SPECTROSCOPIC STUDIES OF LITHIUM AND SODIUM COMPLEXES WITH THE DILACTAM OF C222 CRYPTAND

Thesis for the Degree of M. S.
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ABSTRACT

SPECTROSCOPIC STUDIES OF LITHIUM AND SODIUM COMPLEXES WITH THE DILACTAM OF C222 CRYPTAND

By

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The dilactam of the C222 cryptand was synthesized. The complexing ability of the dilactam with lithium and sodium ion in different solvents was studied using lithium-7 and sodium-23 NMR.

The addition of the dilactam to a lithium or sodium salt solution results in a definite shift of the chemical shift of the ^{7}Li or ^{23}Na resonance when complexation takes place. The rate of exchange of the metal ion between the two sites, i.e., the free ion in the bulk solution and the complex is fast compared to the NMR time scale, and in all cases only one population-average resonance was observed. The ^{7}Li chemical shifts were determined as a function of dilactam/Li^{+} mole ratios. In dimethylsulfoxide, water, methanol and dimethylformamide solutions there was not enough evidence that complexation is occurring because there is not enough change of the chemical shift from the position characteristic of the solvated Li^{+} ion in the above solvents. In the case of formamide, acetone, tetrahydrofuran, pyridine, propylene carbonate, acetonitrile and nitromethane solutions, there is a Li^{+}-dilactam complex formed, as shown by the variation of the chemical shift.

Formation constants of the Li^+-dilactam complexes were determined in pyridine, tetrahydrofuran, nitromethane and acetonitrile solutions. The values obtained were: $K_{Py} = 440 \pm 97$, $K_{THF} = 1327 \pm 263$, $K_{CH_3NO_2} = 4053 \pm 2040$ and $K_{CH_3CN} = 1348 \pm 372$ when LiBr was used as the salt.

The Na^+-dilactam complex is very strong in the case of dimethylformamide solutions. In DMSO it cannot be unambiguously determined if complexation takes place or not because of the broadening of the ^{23}Na resonance peak upon addition of dilactam to the sodium solution.

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Finally, my very special thanks to Dr. Christina Zioudrou of A.E.C. laboratory in Greece, for introducing me to research, and her encouragement and friendship. To her, I dedicate this thesis.

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CHAPTER I

HISTORICAL PART

HISTORICAL

In recent years, macrocyclic polyethers have been synthesized which are capable of forming strong complexes with the alkali and alkaline earth metal ions.

Cyclic polyethers or "crown" ethers, developed by Pedersen (1) in 1967, were the first such complexing agents to appear. A typical crown is shown in Figure 1. These macrocyclic ligands form a central, two-dimensional cavity, the diameter of which can be varied by changing the number of methylene groups and/or of ether oxygens in the ring.

Shortly thereafter, Lehn and coworkers (2,3) introduced a new class of complexing agents, diaza-polyoxamacrocycles called "cryptands" which form stronger complexes with alkali metal cations than do the crown ethers. The term cryptand refers to the ligand and cryptate to the complex.

These ligands form a three-dimensional central cavity and often form an inclusion-type complex with the metal ion trapped inside this cavity. By changing the number of ether bridges we can vary the size of the ligand's cavity to accomodate different cations (see Fig. 2).

In macrobicyclic complexes, the ligand may exist in three forms differing by the configuration of the bridgehead nitrogens: exo-exo (x-x), exo-endo (x-n) and endo-endo (n-n) (Fig. 3).

These forms can easily interconvert by nitrogen inversion. Although it is not known in which conformation the free ligand exists

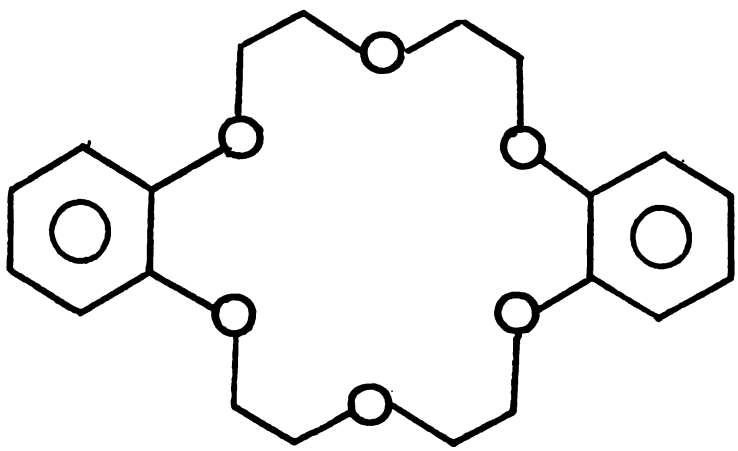
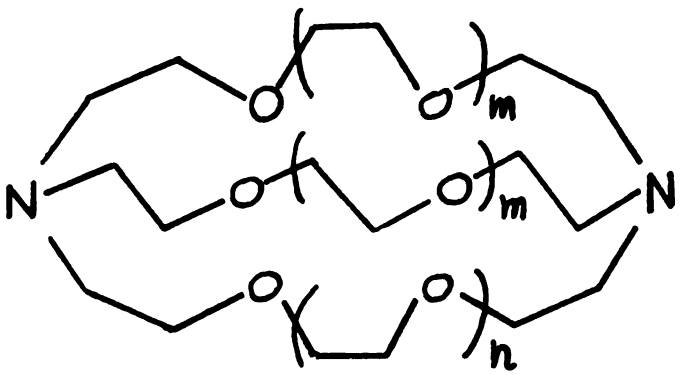


Figure 1. Dibenzo-18-crown-6. The number 6 refers to the total number of oxygens and 18 to the total number of atoms in the polyether ring.

a)



b)

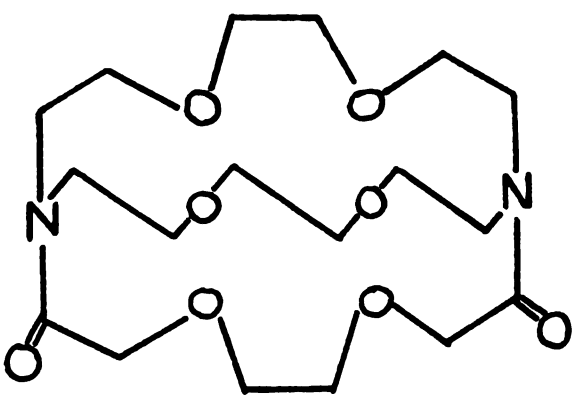


Figure 2. a) C-211 m = 0, n = 1

C-221 m = 1, n = 0

C-222 m = n = 1

b) The dilactam of C-222

in solution, the endo-endo form should be strongly favored in the complex since it allows both nitrogen atoms to participate in the complexation interactions. Crystal structure determination of the free ligand C222 and of several cryptates (4-8) showed that the cation was indeed contained in the three-dimensional molecular cavity and that in all cases the ligand was in the endo-endo form.

Figure 4, shows the structures of the free ligand [C-222] and of its rubidium thiocyanate cryptate. The ligand molecule is flattened and elongated when free, but becomes swollen in the complex. In the series [C-222, M^+], where $M^+ = Na^+$, K^+, Rb^+, Cs^+, a progressive opening of the molecular cavity, involving torsion of the ligand around the N.....N axis, has been observed.

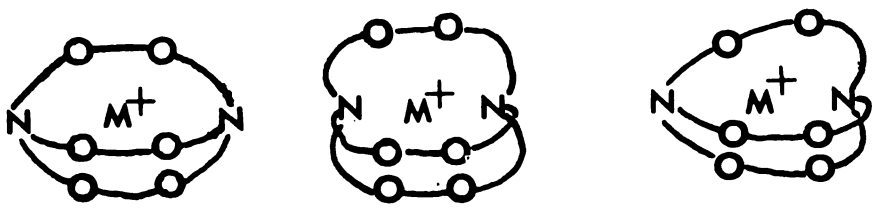
Since the cations are occluded in the central cavity of the ligand, the relationship between the size of the cavity and the diameter of the desolvated cation drastically affects the relative stabilities of the complexes.

Formation constants of alkali-macrocyclic ligand complexes have been obtained (9,10) potentiometrically in aqueous and methanolic solutions.

In the case of weaker complexes, the solvating ability of the solvent used plays an important role in the complexation reaction.

The selectivity of the ligand is directly related to the strength of the complexes. The syntheses of different types of cryptands have been performed in order to better match the size of the given cation by varying the length and the nature of the bridges (11,12).

Also, the alkaline earth-alkali cation complexation selectivity may be controlled by using different cryptands. Lehn, et al. (13),



exo-exo endo-endo exo-endo

Figure 3. Exo-exo, endo-endo and exo-endo conformation of 222 cryptate.

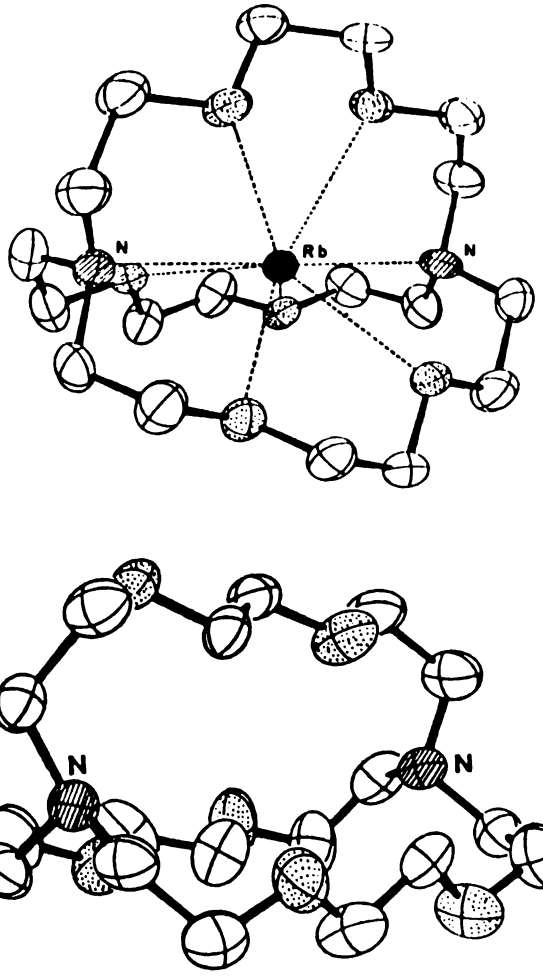


Figure 4. Crystal structure and conformation of a) its RbSCN cryptate and b) the free macrobicyclic ligand C222 (from ref. 10).

investigated the complexation selectivity for Na^+, K^+ and Ba^{2+} in methanol and water solutions.

Two comprehensive review papers, on macrocyclic ligands synthesized have been recently published (10,14).

Since cryptands form strong complexes with alkali metals, while other groups of ligands, e.g., the tetrazoles which have been studied in our laboratory (15,16) do not, the study of their complexation reaction is of considerable interest. Lehn et al. (17) studied the kinetics of the complexation by temperature dependent proton NMR on K^+-C222 and Na^+-C222 cryptates in D_2O solutions.

All the alkali metal ions possess at least one isotope with a magnetic nucleus, e.g., ^7Li, ^{23}Na, ^{39}K, ^{87}Rb, and ^{133}Cs. Since alkali metal NMR, particularly sodium-23 NMR (18-26) and lithium-7 NMR (27-32) have proven to be sensitive probes of the immediate chemical environment of alkali metal ions, investigation of the complexation reaction by using NMR technique has aroused the interest of many researchers.

Recent development of high resolution NMR pulse Fourier transform techniques (33-34), has made possible the investigation of nuclei with low natural abundance.

A more extensive historical and theoretical discussion on ^{23}Na NMR and ^7Li NMR can be found in the Ph.D. theses of M. S. Greenberg and Y. M. Cahen (35-36).

Dye and Ceraso (37) studied the exchange rates of sodium-C222 cryptate in ethylenediamine by using the sodium-23 NMR technique. They found an activation energy of 12.2 ± 1.1 kcal mol^{-1} for the dissociation of the complex. The rate of dissociation of the complex

is also similar to that found by Lehn, et al. (17), for aqueous solutions.

Since the stable sodium cryptate complexes have well-defined coordination shells, Lehn and Kintzinger (38) found ^{13}C and ^{23}Na NMR relaxation studies to be excellent techniques for the study of the ^{23}Na nuclear quadrupole moment. Correlation times were also obtained from the ^{13}C relaxation times (T_1) of the methylene carbons of these complexes.

Alkali metals can be solubilized in nonpolar solvents by adding an appropriate cryptand to the solution (39). Dye and coworkers (40-41) first found optical evidence for the existence of alkali metal anions (Na^-, K^-) in amine and ether solutions in which they used cryptand or crown to dissolve alkali metals. They were able to crystallize the Na^+-C222-Na^- compound (42) and determine its crystal structure (43). They were also able to monitor the ^{23}Na chemical shift of the sodium anion (44).

Complexation studies were extended by Y. M. Cahen, J. L. Dye and A. I. Popov (45) to lithium ion complexes with different cryptands in water and several non-aqueous solvents. They found that the chemical shift of the lithium ion complexed by C211 is essentially solvent and anion independent, indicating that the lithium ion is completely shielded by the cryptand molecule, as was expected. On the other hand, the chemical shifts of Li^+-C221 and especially Li^+-C222 complexes are solvent dependent.

They also determined the formation constants of Li^+-C222 in water and pyridine by using ^7Li NMR technique. The values obtained were $\log K = 0.99 \pm 0.15$ for water and $\log K = 2.94 \pm 0.10$ for pyridine.

By using temperature dependent ^{7}Li NMR they studied (46) the kinetics of complexation reactions of the lithium ion with cryptand C221 in pyridine, water, dimethylsulfoxide, dimethylformamide, and formamide and with C221 in pyridine. Activation energies (E_a), rate constants (k_b), and values of $\Delta H_o^{\ddagger}$, $\Delta S_o^{\ddagger}$, and $\Delta G_o^{\ddagger}$ for the release of Li^+ from the cryptates in the above solvents, are reported. Using also the formation constant of Li^+-C211 cryptate in water and having calculated the rate constant k_b for the backward reaction, they calculated the rate constant for the forward reaction. They report $k_f = 0.98 \times 10^3 \text{ sec}^{-1}$.

The cryptand molecule is strongly basic in water solutions. It has two nitrogen atoms available for protonation. The equilibrium can be represented by the following equations:

$$CH_2^{++} \underset{\longleftarrow}{\xrightarrow{K_1}} CH^+ + H^+$$

$$CH^+ \underset{\longleftarrow}{\xrightarrow{K_2}} C + H^+$$

For the C222 cryptand K_2 and K_1 were determined to be $1.53 \pm 0.08 \times 10^{-10}$ and $6.3 \pm 0.3 \times 10^{-8}$ respectively (47). Since the cryptand molecule is easily protonated, the complexation is pH dependent. By decreasing the pH of a cryptate solution under a certain pH value, the complex is dissociated and the cryptand is protonated.

The dilactam of the C222 cryptand (see fig. 2b) is a precursor of the C222 cryptand. It is a diamide,therefore,it is expected to be much less basic than the C222 cryptand. The complexation reaction of the dilactam is expected to be less pH dependent than the complexation

of the cryptand itself. There are no reports in the literature on complexation studies of this ligand. The subject of this thesis is the synthesis and the spectroscopic study of the complexation of the dilactam with alkali-metal ions.

CHAPTER II

EXPERIMENTAL PART

EXPERIMENTAL

SALTS

Sodium tetraphenylborate (J. T. Baker) was used without further purification except for drying. It was dried under vacuum at 60°C for 72 hours. Lithium perchlorate (Fisher) and lithium bromide (reagent grade, Matheson Coleman and Bell) were dried at 190°C for several days.

After drying the sodium salt was stored in a vacuum dessicator charged with barium oxide, and lithium salts were stored in a dry box under dry nitrogen atmosphere.

In the synthesis part, triethylene glycol (Aldrich, $n_D^{20} = 1.4550$) and oxalyl chloride (Aldrich 98%) were used without further purification. The alumina used for the columns was Alcoa type F-1 80-100 mesh.

SOLVENTS

Nitromethane was fractionally distilled and dried for 24 hours over freshly activated 5A Linde molecular sieves. Dimethylsulfoxide was dried over Linde 4A molecular sieves and vacuum distilled.

Methanol was first fractionally distilled from calcium hydride and then from magnesium turnings in a nitrogen atmosphere. Dimethylformamide was vacuum distilled over phosphorus pentoxide. Acetone was distilled over Drierite and further dried over molecular sieves. Tetrahydrofuran was fractionally distilled from calcium hydride in nitrogen atmosphere. Propylene carbonate was dried over Linde 4A

molecular sieves followed by vacuum distillation. Acetonitrile was refluxed over calcium hydride and then fractionally distilled over granulated barium oxide. Formamide was purified by six fractional freezings. Pyridine was refluxed over granulated barium oxide and then fractionally distilled in nitrogen atmosphere.

The molecular sieves used were activated by heating them at 500°C under dry argon atmosphere for 12 hours. Analyses for water content, where possible, were carried out with an automatic Karl Fisher titrator Aquatest II from Photovolt Corp. In all solvents the water content was <100 ppm. Important solvent properties and solvent abbreviations used in this thesis are listed in Table I.

Benzene used in the synthesis was dried by refluxing several hours over calcium hydride first and over sodium metal after and distilled under nitrogen.

SAMPLE PREPARATION

Since lithium salts are very hygroscopic, the water content of each solution was carefully maintained at the lowest possible level so that its total concentration remained less than 1% of the salt concentrations. All lithium salt solutions were prepared in a dry-box under nitrogen atmosphere.

Dilute solutions of the salt were prepared by appropriate diluations of a stock solution. Ligand was weighed out in the desired amount into a 1 ml volumetric flask and then introduced into a dry-box for subsequent manipulation.

Table I. Key Solvent Properties and Correction for Magnetic Susceptibility on DA-60

Solvents	Volumetric Susceptibility X 10^6	Dielectric Constant	Gutmann's Donor Number	Correction on DA-60 (ppm)
Acetone	-0.460	20.7	17.0	-0.545
Acetonitrile	-0.534	37.5	14.1	-0.390
Dimethylformamide (DMF)	-0.573	36.71	26.6	-0.308
Dimethylsulfoxide (DMSO)	-0.605	46.68	29.8	-0.241
Formamide	-0.551	109.5	24.7*	-0.354
Methanol	-0.515	32.7	25.7*	-0.429
Nitromethane	-0.391	35.9	2.7	-0.689
Propylene Carbonate (PC)	-0.634	65.0	15.1	-0.180
Pyridine	-0.612	12.40	33.1	-0.226
Tetrahydrofuran (THF)	-0.613	7.58	20.0	-0.224
Water	-0.720	78.54	33.0*	0.000

*Predicted (35)

INSTRUMENTAL MEASUREMENTS

Lithium-7 and Sodium-23 NMR

Sodium-23 and lithium-7 NMR measurements were made on a Fourier transform instrument using the magnet of a Varian DA-60 NMR spectrometer equipped with a wide-band probe capable of multinuclear operation (48), and computer controlled rf pulse generation and data collection which has been described previously (49). An external ^{1}H field lock was used to maintain field stability. A Nicolet Instrument Corporation 1082 computer was used. The computer program (49) was used to generate a single rf pulse and to collect the resultant free induction decay (FID) signal. Data treatment was performed by the Nicolet FT-NMR Program (NIC-80/S-7202-D) (50). The instrument was operated at a field of 1.4092 T and at frequencies of 15.87 MHz and 23.32 MHz for ^{23}Na and ^{7}Li respectively.

The references used were 4.0 M $LiClO_4$ in water for the lithium-7 measurements and 3.0 M NaCl in water and 2.5 M $NaClO_4$ in methanol for the sodium-23 measurements. 10 mm NMR tubes were used.

All the chemical shifts reported in this thesis are with respect to 4.0 M $LiClO_4$ in water and 3.0 M NaCl in water. A positive shift from the reference is upfield.

The chemical shifts reported are corrected for differences in bulk diamagnetic susceptibility between sample and reference according to the relationship of Live and Chan for non-superconducting spectrometers (51).

$$\delta_{corr} = \delta_{obs} + \frac{2\pi}{3} (X_v^{ref} - X_v^{sample}) \qquad (1)$$

Where X_v^{ref} and X_v^{sample} are the volume susceptibility of the reference and sample solutions respectively and δ_{obs} and δ_{corr} the observed and the corrected chemical shifts. Values of δ_{corr} were calculated on the basis of published magnetic susceptibilities of various solvents (52). The magnitude of corrections for various solvents are shown in Table I.

Temperatures were measured with a digital readout calibrated thermocouple.

Proton NMR measurements were made by using a Varian T-60 spectrometer.

Infrared Spectra

Infrared measurements in the 4000-600 cm^{-1} spectral region were obtained on the Perkin Elmer Model 225 Spectrophotometer. The mull samples were held between potassium bromide salt plates when the sample was not in a potassium bromide pellet form.

Data Handling

The CDC-6500 computer was used to trace the nmr data. Program KINFIT (53) was employed to determine complexation constants.

CHAPTER III

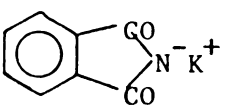
SYNTHESIS OF THE DILACTAM OF THE CRYPTAND C222

SYNTHESIS OF THE DILACTAM OF THE CRYPTAND C222

Cryptands were first synthesized by J. M. Lehn and his coworkers (2,3). Important modifications in some steps of the synthesis were made by Dye et al. (54).

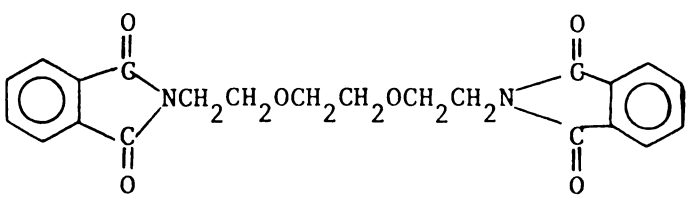
Detailed procedures for both Lehn's high dilution method, and Dye's flow mixing technique as well as procedures for the synthesis of the starting and intermediate compounds, their purification and their properties are given in the following sections.

Synthesis of the Dilactam of C222 Cryptand

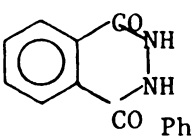
$ClCH_2CH_2OCH_2CH_2OCH_2CH_2Cl$ + 

1,2-Bis(2-chloroethoxy ethane)

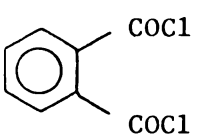
potassium phthalimide

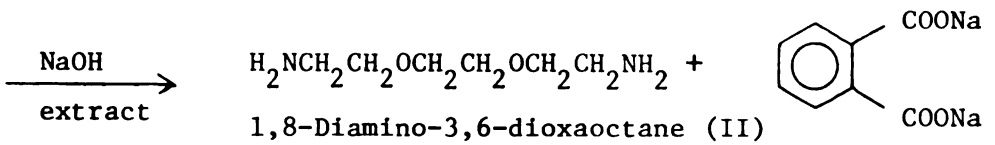
$\xrightarrow{DMF}$ 

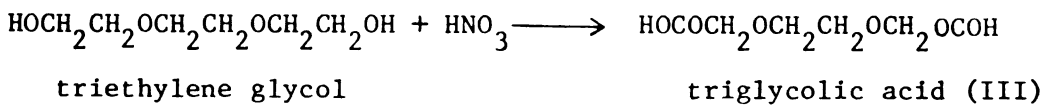
triethylene glycol diphthalimide (I)

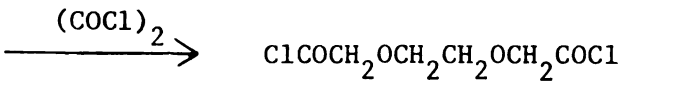
$\xrightarrow[EtOH]{NH_2NH_2}$ $H_2NCH_2CH_2OCH_2CH_2OCH_2CH_2NH_2$ + 

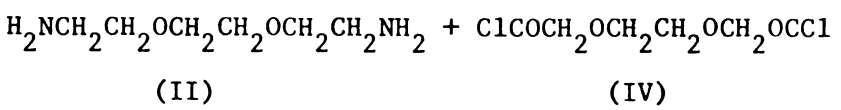
1,8-Diamino-3,6-dioxaoctane Phthalhydrazine

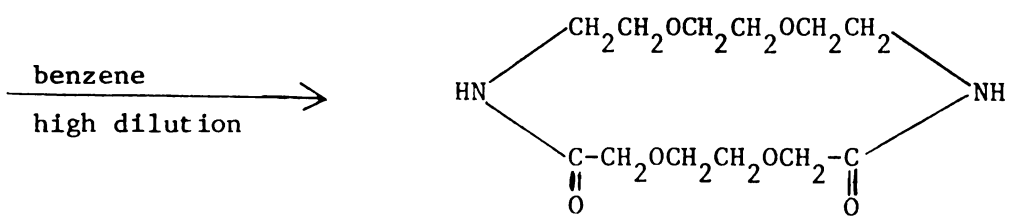
$\xrightarrow{HCl}$ $Cl^-N^+H_3CH_2CH_2OCH_2CH_2OCH_2CH_2N^+H_3Cl^-$ + 


NaOH
extract
$H_2NCH_2CH_2OCH_2CH_2OCH_2CH_2NH_2$ +
1,8-Diamino-3,6-dioxaoctane (II)
COONa
COONa

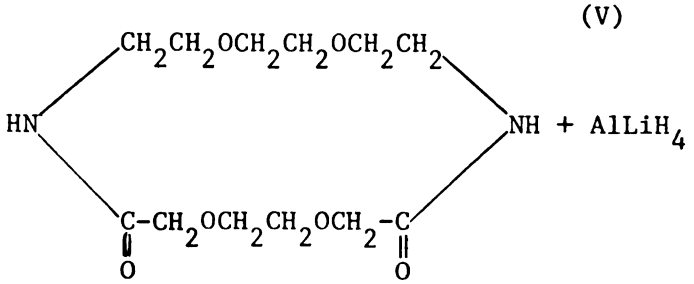

$HOCH_2CH_2OCH_2CH_2OCH_2CH_2OH + HNO_3$
triethylene glycol
$HOCOCH_2OCH_2CH_2OCH_2OCOH$
triglycolic acid (III)


$(COCl)_2$
$ClCOCH_2OCH_2CH_2OCH_2COCl$
triglycolyl chloride (IV)

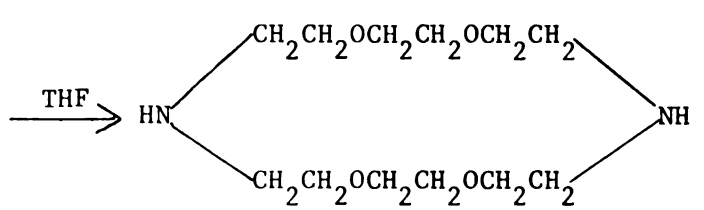

$H_2NCH_2CH_2OCH_2CH_2OCH_2CH_2NH_2$ + $ClCOCH_2OCH_2CH_2OCH_2OCCl$
(II)
(IV)


benzene
high dilution
$CH_2CH_2OCH_2CH_2OCH_2CH_2$
HN
NH
$C-CH_2OCH_2CH_2OCH_2-C$
O
O

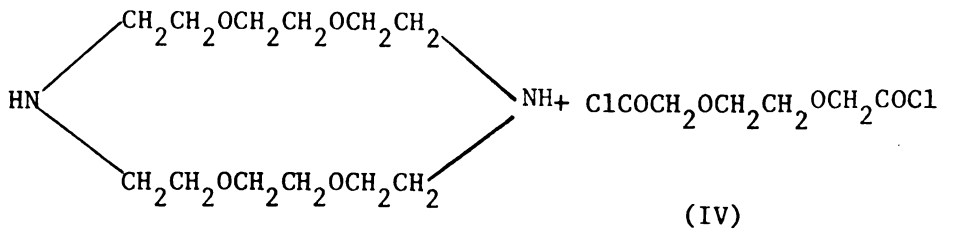
(V)


$CH_2CH_2OCH_2CH_2OCH_2CH_2$
HN
NH + $AlLiH_4$
$C-CH_2OCH_2CH_2OCH_2-C$
O
O

V

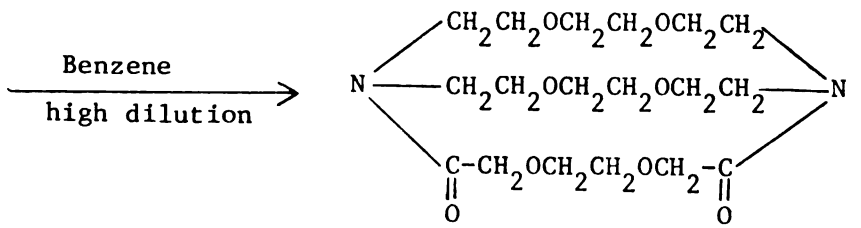

THF
HN
NH
$CH_2CH_2OCH_2CH_2OCH_2CH_2$
$CH_2CH_2OCH_2CH_2OCH_2CH_2$

VI

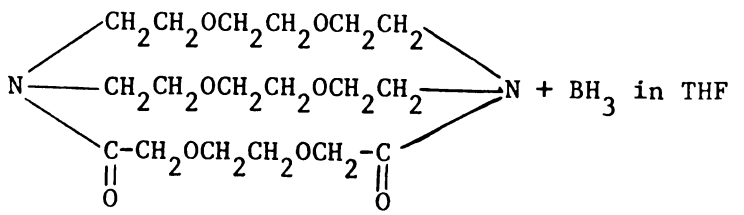


(VII)

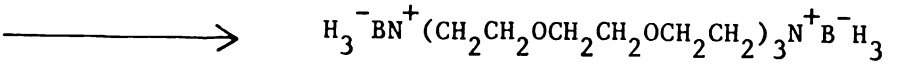
(IV)



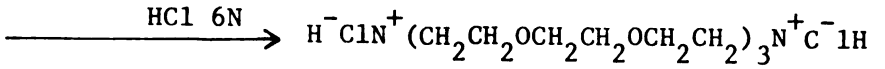
(VIII)



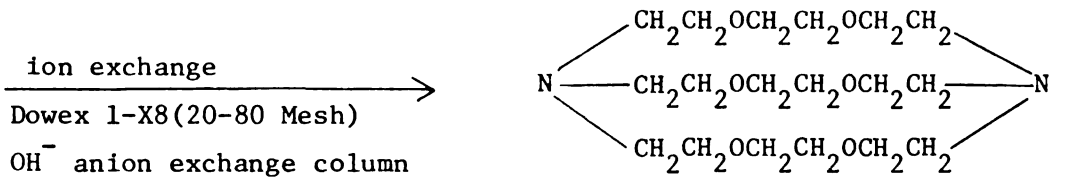
(VIII)



Diborane of "2,2,2-cryptand" (IX)



"2,2,2 cryptand" HCl salt (X)



"2,2,2 cryptand" (XI)

1. Synthesis of Starting Materials

A. Preparation of (1,8-diamino-3,6-dioxaoctane) Hereafter called "Diamine" II

One mole of potassium phthalimide, 1/2 mole of 1,2-(bis-(2-chloroethoxy))ethane and 1 lt of DMF are mixed in a 3-liter flask equipped with a mechanical stirrer.

The solution is heated overnight with an oil bath at 95-100°C. The solution is then cooled to room temperature and poured with stirring into 2 l of ice water. A white precipitate forms. The solution is filtered and the precipitate is recrystallized from glacial acetic acid. The recrystallized product(I) is washed first with 5% Na_2CO_3 and then with distilled water. The obtained product is suspended in ∿2000 ml of 95% ethanol. The ethanol solution is heated to boiling while it is mechanically stirred under reflux. Just after it is brought to boil, 102 ml of 85% hydrazine hydrate is added and refluxing is continued for two hours. Then 225 ml of 10 N HCl are slowly added. The solution is refluxed for another 1/2 hour and most of the solvent is distilled off. Solid sodium hydroxide is added to make the solution strongly basic. This basic solution is extracted with diethyl ether for 1-2 days in a continuous liquid-liquid extractor.

The diethyl ether is then stripped off in a rotatory evaporator. The residue, which contains a large amount of diamine, is twice vacuum distilled to get the pure product II.

B. Preparation of Triglycolyl Chloride (hereafter called "Diacid Chloride") IV

One hundred grams of nitric acid (d = 1.38) in a 500 ml conical flask, are heated in a water bath to 45°C. Four grams of triethylene glycol are added to the nitric acid. The solution is stirred continuously as the temperature is raised to 65°C. After some minutes the solution starts being colored and more and more nitrous vapors are produced. When the reaction is underway, the temperature is stabilized at 45°C. Sixteen grams of triethylene glycol are then added dropwise. The addition takes about one hour, and the temperature is kept constant at 45°C. After the addition is completed the solution is allowed to stand for 20 min at room temperature. It is heated again in a water bath at 45°C for 40 min and then at 80°C for 20 min with continuous stirring. After cooling, the solution is transferred to a 250 ml round bottom flask and the solvent is evaporized in a rotavapor apparatus at 70°C for 3 hr. In order to dry the obtained product, 120 ml of benzene are added to it and an azeotropic distillation of about 10 hours is performed. The product, III, crystallizes in the flask. It is recrystallized from an acetone-benzene mixture.

In order to prepare the triglycolyl chloride, IV, 15 g of dry triglycolic acid, III, and 30 g of oxalyl chloride are added to 100 ml of anhydrous benzene containing three drops of pyridine, in a 250 ml round bottom flask. The flask is topped with a tube filled with $CaCl_2$ and the solution is stirred for 20 hours at room temperature.

After the end of the reaction the solution is quickly filtered, the benzene is evaporated off in a rotavapor, 100 ml of dry benzene are added twice and evaporated off. The brownish oily residue, IV, is crystallized at -70°C. It is recrystallized twice between room temperature and -70°C from ether-petroleum ether mixtures. For the recrystallization the product IV is dissolved in minimum amount of ether at room temperature and then petroleum ether is added slowly until cloudiness appears and then brought to -70°C.

A modification of the above method has been devised (55) for the synthesis of the diacid chloride. Into a 5-liter flask which contains 3150 grams of 60% nitric acid is added 5 grams of triethylene glycol and 3 grams of ammonium metavanadata (NH_4VO_3). The solution is heated to 68-73°C and stirred with a mechanical stirrer. As soon as the brown fumes form, 745 grams of triethylene glycol is dropped into the faslk by means of a dropping funnel over a period of ∿4 hours. The temperature should be maintained at 68-73°C. After the addition has been completed, the solution is stirred for another hour. Then 80% of the nitric acid is removed by distillation.

A green syrup is obtained after distillation. Further evaporation is carried out in an evaporating dish on a hot plate. As the temperature rises the color of the solution changes from green to brown to drak brown to purple and finally to sky-blue at about 140°C. After it is cooled it becomes a hard sky-blue colored solid. An ether Soxhlet extraction is done on the solid. A white solid, triglycolic acid, III, is recovered from the ether solution. (Because the diacid chloride is

unstable, large amounts of triglycolic acid can be prepared and stored for future use.)

Sixty grams of triglycolic acid, III, and 180 ml of $SOCl_2$ (redistilled from commercially available $SOCl_2$) are dissolved in 200 ml of diethyl ether in a 1 l flask. The solution is refluxed for 4 hours. Then the diethyl ether is evaporated off in a rotatory evaporator. The yellow residue is washed twice with diethyl ether and then recrystallized in an ether-petroleum ether mixture at -50°C. Recrystallization is used instead of vacuum distillation, because triglycolyl chloride, IV, decomposes at high temperature. The recrystallized product is pumped to dryness at 15°C. The proton NMR spectrum of IV in deuterated chloroform, shows two resonance peaks, one singlet at 3.75 ppm for the $-OCH_2CH_2O-$ protons and one singlet of equal intensity at 4.52 ppm for the $-OCH_2COCl$ protons.

2. Preparation of 5,12-Dioxo-1,7,10,16-tetraoxa-4,13-diazacyclo-octadecane (1st Cyclization)

The high dilution procedure requires the slow addition with vigorous stirring over a period of about 8 hours, of dilute ($\sim$0.1 M) solutions of the two reagents II and IV in benzene into a reaction flask under nitrogen atmosphere. Completion of the reaction between an amine and an acid chloride requires a base to remove the HCl formed. In this method, either a 2:1 ratio of diamine to diacid chloride is used or else a tertiary amine such as triethylamine is used to scavenge HCl. The flow technique speeds up the addition process without reducing the yields. Figure 5 shows the flow cell that is used to carry out this step.

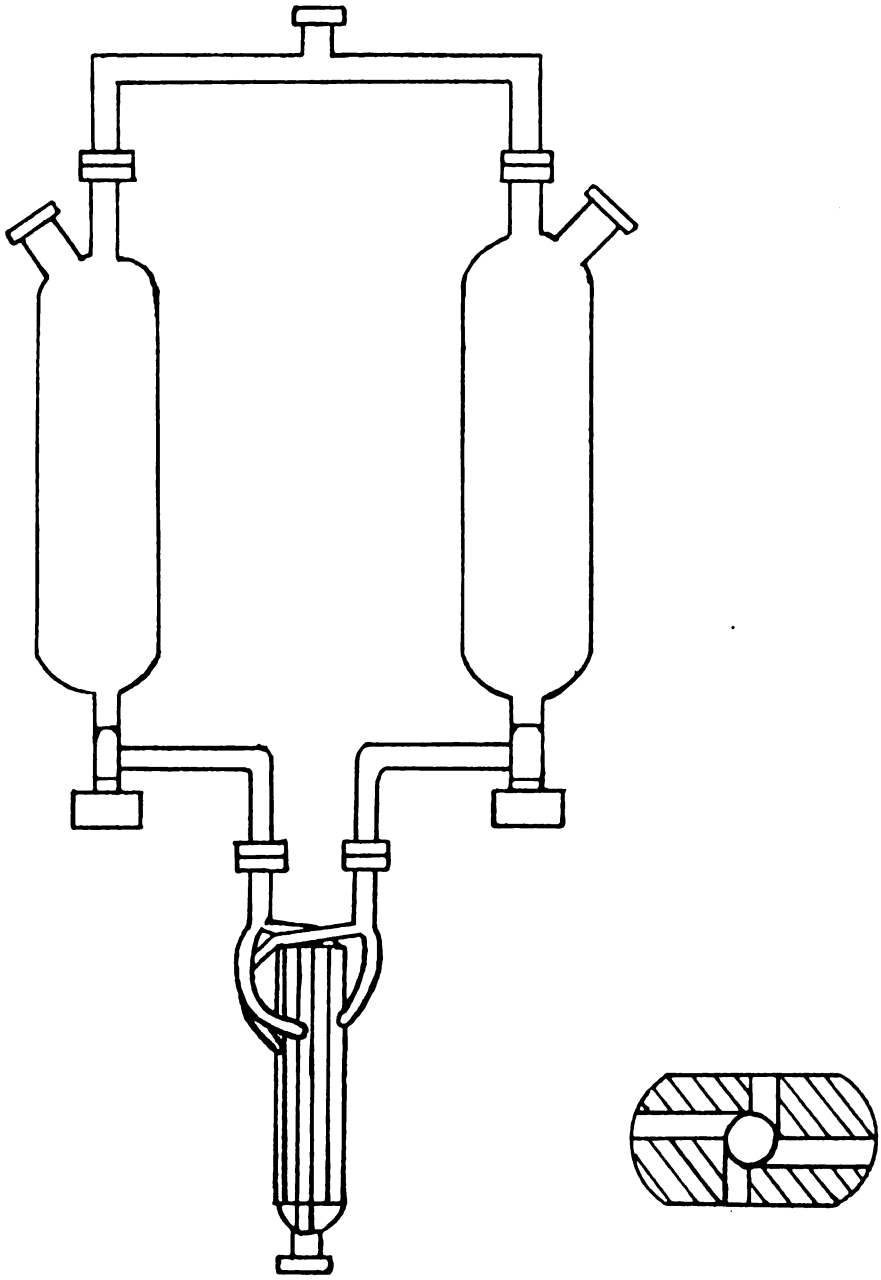


Figure 5. Setup for flow synthesis.

In a typical flow reaction, 200 ml of 0.06 M solution of the diamine, II and 200 ml of a 0.03 M solution of diacid chloride, IV, in dried benzene are allowed to flow through the flow cell under 3 atm pressure. Blockage of the flow tube by the precipitation of the diamine dihydrogen chloride salt can occur at higher reagent concentrations. A high polymer coating on the wall of the mixing cell, or a larger inner diameter capillary tube might help to solve this blockage problem. In the high dilution method, the by-product of the cyclization, hydrogen chloride, is removed with the diamine. The same procedure is used in the flow technique. However, the required excess of amine might either be present in the amine stock solution or it may be in the receiver flask. The diamine can be recovered from the diamine dihydrogen chloride salt with very little net loss of material.

The cyclization product, the dilactam, V, is collected by evaporating the solvent in a rotatory evaporator and purified by elution through an alumina column (80-100 mesh) with benzene. The melting point of V is 110°-111°C and the proton NMR spectrum has a singlet at 3.90 ppm and a multiplet at 3.50 ppm.

3. Preparation of 1,7,10,16-Tetraoxa-4,13-diazacyclooctadecane (1st Reduction)

Freshly distilled over sodium tetrahydrofuran, is placed in a 3 neck round bottom flask. Then 12.0 g of $LiAlH_4$ are added cautiously by stirring the solution. In hot THF 13.8 g of product V are dissolved, placed in a dropping funnel and added dropwise in the flask in order that the reaction temperature does not exceed 30-40°C. It is protected from humidity by covering it with a tube filled with $CaCl_2$.

After the end of the addition it is refluxed for 25 hours. It is cooled to room temperature and the excess of $LiAlH_4$ is destroyed by adding slowly at first a mixture of 20 ml H_2O with 50 ml THF, then 80 ml of 15% NaOH and again the mixture of H_2O with THF until no gas is released. It is filtered under vacuum through a medium sintered glass funnel and the precipitate is washed with hot benzene. The filtrate and the benzene washings are combined and the solvents are evaporated off in a rotovapor apparatus. A white solid, the product VI, is obtained. It is recrystallized from benzene-petroleum ether mixture, and vacuum dried for 24 hours. The proton NMR spectrum of VI in $CDCl_3$ has a singlet and a triplet at 3.58 ppm due to the $-CH_2-O$ protons a triplet at 2.78 ppm due to the NCH_2- protons, and a singlet at 2.25 ppm due to the -NH protons. The melting point of VI is 115-116°C.

4. Preparation of 2,9-Dioxo-4,7,13,16,21,24-hexaoxa-1,10-diaza-bicyclo(8,8,8)hexacosane (Dilactam of the C222 Cryptand) (2nd Cyclization)

A solution of 26.2 grams of the first reduction product, VII, in 500 ml of dry benzene and a solution of 11.0 grams of diacid chloride, IV, in 500 ml of dry benzene are added into 1 liter of dry benzene in a 5 l flask.

For the second cyclization instead of the previous high dilution method, the flow synthesis technique is also applied with similar results.

The product, VIII, the dilactam of C222 cryptand is obtained which is purified by elution through an alumina column (80-100 mesh) using benzene as the eluent. The melting point of XIII is 114°C.

The proton NMR spectrum of XIII in deuterated chloroform has several peaks between 3.3 and 4.6 ppm.

By reduction of the dilactam, VIII, and then purification, the C222 cryptand can be obtained. The detailed procedure is as follows.

5. Preparation of 2,2,2 Cryptand (2nd Reduction)

Ten grams of the second cyclization product, VIII, is dissolved in 200 ml of tetrahydrofuran. One hundred fifty ml of 1 M solution of borane in THF is slowly added to the flask at 0°. After the addition has been completed, the solution is stirred for a half hour at this temperature and then refluxed for an additional hour. A white precipitate forms during this process. The solution is cooled to room temperature and excess reagent is decomposed by adding 50 ml of H_2O. (The solution must become clear after the addition of H_2O.) Solvents are evaporated. Approximately 10 grams of the product (diborane adduct) IX, are formed. The diborane adduct is dissolved in 200 ml of 6N hydrochloric acid, the solution is refluxed for an hour and then evaporated to dryness. The white crystalline solid cryptand C222·2HCl, X, is dissolved in 100 ml of conductance water and the solution is passed through an anion exchange column (Dowex 1-X8, 20-80 mesh). The column is washed continuously with conductance water until the eluent is neutral. The solution is evaporated and further drying of the product XI, is done by using the azeotropic mixture evaporation technique. In this case, dry benzene is added to the wet solid and evaporated. The white solid "2,2,2-crypt" so obtained is vacuum dried for a day before any further purification. The melting point of C222 XI, is 68-69°C. The proton NMR spectrum of XI in

$CDCl_3$ has a triplet at 2.65 ppm due to NCH_2 protons, a triplet at 3.60 due to OCH_2 protons and a singlet at 3.68 due to OCH_2CH_2O protons.

6. Purification of Final Product

Purification of the final product, XI, is carried out in three steps. The first step is n-hexane extraction. This is followed by vacuum sublimation and finally by the zone melting method (47).

The compound is stored in the dark under vacuum.

Synthesis Experimental

Since the synthesis of the C222 dilactam was performed in collaboration with Dr. Dye's research group, it will be indicated in this section which steps were performed in this investigation, which method of the previous described ones was followed, the quantities that were used and the yield of the reactions.

For the synthesis of the triglycolyl chloride IV, both methods (pp 19-20) were used. Two batches of diacid chloride were prepared. In Lehn's method the quantities used are the ones described previously. In the preparation of the diacid, III, the yield of the reaction was about 65%.

The ^1H NMR spectrum in D_2O gave two singlets, one at 3.70 ppm for the $-OCH_2CH_2O-$ protons and one at 4.20 ppm for the $-OCH_2COO-$ protons.

Proton NMR shows no impurities in the spectrum which has two singlets one at 3.65 ppm and one at 4.30 ppm. The other method of the diacid chloride preparation was also followed exactly as it was described previously (pp 20-21).

In the purification of the first cyclization product, the dilactam, V, the yield was 82%. M.P. 113°C. ^{1}H NMR shows no impurities.

NMR spectrum has a singlet at 4.00 ppm due to $-COCH_2-$ protons and a multiplet at 3.5 ppm due to $-OCH_2-$ and $-NCH_2-$ protons.

For the reduction of the dilactam, V, the quantities used were three times larger than the ones described on page 23.

After two recrystallizations from benzene-petroleum ether the yield was 60%. The pure compound has a m.p. of 114-116° and the PMR spectrum shows at 3.58 ppm (stt) 16 protons ($-OCH_2-$), at 2.78 ppm (t) 8 protons $-NCH_2-$ and at 2.10 ppm -NH.

For the second cyclization the flow technique was used. The yield was 90%.

To purify the dilactam of C222, VIII, two recrystallizations from benzene-petroleum ether were performed but the PMR spectrum showed a small impurity from unreacted monocyclic amine. Finally it was purified by elution through an alumina column using dry benzene as an eluent. The M.P. of the compound is 113-114°C. The PMR spectrum is given in Figure 6.

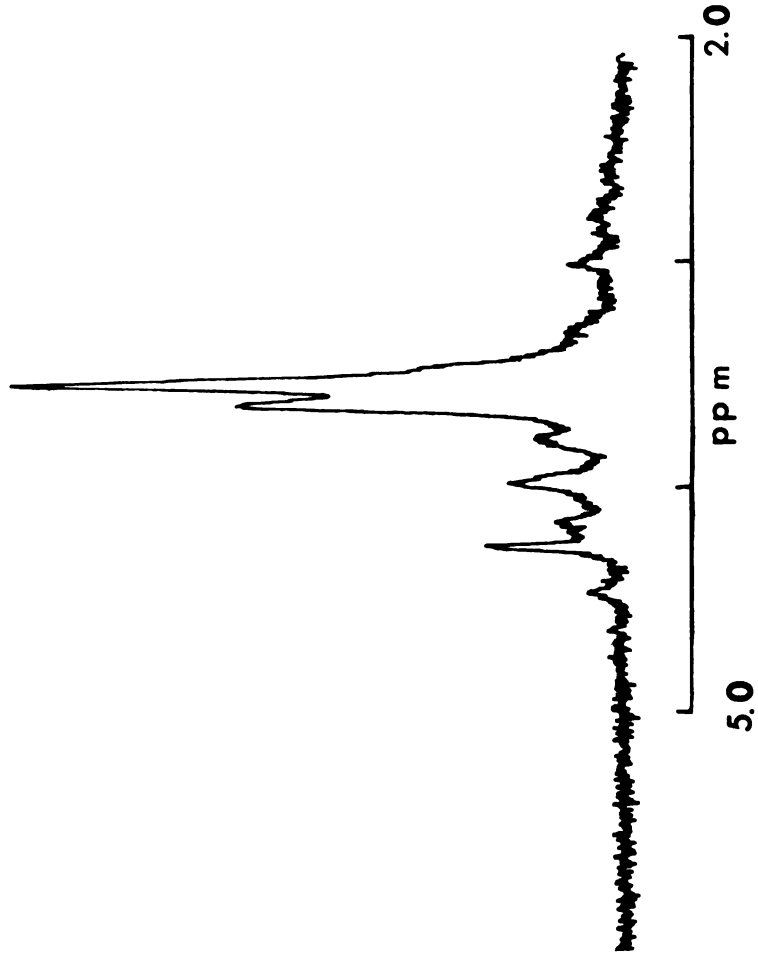


Figure 6. Proton NMR spectrum of the dilactam of C222 cryptand.

CHAPTER IV

SPECTROSCOPIC STUDIES OF COMPLEXATION OF ALKALI METAL IONS, WITH THE DILACTAM OF C222

SPECTROSCOPIC STUDIES OF COMPLEXATION OF ALKALI METAL IONS, WITH THE DILACTAM OF C222

1. Introduction

Nuclear magnetic resonance (NMR) has become a powerful tool for the investigation of complexation reactions. The chemical shifts and line widths of the nuclear resonances of alkali metal ions nuclei can give information about ion-ligand, ion-solvent and ion-ion interactions.

Sodium-23 has a large quadrupole moment (0.1 e X 10^{-24} cm^2), and its chemical shift range is rather large (about 40 ppm). These two factors make ^{23}Na nucleus a sensitive probe of the electronic environment around the nucleus as previous studies in this laboratory (19-22) and elsewhere (18,25,55) have shown.

Lithium-7 nucleus is highly suitable for nuclear magnetic resonance studies because the resonance lines of Li^+ ion in solutions are exceptionally narrow and chemical shifts can be measured with considerable accuracy (27). Both ^{23}Na NMR and ^{7}Li NMR have been found useful techniques for determination of the formation constants of weak and medium strength complexes (15,16,45).

The purpose of this study is the investigation of the complexation reaction of Li^+ ion and Na^+ ion with the dilactam of C222 in different solvents and the determination of the formation constants, where possible. The addition of the dilactam to a lithium or sodium salt

solution results in a definite shift of the chemical shift of the ^{7}Li or ^{23}Na resonance when complexation takes place. If the rate of exchange of the metal ion between the two sites, free ion in the bulk solution and the complex, is greater than $\sqrt{2}/\pi\Delta\nu$, where $\Delta\nu$ is the difference between the characteristic resonance (in Hz) of each site, only one population-average resonance is observed. In all cases in this study only one resonance line is observed.

2. Lithium-7 NMR Study

The ^{7}Li chemical shifts were determined as a function of dilactam/Li^{+} mole ratios. The results are shown in Table II. Typical spectra obtained with the dilactam of C222 are shown in Figure 7.

In dimethylsulfoxide, water, methanol and dimethylformamide solutions, the solvent molecules have a strong solvating ability and compete quite successfully with the ligand. There is not enough evidence that complexation is occurring because there is not enough change of the chemical shift from the position characteristic of the solvated Li^{+} ion in the above solvents. In the case of formamide, a solvent with a medium solvating ability, and of acetone and tetrahydrofuran with medium to low solvating ability, a lithium complex is formed, as shown by the variation of the chemical shift (Table II). In order to determine the formation constants of Li^{+}-dilactam complexes in pyridine, tetrahydrofuran, propylene carbonate, acetonitrile and nitromethane solutions, the ^{7}Li chemical shifts were measured as a function of ligand/Li^{+} mole ratio (Table III).

The exchange of Li^{+} ion from the bulk solution and the complex is fast compared to the NMR time scale, therefore, only the population-average chemical shift is observed,

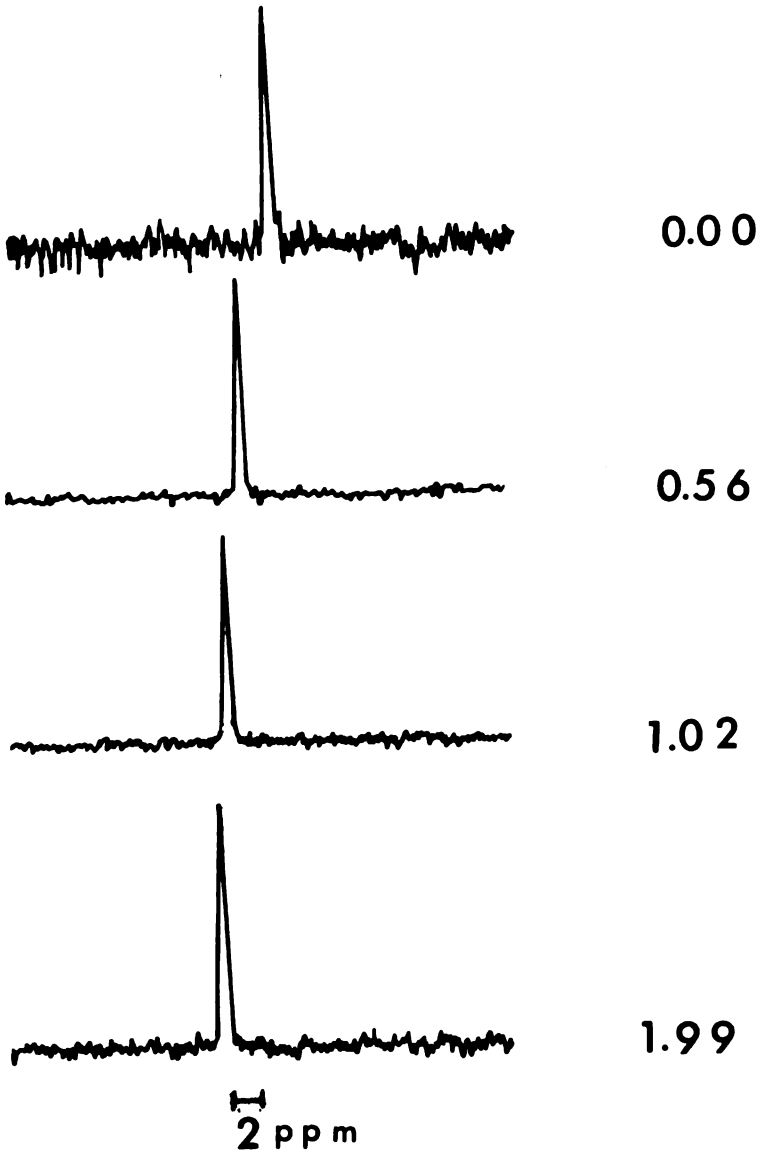


Figure 7. Change of ^{7}Li chemical shift with dilactam/Li^{+} mole ratio at constant [Li^{+}] = 0.015 M in acetonitrile.

Table II. ^{7}Li-NMR Study of the Dilactam of C222, Lithium Complexes in Various Solvents at Constant Temperature 33 ± 2°C

Solvent	Salt	$[Li^+]$ (M)	[Dilactam]/$[Li^+]$	^{7}Li Chemical Shift (ppm)[a]
DMSO	$LiClO_4$	0.020	0.0	1.16
			0.5	1.12
			1.0	1.08
			2.0	1.12
H_2O	$LiClO_4$	0.015	0.0	0.00
			0.5	0.05
			0.9	0.05
			2.1	0.15
Formamide	$LiClO_4$	0.015	0.0	-0.50
			0.5	-0.52
			1.1	-0.41
			2.0	-0.35
Acetone	$LiClO_4$	0.015	0.0	-1.55
			0.5	-1.22
			1.0	-1.03
			2.0	-0.91
CH_3OH	$LiClO_4$	0.015	0.0	0.45
			0.5	0.34
			1.0	0.39
			2.0	0.37

Table II Continued

DMF	$LiClO_4$	0.10	0.0	-0.43
			0.1	-0.38
			0.5	-0.39
			1.0	-0.35
			1.5	-0.44
			2.0	-0.44
THF	$LiClO_4$	0.019	0.0	0.93
			0.1	0.72
			0.3	0.57
			1.0	0.13
			2.0	-0.31

[a]Lithium-7 chemical shift vs 4.0 M $LiClO_4$ in water (corrected for magnetic susceptibility)

Table III. ^{7}Li Chemical Shifts as a Function of Ligand/Li^{+} Mole Ratio in Different Solvents at 33 ± 2°C

Pyridine $[LiClO_4]$ = 0.020 M		THF $[LiClO_4]$ = 0.010 M	
[Dil]/[Li^{+}]	δ(ppm)[a]	[Dil]/[Li^{+}]	δ(ppm)[a]
0.00	-2.27	0.00	0.87
0.15	-1.99	0.25	0.68
0.30	-1.86	0.40	0.49
0.46	-1.68	0.64	0.22
0.61	-1.51	0.71	0.16
0.77	-1.38	1.20	-0.10
0.89	-1.26	1.33	-0.18
1.04	-1.16	1.68	-0.19
1.25	-1.11	1.78	-0.20
1.50	-1.05	2.00	-0.24
1.69	-1.00	2.27	-0.26
2.05	-0.91	2.84	-0.26
2.25	-0.94		
2.39	-0.91		
PC $[LiClO_4]$ = 0.011 M		CH_3NO_2 $[LiClO_4]$ = 0.015 M	
0.00	0.80	0.00	0.18
0.21	0.55	0.20	0.02
0.35	0.35	0.27	-0.08
0.53	0.18	0.40	-0.10
0.65	-0.02	0.59	-0.24

Table III Continued

0.92	-0.11	0.67	-0.36
1.20	-0.14	0.80	-0.40
1.32	-0.07	0.92	-0.56
1.48	-0.05	1.13	-0.69
1.69	-0.20	1.33	-0.75
1.85	-0.24	1.47	-0.73
2.26	-0.33	1.67	-0.79
2.66	-0.35	2.04	-0.77
3.16	-0.35	2.40	-0.79
		3.00	-0.77
		3.33	-0.77

Acetonitrile [$LiClO_4$] = 0.015		Acetonitrile [LiBr] = 0.015	
0.00	2.58	0.00	2.02
0.15	2.16	0.13	1.68
0.31	1.75	0.33	1.22
0.40	1.54	0.40	1.05
0.56	1.11	0.60	0.74
0.67	0.95	0.67	0.59
0.77	0.64	0.82	0.27
0.95	0.20	0.93	0.09
1.02	0.17	1.17	-0.06
1.12	0.03	1.27	-0.12
1.30	-0.01	1.58	-0.16

Table III Continued

1.48	-0.06	2.13	-0.35
1.70	-0.08	2.37	-0.31
1.91	-0.08	3.02	-0.37
1.99	-0.14	3.58	-0.35
2.37	-0.14		
3.00	-0.18		

[a]Lithium-7 chemical shift *vs* 4.0 *M* $LiClO_4$ in water (corrected for magnetic susceptibility)

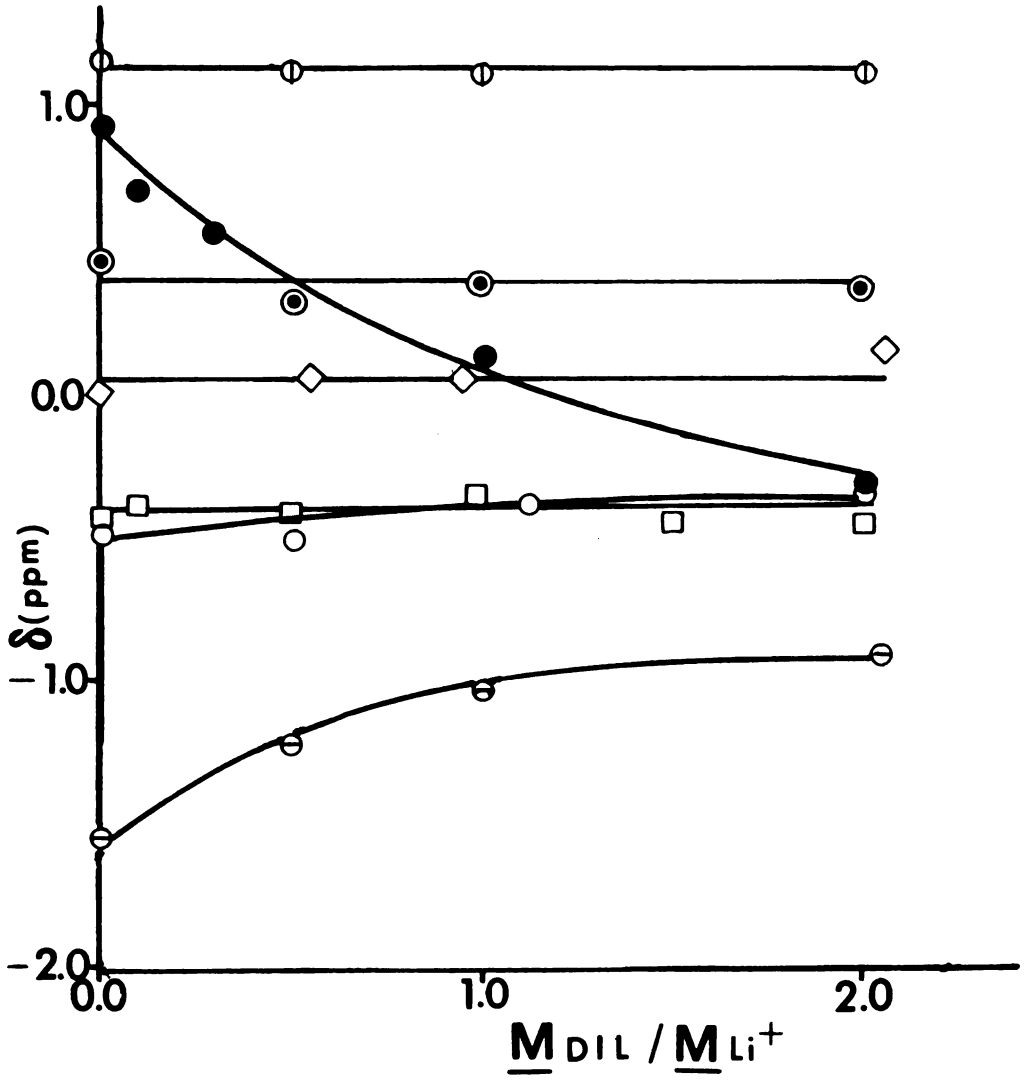


Figure 8. Plot of ^{7}Li chemical shift with reference to 4.0 M aqueous $LiClO_4$ vs mole ratio of dilactam to Li^+ at ⦶ $[Li^+]$ = 0.02 M in DMSO, ● $[Li^+]$ = 0.019 in THF, ◉ $[Li^+]$ = 0.015 M in MeOH, ◇ $[Li^+]$ = 0.015 M in H_2O, ○ $[Li^+]$ = 0.015 in formamide, □ $[Li^+]$ = 0.10 M in DMF, ⊖ $[Li^+]$ = 0.015 M in acetone.

$$\delta_{obs} = \delta_M X_M + \delta_{ML} X_{ML} \tag{2}$$

where δ_{obs} is the observed chemical shift, X_M and X_{ML} are the mole fractions of the free and complexed metal ion respectively while δ_M and δ_{ML} are the respective chemical shifts for the two species. Assuming a 1:1 complex, we have the equilibrium

$$M + L \rightleftarrows ML \tag{3}$$

where L is the ligand. The formation constant of the complex, in concentration units, becomes

$$K = \frac{C_{ML}}{C_M C_L} \tag{4}$$

where C_M and C_{ML} are the equilibrium concentrations of the free ligand and the complex respectively.

$$\delta_{obs} = (KC_M^t - KC_L^t - 1) \pm (K^2 C_L^{t\,2} + K^2 C_M^{t\,2} - 2K^2 C_M^t C_L^t + 2KC_L^t + 2KC_M^t + 1)^{1/2}$$

$$\frac{\delta_M - \delta_L}{2KC_M^t} + \delta_{ML} \tag{5}$$

In eq. (5), C_M^t and C_L^t, the total concentration of the metal ion and of the ligand respectively, are known and δ_M can be easily determined from measurements on solutions of lithium salts without the ligand. Eq. (5) then contains two unknowns K and δ_{ML}. In the case of a rather strong complex δ_{ML} can be determined experimentally by the addition of such excess of L that essentially all of the metal is complexed.

In the case of weak complexes eq. (5) is solved by the following procedure. The experimental parameters δ_{obs}, C_M^t, C_L^t and δ_M are substituted into the equation, and K and δ_{ML} are varied until the

calculated chemical shifts correspond to the experimental values within the error limits. The data were analyzed on a CDC-6500 computer using the FORTRAN IV program KINFIT (54).

The values obtained were K = 440 $\pm$ 97 in pyridine, K_f = 1327 $\pm$ 263 in tetrahydrofuran, K_f = 4053 $\pm$ 2040 in nitromethane and K_f = 1686 $\pm$ 274 in acetonitrile.

In all the above cases $LiClO_4$ was used as the lithium salt.

In pyridine which has strong solvating ability the complex is weaker than in THF which has a medium to low solvating ability. In acetonitrile and nitromethane with low solvating ability the complexes are even stronger.

By changing the anion from perchlorate to bromide in the case of acetonitrile we end up with a value of K_f = 1348 $\pm$ 372 which is essentially the same as in the case of the perchlorate anion. This is an indication that the lithium ion complexed by the dilactam is independent from the counter ion. In the case of propylene carbonate the determination of the formation constant was not possible, because it exists an anomaly, probably due to a secondary reaction.

All the above values are the concentration constants. However, since the complexation reaction

$$Li^+ + \text{Dilactam} \rightleftarrows Li^+ - \text{Dil} \qquad (6)$$

does not involve separation of charges, these values should represent reasonable approximations of the thermodynamic constants.

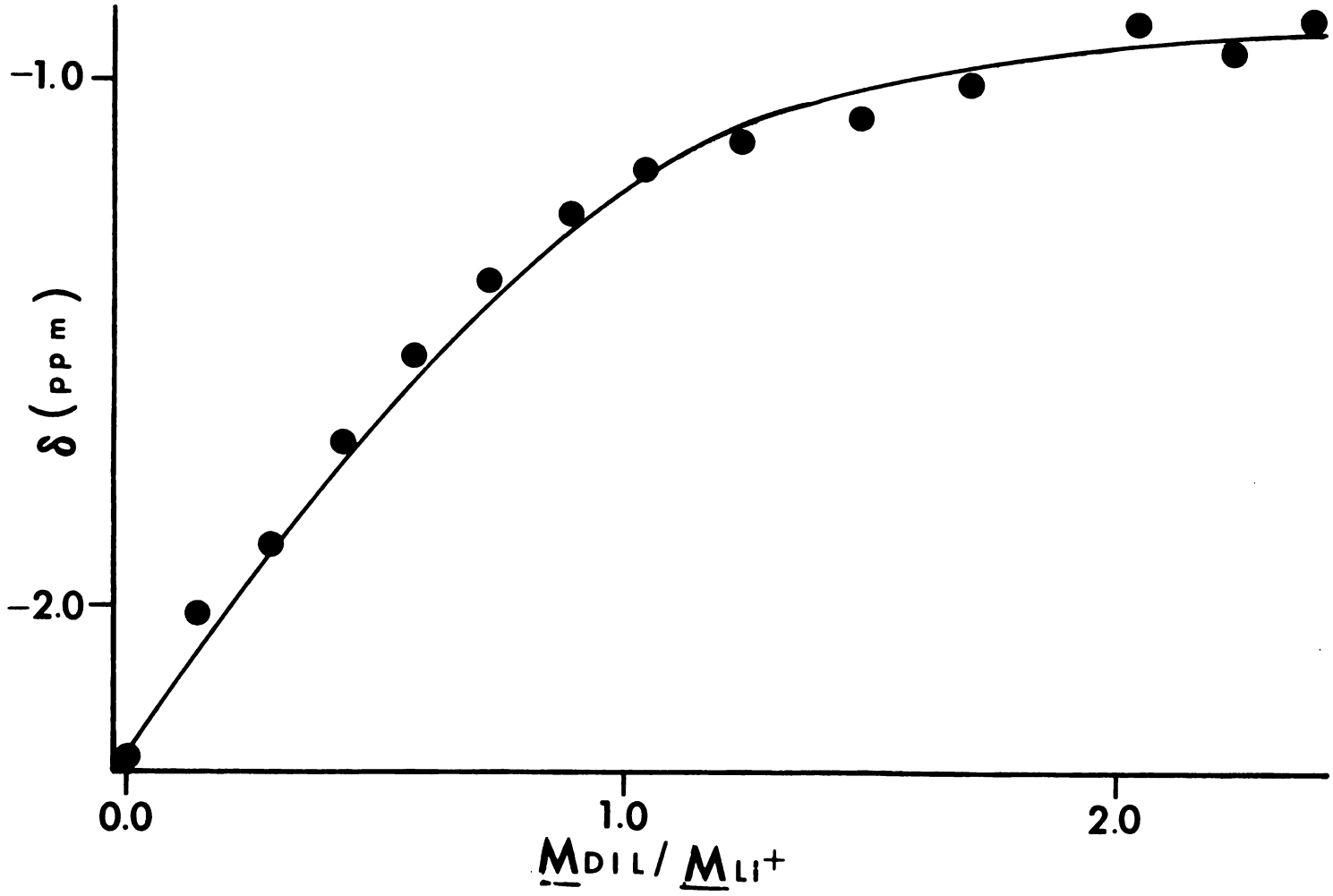


Figure 9. Plot of ^{7}Li chemical shift with reference to 4.0 M aqueous $LiClO_4$ vs mole ratio of dilactam to Li^+ at constant $[Li^+]$ = 0.020 M in pyridine. Solid line is computer-generated curve and dots are experimental points.

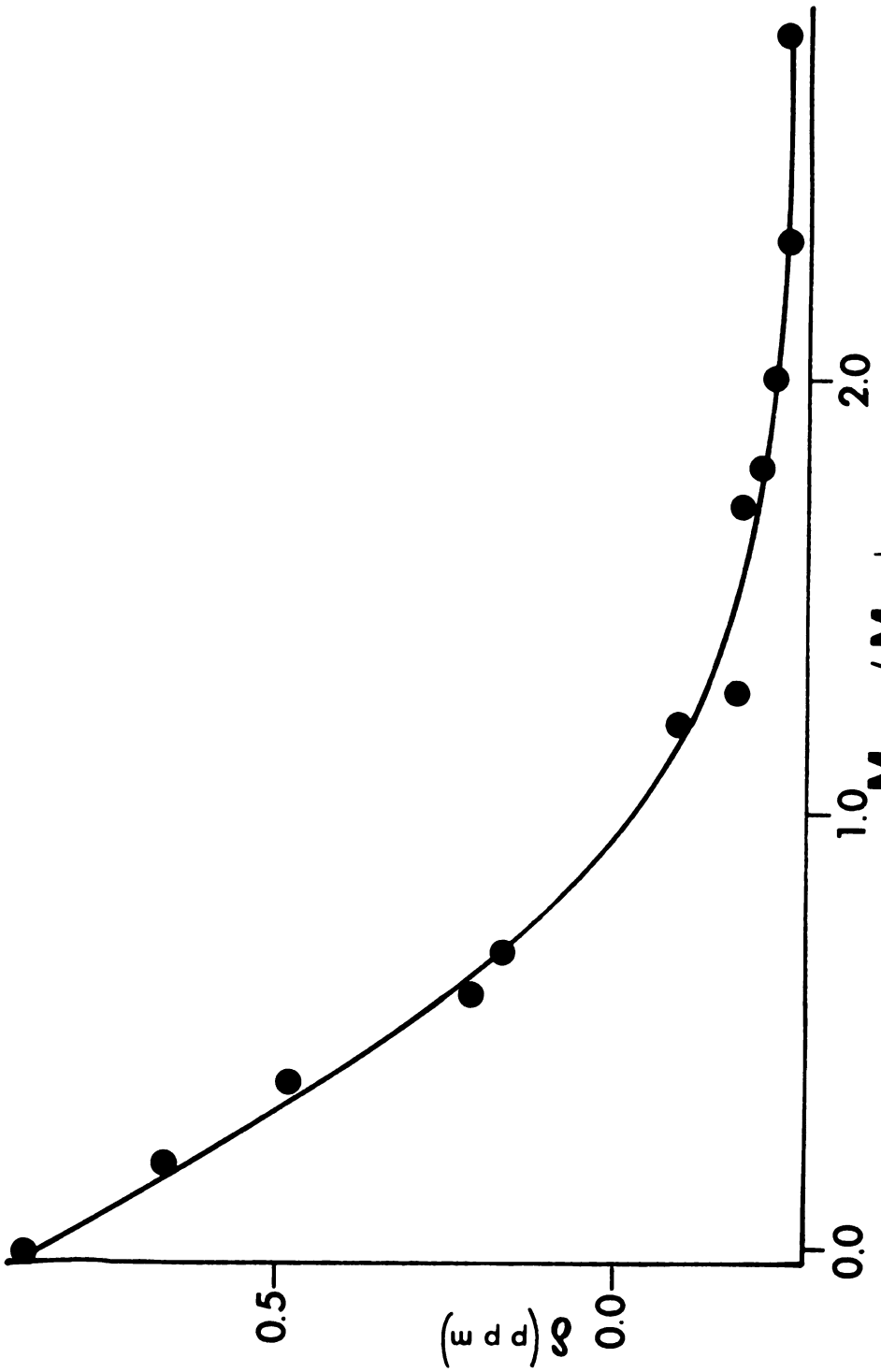


Figure 10. ^{7}Li chemical shift with reference to 4.0 M aqueous $LiClO_4$ vs mole ratio of dilactam to Li^+ at constant $[Li^+]$ = 0.010 M in THF. Solid line is computer-generated curve and dots are experimental points.

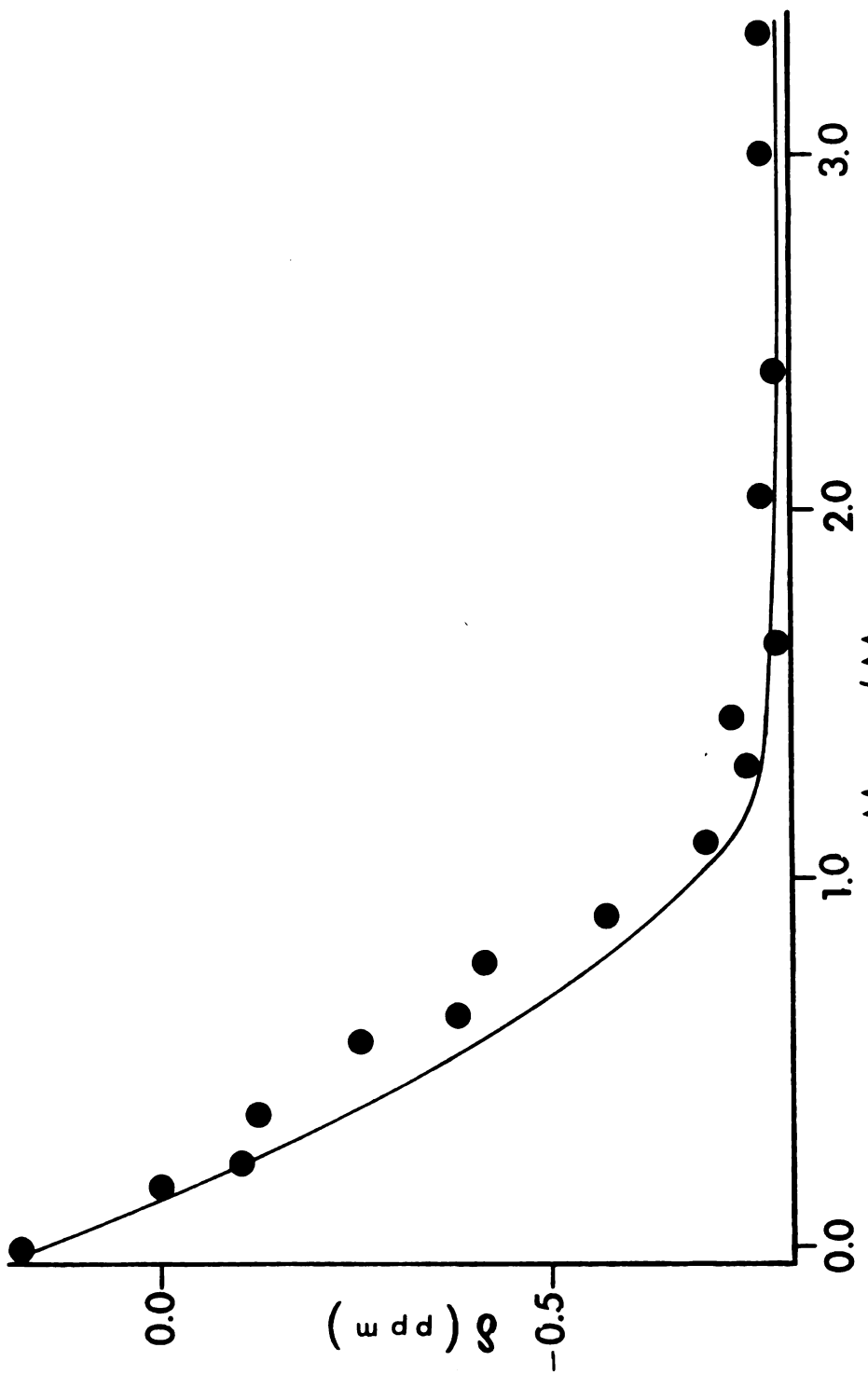


Figure 11. ^{7}Li chemical shift with reference to 4.0 M aqueous $LiClO_4$ vs mole ratio of dilactam to Li^+ at constant $[Li^+]$ = 0.015 M in nitromethane. Solid line is computer-generated curve and dots are experimental points.

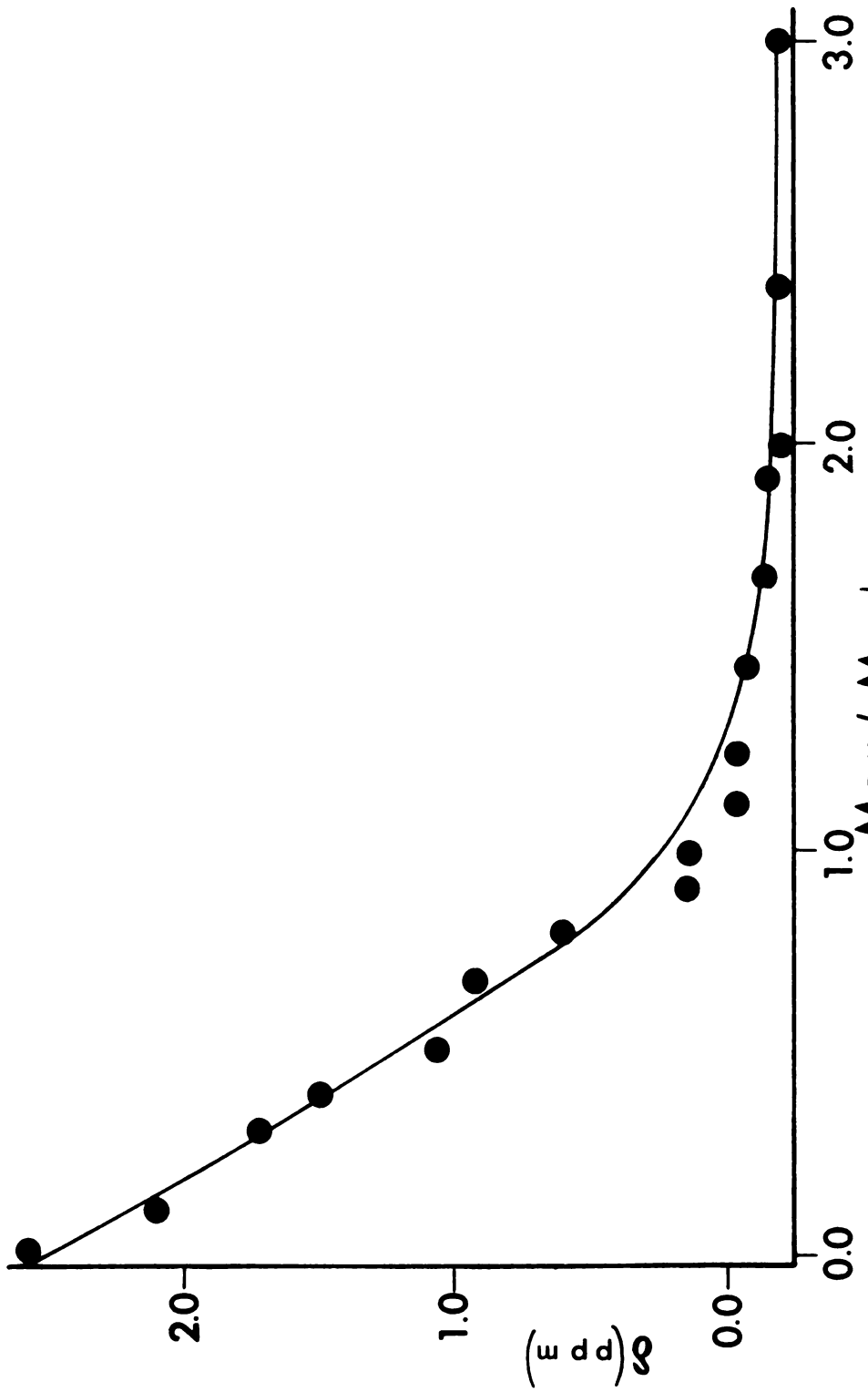


Figure 12. ^{7}Li chemical shift with reference to 4.0 M aqueous $LiClO_4$ vs mole ratio of dilactam to Li^+ at constant $[Li^+]$ = 0.015 M in acetonitrile. Solid line is computer-generated curve and dots are experimental points.

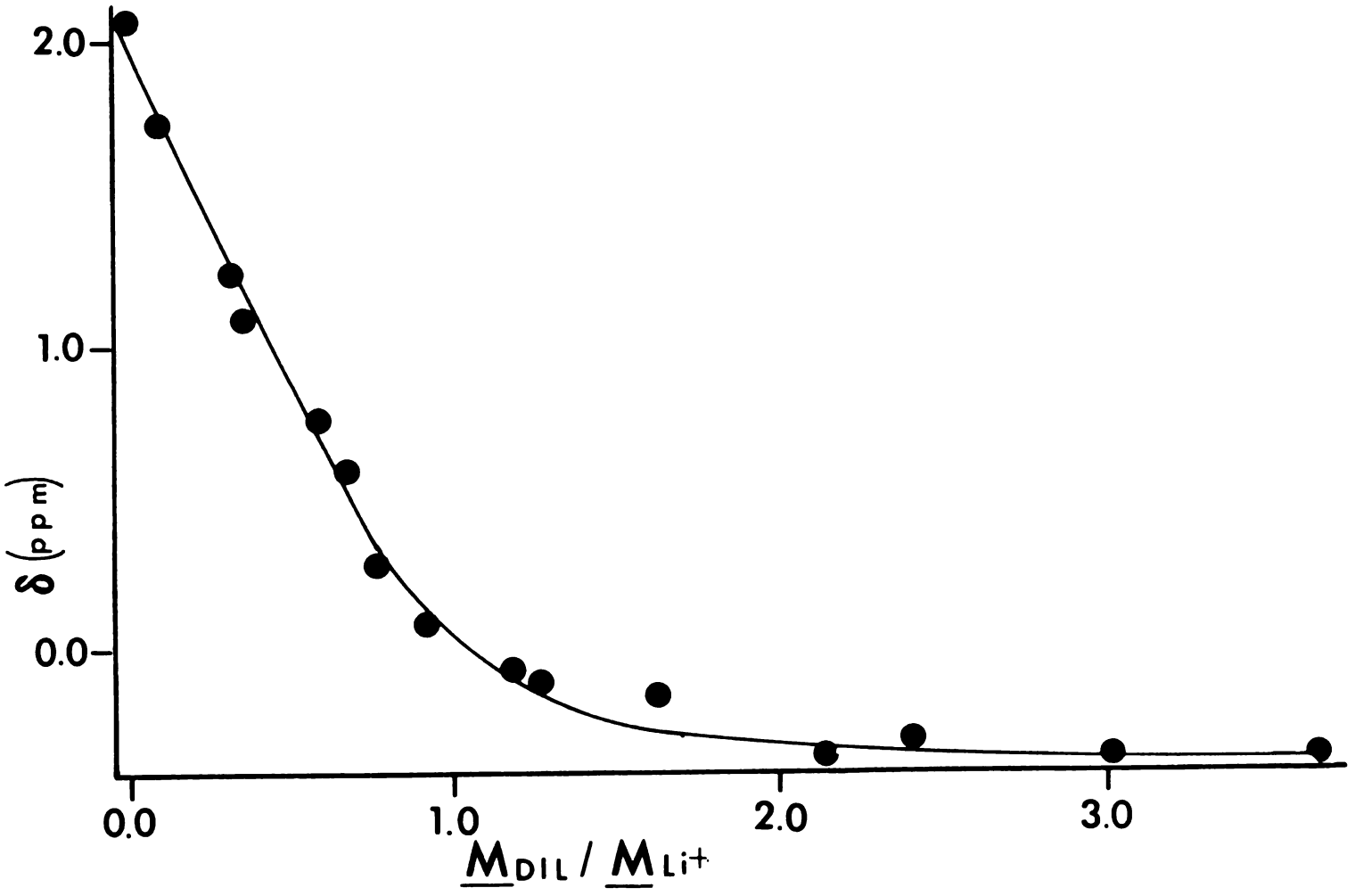


Figure 13. Plot of ^{7}Li chemical shift with reference to 4.0 M aqueous $LiClO_4$ vs mole ratio of Dil/Li^+ at constant [LiBr] = 0.015 M in acetonitrile. Solid line is computer-generated curve and dots are experimental points.

Table IV. Limiting Chemical Shifts and Formation Constants of the Dil-Li^+ Complex in Various Solvents

Salt	Solvent	δ_{ML} (ppm)[a]	δ_{ML} (ppm)[b]	K_f[b]
$LiClO_4$	CH_3CN	-0.16	-0.22	1686 ± 274
LiBr	CH_3CN	-0.35	-0.41	1348 ± 372
$LiClO_4$	THF	-0.26	-0.31	1327 ± 263
$LiClO_4$	Pyridine	-0.91	-0.80	440 ± 97
$LiClO_4$	CH_3NO_2	-0.77	-0.78	4053 ± 2040

[a]Experimentally determined values

[b]Computer calculated values

3. Sodium-23 NMR Study

The sodium-23 chemical shifts were determined in several solvents as a function of dilactam/Na^+ mole ratios. The results are shown in Tables V and VII.

In the case of dimethylformamide solutions the complex is very strong, the plot of the chemical shift as a function of the mole ratio, consists of two linear parts. At a mole ratio of 1:1 essentially all of the sodium ion is complexed.

In dimethylsulfoxide solutions two sodium concentrations were used, 0.20 M and 0.10 M. Addition of dilactam resulted in appreciable broadening of the ^{23}Na resonance. The full width at half height in the case of dimethylsulfoxide increases from fifty up to six hundred hz, therefore, the error in the determination of the chemical shift is relatively large. Consequently it cannot be unambiguously determined if the addition of dilactam results in ^{23}Na chemical shift change or not.

The exchange of Na^+ ion between the bulk solution and the complex is fast on the NMR time scale, and only one population-average resonance is observed. Temperature-dependent study of the exchange was tried in the case of dimethylformamide. As the temperature increases, the exchange becomes faster and the sodium resonance peak narrowed (Table VI). By lowering the temperature the peak broadens very much, to more than two thousand hertz at -35°C and

Table V. ^{23}Na-NMR Study of the Dilactam of C222, Sodium Complexes in DMF at 33 ± 2°C

DMF [$NaBPh_4$] = 0.10 M

[Dil]/[Na^+]	δ(ppm)[a]	$\Delta\nu_{1/2}$(Hz)[b]
0.00	5.07	29
0.09	4.92	46
0.30	4.76	71
0.49	4.29	100
0.72	3.99	124
0.91	3.38	154
1.01	2.93	185
1.09	3.25	195
1.31	3.49	229
1.49	3.08	249
1.69	3.19	244
1.87	3.14	302
1.97	3.28	325
2.19	3.07	332
2.50	3.62	361

[a]Sodium-23 chemical shift vs 3.0 M NaCl in water (corrected for magnetic susceptibility)

[b]Full width at half height

Table VI. Temperature-Dependent Study of the Dilactam of C222, Sodium Complexes in DMF

[Dil]/[Na^+]	T°C	δ(ppm)	$\Delta\nu_{1/2}$(Hz)
	35		
0.00		5.07	39
0.47		3.67	134
1.10		3.70	287
	47		
0.00		5.55	34
0.47		4.46	98
1.10		3.85	212
	56		
0.00		5.53	32
0.47		4.77	75
1.10		3.69	158
	65		
0.00		5.53	29
0.47		4.77	75
1.10		3.55	114
	83		
0.00		5.39	30
0.47		4.77	66
1.10		4.30	107

Table VII. ^{23}Na-NMR Study of the Dilactam of C222, Sodium Complexes in DMSO at 33 ± 2°C

DMSO [$NaB\phi_4$] = 0.1 M

[Dil]/[Na^+]	δ(ppm)[a]	$\Delta\nu_{1/2}$[b]
0.00	0.84	46
0.10	0.84	54
0.30	0.88	93
0.50	0.68	127
0.70	0.84	171
0.93	0.92	247
1.01	0.33	230
1.30	0.68	313
1.60	1.14	361
1.80	-0.27	390
2.00	-0.16	405
2.21	1.29	390
2.55	1.04	510

DMSO [$NaBPh_4$] = 0.2 M

0.00	0.84	49
0.25	0.84	137
0.50	0.78	225
0.75	1.03	337
0.95	1.58	403
1.50	1.76	674

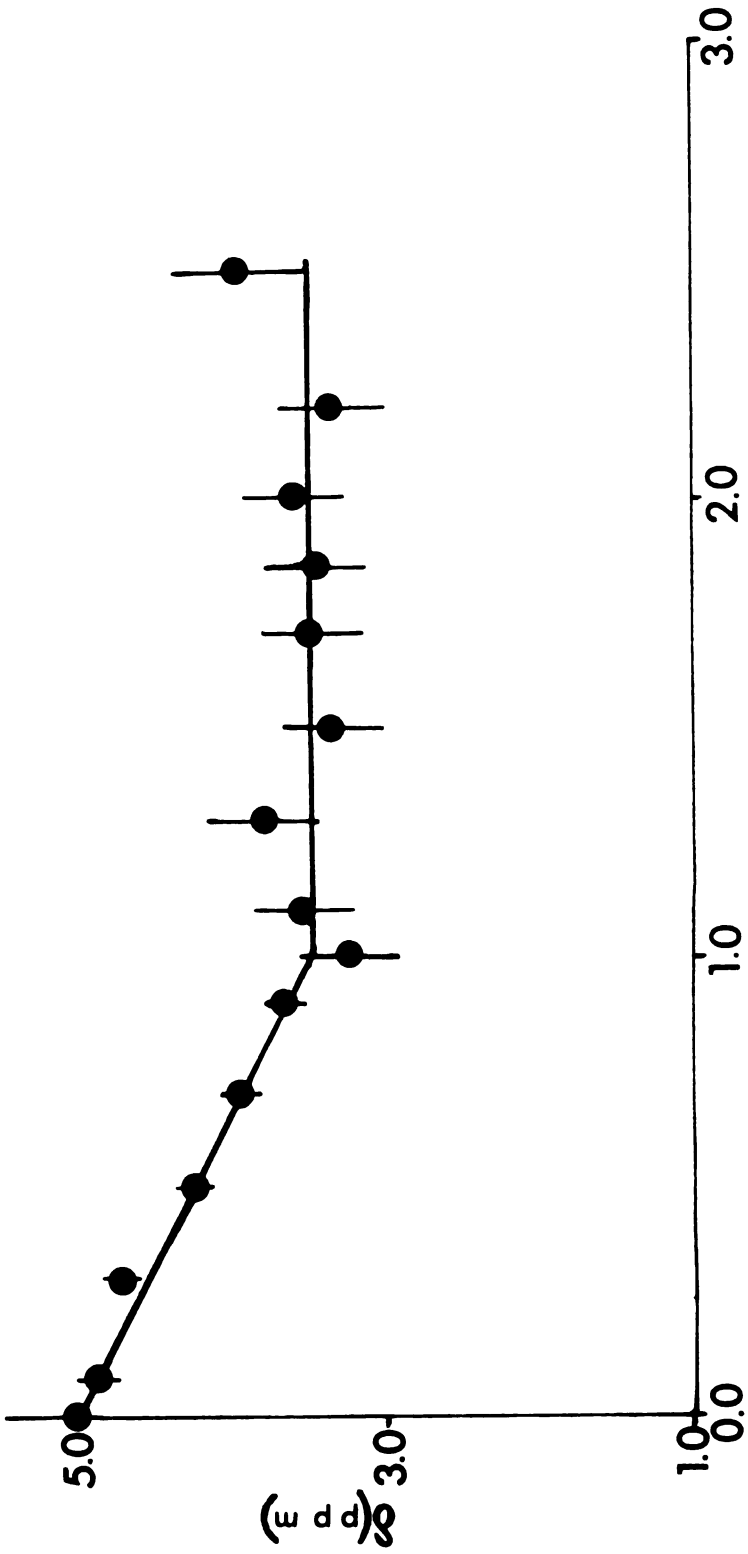


Figure 14. Plot of ^{23}Na chemical shift with reference to 3.0 M aqueous NaCl vs mole ratio of dilactam to Na^+ at constant $[Na^+]$ = 0.1 M in DMF at 33 ± 2°C

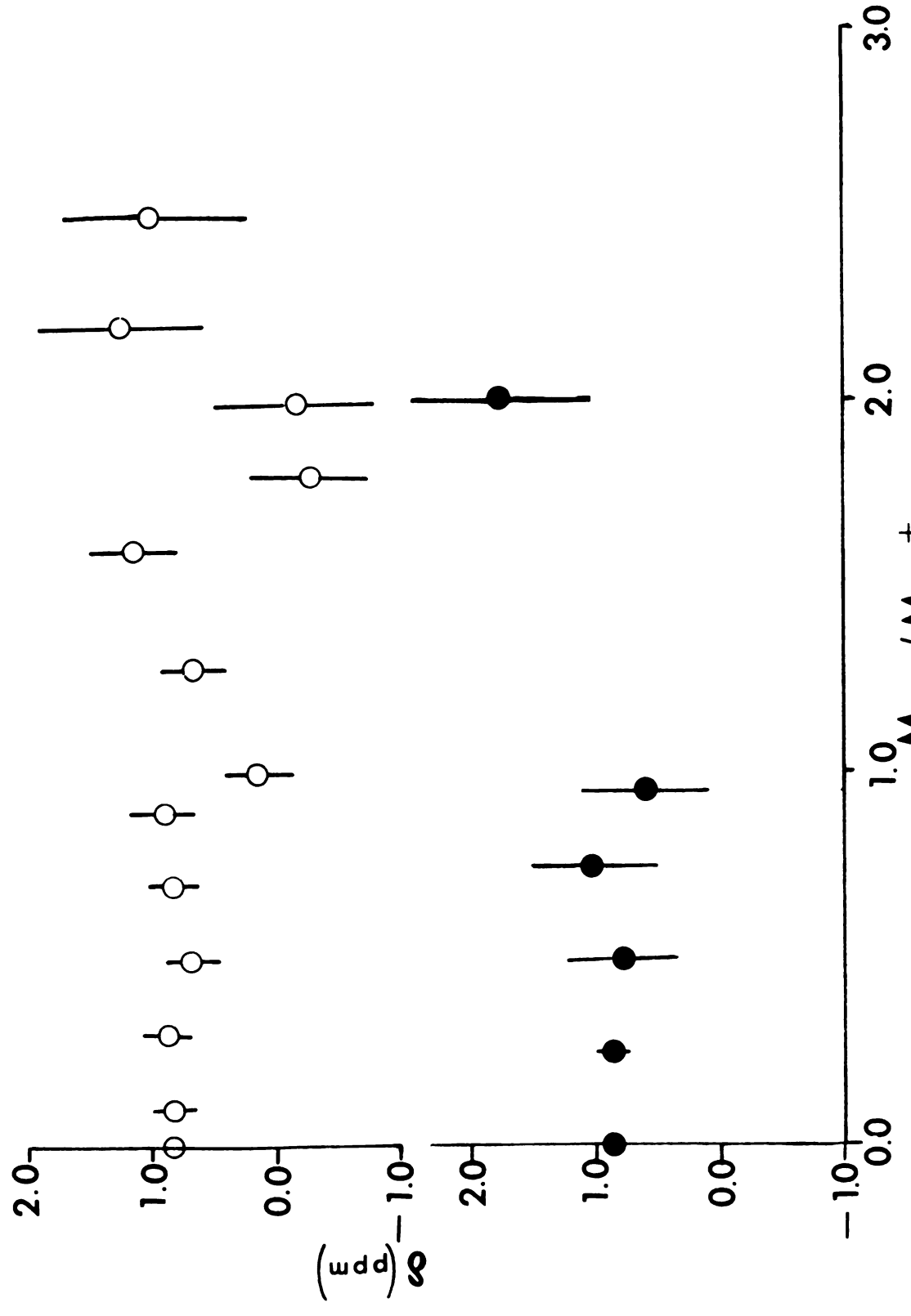


Figure 15. Plot of ^{23}Na chemical shift with reference to 3.0 M aqueous NaCl vs mole ratio of dilactam to Na^+ at $[Na^+]$ = 0.1 M and $[Na^+]$ = 0.2 M in DMSO at 33 ± 2°C

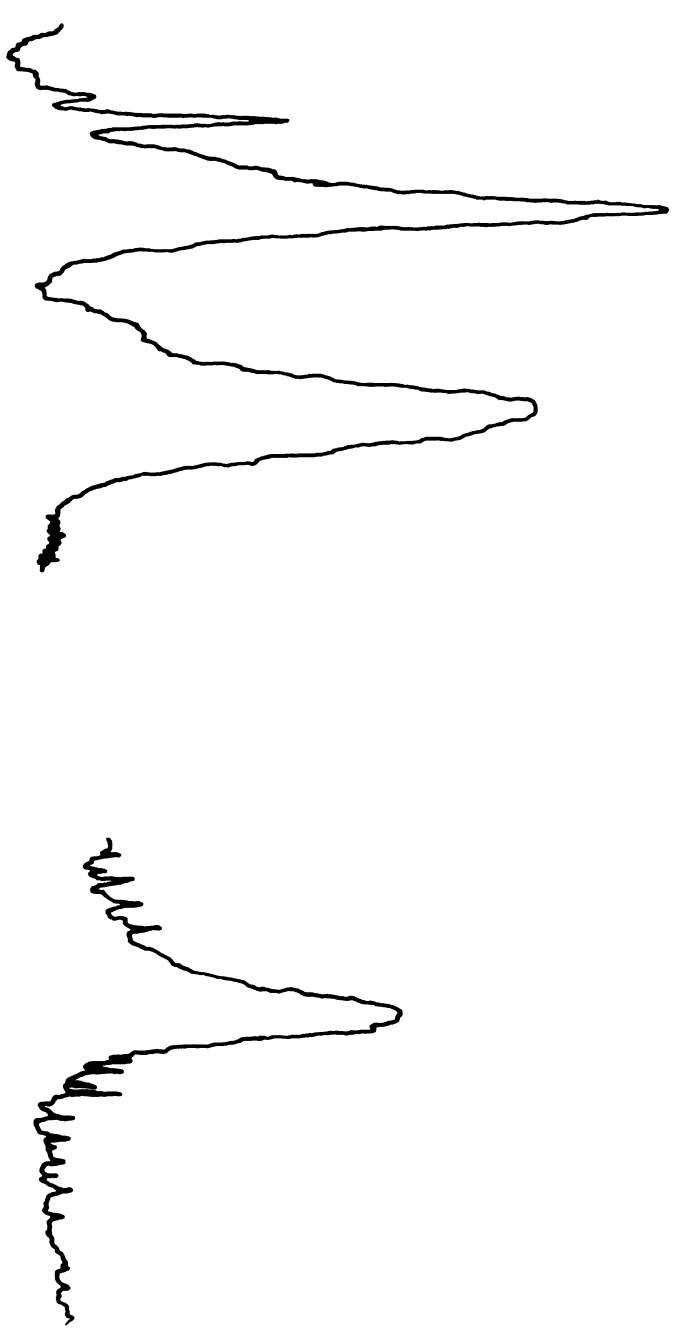


Figure 16. Infrared spectra of dilactam-sodium precipitates from a) DMF solution and b) pyridine solution.

makes the study very difficult. Other solvents were tried for the chemical shift study. Nitromethane, water, propylene carbonate, acetone, methanol, diglyme, benzene, chloroform were tried. In all of them precipitation occurred upon the addition of dilactam to the sodium salt solution. When pyridine, tetrahydrofuran and acetonitrile were used, the dilactam and the sodium tetraphenylborate initially went into solution, but after some minutes a precipitate appeared. In ethylenediamine solution a reaction took place and after a while a precipitate came out of the solution.

The infrared spectra of the precipitates and of the neat dilactam were taken. Dilactam shows a carbonyl absorption band at 1640 cm^{-1}. The precipitates from the water, methanol and ethylenediamine solutions show also a carbonyl absorption band at the same frequency as the neat dilactam, i.e. at 1640 cm^{-1}. The pyridine, nitromethane, and acetonitrile precipitates show two carbonyl absorption bands, one at 1640 cm^{-1} and a second one at 1790 cm^{-1}. The latter spectra were taken with the sample in potassium bromide pellets and in Nujol mulls. In both cases both of the carbonyl peaks were present. In order to see if the Dil-Na^{+} complex has one or two carbonyl absorption bands, a solution of mole ratio of Dil/Na^{+} of 3.40 in dimethylformamide was vacuum dried. The infrared spectrum of the powder obtained showed only one carbonyl absorption band at 1635 cm^{-1}. From the NMR we know that at this mole ratio all of the sodium is complexed. When the melting point of the above powder was taken, a small portion of the sample melted at 114°C, which is probably the excess dilactam, and the main portion

of the sample melted between 185-195°C, which seems to be the melting point region of the Dil-Na^+ complex since the m.p. of the sodium salt is greater than 300°C.

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