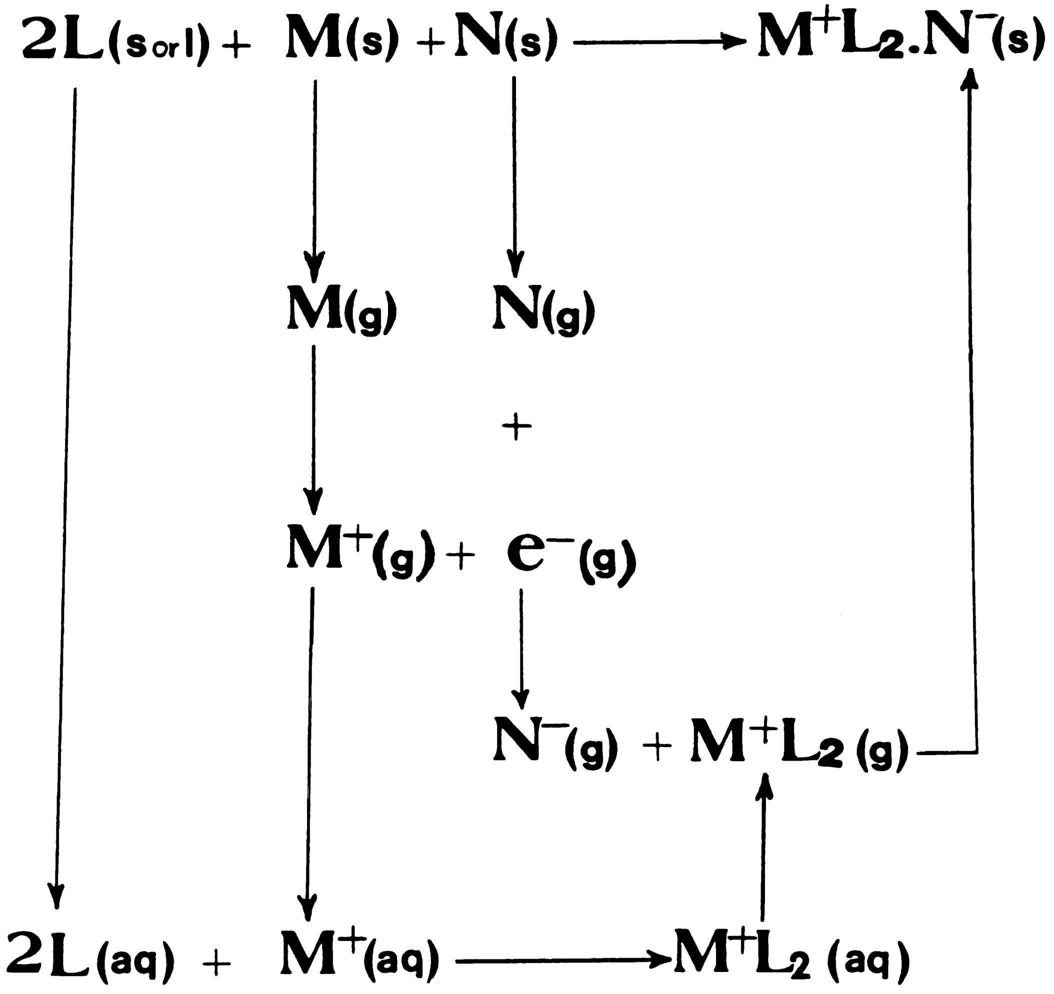

Fig. 10 Modified Born-Haber cycle used to estimate the stability of $M^+L_2.N^-(s)$.

$$M(g) \longrightarrow M^+(g) + e^-(g) \tag{18}$$

$$N(g) + e^-(g) \longrightarrow N^-(g) \tag{19}$$

$$M^+(g) \longrightarrow M^+(aq) \tag{20}$$

$$2L(\text{s or liq}) \longrightarrow 2L(aq) \tag{21}$$

$$M^+(aq) + 2L(aq) \longrightarrow M^+L_2(aq) \tag{22}$$

$$M^+L_2(aq) \longrightarrow M^+L_2(g) \tag{23}$$

$$N^-(g) + M^+L_2(g) \longrightarrow M^+L_2.N^-(s) \tag{24}$$

1. Enthalpy and free energy of metal atomization, ionization, electron affinity and aquation.

Details for the calculation of these quantities have already been made by Van Eck [63] and only the results will be reproduced here in Table 3. They were used without any change to calculate the overall energies.

2. Free energy of ligand solvation.

$$2L(\text{s or liq}) \longrightarrow 2L(aq) \ .$$

The energies of ligand solvation are not yet available. The ethers 12C4, 15C5 and 18C6 whose sandwich compounds are considered here are all neutral water soluble ligands and might have similar negative solvation energies. Since no

Table 3 Enthalpy and Free Energy of Metal Sublimation, Ionization, Electron Affinity and Hydration.[a]

Metal	ΔH°_{subl}	ΔG°_{subl}	ΔH°_{ioniz}	ΔG°_{ioniz}	ΔH°_{EA}	ΔG°_{EA}	ΔH°_{hyd}	ΔG°_{hyd}
Li	+38.40	+30.60	+124.89	+123.81	-14.89	-12.99	-132.1	-122.1
Na	+25.75	+18.48	+119.07	+117.99	-13.23	-11.33	-106.0	-98.2
K	+21.30	+14.50	+100.65	+99.57	-12.14	-10.25	-85.8	-80.6
Rb	+20.51	+13.35	+96.89	+95.81	-11.80	-9.90	-79.8	-75.5
Cs	+18.30	+11.90	+90.36	+89.28	-11.43	-9.53	-72.0	-67.8

[a] Energies are in Kcal mol^{-1}. Table is reproduced from reference 63.

data are available, it is assumed for the presence calculations that

$$\Delta G^\circ_{L\rightarrow L(aq)} = 0$$

The error incurred is probably within ±2 Kcal mol^{-1}.

3. Complex desolvation: $M^+L_2(aq) \longrightarrow M^+L_2(g)$.

The enthalpies and free energies for this process were calculated from the Born equation [68]. The application of this equation requires an estimate of the complexed cation radius. For the transfer from the vacuum to a solvent of dielectric constant D, of a mole of ions of radius r, the thermodynamic quantities are:

$$\Delta H^\circ_t = -\frac{Ne^2}{2r}\left[1 - \frac{1-LT}{D}\right] \tag{25}$$

and

$$\Delta G^\circ_t = -\frac{Ne^2}{2r}\left[1 - \frac{1}{D}\right] + RT \ln \frac{V_2}{V_1} \tag{26}$$

where e = charge of the ion, $L = -(\partial \ell n D/\partial T)_p$. Thus from H_2O into vacuum, $L_{vac} = 0$, $L_{H_2O} = 4.63 \times 10^{-3}$, $V_1 = 1\ \ell$, $V_2 = 24.2\ \ell$ and one has at $T = 298$ K:

$$\Delta H^\circ_t = \frac{166.8}{r_{M^+L_2}(\text{Å})} \ (\text{Kcal mol}^{-1}) \tag{27}$$

$$\Delta G^\circ_t = \frac{163.9}{r_{M^+L_2}(\text{Å})} - 1.89 \ (\text{Kcal mol}^{-1}) \tag{28}$$

where $r_{M^+L_2}$ represents the radius of the sandwich complexed cation. 1.89 Kcal mol^{-1} arises from an entropy change due to a volume change in going from the hypothetical state of 1 mol/liter to a gaseous state at standard conditions. The calculations were carried out with estimates of complexed cation radii obtained from Equation (29):

$$r_{M^+L_2} = \left[r_{M^+} + \frac{3}{4\pi} (2V_L) \right]^{1/3} \qquad (29)$$

in which r_{M^+} = radius of the enclosed cation (Pauling radii were used) [69], $V_L = \Sigma_{i=1}^{n} V_i$ with $V_i = 11.5$ Å^3 for an oxygen atom and 33.5 Å^3 for a CH_2 group.

Equation (29) was derived from an expression established by Lehn for ligand thickness calculations, on the assumption that the total volume of the ligand is spread around the cation [70]. The results of the evaluated energies of complex desolvation are given in Table 4, with an estimated accuracy of ±4 Kcal mol^{-1}. Although the absolute values may have that much error, the relative values should be more accurate (within ±2 Kcal mol^{-1}) due to the fact that the radii $r_{M^+L_2}$ do not vary much from one cation to another.

4. <u>Complexation: $M^+(aq) + 2L(aq) \longrightarrow M^+L_2(aq)$</u>.

It has been experimentally proven that sandwich-type complexes form by a two-step reaction in many nonaqueous

Table 4 Complex Desolvation Enthalpies and Free Energies.

M^+L_2	r_{M^+} (Å)	$r_{M^+L_2}$ (Å)	V_L (Å)	ΔH° (Kcal mol^{-1})	ΔG° (Kcal mol^{-1})
$Li^+(12C4)_2$	0.60	5.31	314.0	31.4	29.0
$Na^+(12C4)_2$	0.95	5.32	314.0	31.4	28.9
$K^+(12C4)_2$	1.33	5.34	314.0	31.2	28.8
$Rb^+(12C4)_2$	1.48	5.35	314.0	31.2	28.7
$Cs^+(12C4)_2$	1.69	5.37	314.0	31.1	28.6
$Na^+(15C5)_2$	0.95	5.73	392.5	29.1	26.7
$K^+(15C5)_2$	1.33	5.75	392.5	29.0	26.6
$Rb^+(15C5)_2$	1.48	5.76	392.5	29.0	26.6
$Cs^+(15C5)_2$	1.69	5.77	392.5	28.9	26.5
$Cs^+(18C6)_2$	1.69	6.12	471.0	27.3	24.9

solvents. The first process involves monoligand complex formation as:

$$M^+ + L \underset{}{\overset{K_1}{\rightleftharpoons}} M^+L \ .$$

It is followed by the addition of a second ligand yielding a sandwich compound which forms by the reaction:

$$M^+L + L \overset{K_2}{\rightleftharpoons} M^+L_2 \ .$$

It will be assumed here that the same processes occur in aqueous solutions. In order to conveniently use the currently available complexation data, each step has been taken separately. There are as yet no reported thermodynamic quantities measured by the same technique for both processes in aqueous solution for the ligands considered.

For the first step of complexation, the free energies of formation of 1:1 complexes between 15C5, 18C6 and the alkali metal cations Na^+, K^+, Rb^+ and Cs^+ in water were calculated from the formation constants obtained by calorimetric titrations and reported by Izatt _et_ _al_. [71]. Energies corresponding to the second process are not available for reactions in aqueous solutions and therefore were derived by treatment of data from nonaqueous solutions. The proportionality relationships that were found between the formation constants K_1 and K_2 in the nonaqueous solvents are assumed to be conserved in water.

From the data on the complexation of Cs^+ by 18C6 which were measured by ^{133}Cs NMR techniques in nonaqueous solvents and summarized in Table 5-a, it was found that:

$$\log\frac{k_1}{k_2} \cong 3 \ . \tag{30}$$

Likewise, the relation:

$$\log\frac{K_1}{K_2} \cong 2 \tag{31}$$

was derived upon consideration of the complexation parameters of K^+ by 15C5 reported by Shih [48].

Data were lacking to provide such a relationship for Na^+, Rb^+ and Cs^+ with 15C5 and mainly for the case of Na^+ with 15C5, information over a wide range of solvents was not available. In Table 5-b, K_2 values were calculated for $Cs^+(15C5)_2$ and $Cs^+(18C6)_2$ by using K_1 for process 1, as outlined above, and Equation (30), while for $Na^+(15C5)_2$, $K^+(15C5)_2$, and $Rb^+(15C5)_2$, respective K_1 values are used along with relation (31).

The reactions of the alkali metal cations with 12C4 in water and many other nonaqueous solvents were very weak so that K_1 values in aqueous solutions and K_2 values in numerous nonaqueous solvents were not measured [45,72].

Table 5-a Formation Constants of 1:1 and 2:1 Complexes of Cs^+ with 18C6 and K^+ with 15C5.

Cation	Macrocycle	Solvent	$\log K_1$	$\log K_2$	$\log \frac{K_2}{K_1}$	Reference
Cs^+	18C6	Propylene Carbonate	4.45 ± 0.06	1.05 ± 0.02	3.4	78
		Dimethyl formamide	4.62 ± 0.05	1.65 ± 0.02	3.0	78
		Dimethyl Sulfoxide	3.04 ± 0.04	0.00 ± 0.15	3.0	47
K^+	15C5	Dimethyl formamide	4.11 ± 0.09	1.57 ± 0.13	2.5	48
		Dimethyl sulfoxide	2.91 ± 0.10	1.33 ± 0.33	1.6	48

Table 5-b Complex Formation Enthalpies[a] and Free Energies.

M^+L_2	$\log K_{1_{meas}}$	$\log K_{2_{calc}}$	$\Delta H^\circ_{1_{meas}}$ (Kcal mol^{-1})	$\Delta G^\circ_{1,2_{calc}}$ (Kcal mol^{-1})
$Li^+(12C4)_2$	—	—	~0	~0
$Na^+(12C4)_2$	—	—	~0	~0
$K^+(12C4)_2$	—	—	~0	~0
$Rb^+(12C4)_2$	—	—	~0	~0
$Cs^+(12C4)_2$	—	—	~0	~0
$Na^+(15C5)_2$	0.70	-1.30	0.80	0.82
$K^+(15C5)_2$	0.74	-1.30	0.70	0.71
$Rb^+(15C5)_2$	0.62	-1.40	1.04	1.04
$Cs^+(15C5)_2$	0.80	-2.20	1.92	1.92
$Cs^+(18C6)_2$	0.99	-2.00	1.40	1.40

[a] ΔH_2 is unknown in aqueous solutions.

Thermodynamic values of ΔG° and ΔH° were estimated as $\cong 0$ for these sandwich complexes.

Results for the complexation reactions are entered in Table 5-b with an estimated accuracy of ±2 Kcal mol^{-1}.

5. <u>Lattice energies: $M^+L_2(g) + N^-(g) \longrightarrow M^+L_2.N^-(s)$</u>.

So far, among the alkalide and electride crystals, a crystal structure is known only for $Na^+C222.Na^-(s)$. Therefore the Kapustinskii equation (Eq. (32)) [73] was used to estimate the lattice energy of the sandwich alkalide compounds studied.

$$\Delta H^\circ_{Lat} = \frac{-287.2\ \nu Z_+ Z_-}{r_{M^+L_2} + r_{N^-}} \left[1 - \frac{0.345}{r_{M^+L_2} + r_{N^-}} \right] \text{Kcal mol}^{-1} \qquad (32)$$

with ν = number of ions in the chemical formula of the salt and $\nu = 2$ for $M^+L_2.N^-(s)$; $Z_+ = Z_- = 1$; $r_{M^+L_2} + r_{N^-}$ denotes the interionic distance in the crystal and r_{N^-} can be estimated as: $r_{N^-} = 2r_N - r_{N^+}$.

The Kapustinski equation gives very accurate results for simple salts such as the alkali halides and its application here requires the estimates of the interionic distances in the compounds. Direct evaluation from a summation of $r_{M^+L_2}$ and r_{N^-} probably does not accurately reproduce the actual interionic distances. These values are excessively large for the reasons that this does not take into account the compression caused by the softness of these anions, and the lack of sphericity of the complexed cations M^+L_2 as well as the anions. Therefore, space filling models were used in which the interionic distances were directly measured. The representation of these sandwich alkalides (as shown in Figure 11) for $Cs^+(18C6)_2Cs^-$ and $Na^+(12C4)_2.Na^-$ were based on the knowledge of the structure of some crown ether sandwich halides such as $Na^+(12C4)_2.Cl^-.5H_2O$ [74], $Ba^{2+}(15C5)_2.Br_2^-.2H_2O$ [75] and $Cs^+(15C5)_2.I^-$ [76]. The crystal structures of these compounds show respectively D_4 and D_5 symmetry arrangements of the ligands around a cation. The site of the anion in the representations shown in Figure 11 is expected to be the most likely position for all the anions. The free energies were estimated from Equation (14) in which the entropy values used were obtained from a scale established by plotting the entropies of the alkali halides vs. the interionic distances in these salts [63]. This scale is:

$$\Delta S^\circ_{Lat} = -48.70 - 27.57 \times \frac{1}{r_{M^+L_2} + r_{N^-}} \text{ cal mol}^{-1} \text{ deg}^{-1} . \qquad (33)$$

Three spheres of relative radii r_1, r_2 and r_3 ranging between the van der Waals radii for Li^+ and Na^+, K^+ and Rb^+, and Cs^+ respectively were used for the cations while three others of the size of the anions estimated from the relation $r_{N^-} = 2r_N - r_{N^+}$ were also used. The lattice

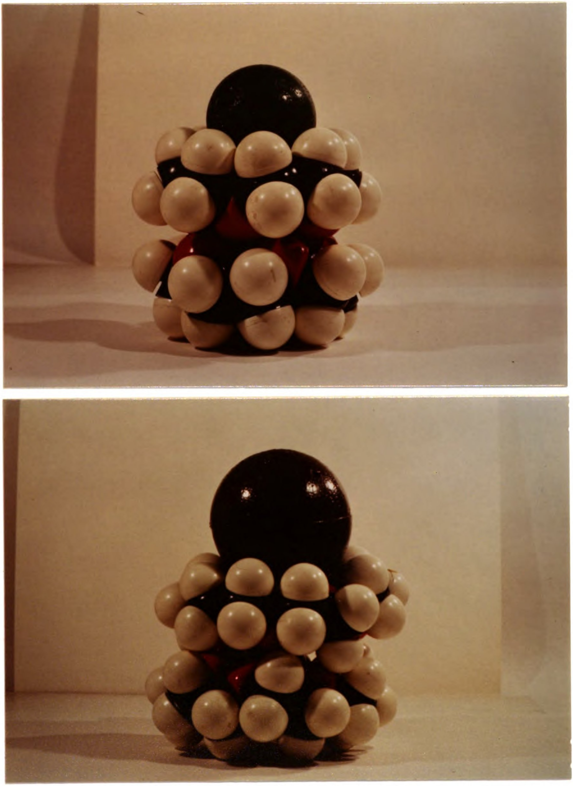

Fig. 11 Representation of $Cs^+(18C6)_2.Cs^-$ and $Na^+(12C4)_2.Na^-$ Systems.

energies are given in Tables 6-8 for the three sets of cases outlined above. The estimated error is within ±5 Kcal mol^{-1}.

6. $\underline{2L + M(s) + N(s) \longrightarrow M^{+}L_{2}.N^{-}(s)}$.

The overall free energies were obtained by summing the energies of all the steps involved in the modified Born-Haber cycle. The results are summarized in Tables 9-13.

B. Discussion

The calculated free energies of formation of the sandwich type alkalides may be in error by as much as 15 Kcal mol^{-1}. This error is caused by all of the approximations required. The experimental energies of sublimation, ionization, electron affinity and aquation of the alkali metals introduce a very small error. Moreover, the approximations made for the quantities of the second complexation step in aqueous solution probably lead to an insignificant error contribution. This can be explained by the relatively low formation constants of the crown ether complexes of the alkali metals observed in aqueous solution ($K_1 \leq 10^2$), which leads to a small contribution of the complexation energy to the overall energy.

Table 6 Lattice Energies and Entropies for Sodide Salts.[a]

Salt	$-\Delta H^{\circ}_{Lat}$ (Kcal mol^{-1})	$-\Delta S^{\circ}_{Lat}$ (cal mol^{-1} deg^{-1})	$-\Delta G^{\circ}_{Lat}$ (Kcal mol^{-1})	r_{N^-} calc (Å)	$(r_{M^+L_2}+r_{N^-})$ model (Å)	$(r_{M^+L_2}+r_{N^-})$ calc (Å)
$Li^+(12C4)_2 \cdot Na^-$	76.0	52.5	60.3	2.72	7.2	8.03
$Na^+(12C4)_2 \cdot Na^-$	76.0	52.5	60.3		7.2	8.04
$K^+(12C4)_2 \cdot Na^-$	73.1	52.4	57.5		7.5	8.06
$Rb^+(12C4)_2 \cdot Na^-$	73.1	52.4	57.5		7.5	8.07
$Cs^+(12C4)_2 \cdot Na^-$	68.7	52.2	53.1		8.0	8.09
$Na^+(15C5)_2 \cdot Na^-$	90.2	53.3	74.3		6.0	8.45
$K^+(15C5)_2 \cdot Na^-$	90.2	53.3	74.3		6.0	8.47
$Rb^+(15C5)_2 \cdot Na^-$	90.2	53.3	74.3		6.0	8.48
$Cs^+(15C5)_2 \cdot Na^-$	88.8	53.2	73.0		6.1	8.49
$Cs^+(18C6)_2 \cdot Na^-$	101.3	53.9	85.2		5.3	8.84

[a] The values for lithide salts are the same because the same sized model there was used for Li^- and Na^-.

Table 7 Lattice Energies and Entropies of Potassides.[a]

Salt	$-\Delta H^{\circ}_{Lat}$ (Kcal mol^{-1})	$-\Delta S^{\circ}_{Lat}$ (cal mol^{-1})	$-\Delta G^{\circ}_{Lat}$ (Kcal mol^{-1})	$r_{N^-_{calc}}$ (Å)	$(r_{M^+L_2} + r_{N^-})_{calc}$ (Å)	$(r_{M^+L_2} + r_{N^-})_{meas}$ (Å)
$Li^+(12C4)_2 \cdot K^-$	70.4	52.2	54.8	3.27	8.58	7.8
$Na^+(12C4)_2 \cdot K^-$	70.4	52.2	54.8		8.59	7.8
$K^+(12C4)_2 \cdot K^-$	68.7	52.2	53.1		8.61	8.0
$Rb^+(12C4)_2 \cdot K^-$	68.7	52.2	53.1		8.62	8.0
$Cs^+(12C4)_2 \cdot K^-$	61.3	51.8	45.9		8.64	9.0
$Na^+(15C5)_2 \cdot K^-$	79.1	52.7	63.4		9.0	6.9
$K^+(15C5)_2 \cdot K^-$	79.1	52.7	63.4		9.02	6.9
$Rb^+(15C5)_2 \cdot K^-$	79.1	52.7	63.4		9.03	6.9
$Cs^+(15C5)_2K^-$	75.0	52.5	59.3		9.04	7.3
$Cs^+(18C6)_2 \cdot K^-$	90.9	53.3	75.0		9.39	5.95

[a] The same model spheres were used for K^- and Rb^-; therefore the values for the potassides hold also for the rubidides.

Table 8 Lattice Energies and Entropies for Cesides.

Salt	$-\Delta H^\circ_{Lat}$ (Kcal mol^{-1})	$-\Delta S^\circ_{Lat}$ (cal mol^{-1})	$-\Delta G^\circ_{Lat}$ (Kcal mol^{-1})	$r_{N^-_{calc}}$ (Å)	$(r_{M^+L_2} + r_{N^-})$ calc (Å)	$(r_{M^+L_2} + r_{N^-})_{meas}$ (Å)
$Li^+(12C4)_2Cs^-$	65.6	52.0	50.1	3.55	8.86	8.4
$Na^+(12C4)_2Cs^-$	65.6	52.0	50.1		8.87	8.4
$K^+(12C4)_2Cs^-$	64.1	51.9	48.6		8.89	8.6
$Rb^+(12C4)_2Cs^-$	64.1	51.9	48.6		8.90	8.6
$Na^+(15C5)_2Cs^-$	73.1	52.4	57.5		9.28	7.5
$K^+(15C5)_2Cs^-$	73.1	52.4	57.5		9.30	7.5
$Rb^+(15C5)_2Cs^-$	73.1	52.4	57.5		9.31	7.5
$Cs^+(15C5)_2Cs^-$	71.3	52.3	55.7		9.32	7.7
$Cs^+(18C6)_2Cs^-$	80.8	52.8	65.1		9.67	6.75
$Cs^+(12C4)_2Cs^-$	56.6	51.5	41.2		9.92	9.80

Table 9 $\Delta H^\circ_{formation}$ and $\Delta G^\circ_{formation}$ of Lithide Salts.

Salt	ΔH°[a] (Kcal mol^{-1})	ΔG° (Kcal mol^{-1})
$Li^+(12C4)_2 \cdot Li^-$	+10.1	+18.6
$Na^+(12C4)_2 \cdot Li^-$	+17.7	+24.5
$K^+(12C4)_2 \cdot Li^-$	+17.8	+22.4
$Rb^+(12C4)_2 \cdot Li^-$	+19.2	+22.5
$Cs^+(12C4)_2 \cdot Li^-$	+22.6	+26.5
$Na^+(15C5)_2 \cdot Li^-$	-0.3	+9.1
$K^+(15C5)_2 \cdot Li^-$	-5.6	+4.1
$Rb^+(15C5)_2 \cdot Li^-$	-2.0	+4.6
$Cs^+(15C5)_2 \cdot Li^-$	-1.0	+6.4
$Cs^+(18C6)_2 \cdot Li^-$	-17.6	-7.9

[a] ΔH° values do not include those of the complexation reaction $M^+L_{(aq)} + L_{(aq)} \rightleftharpoons M^+L_{2(aq)}$ since they are not yet available.

Table 10 $\Delta H^\circ_{formation}$ and $\Delta G^\circ_{formation}$ of Sodide Salts.

Salt	ΔH°[a] (Kcal mol^{-1})	ΔG° (Kcal mol)
$Li^+(12C4)_2.Na^-$	-0.9	+8.2
$Na^+(12C4)_2.Na^-$	+6.7	+14.0
$K^+(12C4)_2.Na^-$	+6.8	+11.9
$Rb^+(12C4)_2.Na^-$	+8.2	+12.0
$Cs^+(12C4)_2.Na^-$	+11.6	+16.0
$Na^+(15C5)_2.Na^-$	-11.3	-1.4
$K^+(15C5)_2.Na^-$	-16.6	-6.4
$Rb^+(15C5)_2.Na^-$	-13.0	-5.9
$Cs^+(15C5)_2.Na^-$	-12.0	-4.1
$Cs^+(18C6)_2.Na^-$	-28.6	-18.4

[a] ΔH° values for 2:1 complex formation are not included since these data were not available.

Table 11 $\Delta H^\circ_{formation}$ and $\Delta G^\circ_{formation}$ of Potasside Salts.

Salt	ΔH°[a] (Kcal mol^{-1})	ΔG° (Kcal mol^{-1})
$Li^+(12C4)_2.K^-$	+1.4	+10.8
$Na^+(12C4)_2.K^-$	+9.0	+16.6
$K^+(12C4)_2.K^-$	+7.8	+13.4
$Rb^+(12C4)_2.K^-$	+9.3	+13.5
$Cs^+(12C4)_2.K^-$	+15.6	+20.3
$Na^+(15C5)_2.K^-$	-3.5	+6.6
$K^+(15C5)_2.K^-$	-8.9	+1.6
$Rb^+(15C5)_2.K^-$	-5.2	+2.2
$Cs^+(15C5)_2.K^-$	-1.6	+6.8
$Cs^+(18C6)_2.K^-$	-21.6	-11.1

[a] ΔH° for the complexation process:

$$M^+L_{(aq)} + L_{(aq)} \rightleftharpoons M^+L_{2\,(aq)}$$

are not included since they are not available.

Table 12 $\Delta H^\circ_{formation}$[a] and $\Delta G^\circ_{formation}$ of Rubidide Salts.

Salt	ΔH°[a] (Kcal mol^{-1})	ΔG° (Kcal mole^{-1})
$Li^+(12C4)_2.Rb^-$	+0.9	+10.0
$Na^+(12C4)_2.Rb^-$	+8.5	+15.8
$K^+(12C4)_2.Rb^-$	+7.4	+12.6
$Rb^+(12C4)_2.Rb^-$	+8.8	+12.7
$Cs^+(12C4)_2.Rb^-$	+15.2	+19.5
$Na^+(15C5)_2.Rb^-$	-4.0	+5.8
$K^+(15C5)_2.Rb^-$	-9.3	+0.8
$Rb^+(15C5)_2.Rb^-$	-5.7	+1.4
$Cs^+(15C5)_2.Rb^-$	-2.0	+6.0
$Cs^+(18C6)_2.Rb^-$	-22.0	-12.0

[a] ΔH° values for the complex reaction

$$M^+L_{(aq)} + L_{(aq)} \rightleftharpoons M^+L_{2(aq)}$$

are not included because they were not yet available.

Table 13 $\Delta H^\circ_{formation}$ and $\Delta G^\circ_{formation}$ of Ceside Salts.

Salt	ΔH°[a] (Kcal mol^{-1})	ΔG° (Kcal mol^{-1})
$Li^+(12C4)_2.Cs^-$	+3.9	+13.2
$Na^+(12C4)_2.Cs^-$	+11.5	+19.4
$K^+(12C4)_2.Cs^-$	+10.1	+16.0
$Rb^+(12C4)_2.Cs^-$	+11.6	+16.1
$Cs^+(12C4)_2.Cs^-$	+18.0	+23.2
$Na^+(15C5)_2.Cs^-$	+0.2	+10.7
$K^+(15C5)_2.Cs^-$	-5.2	+5.7
$Rb^+(15C5)_2.Cs^-$	-1.5	+6.2
$Cs^+(15C5)_2.Cs^-$	-0.2	+8.5
$Cs^+(18C6)_2.Cs^-$	-13.8	-3.1

[a] Values do not include ΔH° for the complexation reaction

$M^+L_{(aq)} + L_{(aq)} \rightleftharpoons M^+L_{2(aq)}$

since these data are not yet available.

However, the Kapustinskii equation for lattice energy calculations, the halide entropy scale for lattice entropy estimation and the Born equation for ionic solvation may give large contributions to the error. In general, calculations involving the Born equation for ionic solvation are weak, due to the assumptions associated with the derivation of the equation itself. The solvent is treated as a structureless dielectric continuum in which the dielectric constant remains unchanged even in the vicinity of the dissolved ions. This neglects the different contributions of primary and secondary solvation to the overall solvation energy of the ions. Furthermore, the ions are taken as conducting spheres of constant radii r both in the gas phase and in the solution. Any variation of the ionic radii which would presumably lead to the stabilization of the ions in the medium is not taken into account. Entropy changes due to rearrangement of the water structure are also neglected.

The discrepencies due to the Born equation may be partially overcome, for it can be considered that the ligands themselves provide the primary solvation shell of the metal cations so that the energy of primary shell solvation need not be considered. Also, the radii of the complexed cations obtained by ligand thickness calculations which treat the complexed cations as incompressible spheres, are large enough to minimize the errors.

The Kapustinskii equation and the halide lattice entropy scale are also sources of errors that can be overcome only by a knowledge of the structure of these sandwich alkalides. The systematic errors caused by the size estimates are minimized by using space filling models to directly approximate interionic distances.

Although the results entered in Tables 9 through 13 may be in error by up to 15 Kcal mol^{-1}, the <u>relative</u> free energies of formation of these sandwich alkalides should be reliable. The general trend observed from the compounds of 18C6 to those of 12C4 reflects the difference in the flexibility of the macrocyclic rings, the number of donor atoms in the rings, and the steric fit between a cation and the cavity formed for it by two similar ligands. All these factors play important roles in the stability of the compounds. From the largest ring of 18C6 to the smallest of 12C4, the rigidity increases, which makes the complexation less and less favorable for large ions such as Cs^+. Also a poor steric fit may inhibit the formation of compounds of 15C5 with Li^+ and Na^+ and of 12C4 with Li^+. The cations are small compared to the cavity formed by the ligands. In these cases, the donors atoms do not bind strongly enough to the cation to stabilize it.

The calculations show that the sandwich sodide salts (Table 10) are the most stable among the compounds listed. This arises from a good balance between the sum of the sublimation and ionization energies which tends to destabilize a given compound, and the relatively low (more negative) lattice energies of these salts.

In contrast, the calculations indicate that the lithides (Table 9) have the highest free energies of formation. This may result from the hardness of the crystal lattice of lithium metal that leads to a relatively very high atomization energy which adds to the ionization energy. The lattice energies for these salts, although low, are not balanced by the atomization and ionization energies. Concerning the potassides (Table 11) and the rubidides (Table 12), the results indicate that they have comparable stabilities, with energies differing by less than 2 Kcal mol^{-1}. They have thermodynamic stabilities that range between the sodides on one hand and lithides and cesides on the other.

It appears from Tables 9 and 13 that the stabilities of cesides with respect to lithides depends on the ligand used. The reasons are not certain, but probably arise from size estimates of the respective cations and anions. Experimentally observed stabilities indicate that the cesides of any of these ligands should be more stable than the corresponding lithides. For instance, the compound $Cs^+(18C6)_2.Cs^-$ ($\Delta G^\circ_{f_{calc}}$ = -3 Kcal mol^{-1}) has been isolated and is stable up to room temperature, while the corresponding lithide, $Cs^+(18C6)_2.Li^-$ ($\Delta G^\circ_{f_{calc}}$ = -8.0 Kcal mol^{-1}) has not been synthesized to date. It should be noted that one always faces possible solution decomposition or formation of an electride. In general lithium is used in some syntheses to provide a high concentration of solvated electrons which stabilizes the formation of some salts, mainly the electrides. These extra electrons appear as defect electrons and Li^- does not form.

Except for the lithides just discussed, the theoretical calculations give results that are in good agreement with the observed existence of various sandwich alkalide salts. Although instability may merely reflect irreversible decomposition rather than decomplexation, the existence of stable salts at least insures that $\Delta G°$ is negative. The sodides are the most stable in the crystalline form and their metal solutions are less likely to decompose during the syntheses. Isolated salts such as:

$Rb^+(15C5)_2.Na^-(s)$	$\Delta G^\circ_{f_{calc}} = -5.9$ Kcal mol^{-1}
$K^+(15C5)_2.Na^-(s)$	$\Delta G^\circ_{f_{calc}} = -6.4$ Kcal mol^{-1}
$Cs^+(18C6)_2.Na^-(s)$	$\Delta G^\circ_{f_{calc}} = -18.4$ Kcal mol^{-1}
$K^+(12C4)_2.Na^-(s)$	$\Delta G^\circ_{f_{calc}} = +12.0$ Kcal mol^{-1}

are stable up to room temperature. Other salts:

$Cs^+(18C6)_2.K^-$	$\Delta G^\circ_f = -11.1$ Kcal mol^{-1}
$Cs^+(18C6)_2.Rb^-$	$\Delta G^\circ_f = -12.0$ Kcal mol^{-1}

have reasonable stabilities but not as great as those of the corresponding sodides. Lithides and the compounds $Na^+(15C5)_2.M^-(s)$ have not yet been obtained. Insufficient work has been done on the other compounds of the macrocyclic ether 12C4 to give an accurate judgment on their stabilities.

The results of these theoretical calculations are mainly useful guides for the synthesis of heteronuclear alkalides. From a kinetic point of view, it has been reported by Eyring *et al*. [77] that for the alkali metals with 18C6, the complexation rate constants follow the trend $Li^+ < Na^+ < K^+ \sim Rb^+ \sim Cs^+$. The same trend was also found for Na^+, K^+ and Rb^+ with 15C5. If all these arguments are also considered, a metal solution which contains a mixture of Rb and Na metals in the presence of excess 15C5 would more likely yield $Rb^+(15C5)_2.Na^-$ than it would $Na^+(15C5)_2.Rb^-$. The same reasons hold for a compound of stoichiometry $Cs^+(18C6)_2.Na^-$, rather than $Na^+(18C6)_2.Cs^-$. However, for a solution that contains K and Rb metals with 12C4 or 15C5 for instance, it is difficult to predict the stoichiometry of the compound which would result since both anions have similar stabilities. In those situations, a careful analysis of the compounds is essential for stoichiometry assignment.

In conclusion, the present calculations have shown that numerous sandwich alkalide salts of 12C4, 15C5 and

18C6 are moderately stable at room temperature. Greater stability is expected when the syntheses are carried out in poorly solvating solvents such as the amines and ethers, in which the complexation constants are much higher. The entropies are undoubtedly negative for the reactions of formation and therefore increased stability is also expected at low temperatures.

CHAPTER V

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

A. Conclusions

A compound of the crown ether 12-crown-4, and the alkali metals potassium and sodium has been isolated. The stoichiometric analysis revealed a 1:2:1 ratio of K, 12C4 and Na in the system. The content of solvent of crystallization is very small. The compound has a relatively high melting point and melts to give a blue liquid at +60°C that probably still contains dissolved metal.

Optical and ^{23}Na MASS-NMR studies indicate that the anionic species in the system is Na^- although the presence of some K^- could not be completely ruled out.

Magnetic susceptibility measurements have shown that the system is diamagnetic and powder conductivity studies indicate that it is an intrinsic semiconductor with, however, some ionic conductivity.

B. Suggestions for Future Work

The study of $K^+(12C4)_2.Na^-$ systems should be pursued for further characterization. Whether this compound contains trapped electrons is not completely elucidated. They are easily detectable by EPR methods and some work in this area may be fruitful. The photoemission spectrum of the samples would also provide information on the presence of trapped electrons and on the electronic band structure of the compound. In addition, since the compound is quite stable at room temperature, recrystallization might provide crystals of good enough quality for x-ray structure and single crystal conductivity studies.

$K^+(12C4)_2.Na^-$ is probably only the first among numerous compounds that could be prepared with the ligand 12-crown-4. The stabilities of the corresponding alkalides have been predicted and their syntheses and characterization would increase the range of potentially available compounds and also give more insight into their common properties. It would also serve as a check of the results of the theoretical calculations. Synthesis of the corresponding electrides is also needed.

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