





This is to certify that the

thesis entitled

Mult: inclear NMR Study of Complexation of Som Univalent Cations by Crown Ethers in Nonagueous Solvents. presented by

Mujtaba Shamsipur

has been accepted towards fulfillment of the requirements for

Ph. D. degree in Chemistry

Herauch Depr Major professor

8-30-79 Date ____

O-7639

. .

OVERDUE FINES: 25¢ per day per item

RETURNING LIBRARY MATERIALS:

Place in book return to remove charge from circulation records

MULTINUCLEAR NMR STUDY OF COMPLEXATION OF SOME UNIVALENT CATIONS BY CROWN ETHERS IN

NONAQUEOUS SOLVENTS

By

Mojtaba Shamsipur

A DISSERTATION

Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1979

2 . ?: 205 ces orc: 21-Tet? dine the ೆ ಕ್ರ and j Was d âs a SUDDOI the Di soluți

-- --

, et i

ABSTRACT

MULTINUCLEAR NMR STUDY OF COMPLEXATION OF SOME UNIVALENT CATIONS BY CROWN ETHERS IN NONAQUEOUS SOLVENTS

By

Mojtaba Shamsipur

Nuclear magnetic resonance of ¹³C, ²³Na, ¹³³Cs, and ²⁰⁵Tl nuclei were used to study the sodium, potassium, cesium, and thallium(I) ion complexes with dibenzo-30crown-10 (DB30Cl0), dibenzo-24-crown-8 (DB24C8), and dibenzo-21-crown-7 (DB21C7) in nitromethane, acetonitrile, acetone, methanol, dimethylformamide, dimethylsulfoxide, and pyridine solutions.

With the exception of the DB30C10-Na⁺ system, all of the complexes were formed in 1:1 mole ratios. The presence of three sodium DB30C10 complexes, $Na_2(DB30C10)$, $Na_3(DB30C10)_2$, and Na(DB30C10) in nitromethane and acetonitrile solutions was deduced from the behavior of the ²³Na chemical shift as a function of DB30C10/Na⁺ mole ratio. The NMR data support the existence of a "wrap around" structure for the DB30C10 complexes with cesium and potassium ions in solution.

X ÷ 3. D (9] 0 g <u>);</u> 5 9 5 5 r.: in re 23; Whj ą_"e the In ent The stabilities of the sodium, cesium, and thallium(I) ion complexes with both DB24C8 and DB21C7 decrease in the order $T1^+ \cdot Crown > Cs^+ \cdot Crown > Na^+ \cdot Crown$ in solvents of low and medium donicities such as nitromethane, acetonitrile, acetone, and methanol. The ability of the ligands for the formation of a three-dimensional "wrap around" complex with the same cation decreases with decreasing the size of the ligand, <u>i.e.</u>, DB30C10 > DB24C8 > DB21C7. In all cases studied, with the exception of pyridine, there is an expected inverse relationship between the donor strength of the solvents and the stability of the complexes. The extent of the solvent effect on the complex formation constants for the Na⁺, Cs⁺, and T1⁺ ion complexes decreases in the order T1⁺ > Na⁺ > Cs⁺.

The chemical shift of the 133 Cs resonance was studied as a function of the ligand/Cs⁺ ion mole ratio at various temperatures in five solvents, <u>i.e.</u>, nitromethane, acetonitrile, acetone, methanol, and pyridine. From the resulting data ΔG° , ΔH° , and ΔS° values for the complexation reactions between the cesium ion and DB30C10, DB24C8, and DB21C7 were calculated. It was found that in all cases, while the stabilities (or the ΔG° values) of the complexes are not very sensitive to the solvent, the enthalpy and the entropy values vary very significantly with the solvent. In all cases the complexes are enthalpy stabilized but entropy destabilized. From the results, it seems reasonable to assume that the main reason for the negative entropy of complexation is the decrease in the conformational entropy of the ligands upon the formation of a metal complex.

The complexation of Li⁺, Na⁺, Cs⁺, and Tl⁺ ions by 1,10diaza-18-crown-6 (DA18C6) in several nonaqueous solvents was studied by multinuclear NMR technique. The formation constants of the resulting 1:1 complexes were calculated by computer fitting of the mole ratio data. The stabilities of the complexes decrease in the order DA18C6.T1 + > $DA18C6 \cdot Li^+$ > $DA18C6 \cdot Na^+$ > $DA18C6 \cdot Cs^+$. In order to study the effect of the substitution of two nitrogen atoms for the two oxygen atoms in 18-crown-6, the formation constants were compared with those reported for the 18-crown-6 complexes with the same cations. As expected, the sodium and the cesium ion complexes are weakened appreciably by the nitrogen substitution. The sodium and cesium ions as "hard acids", cannot interact as strongly with the substituted nitrogen atoms of the ligand as they can with the oxygen atoms. The effect of the nitrogen substitution on the lithium and thallium(I) ion complexes is exactly the opposite, the stabilities of these complexes are greatly increased. These cations can form partially covalent bonds which cause an increase in the strength of the interaction between the ligand and the cations upon the nitrogen substitution.

The kinetics of the complexation reactions of the cesium ion with DB21C7, DB24C8, and DB30C10 in acetone and methanol were investigated by the temperature dependent 133 Cs NMR. The energies of activation for the release of Cs⁺ from the cesium complexes decrease with decreasing donicity of the solvent as expressed by the Gutmann donor number. They also decrease with the increase in the size of the ligand. The data show that, first, the transition state must involve a substantial ionic solvation and, second, the transition state must be more ordered than the initial and the final states, <u>i.e.</u> the solvated complex and the solvated cesium ion and the free ligand.

٦

To Nahid

i i un th:

ACKNOWLEDGMENTS

The author wishes to express his sincere gratitude to Professor Alexander I. Popov for his guidance, encouragement, and friendship throughout this study.

Professor Stanley R. Crouch is acknowledged for his many helpful suggestions as second reader.

The author acknowledges the financial assistance of the people of Iran, as administered by the Isfahan University of Technology, during the course of this study. The financial aids of the Department of Chemistry, Michigan State University, and the National Science Foundation are also acknowledged.

The help of Mr. Frank Bennis, Mr. Wayne Burkhardt, and Mr. Tom Clarke in keeping the NMR spectrometers in operating condition is acknowledged.

Deep appreciation to my wife, Nahid, for her love, understanding, patience, and encouragement throughout this study.

To her and to our son, Ali, I dedicate this thesis.

iii

CHAP

2

2.2

TABLE OF CONTENTS

Chapter	Pa	.ge
LIST OF TABLES	.vi	11
LIST OF FIGURES	•	xv
LIST OF ABBREVIATIONS	.xx	: ii
CHAPTER 1. HISTORICAL REVIEW	•	1
1.1. Macrocyclic Crown Ethers	•	2
1.1.1. Introduction	•	2
l.l.2. Metal Ion Complexes with Large Crowns	•	3
1.1.3. Thermodynamics of Metal- Complex Formation in Solution .	•	14
1.1.3.1. Open Chain Ligands	•	14
1.1.3.2. Cyclic Ligands	•	21
1.2. Nuclear Magnetic Resonance	•	27
1.2.1. Introduction	•	27
1.2.2. Chemical Shift Measurements	•	28
1.2.3. Multinuclear NMR Studies of Complexation of Tl ⁺ and Alkali Ions in Solution	•	33
1.3. Conclusions	•	40
CHAPTER 2. EXPERIMENTAL PART	•	41
2.1. Synthesis and Purification of Ligands	•	42
2.1.1. Synthesis of Dibenzo-30- Crown-10	•	42
2.1.2. Purification of Ligands	•	43
2.2. Solvents and Salts	•	44
2.2.1. Solvents	•	44

Chapter

Page

	2.2.2.	Salts	5.	•••	•	•	•	•	•	•	•	•	•	•	•	45
2.3.	Sample 1	Prepar	ati	on.	•	•	•	•	•	•	•	•	•	•	•	46
2.4.	Instrum	ental	Mea	sur	eme	nt	s	•	•	•	•	•	•	•	•	46
2.5.	Data Hai	ndling	5.	• •	•	•	•	•	•	•	•	•	•	•	•	48
CHAPTER 3.	MULTI OF DI DIBEN DIBEN WITH I IONS	NUCLEA BENZO- ZO-24- ZO-21- Na ⁺ , A IN NOM	AR N -30- -CRC -CRC -CRC	IMR -CRO)WN-)WN- Cs ⁺ JEOU	STU WN- 8, 7 C , a S S	DY 10 AN OM nd	, PL T VE	EXI 1 ⁺ NT:	ES S	•	•	•	•	•	•	50
3.1.	Introdu	ction.	•		•	•	•	•	•	•	•	•	•	•	•	51
3.2.	Complexa Cs ⁺ Iona	ation s with	of Di	Na ⁺ .ben	, K zo-	; + , 30	а -С	nd roi	wn	-1	0	•	•	•	•	52
	3.2.1.	DB300 Nata	210 and	Com K ⁺ .	ple •	•xe	s .	wi1 •	th •	•	•	•	•	•	•	52
	3.2.2.	DB300	210	Com	ple	xe	S	wi	th	C	s+	•	•	•	•	5 9
3.3.	Complex: Tl ⁺ Ion:	ation s with	of Di	Na ⁺ ben	, C zo-	s+ 24	, -C	ano roi	i vn·	-8	•	•	•	•	•	67
	3.3.1.	DB240	28 C	Comp	lex	es	W	itl	n I	Na	ł	•	•	•	•	67
	3.3.2.	DB240	:8 C	omp	lex	es	W	itl	n (Cs	+	•	•	•	•	72
	3.3.3.	DB240	:8 C	omp	lex	es	W	itl	n'	Tl.	+	•	•	•	•	77
	3.3.4.	Concl	usi	ons	•	•	•	•	•	•	•	•	•	•	•	83
3.4.	Complexa Ions wit	ation th Dit	of enz	Na ⁺ 20-2	, C 1-C	s+ ro	, wn	ano - 7	i ' •	T1 [`]	•	•	•	•	•	86
	3.4.1.	DB210	27 C	omp	lex	es	W	itł	n I	Na	+	•	•	•	•	86
	3.4.2.	DB210	27 C	omp	lex	es	W	itł	1	Cs	+	•	•	•	•	91
	3.4.3.	DB210	27 C	omp	lex	es	W	itŀ	י ר	T1	ł	•	•	•	•	97
	3.4.4.	Concl	usi	ons	•	•	•	•	•	•	•	•	•	•	•	102
3.5.	Discuss	ion	•	•••	•	•	•	•	•	•	•	•	•	•	•	105

CHAPTER 4.	CESIU THERM TION DIBEN	M-133 ODYNAN OF DIN ZO-24-	NMR MICS BENZ(-CRO	STU OF D-30 WN-8	DY THE -CR	OF CO OWN ND	THE MPI -10 DIE	EX EN	4 - 20-	-				
	NONAQ	UEOUS	SOL	VENT	SIU S.	•	•••	1 N •	•	•	•	•	•	109
4.1.	Introdu	ction	• •	• •	••	•	•••	•	•	•	•	•	•	110
4.2.	DB30C10	Comp	lexes	s wi	th	Cs ⁺	••	•	•	•	•	•	•	111
4.3.	DB24C8	Comple	exes	wit	h C	s ⁺	•••	•	•	•	•	•	•	126
4.4.	DB21C7	Comple	exes	wit	h C	s ⁺	•••	•	•	•	•	•	•	139
4.5.	Discuss	ion.	• •	•••	••	•	•••	•	•	•	•	•	•	149
CHAPTER 5.	. LITHI AND T Na +, WITH VARIO	UM-7, HALLIU Cs+, a 1,10-I US NON	SOD JM-20 and DIAZ NAQUI	IUM- 05 N 71+ A-18 EOUS	23, MR ION -CR SO	CE STU CO OWN LVE	SIU DY MPI -6 NTS	M- OF EXI IN	L33 L1 ES	3, 1+,		•	•	156
5.1.	Introdu	ction	••	• •	•••	•	• •	•	•	•	•	•	•	157
5.2.	Results		• •	•••	•••	•	• •	•	•	•	•	•	•	158
	5.2.1.	1,10- Comp:	-Diaz lexes	za-l s wi	8-C th	row Li+	n-6	•	•	•	•	•	•	158
	5.2.2.	1,10- Comp:	-Dia: lexe:	za-l s wi	8-C th	row Na +	n-6	•	•	•	•	•	•	170
	5.2.3.	1,10- Comp:	-Dia: lexe:	za-l s wi	8-C th	row Cs+	n-6	•	•	•	•	•	•	173
	5.2.4.	1,10- Comp:	-Diaz lexe:	za-l s wi	8-C th	row Tl+	n-6	•	•	•	•	•	•	176
5.3.	Discuss	ion.	• •	•••	••	•	•••	•	•	•	•	•	•	177
CHAPTER 6.	. A STU ION C CROWN AND D	DY OF OMPLEX -10, I IBENZ(DYN KES V DIBEN D-21-	AMIC WITH NZO- -CRC	S O DI 24-	F C BEN CRO 7 I	ESI ZO- WN- N	UM 30- 8,	-					
	ACETO	NE ANI) ME:	l'HAN	OL.	•	•••	•	•	•	•	•	•	183
6.1 1	Introduc	tion	••	••	•••	•	•••	•	•	•	•	•	•	184
6 6.2.	Determi of the	nation Linesh	n and hapes	i In s.	ter	pre	tat	i01 •	n •	•	•	•	•	186

Chapter

Ε.

	6.3.	Rea	sult	s a	nd	Di	scu	ssi	Lor	1.	•	•	•	•	•	•	•	•	•	195
APPE	ENDICE	S																		
	APPEN FORMA DESCR SUBRO	DIX TIO IPT UTI	I - N CC ION NE E	DE' DNST OF QUA	TEF ANT CON TI(RMII FS 1 APU: DN	NAT BY FER	ION THH PH	N C E N ROG)F IMR RA	CO T M	MP EC KI	LE HN NF	X IIQ II ·	UE A	NE) •	•	•	211
	APPEN FORMA TION	DIX TIO BY	II N CC THE	– D NST NMR	ETH ANT MH	ERMI F WI ETHO	INA ITH OD.	TIC IC	ON ON	OF PA	C IR	OM F	PL OR	EX MA		•	•	•	•	216
REFE	RENCE	s.	••	• •	•	•		•	•	•	•	•	•	•	•	•	•	•	•	223

LIST OF TABLES

Table		Page
I	Experimental Conditions for Metal	
	Ion NMR	. 47
1	Thermodynamic Parameters for the	
	Complexation of Large Crown Ethers	
	with Cations in Solution	. 11
2	Thermodynamic Data for Diethylene-	
	triamine Complexes with Some Metal	
	(II) lons in 0.1 <u>M</u> KCl at 25°C	13
3	Thermodynamic Data for Metal (II)-	
	Polyamine Complexes (Chelate	
	Effect)	. 17
4	Thermodynamic Data for Reaction	
	(2) for Different Metal (II) Ions	. 19
5	Nuclear Properties of Alkali	
	Elements and Thallium	35
6	Key Solvent Properties and Cor-	
	rection for Magnetic Susceptibility	
	on DA-60	49
7	Mole Ratio Study of Dibenzo-30-	
	Crown-10 Complexes with 0.05 \underline{M}	
	Sodium Tetraphenylborate in Various	
	Solvents at 30°C	53

Table

Page

8	Mole Ratio Study of Dibenzo-30-
	Crown-10 Complexes with 0.005 \underline{M}
	Cs ⁺ Ion in Various Solvents at
	30°C 60
9	Formation Constants and the
	Limiting Chemical Shifts of
	DB30Cl0.Cs ⁺ Complexes in Various
	Solvents 66
10	Mole Ratio Study of Dibenzo-24-
	Crown-8 Complexes with 0.025 <u>M</u>
	Sodium Tetraphenylborate in
	Various Solvents at 30°C 68
11	Formation Constants and the
	Limiting Chemical Shifts of
	DB24C8·Na ⁺ Complexes in
	Various Solvents
12	Mole Ratio Study of Dibenzo-24-
	Crown-8 Complexes with 0.005 \underline{M}
	Cs [†] Ion in Various Solvents
	at 30°C
13	Formation Constants and the
	Limiting Chemical Shifts of
	DB24C8.Cs Complexes in
	Various Solvents 76

14	Mole Ratio Study of Dibenzo-24-
	Crown-8 Complexes with 0.005 \underline{M}
	TlClO ₄ in Various Solvents at
	30°C
15	Formation Constants and the
	Limiting Chemical Shifts of
	DB24C8.T1 ⁺ Complexes in Various
	Solvents 82
16	Formation Constants of 1:1 Com-
	plexes of Na^+ , Cs^+ , and Tl^+
	Ions with Dibenzo-24-Crown-8
	in Various Solvents 84
17	Mole Ratio Study of Dibenzo-21-
	Crown-7 Complexes with 0.025 \underline{M}
	NaBPh ₄ in Various Solvents at
	30°C
18	Formation Constants and the
	Limiting Chemical Shifts of DB21C7
	·Na ⁺ Complexes in Various Solvents 92
19	Mole Ratio Study of Dibenzo-21-
	Crown-7 Complexes with 0.005 \underline{M}
	CsSCN in Various Solvents at
	30°C
20	Formation Constants and the
	Limiting Chemical Shifts of

х

	DB21C7 • Cs ⁺ Complexes in Various
	Solvents 96
21	Mole Ratio Study of Dibenzo-21-
	Crown-7 Complexes with 0.005 \underline{M}
	TlClO ₄ in Various Solvents at
	30°C
22	Formation Constants and the
	Limiting Chemical Shifts of
	DB21C7·T1 ⁺ Complexes in
	Various Solvents
23	Formation Constants of 1:1 Com-
	plexes of Na^+ , Cs^+ , and Tl^+ Ions
	with DB21C7 in Various Solvents 103
24	Formation Constants of 1:1 Complexes
	of Na^+ , Cs^+ , and Tl^+ Ions with
	DB21C7, DB24C8, and DB30C10
	in Various Solvents at 30°C 106
25	Cesium-133 Chemical Shifts
	of 0.005 <u>M</u> Cs ⁺ Ion in the
	Presence of DB30Cl0 at Various
	Temperatures
26	Formation Constants of DB30C10
	•Cs ⁺ Complex in Nonaqueous Sol-
	vents at Different Temperatures 122

Table

.

27	Thermodynamic Parameters for the
	Complexation of Cs ⁺ Ion by Dibenzo-
	30-Crown-10 in Various Solvents 124
28	Cesium-133 Chemical Shifts of
	0.005 <u>M</u> Cs ⁺ Ion in the Presence
	of DB24C8 at Various Temperatures 127
29	Formation Constants of DB24C8.Cs ⁺
	Complex in Nonaqueous Solvents at
	Different Temperatures 136
30	Thermodynamic Parameters for the
	Complexation of Cs ⁺ Ion by
	Dibenzo-24-Crown-8 in Various
	Solvents 138
31	Cesium-133 Chemical Shifts of
	0.005 <u>M</u> Cs ⁺ Ion in the Presence
	of DB21C7 at Various Temperatures 140
32	Formation Constants of DB21C7 · Cs ⁺
	Complex in Nonaqueous Solvents at
	Various Temperatures
33	Thermodynamic Parameters for
	the Complexation of Cs ⁺ Ion
	by DB21C7 in Nonaqueous Solvents
	at Different Temperatures 151

Page

34	Entropies of the Complexation of
	Cesium Ion by DB30Cl0, DB24C8, and
	DB21C7 in Various Solvents 153
35	Mole Ratio Study of 1,10-Diaza-18-
	Crown-6 Complex With 0.02 <u>M</u> LiClO ₄
	in Various Solvents at 30°C 159
36	Mole Ratio Study of 1,10-Diaza-
	18-Crown-6 Complex with 0.05 M
	NaBPh ₄ in Various Solvents at
	30°C
37	Mole Ratio Study of 1,10-Diaza-
	18-Crown-6 Complex with Cs ⁺ Ion
	in Various Solvents at 30°C 161
38	Mole Ratio Study of 1,10-Diaza-18-
	Crown-6 Complexes with Tl ⁺ Ion
	in Various Solvents at 30°C 163
39	Formation Constants and the
	Limiting Chemical Shifts of
	1,10-Diaza-18-Crown-6·Li ⁺
	Complexes in Various Solvents 169
40	Formation Constants and the
	Limiting Chemical Shifts of
	1,10-Diaza-18-Crown-6·Na ⁺
	Complexes in Various Solvents 172

41	Formation Constants and the
	Limiting Chemical Shifts of
	l,10-Diaza-18-Crown-6·Cs ⁺
	Complexes in Various Solvents 175
42	Formation Constants and the
	Limiting Chemical Shifts of
	1,10-Diaza-18-Crown-6.T1 ⁺
	Complexes in Various Solvents
43	Formation Constants of Li ⁺ , Cs ⁺ ,
	and T1 ⁺ Ion Complexes of 1,10-
	Diaza-18-Crown-6 and 18-Crown-6
	in Various Solvents 179
44	Temperature Dependence of
	the Rate Constants for the
	Release of Cs ⁺ Ion from
	DB21C7·Cs ⁺ , DB24C8·Cs ⁺ , and
	DB30Cl0·Cs ⁺ Complexes in
	Acetone and Methanol
45	Exchange Rates and Thermodynamic
	Parameters for Release of Cs ⁺
	Ion from Some Large Crown
	Complexes in Acetone and
	Methanol

LIST OF FIGURES

Figure	Page	
1	Structure of Some Large Crown	
	Ethers 4	
2	Crystalline Structure of Some Metal	
	Ion-Crown Complexes. A-(KSCN) ₂ ·DB24C8,	
	B-KI·DB30C10, C-(NaSCN) ₂ DB30C10 7	
3	Sodium-23 Chemical Shifts <u>vs</u> . [DB30Cl0]/	
	[Na ⁺] Mole Ratio in Different Solvents.	
	A-Nitromethane, B-Acetonitrile, C-	
	Pyridine 54	
4	Carbon-13 Chemical Shifts at Various	
	[Metal Ion]/[DB30C10] Mole Ratios	
	(MR) in Nitromethane. A-Sodium	
	Ion at MR=0.0, 1.0, and 2.0; B-	
	Potassium Ion at MR=0.0, 0.5, and	
	1.0 	
5	Carbon-13 Chemical Shifts for	
	the Four Polyether Chain Carbon	
	Atoms at Various [Na ⁺]/[DB30C10]	
	Mole Ratios in Nitromethane 57	
6	Cesium-133 Chemical Shifts <u>vs</u>	
	[DB30Cl0]/[Cs ⁺] Mole Ratio in	

	Different Solvents. A-Nitromethane,
	B-Methanol, C-Acetone, D-Pyridine,
	E-Acetonitrile
7	Computer Fit of the Cesium-133 Mole
	Ratio Data for DB30Cl0-Cs ⁺ in
	Methanol at 30°C 65
8	Sodium-23 Chemical Shifts <u>vs</u> .
	[DB24C8]/[Na ⁺] Mole Ratio in
	Different Solvents 70
9	Cesium-133 Chemical Shifts <u>vs</u> .
	[DB24C8]/[Cs ⁺] Mole Ratio in
	Different Solvents
10	Thallium-205 Chemical Shifts <u>vs</u> .
	[DB21C8]/[T1 ⁺] Mole Ratio in Dif-
	ferent Solvents 80
11	Sodium-23 Chemical Shifts <u>vs</u> .
	[DB21C7]/[Na ⁺] Mole Ratio in
	Different Solvents
12	Cesium-133 Chemical Shifts <u>vs</u> .
	[DB21C7]/[Cs ⁺] Mole Ratio in
	Different Solvents
13	Thallium-205 Chemical Shifts <u>vs</u> .
	[DB21C7]/[T1 ⁺] Mole Ratio

Page

Page	Page	
------	------	--

14	Cesium-133 Chemical Shifts <u>vs</u> .
	[DB30Cl0]/[Cs ⁺] Mole Ratio in
	Nitromethane at Different Tem-
	peratures
15	Cesium-133 Chemical Shifts <u>vs</u> .
	[DB30Cl0]/[Cs ⁺] Mole Ratio in
	Acetonitrile at Different Tem-
	peratures
16	Cesium-133 Chemical Shifts <u>vs</u> .
	[DB30Cl0]/[Cs ⁺] Mole Ratio in
	Acetone at Different Temperatures 118
17	Cesium-133 Chemical Shifts <u>vs</u> .
	[DB30Cl0]/[Cs ⁺] Mole Ratio in
	Methanolat Different Temperatures 119
18	Cesium-133 Chemical Shifts <u>vs</u> .
	[DB30Cl0]/[Cs ⁺] Mole Ratio in
	Pyridine at Different Temperatures 120
19	Van't Hoff Plots for Complexation of
	Cs ⁺ Ion by Dibenzo-30-Crown-10 in
	Various Solvents
20	Cesium-133 Chemical Shifts <u>vs</u> .
	[DB24C8]/[Cs ⁺] Mole Ratio in Nitro-
	methane at Different Temperatures 130
21	Cesium-133 Chemical Shifts <u>vs</u> .
	[DB24C8]/[Cs ⁺] Mole Ratio in

.

Page

	Acetonitrile at Different Tem-
	peratures
22	Cesium-133 Chemical Shifts <u>vs</u> .
	[DB24C8]/[Cs ⁺] Mole Ratio in
	Acetone at Different Temperatures 132
23	Cesium-133 Chemical Shifts <u>vs</u> .
	[DB24C8]/[Cs ⁺] Mole Ratio in
	Methanol at Different Temperatures 133
24	Cesium-133 Chemical Shifts <u>vs</u> .
	[DB24C8]/[Cs ⁺] Mole Ratio in
	Pyridine at Different Temperatures 134
25	Van't Hoff Plots for Complexation
	of Cs ⁺ Ion by Dibenzo-24-Crown-8
	in Various Solvents 137
26	Cesium-133 Chemical Shifts <u>vs</u> .
	[DB21C7]/[Cs ⁺] Mole Ratio in
	Nitromethane at Different Tem-
	peratures
27	Cesium-133 Chemical Shifts <u>vs</u> .
	[DB21C7]/[Cs ⁺] Mole Ratio in
	Acetonitrile at Different Tem-
	peratures
28	Cesium-133 Chemical Shifts <u>vs</u> .
	[DB21C7]/[Cs ⁺] Mole Ratio in
	Acetone at Different Temperatures 145

29	Cesium-133 Chemical Shifts <u>vs</u> .
	[DB21C7]/[Cs ⁺] Mole Ratio in
	Methanol at Different Temperatures 146
30	Cesium-133 Chemical Shifts <u>vs</u> .
	[DB21C7]/[Cs ⁺] Mole Ratio in
	Pyridine at Different Temperatures 147
31	Van't Hoff Plots for Complexation
	of Cs ⁺ Ion by Dibenzo-21-Crown-7
	in Various Solvents 150
32	Lithium-7 Chemical Shifts <u>vs</u> .
	[DA18C6]/[Li ⁺] Mole Ratio in
	Different Solvents
33	Sodium-23 Chemical Shifts <u>vs</u> .
	[DA18C6]/[Na ⁺] Mole Ratio in
	Different Solvents 165
34	Cesium-133 Chemical Shifts <u>vs</u> .
	[DA18C6]/[Cs ⁺] Mole Ratio in
	Different Solvents 166
35	Thallium-205 Chemical Shifts <u>vs</u> .
	[DA18C6]/[T1 ⁺] Mole Ratio in
	Different Solvents 167
36	Cesium-133 NMR Spectra of 0.02 \underline{M}
	CsSCN, 0.01 \underline{M} DB21C7 Solution in
	Acetone at Various Temperatures 196

37	Cesium-133 NMR Spectra of 0.04 <u>M</u>
	CsSCN, 0.02 <u>M</u> DB21C7 Solution in
	Methanol at Various Temperatures 197
38	Cesium-133 NMR Spectra of 0.02 M
	CsSCN, 0.01 \underline{M} DB24C8 Solution in
	Acetone at Various Temperatures 198
39	Cesium-133 NMR Spectra of 0.02 M
	CsSCN, 0.01 <u>M</u> DB24C8 Solution in
	Methanol at Various Temperatures 199
40	Cesium-133 NMR Spectra of 0.01 \underline{M}
	CsSCN, 0.005 \underline{M} DB30C10 Solution
	in Acetone at Various Temperatures 200
41	Cesium-133 NMR Spectra of 0.01 \underline{M}
	CsSCN, 0.005 M DB30Cl0 Solution
	in Methanol at Various Temperatures 201
42	Arrhenius plots of log $k_b \underline{vs}$. l/T for
	the Release of Cs ⁺ Ion in Acetone
	and Methanol with Large Crown
	Ethers. A-DB30Cl0·Cs ⁺ in Methanol,
	B-DB24C8·Cs ⁺ in Methanol, C-DB30Cl0·Cs ⁺
	in Acetone, D-DB21C7·Cs ⁺ in Meth-
	anol, E-DB24C8·Cs ⁺ in Acetone,
	$F-DB21C7 \cdot Cs^+$ in Acetone

Page

LIST OF ABBREVIATIONS

- Ac Acetone
- AN Acetonitrile
- DMF Dimethylformamide
- DMSO Dimethylsulfoxide
- MeOH Methanol
- NM Nitromethane
- PC Propylene carbonate
- Py Pyridine
- TMG Tetramethylguanidine
- TMO Trimethylene oxide
- DB30Cl0 Dibenzo-30-crown-10
- DB24C8 Dibenzo-24-crown-8
- DB21C7 Dibenzo-21-crown-7
- DA18C6 1,10-Diaza-18-crown-6

CHAPTER 1

HISTORICAL REVIEW

1

1.1. MACROCYCLIC CROWN ETHERS

1.1.1. Introduction

Since Pedersen's discovery of macrocyclic polyether (crown) compounds capable of forming stable complexes with the alkali ions (1) the studies of these ligands and their complexes have become a very popular field of research. A large number of such complexes have been isolated in crystalline form and many solution studies have been carried out (2,3). Most of the investigations in solution have been done in water, methanol and/or their mixtures; such studies in other nonaqueous solutions are quite sparse.

A variety of physicochemical techniques have been used for such investigations (3); the choice of favorite technique being dictated by the systems studied as well as by the particular expertise of the investigators.

One of the most interesting characteristics of the macrocyclic compounds is their ability to selectively bind certain cations in solution in the presence of others. The selectivity and stability of crown ether complexes has been reported to be dependent on several important parameters characteristic of the ligand, the cation and the reaction medium. These parameters are: the relative sizes of cation and ligand cavity (4,5), the type and the number of donor atoms in the ring (4,6,7,8), substitution on the macrocyclic ring (9-12), type and charge

2

s ce 30 ci ar: de ex

þe
of cation (13) and the solvent effect (14-16).

Several useful review articles are available on the study of macrocyclic polyethers and their complexes (2,3, 17-19). In this thesis only the studies on the complexes of large crowns and the thermodynamics of the metalcomplex formation in solution will be reviewed.

1.1.2. Metal Ion Complexation with Large Crowns

Despite the very interesting properties of large crowns (<u>i.e.</u>, larger than 18-crown-6), not much attention has been focused on the study of the complexation of metal ions with these ligands. In comparison with approximately three hundred scientific papers on small size crowns, and in particular on different 18-crown-6 derivatives, such investigations on large crown complexes are sparse. The structure of some of these ligands are shown in Figure 1.

Pedersen (1) was the first to report the isolation of cesium ion complexes with dibenzo-24-crown-8 and dibenzo-30-crown-10 in methanol solution and to study the effect of complexation on the ultraviolet spectra of large crowns. He likewise (20) studied complexation of alkali and alkali earth cations with 21-crown-7 and 24-crown-8 derivatives using ultraviolet spectroscopy and solvent extraction methods.

The effect of dicyclohexyl-24-crown-8 on the ionic permeability of natural membranes such as HK and LK sheep







Figure 1. Structure of Some Large Crown Ethers.

red cells has been studied by Tosteson (21). He showed that this ligand notably increases potassium permeability more than sodium permeability, while the behavior is opposite in the case of cyclohexyl-15-crown-5. It has been reported (22) that cyclic polyethers exhibit specific influences on cation transport in rat liver mitochondria. Dicyclohexyl-21-crown-7 was most effective in the presence of potassium or rubidium ions. Dicycloxyl-30-crown-10 was displayed striking specifity in that it was very active with rubidium present and much less active with potassium.

The stoichiometry of crystalline complexes of alkali cations with large crowns has been investigated (23-25), and the crystalline structure of some of these complexes has been reported (26-29). The stoichiometry of such compounds depends on the relative sizes of the cation and the cavity size of the macrocycle, the flexibility of the crown molecule, and the nature of the anion and of the solvent (17). For dibenzo-24-crown-8-K⁺ and dibenzo-30crown-10-Na⁺ systems the ratio of two metal ions to one crown ether has been found so far (24).

Mercer and Truter (27) have reported the structure of the 2:1 (metal to ligand) complex between KSCN salt and dibenzo-24-crown-8, isolated from methanol solution. According to them, each one of the K^+ ions, located inside the ring, are bound to the five oxygen atoms of the

ligand, two nitrogen atoms of bridging thiocyanate groups, and two carbon atoms of a benzene ring (Figure 2a). In another publication (25). Truter and co-workers have shown that when potassium tetraphenylborate was used instead of potassium thiocyanate, only the 1:1 complex was formed since the tetraphenylborate anion cannot be coordinated with the metal ion.

The crystalline structure of the 1:1 complex between KI and dibenzo-30-crown-10 has been studied by Bush and Truter (26). They showed that the potassium ion is completely located inside the cavity which is created by the twisting of the ligand around the cation, all the oxygen atoms are coordinated with the cation to form a so called "wrap around" complex (Figure 2b).

Owen and Truter (29) recently have reported the crystalline structure of the 2:1 (metal to ligand) complex of sodium isothiocyanate with dibenzo-30-crown-1 (29), determined from x-ray diffraction measurements. Each ligand complex with two Na⁺ ions, and each cation is coordinated to six oxygen atoms in the ring and also to one isothiocyanate anion, through the nitrogen atom. The ligand is in an extended conformation, twisted so that the molecule assumes a figure eight configuration, with the Na⁺ ions at the center of two loops (Figure 2c).

The stability constants for the 1:1 complexes of large crown ethers (<u>i.e.</u>, 21, 24, 30, and 60-membered rings)



Figure 2. Crystalline Structure of Some Metal Ion-Crown Complexes. A-(KSCN)₂·DB24C8, B-KI·DB30C10, C-(NaSCN)₂DB30C10.

with alkali ions has been determined by Frensdorff (4) in water and methanol solutions using potentiometric measurements with cation-selective electrodes. He pointed out that the selectivity order is governed by the relative sizes of the cation and the cavity of the ligand. From the increase of K⁺ stability constants between 24crown-8 and 30-crown-10 it was suggested that a "wrap around" complexing might occur with polyethers, such as that observed for K⁺-valinomycin (30).

Rechnitz and Eyal (31) constructed liquid membrane electrodes with dibenzo-30-crown-10 in the membrane phase (nitrobenzene) to measure the crown's electrochemical activity, and to determine the crown-metal ion complex formation constant. The potentiometric selectivity ratio for the crown ether in nitrobenzene for the Rb⁺, Cs⁺, Na⁺, and NH_{μ}⁺ ions with respect to K⁺ ion has been determined, and formation constants of rubidium and potassium ion complexes with dibenzo-30-crown-10 have been reported. The ΔG° and ΔH° parameters for complex formation of dibenzo-30-crown-10 and Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, NH₁⁺ and T1⁺ in methanol has been determined by Chock (32), who has studied the ultraviolet spectra of the ligand at different temperatures. With the exception of the ammonium ion, a good correlation between the stability constant of the complex and the size of metal ion was observed.

In an attempt to elucidate the solution structure of a number of crown ethers. Live and Chan (33) carried out a careful measurement on the ^{1}H and ^{13}C NMR spectra of the ligands and their metal complexes in water, wateracetone, acetone, and chloroform solutions. From the data. the authors have concluded that the structure of K^+ dibenzo-30-crown-10 in solution is similar to that in crystalline state (26) where K^+ ion is completely surrounded by the ligand to form a "wrap around" complex. On the basis of the proton NMR spectrum of Na⁺ dibenzo-30-crown-10 complex in acetone, which did not resemble the one for K⁺, they proposed a twisted configuration for the complex Their ¹³C NMR results support these concluin solution. sions. The stability constants for 1:1 complexes of the ligand with Na⁺, K⁺, and Cs⁺ in acetone have been determined from the ¹H NMR data.

Izatt and co-workers (3^4) have reported thermodynamic parameters for complexation of Na⁺, K⁺, Rb⁺, and Cs⁺ ions with dibenzo-24-crown-8 and dibenzo-27-crown-9 in methanolwater mixtures which have determined calorimetrically. They pointed out that the entropy changes for a 1:1 reaction of a given cation become more negative with increased size of the polyether ring which seem to indicate an increased conformational change of the ligand upon complex formation.

The stability of thallium and alkali metal ion

С a Ľ. u: Vθ c: 0: 1-<u>1r</u> сc me c] 11. cr ti ri cor are complexes with dibenzo-24-crown-8, dibenzo-30-crown-10 and their benzo group derivatives in acetonitrite and methanol has been investigated by Mittal and co-workers using polarographic methods (35). The nature of the solvent was found to affect the stability constants of the complexes.

Recently, Lehn and co-workers (36) reported formation of stable and selective complexes between guadinium and imidazolium ions and chiral hexacarboxylate-27-crown-9 in aqueous solution. The stability constants of the complexes were measured potentiometrically by a competition method using a $\rm NH_{ll}^{+}$ -selective electrode. They have concluded that the presence of anionic carboxylate groups in the ligand markedly increases the stability of the crown complexes and that the selectivity of the complexation arises from central discrimination of the macrocyclic ring.

The literature reported thermodynamic values for the complexation reaction of metal ions with large crowns are listed in Table 1.

Ĉ Thermodynamic Parameters for the Complexation of Lange Table 1.

	Cations	s in Solutio	'n.				
Ligand	Cation	Solvent	Method	Log K _f	AH (Kcal/mole)	∆S (cal/mole deg)	Ref.
21C7	к+	MeOH	pot	4.41	8	8	7
	Cs+	MeOH	pot	5.02	8 8 1 1	6 8 1	-7
DC21C7	Cs+	water	pot	1.9	8	6 8 3	4
DB21C7	Na+	MeOH	pot	2.4	8 8 8	1	4
	¥+	MeOH	pot	4.30	8	L I I I	4
	Cs+ 0	MeOH	pot	4.20	5 8 5 8	8	4
24C8	+×	MeOH	pot	3.48	6 8 8 8	8 8 8	4
	Cs+	MeOH	pot	4.15	8 8 8		4
DC24C8	Cs+	water	pot	1.9	8 8 8	8	4
DB24C8	Na+	AN	polarog	4.00	8	1 0 1 1	35
		70% MeOH	cal	1.54	-7.75	-18.9	34
	к+	AN	polarog	3.70	1	8 8 8	35
		MeOH	polarog	3.20	8	8	35
		MeOH	pot	3.49	6 1 8 8	8 8 1	4
		70% MeOH	cal	2.42	-8.54	-17.6	34
	Rb+	70% MeOH	cal	2.55	-8.72	-7.6	34
	Cs+	AN	polarog	3.80		8	35

Thermodynamic Parameters for the Complexation of Large Crown Ethers with Table 1.

Ligand	Cation	Solvent	Method	Log K _f	AH (Kcal/mole)	ΔS (cal/mole deg)	Ref.
	Cs+	МеОН	pot	3.78	8	1	4
		70% MeOH	cal	2.48	-8.93	-18.6	34
	+11	AN	polarog	4.80	8	8	35
		MeOH	polarog	3.40	L 3 8	L 1 1	35
DB27C9	Na+	70% MeOH	cal	1.50	-11.74	-32.5	34
	+ *	70% MeOH	cal	2.86	-9.50	-18.8	34
	Cs+	70% MeOH	cal	1.42	-6.14	-14.1	34
DB30C10	Na+	MeOH	pot	2.0	8 8 8	8	4
		MeOH	spec	2.11	-4.0	-3.7	32
		AN	polarog	3.60	8 8 8	8	35
		AC	NMR	2.54	8	8	33
	к+	MeOH	pot	4.60	1 8 1 1	 	4
		MeOH	spec	4.57	-11.5	-17.7	32
		MeOH	polarog	3.90	8	1 1 1 5	35
		AN	polarog	4.70		8	35
		AC	NMR	4.30	8 8 8	8 8 8	33
		50% THF	pot	1.35	8 8 1	8 8 8	31
	Rb+	МеОН	spec	4.64	-12.7	-21.4	32

Table 1. Continued.

Table 1. Continued

Ligand	Cation	Solvent	Method	Log K _f	ΔH (Kcal/mole)	ΔS (cal/mole deg)	Ref.
	Rb ⁺	AN	polarog	4.70		8	35
		50% THF	pot	1.56	L 	1 1 1	31
	Cs+	MeOH	spec	4.23	-11.2	-18.2	32
		AN	polarog	3.50	8	8 8 8	35
		AC	NMR	4.23	1	1 6 1	33
	ד ו +	MeOH	spec	4.51	-11.0	-16.3	32
		MeOH	polarog	4.10	7 1 8		35
		AN	polarog	5.60	l 1 1 1	8 8 8 1	35
	+ [¶] HN	МеОН	spec	2.43	-5.5	-7.3	32
DB60C10	к+1	MeOH	pot	3.90	8	8	ħ

Table 1. Continued.

e: e: £. er 52 πc tĿ

1.1.3. Thermodynamics of Metal-complex Formation in Solution

1.1.3.1. <u>Open Chain Ligands</u> - The thermodynamics of metal ion complexes of a number of polyamine systems have been investigated calorimetrically by Paoletti <u>et al</u>. (37-40) in aqueous solutions. The ligand studies were diethylene triamine (dien) (30), n=1; triethylene tetramine (trien) (38), n=2; tetraethylenepentamine (tetren) (39), n=3; and N,N,N',N'-tetra-(2-aminoethyl)-ethylenediamine (Penten) (40). Some of the thermodynamic data for these complexes are listed in Table 2.

H₂N-CH₂-CH₂+CH₂-CH₂+nNH₂

Polyamines' Structure

It is seen that there is a tendency for successive enthalpy changes to become more exothermic, while the entropy changes for 1:1 complexes are positive, those for the second step reactions are negative. The overall entropy changes, however, are positive in all cases and the complexes are both enthalpy and entropy stabilized.

The nature of the chelate effect can be examined in more detail using the available thermodynamic data for the polyamine complexes for the following reaction.

M ²⁺	∆G (Kcal/mole)	ΔH (Kcal/mole)	ΔS (cal/mole deg)
Co ²⁺ +dien	-10.90	-8.15	9.0
Codien ²⁺ +dien	-8.00	-10.25	-7.5
Ni ²⁺ +dien	-14.45	-11.85	8.5
Nidien ²⁺ +dien	-10.90	-13.45	-8.5
Cu ²⁺ +dien	-21.55	-18.00	12.0
Cudien ²⁺ +dien	-7.10	-8.15	-3.5
Zn ²⁺ +dien	-12.00	-6.45	18.5
Zndien ²⁺ +dien	-7.50	-10.15	-9.0

Table 2. Thermodynamic Data for Diethylenetriamine Complexes with Some Metal (II) Ions in 0.1 <u>M</u> KCl at 25°C.

h 4 С t. 1 er St in th an

$$M(NH_3)_n^{2+} + L \ddagger ML^{2+} + n NH_3$$
 (1)

Some of the results obtained are shown in Table 3. It can be seen that the complexes are stabilized with respect to the corresponding ammonia complexes not only by enthalpy changes but also by the large positive entropy changes for the reactions. From the data, it is clear that the large negative free energy changes can be attributed to the positive entropy changes accompanying the release of increasing numbers of ammonia molecules.

Extensive calorimetric studies have been made of the formation of metal complexes with aminopolycarboxalate ions such as ethylendiamine tetraacetic acid and its homolagues (42-48). Schwarzenbach (41) has shown that in ligands with more than two donor atoms the presence of a nitrogen atom meets the requirements for the formation of relatively strain-free chelate rings. These ligands have been found to be stabilized by positive entropy changes resulting from charge neutralization and subsequent solvent release from the solvation shells of interacting ions. Thermodynamics data are obtained from those available for methyliminodiacetate (mIDA) (42) and ethylendiamine tetraacetate homologues:

M ²⁺	L	∆G (Kcal/mole)	∆H (Kcal/mole)	ΔS (cal/mole) deg)	Ref.
N1 ²⁺	dien	-5.33	-1.35	13.4	37
Cu ²⁺	dien	-7.24	-3.00	14.2	37
N1 ²⁺	trien	-8.09	0	27.1	38
Cu ²⁺	trien	-10.20	-1.55	29.0	38
V1 ²⁺	tetren	-12.10	-1.40	35.9	39
2+	tetren	-14.65	-1.75	43.3	39
Vi ²⁺	penten	-15.44	+1.35	56.0	40

Table 3. Thermodynamic Data for Metal (II)-Polyamine Complexes (Chelate Effect).

1	
	(
T	
	~
	wł
	pa
	ch
	are
	Che
	1s
	£at.
T	numi
	hora



in which n=2 for EDTA (42); n=3 for TMTA (44); n=4 for TETA (44); n=5 for PETA (45); n=6 for HDTA (45); and n=8 for ODTA (45).

The existence of thermodynamic data on mIDA and EDTA metal complexes (mIDA constitutes one half of EDTA) makes it possible to examine the chelate effect in more detail considering the following reaction.

$$M(mIDA)_{2}^{2-} + EDTA^{4-} \ddagger MEDTA^{2-} + 2mIDA^{2-}$$
 (2)

The data for the above reaction is given in Table 4. The positive values for ΔS clearly show the chelate effect which reflects the increase in the number of solute particles in the reaction (2). The endothermic enthalpy changes for some of the metal ions such as Ca²⁺ and Mn²⁺ are probably due to the strain involved in fitting another chelate ring around the metal ions. The chelate effect is smallest with these metal ions.

Another interesting point to consider is to investigate the variation of the chelate effect with n, the number of methylene groups in the central chain of EDTA homologues. The following reaction should be considered:

M2+	ΔG (Kcal/mole)	ΔH (Kcal/mole)	ΔS (cal/mole deg)
 Mg ²⁺	-3.65	1.31	17.1
Ca ²⁺	-5.27	-4.62	2.7
Mn ²⁺	-5.68	-4.33	3.1
Co ²⁺	-3.21	1.28	15.3
N1 ²⁺	-3.57	0.10	12.5
Cu ²⁺	-1.17	3.96	17.4
Zn ²⁺	-3.23	0.98	14.6
Ca ²⁺	-5.27	-1.78	11.9

Table 4.	Thermodynamic I	Data for	Reaction	(2)	for	Dif-
	ferent Metal (1	II) Ions.	•			

$$M(mIDA)_2^{2-} + L^{4-} \stackrel{*}{\to} ML^{2-} + 2mIDA^{2-}$$
 (3)

Anderegg in a series of publications (41-45) has reported the thermodynamic data for several metal (II) ion complexes with EDTA and its homologues. He has pointed out that an increase in the number of methylene groups causes the stability of ML to decrease rapidly. The entropy changes were not appreciably different, indicating that the coordination in the complexes is approximately the same.

The factors involved in determining enthalpies and entropies of metal chelate formation in aqueous solution (100) are given below:

Enthalpy Effects

Variation of bond strength with electronegatives of metal ions and ligand donor atoms. Ligand field effects. Steric and electrostatic repulsions between ligand donor groups in the complex. Enthalpy effects related to the conformation of the uncoordinated ligand. Other coulombic forces involved in chelate ring formation.

Entropy Effects

Number of chelate rings. Size of the chelate ring. Changes of solvation on complex formation. Arrangement of chelate rings. Entropy variations in uncoordinated ligands. Effects resulting from differences in configurational entropies of the ligand in complex compounds.

1.1.3.2. <u>Cyclic Ligands</u> - It has been shown that cyclic ligands form much more stable complexes than their corresponding open chain analogs with metal ions. This enhancement in stability was called the "macrocyclic effect" first by Cabbiness and Margerum (46) who observed an appreciable enhancement in the stability of copper complex with a tetramine macrocyclic ligand compared to similar non-cyclic tetramine ligands. According to them the important factors responsible for this effect are the solvation and the configuration of the ligand.

On the basis of the results obtained from a study of copper (II)-tetramine complexes, Paoletti <u>et al</u>. (47) proposed that both entropy and enthalpy terms contribute to the macrocyclic effect, in contrast to the chelate effect which results only from an entropy factor. In a later publication on the study of Ni(II)-tetramine complexes

in water, Hinz and Margerum (48) concluded that the enhanced stability with the cyclic vs. the open-chain ligand is almost entirely due to a more favorable enthalpy change. They have pointed out that the release of water from the metal ion and the ligand results in a positive entropy contribution because the number of independent particles would increase, but this positive contribution is offset by a negative contribution due to the loss of configurational entropy of the ligand upon complexation. The noncyclic ligand would be expected to undergo a much larger loss of configurational entropy than the cyclic ligand. Dei and Gori (49) also emphasized the enthalpy stabilization to explain the macrocyclic effect in a study of ΔH of Cu (II)-tetramine complexes in water.

Kodoma and Kimura (50,51) studied polarographically the complexation of copper (II) with 1,4,7,10-tetrazacyclododecane in water. They found that the stability constant for the 1:1 complex is more than 10^4 -fold greater than that for corresponding open-chain tetraamine. Despite the unfavorable enthalpy term, the large increase in the stability of the copper complex with the cyclic ligand was entirely attributed to the favorable entropy term. The same authors (52) determined thermodynamic values for the complexation of 18-crown-6 and tetraglyme with Pb²⁺ and Tl⁺ ions using polarographic measurements. Again, the stabilities of macrocyclic complexes were much greater

than those of tetraglyme complexes, and this macrocyclic effect was explained in terms of entropy. Frensdorff (4) has also compared the stability of Na⁺ and K⁺ complexes with 18-crown-6 and pentaglyme in methanol. He has noted a 10^3 to 10^4 enhancement of the stability constant of cyclic ligand complexes.

Recently Arnud-neu <u>et al</u>. (52) have reported results of calorimetric and radiocrystallographic studies of Cu (II) and Pb (II) complexes in aqueous solution with 1-oxa-4,13,dithia-7,10-diaza-cyclopentadecane and its corresponding open-chain homolog. According to the above authors macrocyclic effect is both enthalpy and entropy dependent.

One of the first thermodynamic studies on the metal ion-crown complexes by calorimetric titration has been done by Izatt and co-workers $(53,5^4)$ who determined the stability, the enthalpy, and the entropy values for the complexation reaction between different metal ions and dicyclohexyl-18-crown-6 in aqueous solution. The alkali metal ion stability order was found to be identical with the permeability order for these metal ions with the antibiotics valinomycin and monactin. All complexes were enthalpy stabilized but entropy destabilized. Thermodynamic properties of alkali complexes of various carrier antibiotics in methanol and ethanol by Simon <u>et al</u>. (55-57). They used a computerized microcalorimeter for the

thermodynamic measurements.

Schori and Jagur-Grodzinski (58) have studied the thermodynamics of the complexation of dibenzo-18-crown-6 and its derivatives with sodium ion in dimethylformamide and dimethoxyethane solutions at different temperatures by electrical conductance measurements. In dimethoxyethane as solvent, the complexation reaction was found to be both enthalpy and entropy driven. Hogen-Esch and Smid (59) also used conductometric measurements to study the thermodynamics of the dissociation of fluorenyl salts and their complexes with dimethyldibenzo-18-crown-6 in tetrahydrofuran and tetrahydropyran. The complexes were found to be entropy destabilized in both solvents.

Izatt and co-workers (60) have reported Log K, ΔH , and ΔS values for the 1:1 complexes of Na⁺, K⁺, Rb⁺, Cs⁺, Ag⁺, Tl⁺, NH⁺₄, CH₃NH⁺₃, Ba²⁺, Ca²⁺, Sr²⁺, Pb²⁺, and Hg²⁺ ions with 15-crown-5, 18-crown-5, 18-crown-6 and different isomers of dicyclohexo-18-crown-6 in water which were determined by calorimetric titration. For most of the complexation reactions they studied both the entropy and the enthalpy were negative. The authors could not find any reproducible trends in ΔH or ΔS among the reactions studied to be able to explain the macrocyclic effect.

Izatt <u>et al</u>. (61) synthesized new crown ethers by introducing a pyridine ring in 18-crown-6 capable of

forming stable complexes with many metal ions. They studied the thermodynamics of complexation of these ligands with Na⁺, K⁺, Ag⁺ and Ba²⁺ ions in methanol using calorimetric measurements. The ligands were found to form unusually stable complexes with the above ions in which the entropy term favors complexation of the ligands over 18-crown-6 (more negative ΔS) but the enthalpy term does not (more positive ΔH). The same authors (62) synthesized two ligands analogous to 18-crown-6 having carbonyl groups available for cation complexation as does valinomycin. They determined log K, ΔH , and T ΔS values for the reaction of these ligands with Na^+ , K^+ , and Ba^{2+} ions in methanol. The decreased stabilities of the cation complexes with these ligands, compared with those with 18-crown-6, were found to be due to less exothermic ΔH values, but more favorable $T\Delta S$ values.

Mei <u>et al</u>. (63,64) studied the thermodynamics of complexation of Cs⁺ ion with 18-crown-6 in various nonaqueous solvents by cesium-133 NMR. The behavior of the ¹³³Cs chemical shift as a function of 18-crown-6/Cs⁺ mole ratio indicates a two step reaction, first formation of a stable 1:1 complex followed by the addition of a second molecule of the ligand to give a 2:1 sandwich compound. It was found that the stability of the 2:1 complex in pyridine increases with decreasing temperature and that the complex is enthalpy stabilized but entropy

destabilized.

Izatt <u>et al</u>. (65) determined calorimetrically the free energy, enthalpy, and entropy of complexation of ammonium and substituted ammonium cations with 18-crown-6 again in methanol solution. The complexes with secondary and tertiary ammonium ions were found to be much weaker than those with the primary amines. The binding of all these ions involves hydrogen bonding with ether oxygens in addition to the ion-dipole forces. The thermodynamics of 18-crown-6 complexes with arenediazonium and anilinium salts in methanol have also been studied by the same authors (66).

Izatt <u>et al</u>. (67) have compared the stabilities of several sulfur derivatives of 9-crown-3, 12-crown-4, 15-crown-5, 18-crown-6, and 24-crown-8 complexes with Ag^+ , Tl^+ , Pb^{2+} , and Hg^{2+} ions with their polyether analogs. Values of log K, ΔH , and ΔS have been reported for the different complexes in water or water-methanol sol. Many of cyclic thio ethers were found to form 1:2 (cation to ligand) complexes with Ag^+ and Hg^{2+} ions but only 1:1 complexes were found for Tl^+ and Pb^{2+} ions.

Despite existence of much thermodynamic data on the various complexes with cyclic polyethers and their noncyclic analogs, the source of the macrocycle effect has not been completely defined, and further investigation seems to be needed to have a general understanding of this effect.

1.2. NUCLEAR MAGNETIC RESONANCE

1.2.1. Introduction

Since the discovery of nuclear magnetic resonance (NMR) spectroscopy in the 1940's (68,69) this technique has had a spectacular growth and a wide application to many chemical problems. Because of its steady development, both theoretical and instrumental, nuclear magnetic resonance spectroscopy has now reached such an advanced stage that it is a nearly indispensable tool with chemists.

In recent years the use of nuclear magnetic resonance has become quite popular in studies of electrolyte solutions. This is because of the presence of extremely rapid and generally random molecular motions in electrolyte solutions which can result in narrow resonance lines even for nuclei with quadropole moment. Proton NMR is useful for the studies of ionic interactions as well as for the determination of solvation numbers. Resonance frequencies of metal ions are very sensitive probes of the immediate chemical environment of metal cation and therefore can detect very weak ion-ion, ion-ligand, and ion solvent interactions. Despite this tremendous sensitivity to environment, metal ions give a generally weak resonance signal which necessitates special instrumentation for measurement of the interactions.

1.2.2. Chemical Shift Measurements

Only nuclei possessing angular momentum P (nuclear spin I) are suitable probes for nuclear magnetic resonance. The angular momentum imparts a magnetic moment $\mu = \gamma P$ to these nuclei. The ratio γ between the magnetic moment and the angular momentum is designated as the magnetogyric ratio.

When the spinning nuclei are placed in a magnetic field, ${\rm H}_{\rm o}$, their spin axes precess about the field direction. By increasing the strength of the magnetic field, the nuclei cannot be forced to become aligned with the field direction, but they only precess faster. They can be made to flip over, however, by applying a second, much weaker magnetic field, H_1 , at right angles to H_0 , and causing this second field to rotate at exactly the precession frequency v_0 . The magnetic vector of a radio-frequency field supplied by a transmitter coil with its axis perpendicular to H_0 , is used for this purpose conveniently. When the frequency of this field equals v_0 , the nuclei flip over and induce a voltage in a receiver coil placed at right angles to both H_0 and the transmitter coil. This voltage can be amplifield and recorded conveniently. Alternatively, both coils can be combined in one and the flipping of the nuclei can be observed as an absorption of energy from the radiofrequency field.

According to quantum mechanics there are 2I + 1 possible orientations for a magnetic nucleus in an external field of strength H_0 . The energy level separations are given by:

$$\Delta E = \frac{\mu H_0}{I} = \chi H_0 h$$

where h is Plank's constant divided by 2π and μ is the magnetic moment. The transitions occur between the levels by irradiation of the Larner frequency, equal to the energy separation of the nuclear spin states. Actually, resonance occurs at the field experienced by the nucleus, H, which is different from H_0 , given by

$$H = H_{\gamma}(1-\sigma)$$

where σ is known as screening (or shielding) constant.

According to Ramsey equation (70-72) the screening constant, σ , is the sum of various diamagnetic (shielding) and paramagnetic (deshielding) contributions:

$$\sigma = \sigma_d + \sigma_p$$

where σ_p and σ_d are the paramagnetic and diamagnetic components, respectively. He expressed these terms theorem retically from perturbation theory as follows:

$$\sigma = \frac{e^2}{2mc^2} \{ \langle \psi_0 |_{K}^{\Sigma} \frac{r^2 \kappa^2 - \hat{r}_{K} \hat{r}_{K}}{r_{K}^3} | \psi_0 \rangle +$$

$$\sum_{m} (E_{0} - E_{m})^{-1} [\langle \psi_{0} | \sum_{K} \hat{\ell}_{K} | \psi_{m} X \psi_{m} | \sum_{K} \frac{\hat{\ell}_{K}}{r_{K}^{3}} | \psi_{0} \rangle]$$

where

- e : electronic charge
- m: mass of the electron
- c : velocity of light
- $\boldsymbol{\hat{\iota}}_{K}$: angular momentum of the $\textbf{K}^{\texttt{th}}$ electron
- r_{K} : radial distance of the Kth electron from the Kth electron from the origin at the nucleus.

The diamagnetic component, σ_d , depends on ground state electronic wave functions and is a function of the symmetry of the electronic distribution and the density of circulating electrons. The magnitude of the paramagnetic contribution, σ_p , is zero for ions with spherically symmetrical S states but it is substantial for atoms involved in chemical bonding. It is determined by several factors. (i) The inverse of the energy separations ΔE between ground and excited electronic states of the molecule. (ii) The relative electron densities in the various p, d, and higher states involved in bonding, <u>i.e.</u>, upon the degree of asymmetry in electron distribution near the nucleus. (iii) The value of $\langle 1/r^3 \rangle$, the average inverse cube distance from the nucleus to the orbitals concerned. Usually the contributions to σ_d and σ_p for a nucleus are considered only for the electrons immediately neighboring, or local to, that nucleus. More distant electrons give rise to long range effects on both σ_p and σ_d which are large but cancel to make only a small net contribution to σ . Generally, downfield shifts are referred to as paramagnetic and upfield shifts as diamagnetic.

Kondo and Yamashita (73) have proposed the theory of paramagnetic interaction. They suggested that the paramagnetic shift of cations and anions in alkali halide crystals is due to the short range repulsive forces between the closed shell of the ions. These forces can excite p orbital electrons of the alkali nuclei to the higher states, so that the net result would be a decrease in the shielding of the nucleus.

The success of the Kondo-Yamashita theory in interpreting chemical shifts in solids suggested that it may also provide some way for interpretation of the chemical shifts in solution. In this case, however, the problem is more complex. In solids the relative positions and distances of separation of the ions are known, but in the solution the environment of the nucleus will vary randomly with time because of the diffusion of the ions and solvent molecules through the solution and the observed chemical
shift will result from an average of many instantaneous values.

Deverell and Richards (74) applied Kondo-Yamashita theory to provide a qualitative interpretation of the cation chemical shifts in aqueous solutions. They suggested that at infinite dilution, where the only interactions present are between the ion and water molecules, the contribution to the paramagnetic chemical shift is

$$\sigma_{aq}^{o} = -16\alpha^{2} < \frac{1}{r^{3}} >_{np} \cdot \frac{1}{\Delta} \cdot \Lambda^{o}$$
 ion-water

where α is the fine-structure constant, $\langle \frac{1}{r^3} \rangle_{np}$ is the average over the outer p orbitals of the central ion, Δ is the mean excitation energy, and $\Lambda_{\text{ion-water}}^{\circ}$ is an approximate sum of the overlap integrals of the orbitals of the central ion and surrounding water molecules.

By increasing the concentration of the solution the interactions between the ions during the collisions will also contribute to the chemical shift. The chemical shift at concentration of c can be expressed as:

$$\sigma = -16\alpha^{2} < \frac{1}{r^{3}} np \cdot \frac{1}{\Delta} \cdot \left[\Lambda_{\text{ion-water}}^{(c)} - \Lambda_{\text{ion-ion}}^{(c)}\right]$$

where $\Lambda_{\text{ion-water}}^{(c)}$ and $\Lambda_{\text{ion-ion}}^{(c)}$ represent the ion-water and ion-ion, respectively. Ikenberry and Das introduced a more exact equation by including the effects of overlap and charge transfer covalency. The magnitude of paramagnetic screening for an alkali nucleus is proportional to $\langle \frac{1}{r^3} \rangle_{\text{np}} \cdot \frac{1}{\Delta}$. Since the $\langle \frac{1}{r^3} \rangle$ and $\frac{1}{\Delta}$ both increase with increasing atomic number (75), the magnitude and the range of σ_p increases from Li⁺ to Cs⁺ ions. Therefore, the range of chemical shift varies from about 10 ppm for Li⁺ to several hundred ppm for Cs⁺ ion.

1.2.3. Multinuclear NMR Studies of the Complexation of T1⁺ and Alkali Ions in Solution

During the past decade the use of multinuclear NMR for the studies of the thermodynamics and kinetics of reactions in solutions has been expanded very rapidly. In particular, multinuclear NMR has been widely used to study the behavior of alkali ions in solutions.

Since the advent of new macrocyclic ligands, such as crowns, discovered by Pedersen (1), and cryptands, discovered by Lehn (76), capable of forming strong complexes with alkali ions, the studies of the alkali ion complexes with these ligands have become a very popular field of research. Among a variety of physicochemical techniques used for such investigations, alkali metal NMR has been shown to be very popular.

The nuclear properties of alkali elements as well as of thallium are shown in Table 5. All alkali nuclei have at least one isotope with non-zero spin. In all cases I is equal or greater than 1/2 and, therefore, the nuclei have a quadropole moment. Thus it should be expected that the alkali resonances would have broad lines. In practice, however, the natural line width of ²³Na and specially of 7 Li, 133 Cs and 205 Tl nuclei are quite narrow so that in most cases chemical shifts can be measured precisely. Relative sensitivities are generally adequate for all of them except 39K. Thallium-205 is shown to be an ideally suited NMR probe for potassium in biological systems. The chemical properties and ionic radii (1.44 Å and 1.54 Å)of K^+ and Tl^+ are similar so that Tl^+ can replace K^+ in several enzymes without loss of activity.

Lithium-7 NMR has been used for determining formation constants of lithium complexes with pentamethylentetrazole in nitromethane (77). It was found that lithium ion forms a fairly strong complex with a convulsant tetrazole in nitromethane.

Lithium ion complexes with cryptands C222, C221 and C211 in water and in several non-aqueous solvents have been studied by Cahen <u>et al</u>. using ⁷Li NMR technique (78). They showed that the first two ligands form weak 1:1 complexes with Li⁺ ion in solvents of low donicity such as nitromethane. On the other hand, cryptand 211 was found

Sensitivity Relative to lH at Constant Field	0.294	9.27 x 10 ⁻²	5.08 x 10 ⁻⁴	0.177	4.74 x 10 ⁻²	0.192
Spin	3/2	3/2	3/2	3/2	7/2	1/2
Natural Abundance (<i>X</i>)	42.57	100	93.08	72.8	100	70.48
NMR Frequency (MHz) at 14.09 Kgauss	23.315	15.868	2.800	19.630	7.864	34.319
Nucleus		²³ Na	39 K	⁸⁷ Rb	133 _{Cs}	205 _{T1}

.

Nuclear Properties of Alkali Elements and Thallium. Table 5. to form much more stable complexes and two 7 Li resonances (corresponding to the free and the complexed Li⁺) were observed for solutions containing excess of the Li⁺ ion. The resonance of the Li⁺ ion inside the cryptand cavity was found to be completely independent of the solvent indicating that the ligand completely insulates the cation from the solvent.

The kinetics of the complexation reaction of the Li⁺ ion with cryptand C211 in water and several non-aqueous solvents have been investigated by temperature-dependent ⁷Li NMR (79). The activation energy for the release of Li⁺ from the complex was found to be larger in solvents with higher Gutmann donor number. The exchange rates and thermodynamic parameters of lithium cryptate exchange in various solvents were determined from the ⁷Li NMR temperature-dependent data.

Hourdakis and Popov (80) have used ^{7}Li , ^{23}Na , and ^{133}Cs NMR to study alkali complexes with cryptand C222-dilactam in various solvents. They found out that the complexing ability of the dilactam is similar to, but weaker than, that of the cryptand C222. Recently, Smetana and Popov (81) have studied complexes of Li⁺ ion with several crowns in various solvents using ^{7}Li NMR.

Sodium 23 NMR measurements have been obtained on many antibiotic ionophores in chloroform and methanol solutions (82). In all cases, addition of ionophores to the sodium

ion solution broadens the 23 Na resonance lines. Despite the similar nature of the complexes, the 23 Na chemical shifts were found to be very different for different antibiotics. The complexation of Na⁺ ion with pentamethylene tetrazole in nitromethane has also been studied by 23 Na NMR (83).

Addition of the crowns, such as 18-crown-6 derivatives, to the sodium salt solutions of various solvents (84,85) has been shown to result in a very appreciable broadening of the sodium-23 resonance so that the resonance line could not be detected. This is because most crown ethers tend to form two-dimensional complexes with the alkali ions which could distort the spherically symmetrical electric field around the solvated sodium ion and, therefore, broaden the ²³Na resonance line.

Grandjean <u>et al</u>. (86) have determined the thermodynamic parameters for complexation of a heptadentate noncyclic crown ether with Na⁺ ion in pyridine by 23 Na-NMR spectroscopy. Using 23 Na resonance line broadening measurements, they have determined the relaxation rate, and by measurement of relaxation rate as a function of composition have calculated complex formation constants at different temperatures. From the resulted thermodynamic parameters they have concluded that the complex has a "wrap around" structure.

Sodium-23 NMR has been extensively used to study the

exchange kinetics of Na⁺ ion with crowns (87,88) and cryptand (89,91) in different solvents. Shchori <u>et al</u>. (87,88) have investigated the kinetics of Na⁺ complexes of dicyclohexyl-18-crown-6 and dibenzo-18-crown-6 and its derivatives in various solvents. The life times of free and complexed sodium ion and the pseudo first-order rate constant for the decomplexation reaction have been found from line shape analysis as a function of temperature. Different substituent groups on the ligands had a significant effect on the decomplexation reaction.

Dye and co-workers (89,91) obtained two 23 Na resonance signals for Na⁺-C222 cryptate solutions with the excess of the sodium salt in various solvents. One resonance corresponds to the sodium ion inside the cryptand cavity, and the other corresponds to the uncomplexed solvated sodium ion. The rate constants, activation energies and thermodynamic parameters for the decomplexation reaction were obtained from line shape analysis of the 23 Na NMR temperature-dependent data.

Shih and Popov (92) studied complexation reaction between K^+ ion and several crowns and cryptands in various non-aqueous solvents by ³⁹K NMR spectroscopy. They found evidence for formation of an inclusive complex between K^+ ion cryptand C222 but an exclusive one for K^+ -C221 cryptate in solution. The K^+ -18-crown-6 complexes were found to be quite stable in non-aqueous solvents. The 15-crown-5's

were found to form both 1:1 and 2:1 sandwich complexes with K^+ in all non-aqueous solvents used.

Shporer and Luz (93) studied the longitudinal relaxation time T_1 of the potassium-39 nucleus as a function of temperature in methanol solutions in the presence of dibenzo-18-crown-6 using ³⁹K-NMR technique. The rate of the decomplexation reaction and the activation energy for the reaction were then calculated from the resulting data.

Popov and co-workers (63,96,94-96) have obtained interesting results from a cesium-133 NMR study of both the kinetics and thermodynamics of crowns and cryptands complexes with Cs⁺ ion in non-aqueous solvents. From ¹³³Cs chemical shift measurement as a function of ligand to metal ion mole ratio, they have obtained evidence of a two-step complexation reaction between Cs⁺ ion and 18crown-6's ligands (63,64,94). The formation of a 1:1 complex is followed by the addition of a second molecule of crown to give a 2:1 sandwich complex. The thermodynamic and kinetic parameters for the two step reaction of Cs⁺ ion with 18-crown-6 in pyridine have been obtained from the mole ratio data at different temperatures (64).

The chemical shift of the 133 Cs resonance was studied as a function of cryptand C222 to Cs⁺ at various temperatures in different solvents (95). The formation constants for Cs⁺-C222 cryptate were then determined from the resulting data. The limiting chemical shifts for Cs⁺-C222

complex in dimethylformamide, propylenecarbonate and acetone were found to approach to the same value at about -100°C. From these results the authors suggested that the complex is exclusive at higher temperatures but inclusive at lower temperatures. The thermodynamic parameters were calculated by analysis of the data obtained at different temperatures.

Thallium-205 NMR has been used to study the metal ion binding to biological macromolecules such as pyruvate kinase (97). It also has been used to investigate complexation of Tl⁺ ion with crowns (98) and antibiotics (99).

1.3. CONCLUSIONS

From the above discussion, it is evident that multinuclear NMR provides a very powerful tool for studies of complexation reactions in solution. The full potential of this method has not been realized; however, with continuous improvement in NMR instrumentation its increasing usefulness for different kinds of studies can be predicted. Information on the thermodynamics and kinetics of complexation reaction can also be obtained by this method. The subject of this thesis is a multinuclear NMR study of thermodynamics and kinetics of large crowns in various nonaqueous solutions.

CHAPTER 2

EXPERIMENTAL PART

2.1. SYNTHESIS AND PURIFICATIONS OF LIGANDS

2.1.1. Synthesis of Dibenzo-30-Crown-10

The method for synthesis of dibenzo-30-crown-10 was essentially based on Pedersen's (1) published method for the synthesis of benzo-15-crown-5. By reacting catechol with 1,11-dichloro-3,6,9-trioxaundecane both benzo-15crown-5 and dibenzo-30-crown-10 are formed. The main product of the reaction is benzo-15-crown-5. The procedure is slightly modified for separation of dibenzo-30-crown-10 from benzo-15-crown-5.

Catechol (88 g, 0.8 mole) was dissolved in 800 ml of dried n-butanol containing 0.8 mole of KOH (53 g, 85% pure) in a 2.5 liter three necked flask, equipped with a thermometer, a dropping funnel, and a condenser. The equipment was under a nitrogen atmosphere. The mixture was heated to reflux, when solution became muddy-whitegreenish in color.

1,11-Dichloro-3,6,9-trioxaundecane (93 g, 0.4 mole), prepared according to Pedersen's method (1), was then added dropwise over four hours with continued heating, and the mixture was further heated for an additional three hours. The mixture was then cooled to room temperature, and 0.8 mole of KOH (53 g, 85% pure) was added. The mixture was again heated to reflux. Another 0.4 mole (93 g) of 1,11dichloro-3,6,9-trioxaundecane was then added dropwise

over four hours. The mixture was refluxed for about 24 hours, while the color of the solution changes to dark brown, and then was cooled and evaporated under vacuum in a roto-vac apparatus.

After cooling the mixture, a solution of 20 ml of concentrated HCl in 150 ml water and 500 ml of chloroform was added. The chloroform layer (lower layer) was then separated and was washed three times with 400 ml of each of saturated NaCl-50% NaOH solutions, and once with 400 ml of saturated NaCl solution (separation of phases was slow). The chloroform solution was then dried over Na_2SO_4 .

The chloroform was then evaporated using a roto-vac. A soft solid was then obtained which was suspended in a warm (80-90°C) n-heptane solution in a continuous liquidliquid extractor for several days. After cooling the yellow n-heptane extract to about 40-50°C, two layers were obtained. The upper layer containing benzo-15-crown-5 was separated. The lower layer was recrystalized from pure acetone to give white plate crystals of dibenzo-30crown-10 with a melting point of 106.5°C. The yield of reaction for benzo-15-crown-5 and dibenzo-30-crown-10 were found to be 37% and 3%, respectively.

2.1.2. Purifications of Ligands

Some dibenzo-30-crown-10 was obtained through the courtesy of DuPont company. The ligand was recrystallized

from acetone and vacuum dried. Dibenzo-21-crown-7 and dibenzo-24-crown-8 (Parish Chemical Company) were recrystallized from n-heptane and dried under vacuum for three days. The melting points of well defined crystals were found to be 107 and 103°C, respectively, which are the same as the reported values (17). 1,10-Diaza-18crown-6 (Merck Company) was recrystallized from reagent grade n-heptane and dried under vacuum for several days. Benzo-15-crown-5 was recrystallized from pure n-heptane and vacuum dried for 72 hours.

2.2. SOLVENTS AND SALTS

2.2.1. Solvents

Reagent grade acetone (Mallinkrodt) was refluxed over calcium sulfate, fractionally distilled, and dried over 4A Linde molecular sieves. Spectrophotometric grade nitromethane (Aldrich) was refluxed over night over phosphorus pentoxide, fractionally distilled, and dried over activated molecular sieves for 24 hours. Dimethylsulfoxide (Fisher) was dried over Linde 4A molecular sieves and vacuum distilled. Dimethylformamide (Fisher) was vacuum distilled over phosphorus pentoxide. Propylene carbonate (Aldrich) was dried for 48 hours over Linde 4A molecular sieves followed by vacuum distillation. Acetonitrile (Mallinkrodt) was refluxed over calcium hydride, fractionally

distilled and dried over molecular sieves. Trimethylene oxide (Aldrich) was dried over activated molecular sieves for 48 hours. Tetramethylguanidine (Eastman) was refluxed over granulated barium oxide and fractionally distilled.

The molecular sieves used were activated by heating them at 600°C for 12 hours under a nitrogen atmosphere. Analyses for water in solvents were carried out with an automatic Karl Fischer Aquatest (Photovolt Corp.) titrator. The water content of the solvents after drying was found to be less than 100 ppm.

2.2.2. Salts

Lithium perchlorate (Fisher) was dried at 190°C for several days. Sodium tetraphenylborate (J. T. Baker) was dried under vacuum at 60°C for 72 hours. Potassium hexafluorophosphate (Pfaltz & Bauer) was purified by recrystallization from water and dried under the vacuum at 110°C for 72 hours. Cesium thiocyanate (Pfaltz & Bauer) was recrystallized from reagent grade methanol and dried under vacuum for several days. Cesium tetraphenylborate was prepared by mixing tetrahydrofuran solution of sodium tetraphenylborate with equimolar amount of concentrated aqueous solution of cesium chloride (Ventron Alfa Product). The resulting fine white precipitate was collected, washed several times to remove any adhering sodium salt and dried under vacuum at 70°C for 72 hours. Thallium (I)

perchlorate (K & K) was recrystallized from water and dried at 110°C for 24 hours.

2.3. SAMPLE PREPARATION

All solutions were prepared in a dry-box under a nitrogen atmosphere to maintain their water content at the lowest possible level. Dilute solutions of the salts were prepared by appropriate dilution of a stock solution. The ligand solutions were prepared by proper dilution of a stock solution (if the ligand was soluble enough) or by weighing out in the desired amount into a 2 ml volumetric flask followed by dilution with the solvent or the solution.

2.4. INSTRUMENTAL MEASUREMENTS

Lithium-7, sodium-23, cesium-133, and thallium-205 NMR measurements were carried out on a modified Varian Associate DA-60 spectrometer equipped with a wide-band probe capable of multinuclear operation (101), operating at a field of 14.09 kgauss in a pulsed Fourier transform mode. The spectrometer is equipped with an external proton lock to maintain the field stability. The NMR spectrometer is interfaced to a Nicolet 1083 computer for pulse generation, data collection, and data treatment. A previously described program (102) was used for pulse generation and collection of the resultant free induction decay (FID) signal. Data treatment was performed using the Nicolet FT-NMRD program (NIC-80/S-7202-D) (103). The experimental conditions are given in Table I.

Nucleus	Resonance Frequency (MHz)	External Reference Solution
7 _{L1}	23.32	4.0 M LiClO ₄ in H ₂ O
²³ Na	15.87	3.0 M NaCl in H ₂ O
133 _{Cs}	7.87	0.5 M CsBr in H ₂ O
205 _{Tl}	34.61	0.3 M TINO ₃ in H_2O

Table I. Experimental Conditions for Metal Ion NMR.

All the chemical shifts for sodium-23, cesium-133, and thallium-205 reported in this thesis are referred to infinitely dilute aqueous Na⁺, Cs⁺, and Tl⁺ solutions, and the chemical shifts for lithium-7 are referred to a 4.0 M LiClO_4 aqueous solution. <u>Downfield</u> (paramagnetic) chemical shifts from the reference are indicated as <u>negative</u>. In order to keep the chemical shift of external reference constant, an insulated reference tube (64) was used in the measurements of cesium-133 chemical shifts as a function of temperature.

The reported chemical shifts are also corrected for the differences in the bulk diamagnetic susceptibility between the sample (nonaqueous) and the reference (aqueous) solutions according to the Live and Chan (104) equation for non-superconducting spectrometers

$$\delta_{\text{corr}} = \delta_{\text{obs}} + \frac{2n}{3} \left(X_V^{\text{ref}} - X_V^{\text{sample}} \right)$$

where X_V^{ref} and X_V^{sample} are the volume susceptibility of the reference and the sample solutions, respectively. The magnitude of corrections, calculated on the basis of the published susceptibilities (105), and the physical properties (106,107) for the solvents used in this study are shown in Table 6.

Carbon-13 NMR spectra were obtained on a Varian CFT-20 spectrometer operating at a field of 18.68 kgauss in a pulsed Fourier transform mode. Acetone was used as an external reference and D_2O was used to lock the system. All carbon-13 chemical shifts are reported with respect to TMS.

2.5. DATA HANDLING

The complex formation constants were obtained by fitting the chemical shift-mole ratio data to appropriate equations (which will be discussed in detail later) using the least squares program KINFIT (108) on a CDC-6500 computer. A linear least squares program was used to obtain enthalpies and entropies.

Solvent	Dielectric Constant	Donor Number ^a	Volumetric Susceptibility ^b (-Kx10 ⁶)	Correction on DA-60(ppm)
Acetone	20.7	17.0	0.460	-0.545
Acetonitrile	38.8	14.1	0.529	-0.390
Dimethylformamide	36.7	26.6	0.500	-0.308
Dimethylsulfoxide	46.7	29.8	0.630	-0.241
Methanol	32.7	25.7 ^c	0.530	-0.429
Nitromethane	35.9	2.7	0.391	-0.689
Propylene Carbonate	65.0	15.1	0.634	-0.180
Pyridine	12.4	33.1	0.612	-0.226
Tetramethylguanidine	0.11		0.590	-0.272

Key Solvent Properties and Correction for Magnetic Susceptibility on DA-60. Table 6.

^aReference (106).

^bReference (105).

^cReference (107).

CHAPTER 3

.

MULTINUCLEAR NMR STUDY OF DIBENZO-30-CROWN-10, DIBENZO-24-CROWN-8, AND DIBENZO-21-CROWN-7 COMPLEXES WITH Na⁺, K⁺, Cs⁺, and Tl⁺ IONS IN NONAQUEOUS SOLVENTS

3.1. INTRODUCTION

Previous studies in our laboratories (109-112) and elsewhere (113-117) have shown that the nuclear magnetic resonance of thallium and alkali nuclei offers a very sensitive technique for the studies of changes in the immediate chemical environment of the thallium and alkali ions in solution. The chemical shifts and line width of the resonances can given information about ion-ion, ionsolvent, and ion-ligand interactions. During the past decade alkali metal NMR has been used extensively to study the thermodynamics and kinetics of the complexation reaction between alkali metal ions and crowns and cryptands (109-118).

Among the crown ethers, large molecules such as dibenzo-30-crown-10 and dibenzo-24-crown-8 have some interesting properties. These are very flexible molecules with enough oxygen atoms in the ring so that they can twist around a metal ion with a suitable size to envelope it completely and form a three-dimensional "wrap around" complex (26).

Alkali complexes of dibenzo-30-crown-10, dibenzo-24crown-8, and dibenzo-21-crown-7 have been studied by potentiometry (4,31), polarography (35), calorimetry (34), spectrometry (32), and proton and carbon-13 NMR (33) in different solvents. The purpose of the study described in this chapter was to investigate Na⁺, K⁺, Cs⁺, and T1⁺ ion complexes of the above mentioned ligands in a number of nonaqueous solutions by the multinuclear NMR technique.

3.2. COMPLEXATION OF Na⁺, K⁺, AND Cs⁺ IONS WITH DIBENZO-30-CROWN-10

3.2.1. DB30C10 Complexes with Na⁺ and K⁺

Sodium-23 chemical shifts were determined as a function of dibenzo-30-crown-10/sodium ion mole ratios in nitromethane, acetonitrile, and pyridine solutions. The resulting data are given in Table 7 and the mole ratio plots are shown in Figure 3. In all cases only one populationaverage resonance was observed indicating that the exchange of the metal ion between the bulk solution and the complex is faster than the NMR time scales. In the case of pyridine solutions, the addition of the ligand to the Na⁺ solution produces a gradual diamagnetic shift of sodium-23 resonance which begins to level off at a mole ratio of about 1, which indicates the formation of a 1:1 complex of the sodium ion with the ligand.

On the other hand, in the case of nitromethane and acetonitrile solutions, the chemical shift <u>vs</u>. mole ratio plots show three distinct inflection points at the ligand/ metal mole ratios of about 0.5, 0.7, and 1 indicating the formation of three complexes with the respective stoichiometries DB30C10.2Na⁺, 2DB30C10.3Na⁺, and DB30C10.Na⁺. The synthesis and isolation of crystalline 1:2 and 1:1 (ligand to metal ion) complexes of sodium tetraphenylborate and dibenzo-30-crown-10 have been previously

	MM			AN			Py	-
L/Na ⁺	(mqq) ^ð	۵۷ _{1/2} (Hz)	L/Na ⁺	(bpm)	∆v _{1/2} (Hz)	r∕m+	(mpm)	۵۷ _{1/2} (Hz)
0.00	14.08	10	0.00	7.63	11	0.00	-0.77	ττ
0.14	12.51	66	0.19	7.87	33	0.18	0.72	55
0.23	11.43	011	0.38	7.99	63	0.29	1.77	117
0.32	10.77	128	0.49	8.10	79	0.48	3.31	146
0.38	9.71	144	0.61	8.06	7 4	0.78	5.15	161
0.54	9.38	205	17.0	7.77	83	0.92	6.03	185
0.60	11.04	172	0.81	7.95	79	1.16	6.73	203
0.64	11.61	212	06.0	8.16	83	1.40	6.98	220
0.78	11.71	201	0.99	8.47	88	1.84	7.33	225
0.79	11.62	200	1.10	8.55	83	2.16	7.15	228
0.88	10.94	135	1.30	8.62	83			
.99	10.62	190	1.53	8.63	83			
1.16	10.23	135						
1.35	10.24	135						
2.03	10.16	150						
2.42	10.29	ו75						

È r τ -¢ . ſ 1 2 r r



Figure 3. Sodium-23 Chemical Shifts <u>vs</u>. [DB30C10]/[Na⁺] Mole Ratio in Different Solvents. A-Nitromethane, B-Acetonitrile, C-Pyridine.

reported by Truter and coworkers (25). These three species were isolated from acetonitrile solutions in the form of well defined crystals. The melting points of 1:1 and 1:2 (ligand to metal ion) complexes were found to be very close to the reported values. The crystalline structure of the third species which we supposed to be 2:3 complex were determined. The results showed that it is not the 2:3 species, but instead it is the 1:2 complex associated with four molecules of acetonitrile of crystallization. It seems that 2:3 complex is quite unstable and exists only in solution.

It has been shown previously that carbon-13 chemical shifts of the carbons in the ether region of cyclic polyethers are sensitive to the conformational change of the ligand upon complexation (119). In order to get further information about dibenzo-30-crown-10 interactions with the sodium ion, we studied the chemical shift of the polyether chain carbons as a function of sodium and potassium ion concentrations relative to the concentration of the ligand. The results, obtained in nitromethane solutions, are shown in Figures 4 and 5.

In the case of the DB30Cl0- K^+ ion system, the addition of potassium hexafluorophosphate to a DB30Cl0 solution results in a gradual coalescence of the four resonances and only one signal is obtained at equimolar concentrations of the potassium ion and the ligand. This behavior seems



Figure 4. Carbon-13 Chemical Shifts at Various [Metal Ion]/ [DB30C10] Mole Ratios (MR) in Nitromethane. A-Sodium Ion at MR=0.0, 1.0, and 2.0; B-Potassium Ion at MR=0.0, 0.5, and 1.0.



Figure 4. Carbon-13 Chemical Shifts at Various [Metal Ion]/ [DB30C10] Mole Ratios (MR) in Nitromethane. A-Sodium Ion at MR=0.0, 1.0, and 2.0; B-Potassium Ion at MR=0.0, 0.5, and 1.0.



Figure 5. Carbon-13 Chemical Shifts for the Four Polyether Chain Carbon Atoms at Various [Na⁺]/ [DB30C10] Mole Ratios in Nitromethane.

to indicate an essentially equal interaction between the ten oxygens of the polyether ring and the potassium ion. Naturally, such equal interactions is only possible if in solutions the ligand is "wrapped around" the cation as postulated by Live and Chan (33) in solution and shown by Truter and coworkers (26) for the solid complex.

Considerably different behavior is observed in the case of the sodium ion. The details are given in Figure 5. Between mole ratios of 0.0 and 2.0 all four carbons behave quite differently. While the initial addition of the sodium ion results in a chemical shift of carbons 2, 3, and 4, the chemical shift of carbon 1 remains unaffected. On the other hand, between mole ratio of 1.0 and 2.0 the chemical shifts of carbons 2 and 3 remains constant while carbon 4 and especially carbon 1, show a significant downfield shift. Beyond mole ratio of 2.0, the resonance frequencies are constant.

The results show that the addition of the sodium ion to DB30C10 results in at least two conformational changes of the ligand molecule following the formation of DB30C10·Na⁺ and DB30C10·2Na⁺ complexes. No evidence for the formation of the 2DB30C10·3Na⁺ complex was observed; however, it is to be expected that the 23 Na chemical shift is a much more sensitive probe of the sodium ion interaction than the 13 C chemical shift. Once again, these data support the conclusions of Live and Chan (33) that the

DB30Cl0·Na⁺ complex has a different configuration from the DB30Cl0 complex with potassium ion (and presumably with the Cs⁺ and Ba²⁺ ions).

An attempt was made to calculate the formation constants of DB30Cl0 complexes with the potassium ion from the variation of the carbon-13 chemical shift as a function of K⁺/ligand mole ratio. It was found that in nitromethane and acetonitrile solutions log K_f was greater than 5, while in acetone solutions log $K_f = 4.3 \pm 0.1$.

3.2.2. DB30C10 Complexes with Cs⁺

The variation of cesium-133 chemical shift as a function of the ligand/Cs⁺ mole ratio in nitromethane, acetonitrile, acetone, methanol, and pyridine solutions at 30°C are shown in Figure 6 (the data are given in Table 8). It is seen that the shift is diamagnetic in acetonitrile solutions and paramagnetic in all others. The shifts begin to level off at a mole ratio of about 1, indicating the formation of a 1:1 complex. It is interesting to note that the limiting chemical shifts for the complexed cesium tend to approach each other indicating that in the complex the cation is largely insulated from the solution and, once more, confirming the "wrap around" structure.

The formation constants for the DB30Cl0·Cs⁺ complex in different solvents were determined from the variations of the 133 Cs chemical shifts with the ligand/Cs⁺ mole

NM ^a		A	QN d	Ac ^c		MeC	q ^{H(}	Py	υ
L/Cs ⁺ ((mqq) ⁸	L/Cs+	(bpm)	L/Cs+	(mqq) ⁸	L/Cs ⁺	(mqq) ⁸	L/Cs+	(mqq) ⁸
0.00	61.71	0.00	-33.65	00.0	40.01	00.0	46.00	00.0	35.31
0.23	52.4	0.25	-25.21	0.30	36.61	0.22	39.75	0.22	29.49
0.50	39.77	0.50	-16.20	0.64	32.11	0.56	30.02	0.47	24.69
17.0	30.61	0.59	-13.57	0.75	30.71	0.80	23.74	0.66	19.49
0.84	22.70	0.70	-9.77	0.88	29.40	0.86	23.34	0.80	15.69
0.96	22.00	0.81	-6.28	0.99	28.00	0.98	20.47	0.86	14.61
1.15	20.41	0.98	-0.85	1.07	27.61	1.07	19.15	1.03	12.36
1.30	19.40	1.12	2.79	1.23	26.61	1.26	18.2 6	1.10	12.12
1.49	19.40	1.19	4.12	1.36	26.22	1.37	17.61	1.27	11.82
1.68	11.01	1.38	6.98	1.53	26.15	1.60	17.14	1.45	11.58
1.80	19.00	1.60	8.54	1.86	23.99	1.74	17.14	1.77	11.43
2.08	18.92	2.00	9.55					2.18	11.43
acsclo4.	bcsS	CN.	csBPh4.						

Mole Ratio Study of Dibenzo-30-Crown-10 Complexes with 0.005M Cs⁺ Ion in Table 8.



Figure 6. Cesium-133 Chemical Shifts <u>vs</u>. [DB30Cl0]/[Cs⁺] Mole Ratio in Different Solvents. A-Nitromethane, B-Methanol, C-Acetone, D-Pyridine, E-Acetonitrile.

ratio according to the following method. Assuming that only cation-ligand interactions are important, for the two chemical environments of the metal ion, freely solvated and complexed, in which the exchange rate is fast as compared to the NMR time scale, a population average shift is observed

$$\delta_{obs} = X_{M} \delta_{M} + X_{ML} \delta_{ML}$$
(1)

where $\delta_{\rm obs}$ is the observed chemical shift in ppm, $X_{\rm M}$ and $X_{\rm ML}$ are the respective chemical shifts for the two sites. Equation 2 is easily derived from Equation 1 where

$$\delta_{\text{obs}} = \frac{C_{\text{M}}}{C_{\text{M}}^{\text{t}}} \left(\delta_{\text{M}} - \delta_{\text{ML}}\right) + \delta_{\text{ML}}$$
(2)

 C_M is the concentration of free metal ion and C_M^t is the total concentration of metal ion. Assuming formation of a 1:1 complex, we have the equilibrium

where L is the ligand. The concentration equilibrium constant can be written as

$$K_{f} = \frac{C_{ML}}{C_{M}C_{L}}$$
(3)

where C_{ML} is the concentration of the complex, C_M is the concentration of free metal ion, and C_L is the concentration of free ligand. By a simple algebraic substitution, Equation 3 can be written as

$$K_{f} = \frac{C_{M}^{t} - C_{M}}{C_{m}(C_{L}^{t} - C_{M}^{t})}$$
(4)

where C_{L}^{t} is the total concentration of the ligand.

From Equations 2, 3, and 4 we can obtain Equation 5 which relates the observed chemical shift to the formation constant, the total concentrations of the metal ion and the ligand ($C_{\rm M}^{\rm t}$ and $C_{\rm L}^{\rm t}$ respectively), the limiting chemical shift of the complexes metal ion ($\delta_{\rm ML}$), and to the chemical shift of the free metal ion ($\delta_{\rm M}$).

$$\delta_{obs} = [(\kappa_{f}c_{M}^{t} - \kappa_{f}c_{L}^{t} - 1) + (\kappa_{f}^{2}c_{L}^{t^{2}} + \kappa_{f}^{2}c_{M}^{t^{2}} - 2\kappa_{f}^{2}c^{t}c_{L}^{t}]$$

+
$$2\kappa_{f}c_{L}^{t}$$
 + $2\kappa_{f}c_{M}^{t}$ + 1)^{1/2}] $(\frac{\delta_{M}-\delta_{ML}}{2\kappa_{f}c_{M}^{t}})$ + δ_{ML} (5)

In Equation 5, C_M^t and C_L^t are known, δ_M can be easily determined from the measurement on solutions of free metal ion. The equation then contains two unknowns K_f and δ_{ML} . The procedure then is to input the δ_{obs} , C_M^t , C_L^t , and δ_M parameters and vary K_f and δ_{ML} using a computer least squares program KINFIT (108). The procedure will continue until the calculated chemical shifts correspond with the experimental chemical shifts within the error limits. A typical fit of the data for DB30Cl0·Cs⁺ in methanol at 30° C is shown in Figure 7.

The results for the DB30Cl0·Cs⁺ complexes in various solvents are shown in Table 9. It is seen that in acetone solutions the stability of the complex is not affected by a change in the concentration of salt or of the counter ion. It is evident, therefore, that at low concentrations of the cesium salts, which we used, the formation of the complex is unaffected by ion pairing. It is reasonable to assume that the same situation will exist in solvents with higher donicities and/or higher dielectric constants such as nitromethane, acetonitrile, and methanol. Comparison of our values with those reported in the literature (and obtained by different techniques) show a satisfactory agreement (Table 9).

Since the cesium ion is rather weakly solvated because of low charge density of the cation, it is not surprising that the stability of the complex is only marginally dependent on the nature of the solvents.



Solvent	log K _f	δ _{lim} (ppm)
Nitromethane	4.30±0.05	18.58±0.04
Acetonitrile	3.39±0.09	13.56±0.95
Acetonitrile	3.50 ^a	
Acetone	3.99±0.08 ^b	14.69±0.01
Acetone	4.04±0.05 ^c	15.05±0.02
Acetone	3.96±0.07 ^d	15.89±0.07
Acetone	4.05±0.06 ^e	15.28±0.05
Acetone	4.23 ^f	
Methanol	4.18±0.07	16.50±0.11
Methanol	4.23 ^g	
Pyridine	4.41±0.10	11.35±0.02

Table 9. Formation Constants and the Limiting Chemical Shifts of DB30Cl0.Cs⁺ Complexes in Various Solvents.

^aReference 35.

^b0.005<u>M</u>CsSCN.

```
<sup>C</sup>0.005<u>M</u> Cs Picrate.
```

d0.005<u>M</u> CsBPh4.

e0.0025<u>M</u> CsBPh₄.

^fReference 33.

^gReference 4.
3.3. COMPLEXATION OF Na⁺, Cs⁺, and Tl⁺ IONS WITH DIBENZO-24-CROWN-8

3.3.1. DB24C8 Complexes with Na⁺

The complexation between sodium ion and dibenzo-24crown-8 was studied in nitromethane, acetonitrile, dimethylformamide, dimethylsulfoxide, and pyridine. The measured sodium-23 chemical shifts at various ligand to sodium ion mole ratios and the line widths of the resonance lines at the half height at 30°C are listed in Table 10. The mole ratio plots are shown in Figure 8. It is seen immediately that the solvent plays an important role in the complexation reaction. In solvents of high donicity, such as DMF and DMSO, the sodium-23 resonance is almost independent of the ligand/sodium ion mole ratio. This behavior indicates that in these solvents the immediate environment of the sodium ion is not changed upon the addition of the ligand indicating formation of a very weak complex at the best.

On the other hand, in nitromethane, acetonitrile, and pyridine solutions the sodium-23 resonances shift upfield or downfield with some indication of a break at a mole ratio of about 1 implying the formation of a 1:1 DB24C8·Cs⁺ complex. The formation constants and the limiting chemical shifts of the complex in different solvents are given in Table 11. It is obvious that in solvents with low solvating

	pnen	ylborate in v	arious So	LVENTS at	. 30°C.			
	MN			AN			DMF	
L/Na ⁺	(mqq) ⁸	Δν _{1/2} (Hz)	L∕Na ⁺	(ppm)	۵۷ _{1/2} (Hz)	L/Na ⁺	(mpm)	۵۷ _{1/2} (Hz)
0.00	14.04	12	0.00	7.30	11	0.00	4.70	29
0.36	11.73	35	0.35	7.62	18	0.38	4.58	140
0.76	9.19	50	0.78	8.00	34	0.79	4.65	41
0.86	8.93	52	0.85	8.08	39	0.92	4.76	01
0.98	8.58	53	0.98	8.11	38	1.04	4.76	42
1.08	8.20	54	1.10	8.17	0 †	1.17	4.72	45
1.24	7.95	56	1.25	8.22	42	1.28	4.80	43
1.68	7.87	57	1.56	8.27	39	1.74	4.86	47
2.07	7.87	55	1.89	8.28	39	2.38	4.96	L 41
2.57	7.85	57	2.42	8.30	Γħ			

Mole Ratio Study of Dibenzo-24-Crown-8 Complexes with 0.025<u>M</u> Sodium Tetra-Table 10.

	DMSO			Py		
L/Na ⁺	(mqq) ⁸	Δν _{1/2} (Hz)	L/Na ⁺	(ddm)	۸۷ _{1/2} (Hz)	
0.00	11.0	917	00.0	-1.18	20	
0.30	0.30	91	0.34	2.15	56 .	
0.75	0.38	50	0.78	6.04	78	
0.83	0.38	51	0.88	6.92	64	
0.96	0.41	51	0.97	7.20	107	
1.10	0.34	50	1.10	7.70	105	
1.22	0.34	49	1.20	7.90	109	
1.61	0.42	59	1.58	8.26	110	
2.02	0.47	59	1.88	8.73	112	
2.46	0.52	59	2.31	8.82	113	

Table 10. Continued.



Figure 8. Sodium-23 Chemical Shifts <u>vs</u>. [DB24C8]/[Na⁺] Mole Ratio in Different Solvents.

Table 11. Formation Constants and the Limiting Chemical Shifts of DB24CB·Na⁺ Complexes in Various Solvents.

Solvent	log K _f	δ _{lim} (ppm)
Nitromethane	3.74±0.12	7.82±0.01
Acetonitrile	2.95±0.07	8.33±0.01
DMF	∿0	
DMSO	∿ 0	
Pyridine	2.89±0.10	9.20±0.09

abilities the complex is more stable. Once again pyridine seems to be an exceptional case.

The limiting chemical shifts of the complexed sodium ion in nitromethane, acetonitrile, and pyridine solutions are close to each other indicating that in these solvents the complexed sodium ion is no longer exposed to the solvent molecules. This is only possible if the sodium ion is located inside the cavity created by the twisting of the ligand around the cation. Another evidence which supports the formation of such a "wrap around" complex between DB24C8 and the sodium ion is the existence of the relatively narrow signals for sodium-23 resonance in all solutions. The width of the ²³Na resonance lines in this case are less than one half of those observed for Na⁺-DB30C10 system in the same solvents (Table 7). For nuclei such as ²³Na with appreciable quadrupole moment, we expect to have a broader resonance line for a more unsymmetrical environment around the nucleus. Thus existence of relatively narrow ²³Na resonance lines in this case indicates a symmetrical environment around the sodium ion which can only be obtained by the formation of a three-dimensional complex.

3.3.2. DB24C8 Complexes with Cs⁺

Cesium-133 chemical shifts were determined as a function of the ligand to the cesium ion mole ratio. The data

are given in Table 12 and the mole ratio plots are shown in Figure 9. In all cases, the cesium-133 resonance has a gradual shift, paramagnetic or diamagnetic depending on the nature of the solvent, until a mole ratio of about 1 is reached and then begins to level off. This behavior indicates formation of a 1:1 DB24C8·Cs⁺ complex in all solvents.

The formation constants and the limiting chemical shifts of the complex in various solvents are shown in Table 13. From the results it is obvious that solvent plays an important role in the complexation. In strong solvating solvents such as DMF and DMSO the complex is much weaker than in solvents of low and medium donor strength such as nitromethane, acetonitrile and acetone. This behavior shows the existence of a competition between the ligand and the solvent molecules for the cesium ion. The only exception is the case of pyridine where despite the high Gutmann donor number of the solvent the complex is unexpectedly stable. This exception probably results from the relatively weak interaction between the "soft base" nitrogen atom of pyridine and a "hard acid" (cesium ion).

Three different cesium salts at different concentrations were used to investigate the effects of the anion and of the concentration on the complexation of cesium ion with dibenzo-24-crown-8 in acetonitrile solution. The results are also given in Table 13. As seen in all

N	IMa	A	Na	A	1C ^a	Me	OH ^a
L/Cs ⁺	δ _(ppm)	L/Cs ⁺	δ _(ppm)	L/Cs ⁺	δ _(ppm)	L/Cs ⁺	δ(ppm)
0.00 0.21 0.60 0.70 0.94 1.05 1.10 1.18 1.40 1.87 2.39 2.88	57.57 53.31 45.62 44.38 41.37 40.59 40.42 39.86 39.04 38.56 38.42 38.42	0.00 0.25 0.62 0.72 0.84 0.98 1.09 1.13 1.38 1.78 2.32 2.78	$\begin{array}{r} -33.55\\ -23.24\\ -7.50\\ -3.70\\ -0.20\\ 5.85\\ 8.32\\ 8.55\\ 12.12\\ 13.68\\ 14.14\\ 14.22\end{array}$	0.00 0.25 0.60 0.77 0.98 1.12 1.25 1.81 2.19 2.66	19.27 21.14 23.82 25.15 26.69 27.70 28.16 28.48 28.79 29.02 29.04	0.00 0.20 0.54 0.78 0.94 1.02 1.18 1.34 1.60 1.76 2.07 2.78	46.15 44.76 41.50 40.03 39.02 38.63 37.87 37.39 37.09 36.92 36.79 36.70
DN	ſF ^a	DM	so ^a	F	y ^b		
L/Cs ⁺	δ _(ppm)	L/Cs ⁺	δ(ppm)	L/Cs ⁺	δ _(ppm)		
0.00 0.34 0.60 0.80 0.84 0.96 1.12 1.30 1.40 1.85 2.60	0.26 3.12 5.23 6.68 6.86 7.78 8.78 9.71 10.11 12.14 14.20	0.00 0.42 0.71 0.86 1.00 1.14 1.20 1.38 1.85 2.30 2.80	-67.26 -63.27 -60.63 -59.02 -58.53 -57.29 -57.29 -55.90 -52.79 -49.92 -47.52	0.00 0.38 0.56 0.83 0.92 1.05 1.26 1.52 2.03 2.39 2.83	23.99 22.82 22.44 21.75 21.36 21.19 20.98 20.88 20.81 20.79 20.79		

Table 12. Mole Ratio Study of Dibenzo-24-Crown-8 Complexes with 0.005M Cs⁺ Ion in Various Solvents at 30°C.

a_{CsSCN}.

b_{CsBPh4}.



Figure 9. Cesium-133 Chemical Shifts vs. [DB24C8]/[Cs⁺] Mole Ratio in Different Solvents.

Solvent	Log K _f	δ _{lim} (ppm)
Nitromethane	4.11±0.08	38.26±0.03
Acetonitrile	3.94±0.07 ^a	14.86±0.02
Acetonitrile	3.89±0.07 ^b	14.50±0.07
Acetonitrile	3.90±0.04 ^c	14.82±0.06
Acetonitrile	3.97±0.04 ^d	14.23±0.06
Acetone	3.71±0.09	29.24±0.06
Methanol	3.65±0.05	36.47±0.03
Methanol	3.78±0.08 ^e	
Dimethylformamide	2.10±0.04	24.93±0.96
Dimethylsulfoxide	1.61±0.04	-8.32±3.46
Pyridine	4.00±0.03	20.75±0.07

Table 13. Formation Constants and the Limiting Chemical Shifts of DB24CB·Cs⁺ Complexes in Various Solvents.

a0.005<u>M</u> CsSCN.

^b0.010<u>M</u> CsSCN.

^c0.005<u>M</u> CsBPh₄.

^d0.005<u>M</u> CsI.

e_{Reference} 4.

cases the limiting chemical shifts and the stability of the complex are not affected either by a change in the salt concentration or by a change in the anion. It is evident, therefore, that at low concentrations used in this study, the formation of the complex is unaffected by ion pairing. We can assume that in solvents of higher donicities and/or higher dielectric constants the same situation will exist.

The large divergence in DB24C8·Cs⁺ complex limiting chemical shifts (a range of about 46 ppm) probably indicates that the cesium ion is not insulated from the solvent by the ligand. The complex formation constant in methanol solution is in satisfactory agreement with the previously reported value (4).

3.3.3. DB24C8 Complexes with T1⁺

The thallium nucleus, 205 Tl, has very favorable properties for NMR studies. It has a spin of I = 1/2 and its chemical shift is very sensitive to small changes in the chemical environment. The solvent dependence of the thallium-205 chemical shift is over 2600 ppm (116,120) in comparison to a chemical shift range of about 8 ppm for 7 Li (123,124), 30 ppm for 23 Na (123,124), and 130 ppm for 133 Cs (125,126). The thallous ion is a useful probe because its chemistry is very similar to that of the alkali ions (127). In particular, the chemical properties and ionic radii of T1⁺ and K⁺ ions are very close (1.54 Å and 1.44 Å, respectively) (128) so that thallium(I) ion can be used as a NMR probe for potassium. Because of these interesting properties, we were interested in studying the complexation of thallous ion with dibenzo-24-crown-8 in various nonaqueous solvents.

The thallium-205 chemical shift was measured as a function of DB24C8/T1⁺ mole ratio in nitromethane, acetonitrile, acetone, methanol, DMF, DMSO, and pyridine solutions at 30°C. The thallous ion concentration was maintained constant at 0.005 M in all cases. The mole ratio data are given in Table 14 and the variations of the 205 Tl chemical shift as a function of the ligand/Tl⁺ mole ratio are shown in Figure 10. In poor solvating solvents such as nitromethane, acetonitrile, and acetone, the addition of the ligand to the thallous ion solution causes a quite linear change in the 205Tl chemical shift (upfield or downfield) until a mole ratio of 1 is reached. After the mole ratio of 1, further addition of the ligand does not affect the thallium-205 resonance. This behavior indicates the formation of a very stable 1:1 complex between the thallium(I) ion and the ligand in the above solvents. On the other hand, in methanol solution the mole ratio plot shows some curvature around the mole ratio of 1 and a limiting value is obtained at mole ratios greater than 2.5, indicating formation of a weaker 1:1 complex than that in the previous solvents. In solvents of high

1	NM	A	N	A	c	M	eOH
L/T1 ⁺	δ(ppm)	L/T1 ⁺	δ (ppm)	L/T1 ⁺	δ (ppm)	L/T1+	(ppm)
0.00 0.73 0.97 1.11 1.22 1.65 1.88 2.15 2.68	366.6 281.9 250.1 246.9 246.9 246.9 246.9 246.9 246.9	0.00 0.34 0.70 0.85 0.96 1.09 1.21 1.52 1.88 2.19 2.72	209.8 222.4 237.8 243.1 245.6 249.1 249.8 249.8 249.8 249.9 249.9 249.9 250.0	0.00 0.36 0.72 0.82 0.97 1.10 1.31 1.56 1.87 2.23 2.80	206.1 226.4 242.8 249.9 253.4 257.0 258.3 258.9 259.7 259.6 260.1	0.00 0.46 0.75 0.86 1.06 1.15 1.28 1.59 1.79 2.06 2.70	-107.5 -7.7 60.7 78.6 118.2 131.8 143.1 166.3 176.7 187.6 192.3
1	DMF	DM	SO	P	у		
L/T1 ⁺	δ(ppm)	l/T1 ⁺	δ _(ppm)	L/T1 ⁺	δ _(ppm)		
0.00 0.35 0.78 0.94 1.12 1.22 1.46 1.80 2.08	-190.2 -178.3 -163.5 -156.3 -151.5 -148.0 -139.3 -126.2 -115.2 -113.6	0.00 0.45 0.80 0.98 1.10 1.29 1.61 1.83 2.37	-319.3 -320.7 -321.7 -322.0 -322.3 -322.7 -323.4 -324.2 -324.8 -325.7	0.00 0.38 0.67 0.99 1.08 1.22 1.59 1.84 2.35	654.1 603.4 569.1 529.3 516.7 498.8 464.4 441.5 398.5		

Table 14. MOle Ratio Study of Dibenzo-24-Crown-8 Complexes with 0.005M TlClO₄ in Various Solvents at 30°C.



Figure 10. Thallium-205 Chemical Shifts vs. [DB24C8]/[T1⁺] Mole Ratio in Different Solvents.

donicities, such as DMF, DMSO, and pyridine, upon addition of the ligand there is a gradual shift of the 205 Tl resonance which does not reach a limiting value even at a mole ratio of 3 (Figure 10), indicating formation of a weak complex in these solvents.

The formation constants and the limiting chemical shifts of the 1:1 complex of the ligand with the thallous ion in various solvents are given in Table 15. It is immediately obvious that the stability of the complex is very much dependent on the nature of the solvent. The stability of the complex increases with decreasing Gutmann donor number of the solvents. It is interesting to note that in contrast to the sodium and cesium ion complexes with DB24C8, in pyridine solution the DB24C8 \cdot Tl⁺ complex is expectedly weak. The thallous ion as a "soft acid" can strongly interact with the nitrogen atom of pyridine which is a "soft base" so that the resulting DB24C8.T1⁺ in this solvent is weak. As shown in Table 15, the formation constants of the complex in acetonitrile and methanol solutions are in a good agreement with the values reported by Hofmanova et al. (35) who used polarographic technique for the measurements.

The limiting chemical shifts of the complexed thallous ion in solvents of low and medium donicities such as nitromethane, acetonitrile, acetone, and methanol are close to each other (Figure 10). This behavior indicates

Solvent	Log K _f	δ _{lim} (ppm)
Nitromethane	>5	245.00
Acetonitrile	4.81±0.05	250.1±0.1
Acetonitrile	4.80 ^a	
Acetone	4.15±0.05	260.5±0.1
Methanol	3.19±0.07	215.2±3.8
Methanol	3.40 ^a	
Dimethylformamide	1.16±0.21	336 ±94
Dimethylsulfoxide	<1.0	
Pyridine	1.64 0.04	-150 ±46

Table 15. Formation Constants and the Limiting Chemical Shifts of DB24C8.Tl⁺ Complexes in Various Solvents.

^aReference 35.

that the thallous ion is insulated from the solvent by the ligand so that there is only a weak interaction between the solvent molecules and the cation. In solvents of strong solvating ability such as DMF, DMSO, and pyridine, however, the limiting chemical shifts are solvent dependent indicating a strong interaction between the solvent molecules and the cation.

3.3.4. Conclusions

The formation constants of the 1:1 complexes of Na⁺, Cs⁺, and Tl⁺ ions with dibenzo-24-crown-8 in various solvents are compared in Table 16. From the results it is immediately obvious that solvent plays an important role in the complexation reactions. With the exception of the sodium and cesium ion complexes in pyridine solution, in all cases the stabilities of the complexes are decreased with increasing solvating abilities of the solvents. In poor solvating solvents such as nitromethane, acetonitrile, and acetone the stabilities of the Na⁺, Cs⁺, and Tl⁺ complexes decreases in the order DB24C8·Tl⁺ > DB24C8·Cs⁺ > DB24C8·Na⁺.

For large crown ethers such as dibenzo-30-crown-10 and dibenzo-24-crown-8 which are capable of formation of three-dimensional "wrap around" complexes with cations (33), we expect the size of the cation to play an important role in the complexation reaction. The complexation of a cation

Table 16. Formation Constants of 1:1 Complexes of Na⁺, Cs⁺, and Tl⁺ Ions with Dibenzo-24-Crown-8 in Various Solvents.

		Log K _f	
Solvent	Cs ⁺	Tl+	Na ⁺
Nitromethane	4.11±0.08	>5.0	3.74±0.12
Acetonitrile	3.94±0.07	4.81±0.05	2.95±0.07
Acetone	3.71±0.09	4.15±0.05	
Methanol	3.60±0.05	3.19±0.05	
Dimethylformamide	2.10±0.04	1.16±0.21	~0.0
Dimethylsulfoxide	1.61±0.04	<1.0	~0.0
Pyridine	4.00±0.03	1.64±0.04	2.89±0.10

and the ligand with appropriate relative sizes results in the formation of a very strong complex, for example complexation of potassium ion by dibenzo-30-crown-10 (26,33). In the case of the complexation of the ligand with larger cations, the three-dimensional structure cannot be complete and, therefore, a weaker complex will be formed. On the other hand, in the case of the complexation of the ligand with smaller cations, the ligand can still twist around the cation to form the three-dimensional structure, but in this case the oxygen atoms of the ligand will have repulsive forces on each other which, consequently, result in the formation of a weak complex between the cation and theligand.

The formation constants and the limiting chemical shifts obtained in this study support the above conclusions for the complexation of Na⁺, Cs⁺, and Tl⁺ ions by dibenzo-24crown-8. Cesium ion is too large to form a complete "wrap around" complex with the ligand. Thus the cation remains exposed to the solvent molecules which causes the existence of quite scattered limiting chemical shifts of the complex in different solvents (Figure 9). In the case of the sodium ion, despite the smaller size of the cation, the "wrap around" structure can be formed, but because of the repulsive forces of the oxygen atoms of the ring on each other the resulting complex is weak. In this case, the cation is insulated from the solvent by

the ligand and, therefore, the complex limiting chemical shifts in different solvents are close (Figure 8). Thallous ion seems to have the most suitable size for the cavity since the DB24C8 \cdot Tl⁺ complex is the strongest among the series and its limiting chemical shifts are very close.

3.4. COMPLEXATION OF Na⁺, Cs⁺, and T1⁺ IONS WITH DIBENZO-21-CROWN-7

3.4.1. DB21C7 Complexes with Na⁺

The complexation of sodium ion with dibenzo-21-crown-7 was investigated in nitromethane, acetonitrile, acetone, dimethylformamide, dimethylsulfoxide, and pyridine solutions by sodium-23 NMR. The concentration of sodium tetraphenylborate was maintained at 0.025 M while the concentration of the ligand was varied from zero to about 0.075 M. The sodium-23 chemical shifts were determined as a function of DB21C7/Na⁺ mole ratios. The data are given in Table 17 and the mole ratio plots are shown in Figure 11. In DMF and DMSO solutions the ²³Na chemical shift is very little affected by the addition of the ligand, although the resonance line shows some broadening (Table 17). The results seem to indicate the formation of very weak complex at the best in these solvents. This is not surprising since DMF and DMSO are solvents with strong solvating

	WN			AN			Ac	
L∕Na ⁺	(mpm)	۵۷ _{1/2} (Hz)	L/Na ⁺	(mpm) ⁸	∆v _{1/2} (Hz)	L/Na ⁺	(bpm)	4v _{1/2} (Hz)
0.00	13.23	18	0.00	7.17	19	00.00	6.90	20
0.41	11.93	78	0.42	8.34	27	0.42	7.73	31
0.74	10.72	112	0.76	9.21	35	0.70	8.12	91
06.0	10.25	151	0.86	9.42	42	0.87	8.42	53
1.02	06.6	154	0.98	9.67	43	0.98	8.54	55
1.12	9.78	152	1.13	9.88	49	1.11	8.73	58
1.28	9.58	161	1.31	9.97	47	1.35	8.96	66
1.76	9.48	157	1.81	10.05	50	1.84	9.39	67
2.20	9.45	169	2.28	10.12	52	2.29	9.55	70
2.95	04.0	170	3.02	10.20	58	3.02	9.60	75

Mole Ratio Study of Dibenzo-21-Crown-7 Complexes with $0.025\underline{M}$ NaBPh₄ in Various Solvents at 30° C. Table 17.

	DMF			DMSO			Py	
L/Na ⁺	(ppm)	۵۷ _{1/2} (Hz)	L/Na ⁺	(سطط) م	۵۷ _{1/2} (Hz)	L/Na ⁺	(mpm) ⁸	42 (Hz)
0.00	4.57	29	0.00	-0.01	43	0.00	-1.14	17
0.40	4.70	57	0.36	0.05	75	0.38	2.43	116
0.81	4.75	59	0.75	0.09	83	0.60	4.00	184
0.94	4.78	61	06.0	0.13	95	0.85	5.71	210
1.03	4.75	68	1.02	0.18	98	0.98	6.56	209
1.20	4.83	77	1.22	0.14	112	1.14	7.40	240
1.38	4.81	75	1.55	0.17	128	1.35	7.85	269
1.80	4.88	83	1.90	0.18	142	1.83	8.33	279
2.13	4.92	85	2.25	0.19	157	2.39	8.67	304
						3.00	8.95	322

Table 17. Continued.



Figure 11. Sodium-23 Chemical Shifts vs. [DB21C7]/[Na⁺] Mole Ratio in Different Solvents.

abilities which can strongly compete with the ligand for the cation.

On the other hand, a considerable change in 23 Na chemical shifts was observed in nitromethane, acetonitrile, acetone, and pyridine solutions upon the addition of the ligand indicating a change in the chemical environment of the nucleus. The diamagnetic shift of the sodium-23 resonance in acetonitrile, acetone, and pyridine solution (paramagnetic in nitromethane) begins to level off at a mole ratio of about 1, indicating formation of a 1:1 complex between the ligand and the sodium ion. In all cases, the line width of the ²³Na resonance at the half height $(\Delta v_{1/2})$ increases almost linearly with the ligand/Na⁺ mole ratio until a mole ratio of about 1 is reached, and then it remains almost constant upon further addition of the ligand (Table 17). This is not surprising because for a nucleus such as sodium with an appreciable quadrupole moment we expect the line width of the resonance signal to be sensitive to the electrical field gradient around the nucleus. The solvated sodium ion has a symmetrical environment and, therefore, the line width of the resonance signal is small (about 10 to 20 Hz depending on the solvent used). Complexation of the sodium ion with the ligand creates an unsymmetrical environment around the cation which results in the broadening of the resonance signal. As the DB21C7/Na⁺ mole ratio increases, the amount of the complexed sodium

ion increases and, therefore, the ²³Na resonance signal becomes broader. After a mole ratio of 1 is reached, essentially all of the cation is complexed and further addition of ligand has no effect on the sodium-23 resonance. This behavior, once more, confirms the formation of a stable 1:1 complex between DB21C7 and sodium ion.

The formation constant and the limiting chemical shifts of DB21C7·Na⁺ complex in various solvents at 30° C are shown in Table 18. With the exception of pyridine there is an inverse relationship between the donicity of the solvent and the stability of the complex. It has been pointed out previously, however, that being a soft nitrogen donor, pyridine does not strongly solvate a hard ion such as sodium ion (80) and, therefore, a stable complex can be formed between the ligand and the sodium ion in this solvent. The limiting chemical shifts of the complexed sodium ion in nitromethane, acetonitrile, acetone, and pyridine solutions are very close, indicating that the sodium ion is enclosed inside the ligand's cavity so that the solvent molecules can barely interact with the cation.

3.4.2. DB21C7 Complexes with Cs⁺

Cesium-133 NMR was used to study the complexation of the cesium ion with dibenzo-21-crown-7 in various nonaqueous solvents. The 133 Cs chemical shift was determined as a function of the ligand to cesium ion mole ratio.

Table 18. Formation Constants and the Limiting Chemical Shifts of DB21C7 • Na⁺ Complexes in Various Solvents

Solvent	Log K _f	δ _{lim} (ppm)
Nitromethane	3.14±0.05	9.35±0.01
Acetonitrile	2.78±0.08	10.29±0.02
Acetone	2.28±0.08	9.88±0.06
Dimethylformamide	~0.0	
Dimethylsulfoxide	∿0.0	
Pyridine	2.56±0.05	9.47±0.06

The results are shown in Table 19 and in Figure 12. The cesium ion concentration was maintained at 0.005 M. Upon addition of the ligand, the line width observed shows a slight increase from about 4 Hz to 11 Hz. The complexation was studied up to a mole ratio of about 3, where a limiting value for the chemical shift of the complexed cesium ion is reached in nitromethane, acetonitrile, acetone, methanol, and pyridine solutions. The variations of the cesium-133 chemical shift as a function of DB21C7/Cs⁺ mole ratio in the above mentioned solvents show a single inflection point at a mole ratio of about 1, indicating formation of a 1:1 complex between the ligand and the cesium ion.

No evidence for formation of a 2:1 (ligand to metal ion) complex was observed in any of the solvents used. While the existence of a 2:1 complex of the ligand with cesium ion in the solid crystalline state has been demonstrated (23), it does not follow necessarily that it also exists in solution. Frensdorff (4), however, has reported formation of a very weak 2:1 complex between DB21C7 and cesium ion in methanol solution.

The formation constant and the limiting chemical shifts obtained from the computer analysis of the mole ratio data in various solvents are shown in Table 20. The large difference in the limiting chemical shifts of the complex in different solvents is a good indication that the metal ion remains exposed to the solvent. The cesium ion is

]	١M	A	N	A	С	Me	ОН
L/Cs ⁺	δ(ppm)	L/Cs ⁺	^δ (ppm)	L/Cs ⁺	δ(ppm)	L/Cs ⁺	δ _(ppm)
0.00 0.26 0.50 0.77 0.94 1.11 1.28 1.48 1.80 2.25 2.67	57.89 50.43 43.37 35.22 30.75 27.37 25.41 24.86 24.24 24.15 24.07	0.00 0.35 0.64 0.82 0.92 1.04 1.22 1.33 1.50 1.83 2.52 3.21	-31.93 -24.79 -19.06 -15.49 -13.47 -11.76 -9.47 -9.36 -9.05 -8.74 -8.52 -8.40	0.00 0.30 0.56 0.79 0.89 1.03 1.12 1.20 1.43 1.90 2.37 3.16	19.48 16.46 13.82 11.65 10.72 9.67 8.94 8.42 8.42 8.24 88.20 8.10	0.00 0.30 0.54 0.68 0.90 1.03 1.14 1.28 1.46 1.85 2.42 3.04	46.97 39.53 32.86 29.92 24.64 22.40 21.55 20.62 19.90 19.66 19.53 19.34
I	OMF	DM	SO	P	y ^a		
L/Cs ⁺	δ _(ppm)	L/Cs ⁺	δ(ppm)	L/Cs ⁺	δ _(ppm)		
0.00 0.37 0.69 0.86 0.99 1.19 1.31 1.95 2.35 2.94	2.51 2.20 1.88 1.61 1.50 1.41 1.36 1.27 1.19 1.11	0.00 0.30 0.72 0.93 1.06 1.20 1.40 1.82 2.37 3.06	-66.59 -63.18 -58.14 -55.89 -54.27 -53.25 -50.92 -47.36 -43.72 -39.73	0.00 0.17 0.50 0.77 0.91 0.99 1.14 1.29 1.51 1.88 2.37 2.97	24.53 19.80 11.12 3.91 -0.67 -2.30 -5.47 -5.63 -5.78 -5.82 -5.94 -6.05		

Table 19. Mole Ratio Study of Dibenzo-21-Crown-7 Complexes with 0.005<u>M</u> CsSCN in Various Solvents at 30°C.

aCsBPh4.



Figure 12. Cesium-133 Chemical Shifts vs. [DB21C7]/[Cs⁺] Mole Ratio in Different Solvents.

Solvent	Log K _f	δ _{lim} (ppm)
Nitromethane	4.14±0.07	23.78±0.05
Acetonitrile	3.95±0.04	-8.17±0.02
Acetone	3 .9 3±0.06	7.98±0.02
Methanol	3.96±0.06	19.07±0.04
Methanol	4.20 ^a	
Dimethylformamide	2.84±0.10	0.92±0.04
Dimethylsulfoxide	1.72±0.04	-0.96±3.18
Pyridine	4.27±0.07	-6.21±0.03

Table 20. Formation Constants and the Limiting Chemical Shifts of DB21C7.Cs⁺ Complexes in Various Solvents.

^aReference 4.

known as a large cation with a low charge density which cannot be strongly solvated by the solvent molecules. Thus it is not surprising if the stability of the complex in nitromethane, acetonitrile, acetone, methanol, and pyridine is only marginally dependent on the nature of the solvent. In DMF and DMSO, however, the DB21C·Cs⁺ complex is much weaker than that in the above solvents. Dimethylformamide and dimethylsulfoxide are solvents of high donicities, and their interactions even with a large cation such as cesium ion is still strong enough to compete with the ligand for this cation and to prevent formation of a strong complex. The value obtained for the stability constant of the DB21C7·Cs⁺ complex in methanol solution at 30°C is in a satisfactory agreement with the literature reported value in the same solution at $25^{\circ}C$ (4) (Table 20).

3.4.3. DB21C7 Complexes with T1⁺

In order to determine the stoichiometry and the stability of the thallium(I) complex with dibenzo-21crown-7 in various solvents, the thallium-205 NMR chemical shift was measured as a function of DB21C7/T1⁺ mole ratio. The concentration of thallium(I) perchlorate was maintained at 0.005 <u>M</u>, while the concentration of the ligand was varied from zero to about 0.015 <u>M</u>. The data are given in Table 21 and the mole ratio plots are shown in Figure 13. In nitromethane, acetonitrile, and acetone solutions, the

N	M	A	AN Ac		
L/T1 ⁺	δ(ppm)	L/T1 ⁺	δ _(ppm)	L/T1 ⁺	δ _(ppm)
0.00 0.74 0.86 1.01 1.14 1.28 1.43 1.88 2.37 3.14	349.6 319.2 315.4 310.1 309.0 308.8 308.5 308.4 308.3 308.4	0.00 0.37 0.85 1.05 1.15 1.32 1.50 1.98 2.55 3.21	213.9 234.4 260.5 272.2 274.4 274.3 274.6 274.7 274.6 274.5	0.00 0.42 0.54 0.77 0.94 1.06 1.24 1.51 1.63 2.03 2.57 3.09	150.3 202.8 216.8 246.5 262.1 271.6 275.0 277.3 277.9 278.1 278.2 278.3
Me	ОН	D	MF	DMS	0
L/T1 ⁺	δ(ppm)	L/T1 ⁺	δ _(ppm)	L/T1 ⁺	δ _(ppm)
0.00 0.28 0.52 0.76 0.96 1.10 1.23 1.48 1.75 2.20 2.90	-112.0 -39.4 32.0 103.7 130.0 154.1 182.9 188.0 200.2 204.1 207.5 209.1	0.00 0.40 0.70 0.86 1.03 1.13 1.33 1.85 2.42 3.11	-148.5 -94.3 -55.1 -36.0 -15.2 -6.7 15.3 44.4 75.5 101.4	0.00 0.27 0.54 0.82 0.92 1.01 1.16 1.38 1.60 1.80 2.47 3.09	-212.9 -218.3 -223.4 -230.0 -231.9 -233.4 -236.2 -240.3 -246.0 -248.5 -261.0 -273.3

Table 21. Mole Ratio Study of Dibenzo-21-Crown-7 Complexes with $0.005\underline{M}$ TlClO₄ in Various Solvents at 30°C.



Figure 13. Thallium-205 Chemical Shifts <u>vs</u>. [DB21C7]/[T1⁺] Mole Ratio in Different Solvents.

thallous ion resonance shifts either upfield or downfield as the concentration of the ligand increased. Once again mole ratio plots show a break at a mole ratio of 1, indicating formation of a 1:1 complex. The break is more pronounced in the nitromethane and acetonitrile curves compare to that in acetone and methanol plots which is indicative of formation of a stronger complex in the former solvents. No other break is found, indicating that if any 2:1 (ligand to metal ion) complex formation occurs it is negligible.

In solvents of high donicities such as DMF and DMSO only a gradual shift of thallium-205 resonance is observed upon addition of the ligand which does not reach a limiting value even at a mole ratio of about 3. This behavior indicates formation of a weak complex between the ligand and the thallous ion in these solvents. The formation constant and the limiting chemical shift of the DB21C7.T1⁺ complex in various solvents are given in Table 22. It is obvious that the nature of the solvent has a large effect on the stability of the complex. There is an inverse relationship between the Gutmann donor number of the solvent and the complex formation constant. Except for the acetonitrile and acetone cases the complex limiting chemical shifts are different in different solvents, indicating that the complexed thallous ion remains exposed to the solvent. For stable complexes with $K_r > 10^5$, the ²⁰⁵Tl chemical shift-mole ratio plots consist of two straight lines

Table 22. Formation Constants and the Limiting Chemical Shifts of DB21C7.Tl+ Complexes in Various Solvents.

Solvent	Log K _f	δ _{lim} (ppm)
Nitromethane	>5	308.4
Acetonitrile	>5	274.5
Acetone	4.71±0.08	278.5±0.1
Methanol	3.97±0.03	212.7±0.3
Dimethylformamide	2.18±0.02	233.8±8.1
Dimethylsulfoxide	0.63±0.15	
intersecting at 1:1 mole ratio. These kinds of plots cannot be analyzed by our technique, and in such cases we can only conclude that $\log K_f > 5$. This behavior is observed for the DB21C7.T1⁺ complex in nitromethane and acetonitrile solutions which is not surprising since both nitromethane and acetonitrile are poor solvating solvents with respective Gutmann donor number of 2.7 and 14.1.

3.4.4. Conclusions

The formation constants of the 1:1 complexes of Na⁺, Cs⁺, and Tl⁺ ions in various solvents are compared in Table 23. In solvents of low and medium solvating abilities such as nitromethane, acetonitrile, acetone and methanol, the stabilities of DB21C7 complexes with sodium, cesium, and thallium(I) ions decrease in the order DB21C7.Tl⁺ > $DB21C7 \cdot Cs^+ > DB21C7 \cdot Na^+$. The ionic radii of the above cations vary in the order $Na^+ < Tl^+ < Cs^+$. Cesium ion has a diameter of 3.68 Å (128) which is just the right size to fit conveniently inside the cavity of dibenzo-21crown-7 with the size of 3.4-4.3 Å (4), while sodium ion (diameter 2.24 Å) is too small for the ligand's "hole". Thus the DB21C7·Cs⁺ complex is more stable than the DB21C7·Na⁺ complex. In the case of DB21C7·Cs⁺ complex the crown ether only occupies the equatorial coordination sites of the cation. Thus the complexed cesium ion remains exposed to the solvent molecules from the axial positions

Table 23. Formation Constants of 1:1 Complexes of Na⁺, Cs⁺, and Tl⁺ Ions with DB21C7 in Various Solvents.

		Log K _f	
Solvent	Na ⁺	Cs ⁺	T1 ⁺
Nitromethane	3.14±0.05	4.14±0.07	>5
Acetonitrile	2.78±0.08	3.95±0.04	>5
Acetone	2.28±0.08	3.93±0.06	4.71±0.08
Methanol		3.96±0.06	3.97±0.03
Dimethylformamide	∿0.0	2.84±0.10	2.18±0.02
Dimethylsulfoxide	∿0.0	1.72±0.04	0.63±0.15
Pyridine	2.56±0.05	4.27±0.07	

and, therefore, the complex limiting chemical shift is strongly solvent dependent (Figure 12).

In the case of DB21C7 \cdot Na⁺ complex, however, because of the small size of the cation, the ligand is able to twist around the sodium ion to form a three-dimensional array and thus insulate it from the solvent molecules. Consequently, the limiting chemical shift of the complexed cation is essentially solvent independent (Table 18). In the case of the thallium(I) complex, despite the more inconvenient relative sizes of the cation and the ligand than the cesium ion case, the DB21C7.T1⁺ complex is more stable than the DB21C·Cs⁺. This is not surprising since the thallous ion is known to bond to the oxygen atoms of the macrocyclic ligands by an ion-dipole interaction with a covalent contribution (129) which results in the formation of a very strong complex between the cation and the ligand.

In solvents of strong solvating abilities such as DMF and DMSO no evidence for the formation of a complex between the ligand and the sodium ion was observed. The cesium and thallous ions, however, form weak complexes with the ligand in these solvents, but in this case the DB21C7·Cs⁺ complex is more stable than the DB21C7·T1⁺ complex. The smaller stability constant of the thallous ion complex may be related to the preference of thallous ion as a soft acid for the nitrogen and sulfur atoms as soft bases

in the DMF and DMSO structures respectively. Pyridine is an exceptional case where despite the high donicity (Gutmann donor number of 33.1) of the solvent, the resulting complexes of the ligand with sodium and cesium ions are unexpectedly stable. The reason for this behavior has been discussed previously.

3.5. DISCUSSION

The stability constants of Na⁺, Cs⁺, and Tl⁺ ion complexes with dibenzo-21-crown-7, dibenzo-24-crown-8, and dibenzo-30-crown-10 in various solvents at 30°C are shown in Table 24. It is immediately obvious that in all cases the nature of the solvent has a great effect on the stabilities of the complexes. The magnitude of the solvent effect on the complex formation constants decreases in the order of $Tl^+ > Na^+ > Cs^+$. Cesium ion is a large cation with a low charge density which cannot strongly interact with the solvent and, therefore, the stabilities of the cesium ion complexes are only marginally dependent on the nature of the solvent. In the case of the sodium ion complexes the solvent effect is more pronounced, which can be related to the smaller size and consequently to the higher charge density of the sodium ion than that of the cesium ion. Since the thallium(I) ion is bonded to the solvent molecules by an ion-dipole interaction with a covalent

			ATOR CROT ID	61168 ac DO	•		
				Log K _f			
	Na	+		Cs+		Τ	+
Solvent	DB21C7	DB24C8	DB21C7	DB24C8	DB30C10	DB21C7	DB24C8
Nitromethane	3.14±0.0 5	3.74±0.12	4.14±0.07	4.11±0.08	4.30±0.05	>5	>50
Acetonitrile	2.78±0.08	2.95±0.07	3.95±0.04	3.94±0.07	3.39±0.09	> 5	4.81±0.05
Acetone	2.28±0.08	1 8 9 1	3.93±0.06	3.71±0.09	3.96±0.07	4.71±0.08	4.15±0.05
Methanol			3.96±0.06	3.60±0.05	4.18±0.07	3.97±0.03	3.19±0.05
DMF	0.0~	~0°	2.84±0.10	2.10±0.04	- - - -	2.18±0.02	1.16±0.21
DMSO	~0°	~0°0	l.72±0.04	1.61±0.04		0.63±0.15	<1.00
Pyridine	2.56±0.05	2.89±0.10	4.27±0.07	4.00±0.03	4.41±0.10	1 	1.64±0.04

Formation Constants of 1:1 Complexes of Na⁺, Cs⁺, and Tl⁺ Ions with DB21C7, DB24C8, and DB30C10 in Various Solvents at 30°C. Table 24.

contribution, it is not surprising that the stabilities of the complexes depend strongly on the nature of the solvent.

With the exception of the sodium and cesium ion complexes in pyridine solution, there is an inverse relationship between the donicity of the solvent and the stability of the complex. In the case of pyridine, however, we have a solvent with the highest donor strength (<u>i.e.</u>, Gutmann donor number of 33.1) and yet the sodium and cesium ion complexes are strong in this medium. It has been pointed out previously that pyridine as a "soft" nitrogen donor does not solvate strongly "hard" cations such as an alkali ion (80,130).

As can be seen, sodium ion forms a more stable complex with DB24C8 than with DB21C7. While the cavity sizes of both ligands are too large for the small sodium ion, the increased number of the oxygen atoms, as binding sites, in DB24C8 seems to play an important role in the complexation. As discussed in previous sections (3.3.1 and 3.4.1) the limiting chemical shifts of the complexed cations are relatively solvent independent in both cases indicating that the sodium ion is insulated from the solvent by the ligands. According to this picture it is evident that DB24C8 with more binding sites can form a more stable complex with the sodium ion than DB21C7. In the case of the thallous ion complexes the opposite behavior is

seen: DB21C7·T1⁺ is more stable than DB24C8·T1⁺. In this case the relative sizes of the ligand to the cation seem to be the key factor in the complexation reactions. The thallous ion with the size of 3.08 Å has a more convenient fit inside the cavity of DB21C7 (with the size of 3.4-4.3 Å) than with DB24C8 which has a cavity size greater than 4 Å.

With the exception of the DB30Cl0·Cs⁺ complex in acetonitrile solution the stabilities of the cesium ion complexes with the ligands decreases in the order DB30Cl0.Cs⁺ > $DB21C7 \cdot Cs^+ > DB24C8 \cdot Cs^+$ in all solvents used. Dibenzo-30crown-10 is a large molecule with enough oxygen atoms in the ring which can form a stable "wrap around" complex with cesium ion (Sec. 3.2.2). The sizes of the dibenzo-21crown-7 cavity and the cesium ion are very close so that the cation can be held by the ligand to form a stable complex, which is expectedly weaker than DB30Cl0.Cs⁺ complex because of its two-dimensional structure. Dibenzo-24-crown-8 has neither a long enough chain to form a threedimensional complex with the cesium ion nor a convenient cavity size to hold the cation as tight as dibenzo-21crown-7 can. Thus the resulting complex is the weakest in the series.

CHAPTER 4

CESIUM-133 NMR STUDY OF THE THERMODYNAMICS OF THE COMPLEXATION OF DIBENZO-30-CROWN-10, DIBENZO-24-CROWN-8, AND DIBENZO-21-CROWN-7 WITH CESIUM ION IN NONAQUEOUS SOLVENTS

4.1. INTRODUCTION

In order to have a deeper understanding of the thermodynamics of the complexation reactions, it is useful to consider separately the enthalpic and the entropic contributions to the reaction. The change in free energy of complexation, ΔG° , can be divided into two parts: the change in enthalpy, ΔH° , and the change in entropy, ΔS° , of the reaction:

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{1}$$

The complex can be stabilized by meeting one of the following requirements: (a) $\Delta H^{\circ} < 0$ and dominant, $T\Delta S^{\circ} < 0$ (enthalpy stabilized); (b) $\Delta H^{\circ} > 0$, $T\Delta S^{\circ} > 0$ and dominant (entropy stabilized); and (c) either $\Delta H^{\circ} < 0$ and dominant, $T\Delta S^{\circ} > 0$ or $\Delta H^{\circ} < 0$, $T\Delta S^{\circ} > 0$ and dominant (both enthalpy and entropy stabilized).

Presently available thermodynamic data for the complexation of alkali metal ions with uncharged ligands such as crowns and cryptands are not detailed enough to give a clear picture of the thermodynamic behavior of the complexes. The results of the thermodynamic studies, reported so far, show that most of the alkali ion complexes with crowns and cryptands (18) are enthalpy stabilized but entropy destabilized. In particular, the reported

thermodynamic data for the complexation of the cations with large crown ethers (<u>i.e.</u>, 21-crown-7 and larger) are quite sparse. To the best of our knowledge, there are just four papers available (96,33,34,131), reporting the thermodynamic parameters for the complexation of large crowns.

In previous work, Lehn and coworkers (132) and Cahen <u>et al</u>. (110) both noted that the observed chemical shift of the complexed metal ion varied with temperature. Cesium-133 and lithium-7 NMR were used by E. Mei (112) and by A. Hourdakis (133) to determine the thermodynamic parameters for the complexation of the cesium and lithium ions with some crowns and cryptands in nonaqueous solutions.

The results of the study of the stoichiometries and stabilities of Na⁺, K⁺, Cs⁺, and Tl⁺ ion complexes with dibenzo-30-crown-10, dibenzo-24-crown-8, and dibenzo-21-crown-7 in various solvents were discussed in chapter 3. In this chapter we will attempt to evaluate the thermo-dynamic parameters of the complexation reaction between cesium ion and the above mentioned crown ethers.

4.2. DB30C10 COMPLEXES WITH Cs⁺

The method for determining of the thermodynamic values was based on the temperature dependence of the complex formation constant. The complex formation constant is related to the relevant thermodynamic parameters by the following relationships:

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad (1)$$
$$\Delta G^{\circ} = -RT \cdot ln K_{f} \qquad (2)$$
$$ln K_{f} = -\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R} \qquad (3)$$

Thus a plot of $\ln K_{f} \underline{vs}$. 1/T gives a straight line with a slopt of $-\frac{\Delta H^{\circ}}{R}$ and an intercept of $\frac{\Delta S^{\circ}}{R}$, provided that ΔH° is independent of temperature over the temperature range considered.

The variation of the cesium-133 chemical shift was measured as a function of DB30Cl0/Cs⁺ mole ratio in nitromethane, acetonitrile, acetone, methanol, and pyridine at different temperatures. In all cases studied, only one population average signal was observed indicating that the exchange of the metal ion between the two sites (<u>i.e.</u>, free ion in the bulk solution and the complexed ion) is faster than the NMR time scale. The data are given in Table 25 and the mole ratio plots at different temperatures are shown in Figures 14-18.

In all five solvents used, <u>i.e.</u>, nitromethane, acetonitrile, acetone, methanol, and pyridine, the curvature in the mole ratio plots increases with increasing the temperature. This behavior indicates the existence of

Solver	nt: Nitr	omethane				<u></u>
10001	.0/03		Temp	perature,	°C	
	0	10	30	45	60	70
0.00 0.23 0.50 0.71 0.84 0.96 1.15 1.30 1.49 1.68 1.80 2.08 Solver	58.21 48.61 37.71 27.40 23.31 19.82 17.70 17.41 17.41 17.41 17.41 17.42	59.71 50.61 38.21 28.51 24.22 21.11 19.12 18.82 18.30 18.22 18.30 18.22 0.18.22	61.71 52.41 39.72 30.61 25.70 22.00 20.41 19.40 19.40 19.11 19.00 18.92	63.01 53.81 41.30 32.81 27.91 24.22 21.80 21.22 20.21 20.21 19.82 19.61	64.81 55.91 43.21 34.80 30.72 27.00 24.81 23.71 22.60 22.00 21.81 21.30	66.51 57.21 45.42 36.41 32.71 29.62 26.40 24.71 23.52 22.41 22.20 22.11
DB30C1	.0/Cs ⁺		Tom:	onotuno	٥ <i>.</i>	
			leut	berature,		
	18	30	45	60	77	
0.00 0.25 0.50 0.59 0.70 0.81 0.98 1.12 1.19 1.38 1.60 2.00	$\begin{array}{c} -35.10 \\ -26.75 \\ -17.13 \\ -14.81 \\ -10.62 \\ -6.97 \\ -1.08 \\ 3.11 \\ 4.42 \\ 7.37 \\ 8.61 \\ 9.55 \end{array}$	-33.65 -25.21 -16.20 -13.57 -9.77 -6.28 -0.85 2.79 4.12 6.98 8.54 9.55	$\begin{array}{r} -32.41 \\ -23.10 \\ -14.73 \\ -12.71 \\ -9.07 \\ -6.43 \\ -1.70 \\ 2.02 \\ 3.26 \\ 6.13 \\ 8.00 \\ 9.74 \end{array}$	-30.58 -22.33 -14.04 -11.39 -8.36 -5.82 -1.62 1.98 2.48 5.27 7.29 9.28	$\begin{array}{r} -26.00 \\ -19.00 \\ -12.33 \\ -9.85 \\ -7.91 \\ -5.74 \\ -2.25 \\ -0.10 \\ 1.40 \\ 4.19 \\ 6.05 \\ 8.02 \end{array}$	

Table 25. Cesium-133 Chemical Shifts of 0.005<u>M</u> Cs⁺ Ion in the Presence of DB30Cl0 at Various Temperatures.

Table 25. Continued.

Solver DB30CI	nt: Acet LO/Cs ⁺	one		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	90	
	-10	10	20	erature,	50	
0.00 0.30 0.64 0.75 0.88 0.99 1.07 1.23 1.36 1.53	25.13 21.91 17.87 16.55 15.31 13.72 13.26 13.01 12.91 12.91	28.11 24.46 20.20 18.57 17.26 16.17 15.86 15.24 14.93 14.93	29.43 25.78 21.52 20.20 18.49 17.34 17.03 16.10 15.70 15.65	30.87 26.87 22.38 20.97 19.66 18.26 17.87 16.87 16.48 16.41	33.46 29.73 24.77 23.38 22.13 21.06 20.58 19.53 18.80 18.26 18.02	

Solvent: Methanol

DB30C10/Cs⁺

	Temperature, °C						
	0	15	30	45	60		
0.00 0.22 0.56 0.80 0.98 1.07 1.26 1.37 1.60 1.74	42.10 35.05 25.05 17.69 17.00 13.97 13.19 13.15 13.11 13.11 13.11	44.37 37.69 27.38 20.71 19.97 17.30 16.25 15.44 15.28 15.15 15.08	46.00 39.75 30.02 23.74 23.34 20.47 19.15 18.26 17.61 17.14 17.14	47.23 41.18 32.26 27.30 26.25 24.74 23.85 21.50 20.57 19.93 19.75	50.25 45.38 37.46 32.41 31.25 28.95 27.99 26.45 25.67 24.43 23.97		

Table 25. Continued.

Solver	nt: Pyri LO/Cs ⁺	dine				
			Temp	erature,	°C	
	0	10	30	50	65	85
0.00 0.22 0.47 0.66 0.80 0.86 1.03 1.10 1.27 1.45 1.77 2.18	27.17 23.69 18.65 14.64 11.99 11.81 9.02 9.25 9.19 9.17 9.19 9.18	30.05 25.50 20.28 16.56 12.60 11.82 9.80 9.73 9.72 9.62 4.61 9.59	34.39 28.57 23.77 18.57 14.77 13.69 11.44 11.20 10.90 10.66 10.51 10.51	38.12 31.91 26.09 20.82 16.48 15.50 13.06 12.76 11.83 11.75 11.44 11.40	41.68 34.70 27.95 22.52 17.71 16.86 14.46 14.32 13.22 13.22 12.84 12.28 12.15	44.24 37.99 30.82 25.47 21.59 20.43 17.25 17.22 16.01 15.38 14.78 14.37



Figure 14. Cesium-133 Chemical Shifts <u>vs</u>. [DB30C10]/[Cs⁺] Mole Ratio in Nitromethane at Different Temperatures.



Figure 15. Cesium-133 Chemical Shifts <u>vs</u>. [DB30C10]/[Cs⁺] Mole Ratio in Acetonitrile at Different Temperatures.



Figure 16. Cesium-133 Chemical Shifts vs. [DB30C10]/[Cs⁺] Mole Ratio in Acetone at Different Temperatures.



Figure 17. Cesium-133 Chemical Shifts <u>vs</u>. [DB30C10]/[Cs⁺] Ratio in Methanol at Different Temperatures.



Figure 18. Cesium-133 Chemical Shifts <u>vs.</u> [DB30C10]/[Cs⁺] Mole Ratio in Pyridine at Different Temperatures.

an exothermic reaction between the cesium ion and the ligand. The formation constants were computed by the KINFIT program as described previously and the results are listed in Table 26. It is readily seen that lowering the temperature increases the stability of the complex. In most cases at lower temperatures the formation constants were greater than 10^5 and their precise values could not be determined by our technique.

Plots of $\ln K_{f}$ vs. 1/T for the five systems are shown in Figure 19. The slopes and intercepts of the straight lines are calculated by linear least squares fitting of the data, and the corresponding thermodynamic parameters are listed in Table 27. It is seen that the results obtained in methanol solutions agree reasonably well with the results of Chock (32). It is interesting to note that while the stability (or ΔG° values) of the complex is not very sensitive to the solvent (at least in the case of the five solvents studied here), the enthalpy and the entropy values vary significantly with the solvent. Since the cesium ion is rather weakly solvated because of the low charge density of the cation, it is not surprising that the free energy, ΔG° , of the complexation is only marginally dependent on the nature of the solvent. However, the solvation of the ligand would be different in different solvents and because of that the enthalpy of the complexation is solvent dependent. The entropy of the complexation

SolvenSolvent	Temp. (°C)	Log K _f	
Nitromethane	70	3.65±0.04	
	60	3.70±0.02	
	45	3.99±0.10	
	30	4.30±0.05	
	10	4.67±0.14	
	0	>5	
Acetonitrile	77	2.85±0.07	
	60	3.04±0.05	
	45	3.20±0.08	
	30	3.39±0.09	
	18	3.49±0.10	
Acetone	60	3.40±0.08	
	45	3.96±0.07	
	30	4.31±0.14	
	15	4.92±0.20	
Methanol	60	3.36±0.08	
	45	3.70±0.05	
	30	4.18±0.07	
	15	4.65±0.02	
	0	>5	
Pyridine	85	3.52±0.02	
	65	3.81±0.05	
	50	4.13±0.04	
	30	4.41±0.10	
	10	4.81±0.07	
	0	>5	

Table 26. Formation Constants of DB30Cl0.Cs⁺ Complex in Nonaqueous Solvents at Different Temperatures.



Figure 19. Van't Hoff Plots for Complexation of Cs⁺ Ion by Dibenzo-30-Crown-10 in Various Solvents.

Table 27. Thermodynamic Parameters for the Complexation of Cs⁺ Ion by Dibenzo-30-Crown-10 in Various Solvents.

Solvent	ΔG°(30°C) (kcal/mole)	ΔH ^o (kcal/mole)	∆S° (cal/mole °K)
Nitromethane	-5.97±0.07	-7.95±0.39	-6.66±1.25
Acetonitrile	-4.71±0.13	-5.13±0.28	-1.53±0.89
Acetone	-5.50±0.10	-13.48±0.51	-26.19±1.69
Methanol	-5.81±0.10	-12.72±0.34	-22.82±1.11
Methanol ^a	-5.77	-11.2	-18.2
Pyridine	-6.13±0.14	-7.94±0.36	-5.93±1.13

^aReference 32.

in various solvents increases in the order of acetone < methanol < nitromethane < pyridine < acetonitrile. In all cases the complexes are enthalpy stabilized but entropy destabilized.

It should be noted that similar behavior was previously observed in nonaqueous solutions. For example, in the case of the cryptate C222 exclusive complex with cesium ion, the ΔH° and ΔS° values are -12.9 kcal mole⁻¹ and -26.8 e.u. in acetone, -8.6 kcal mole⁻¹ and -13.7 e.u. in propylene carbonate and -5.7 kcal mole⁻¹ and -11.2 e.u. in N,N-dimethylformamide solutions (96). Entropy destabilization was also observed by Izatt et al. for the complexation of sodium and potassium ions by benzo-15-crown-5 and 18-crown-6 in water-methanol mixtures (34) and by Kauffmann et al. for the complexation of potassium and rubidium ions by cryptand C221 and Na⁺, K^+ , Rb⁺, and Cs⁺ ions by cryptand C222 in aqueous solutions (134). In the last case, it was assumed that the decrease in entropy was largely due to the rearrangement of the water structure upon the metastasis of a small inorganic cation into a large hydrophobic organic cation. While this explanation is quite feasible for aqueous solutions, it cannot be carried over to much less structured organic solvents used in this study.

It seems reasonable to assume that the main reason for the negative entropy of the complexation is the decrease

in the conformational entropy of the ligand upon the formation of a metal complex. Large macrocycle ligand such as DB30C10 should be rather flexible in the free state. The degree of flexibility would vary with the solvent, <u>i.e.</u>, with the extent of ligand-solvent interaction. The formation of a rigid three-dimensional complex should decrease the conformational entropy of the ligand and thus, perhaps, give rise to negative entropy of the complexation. At the present time, however, thermodynamic data on the formation of macrocyclic complexes in nonaqueous solvents are quite sparse. Additional work is very necessary before the entropy destabilization of macrocyclic ligands in nonaqueous solvents can be explained satisfactorily.

4.3. DB24C8 COMPLEXES WITH Cs⁺

In order to study the thermodynamic behavior of the complexation reaction between cesium ion and dibenzo-24crown-8, extensive chemical shift-mole ratio studies were made of the Cs⁺-DB24C8 system in nitromethane, acetonitrile, acetone, methanol, and pyridine solutions over a wide temperature range. The measured chemical shifts for different ligand to metal ion mole ratios at various temperatures are given in Table 28 and the corresponding mole ratio plots are shown in Figures 20-24. In all systems

Table 28. Cesium-133 Chemical Shifts of 0.005<u>M</u> Cs⁺ Ion in the Presence of DB24C8 at Various Temperatures.

Solver DB24C8	nt: Nitro S/Cs ⁺	omethane				
			Temperat	ture, °C		
	20	30	45	60	75	90
0.00 0.21 0.60 0.70 0.94 1.05 1.10 1.18 1.40 1.87 2.39 2.88	56.87 52.46 45.09 43.54 40.43 39.60 39.31 39.11 38.42 38.03 37.96 37.96	57.57 53.31 45.62 44.38 41.37 40.42 39.04 39.08 39.08 38.42 38.42	58.47 54.32 46.64 44.94 42.29 41.55 40.90 40.59 39.66 39.29 39.00	61.15 56.48 47.64 46.17 43.46 42.38 41.83 40.66 39.97 39.74 39.53	62.46 57.41 48.88 47.59 45.09 44.24 44.00 43.19 41.79 40.78 40.28 40.11	64.55 59.12 51.06 48.82 46.87 44.55 45.00 44.43 43.38 41.98 41.15
Solver DB24C8	nt: Aceto /Cs ⁺	onitrile				
			Temperati	ure, °C		
	5	30	40	50	60	75
0.00 0.25 0.62 0.72 0.84 0.98 1.09 1.13 1.38 1.78 2.32 2.78	-37.35 -26.65 -8.97 -4.47 0.72 6.46 9.25 9.88 12.51 13.30 13.44 13.44	-33.55 23.24 -7.50 -3.70 -0.20 5.85 8.32 8.55 12.12 13.68 14.14 14.22	-32.08 -22.54 -7.26 -3.47 0.56 5.00 7.54 7.93 11.73 13.05 13.90 13.95	-30.15 -21.41 -7.42 -3.85 0.10 4.36 6.77 7.08 10.64 12.93 13.85 14.10	-29.29 -20.45 -7.03 -3.69 0.09 3.74 6.46 6.96 10.80 12.81 13.75 14.21	$\begin{array}{r} -27.27 \\ -19.52 \\ -6.57 \\ -3.62 \\ -0.21 \\ 2.73 \\ 5.69 \\ 5.90 \\ 9.87 \\ 11.57 \\ 13.67 \\ 14.35 \end{array}$

Table 28. Continued.

Solvent DB24C8/	: Aceto (Cs ⁺	one	Temp	erature.	°C	
	5	15	30	40	55	
0.00 0.25 0.60 0.77 0.98 1.12 1.25 1.43 1.81 2.19 2.66	15.61 18.78 22.43 23.98 26.46 27.39 28.01 28.16 28.16 28.17 28.20 28.24	17.80 20.25 23.12 24.51 26.53 27.60 28.24 28.45 28.45 28.68 28.72 28.84	19.27 21.14 23.82 25.15 26.69 27.70 28.16 28.48 28.79 29.02 29.04	20.30 21.84 24.56 25.43 27.22 28.21 28.50 29.06 29.60 29.83 29.98	22.12 24.06 26.32 26.92 27.94 28.48 29.03 29.10 29.72 30.10 30.29	

Solvent: Methanol

DB24C8/Cs⁺

			Temp	erature,	°C	
	10	20	30	40	50	65
0.00 0.20 0.54 0.78 0.94 1.02 1.18 1.34 1.60 1.76 2.07 2.78	44.11 42.40 39.84 38.21 37.28 37.12 36.56 36.35 36.00 35.96 35.85 35.85	45.34 43.56 40.70 39.14 38.13 37.20 36.65 36.45 36.35 36.25 36.20	46.15 44.76 41.50 40.03 39.02 38.63 37.87 37.39 37.09 36.92 36.79 36.70	47.00 45.42 42.63 40.77 39.77 39.45 38.45 38.45 37.90 37.60 37.30 37.02	47.83 46.43 43.57 41.70 40.77 39.87 39.24 38.67 38.26 37.83 37.43 37.10	48.90 47.40 44.72 42.79 41.93 41.62 40.47 40.06 39.46 38.84 38.20 37.80

Table 28. Continued.

<u>DD2+00</u>	/05		Temp	erature,	°C	
	30	45	60	75	90	
0.00 0.38 0.56 0.83 0.92 1.05 1.26 1.52 2.03 2.39 2.83	23.99 22.82 22.44 21.75 21.36 21.19 20.98 20.88 20.81 20.79 20.79	26.93 25.24 24.56 23.22 22.83 22.13 21.59 21.28 21.20 21.18 21.13	30.50 27.63 26.63 24.69 24.25 23.68 22.77 22.60 22.36 22.28 22.20	34.22 30.66 29.26 27.17 26.70 25.61 24.07 23.46 23.04 22.88 22.80	37.71 33.85 31.80 29.81 28.72 27.87 26.24 24.92 24.25 24.13 23.96	



Figure 20. Cesium-133 Chemical Shifts <u>vs</u>. [DB24C8]/[Cs⁺] Mole Ratio in Nitromethane at Different Temperatures.



Figure 21. Cesium-133 Chemical Shifts <u>vs</u>. [DB24C8]/[Cs⁺] Mole Ratio in Acetonitrile at Different Temperatures.



Figure 22. Cesium-133 Chemical Shifts vs. [DB24C8]/[Cs⁺] Mole Ratio in Acetone at Different Temperatures.



Figure 23. Cesium-133 Chemical Shifts vs. [DB24C8]/[Cs⁺] Mole Ratio in Methanol at Different Temperatures.



Figure 24. Cesium-133 Chemical Shifts vs. [DB24C8]/[Cs⁺] Mole Ratio in Pyridine at Different Temperatures.

studied, the curvature in the mole ratio plots is more pronounced at lower temperatures. This behavior implies that the complex formed is more stable at lower temperatures and that, of course, the complexation reaction is exothermic.

The calculated formation constants of DB24C8.Cs⁺ complex in different solvents at various temperatures are listed in Table 29. It is seen that such as with DB30Cl0 the stability of the complex drastically increases as the temperature is lowered. Plots of $\ln K_{f}$ vs. the reciprocal of absolute temperature gave straight lines in all solvents used (Figure 25) and the ΔH° and ΔS° values were determined in the usual manner for the slope and the intercept of the plots. The calculated thermodynamic parameters for the complexation in various solvents are listed in Table 30. The data clearly show that in all cases studied the complexation reaction is enthalpy stabilized but entropy destabilized. While the stability of DB24D8·Cs⁺ complex (or ΔG°) is only marginally dependent on the nature of the solvent, the changes in enthalpy and particularly in the entropy of the complexation are very solvent dependent. The entropy change for the complexation in various solvents decreases in the order of pyridine > nitromethane > acetonitrile > methanol > acetone.

Izatt and coworkers have studied the thermodynamics of the complexation of the cesium ion with DB24C8 in 70%

Solvent	Temp. (°C)	Log K _f	
Nitromethane	90	3.37±0.05	
	75	3.52±0.03	
	60	3.68±0.04	
	45	3.91±0.03	
	30	4.11±0.08	
	20	4.26±0.06	
Acetonitrile	75	3.19±0.03	
	60	3.45±0.04	
	50	3.57±0.05	
	40	3.77±0.07	
	30	3.94±0.07	
	5	4.50±0.05	
Acetone	55	3.07±0.03	
	40	3.37±0.07	
	30	3.71±0.09	
	15	4.15±0.10	
	5	4.37±0.07	
Methanol	65	2.86±0.06	
	50	3.11±0.04	
	40	3.36±0.10	
	30	3.65±0.05	
	20	3.85±0.06	
	10	4.04±0.10	
Pyridine	90	3.27±0.09	
	75	3.44±0.07	
	60	3.60±0.04	
	45	3.76±0.08	
	30	4.00±0.03	

Table 29. Formation Constants of DB24C8.Cs⁺ Complex in Nonaqueous Solvents at Different Temperatures.


Figure 25. Van't Hoff Plots for Complexation of Cs⁺ Ion by Dibenzo-24-Crown-8 in Various Solvents.

Table 30. Thermodynamic Parameters for the Complexation of Cs⁺ Ion by Dibenzo-24-Crown-8 in Various Solvents.

Solvent	∆G°(30°C) (kcal/mole)	∆H ^o (kcal/mole)	∆S° (cal/mole °K)
Nitromethane	-5.71±0.11	-6.25±0.10	-1.79±0.34
Acetonitrile	-5.47±0.10	-8.12±0.16	-8.66±0.48
Acetone	-5.15±0.13	-11.20±0.52	-20.08±1.71
Methanol	-5.06±0.07	-9.87±0.46	-16.10±1.49
Pyridine	-5.55±0.05	-5.97±0.16	-1.39±0.46

methanol solution by calorimetric titration. They also found negative values for the changes in the enthalpy and the entropy of the reaction (<u>i.e.</u>, $\Delta H^{\circ} = -8.09$ kcal mole⁻¹ and $\Delta S^{\circ} = -14.1$ e.u.). Since dibenzo-24-crown-10 is a rather flexible ligand in free state, it is reasonable to expect that a change in conformation of the ligand, from a "loose" structure in the free state to a "rigid" structure in the complex, contributes to the large negative entropy changes of the reaction as a dominant factor.

4.4. DB21C7 COMPLEXES WITH Cs⁺

The thermodynamics of the complexation of the cesium ion with dibenzo-21-crown-7 was investigated in nitromethane, acetonitrile, acetone, methanol, and pyridine by cesium-133 NMR. The variation of the chemical shift with the changing temperature was studied for the complexation reaction. At each temperature the cesium-133 chemical shift was monitored as a function of DB21C7/Cs⁺ mole ratios. The data are given in Table 31 and the mole ratio plots are shown in Figures 26-30. As the temperature increases, the mole ratio plots show less curvature indicating the formation of a weaker complex at higher temperatures. This trend is evidence of the existence of an exothermic reaction between the cesium ion and the ligand. The calculated formation constants show the same trend (Table 32).

					<u> </u>	
Solven DB21C7	t: Nitron /Cs ⁺	methane	Temperati	ure. °C		
	15	30	45	60	75	90
0.00 0.26 0.50 0.77 0.94 1.11 1.28 1.48 1.80 2.25 2.67	56.95 49.65 42.04 33.57 29.33 25.80 23.68 23.45 23.14 23.06 23.05	57.89 50.43 43.37 35.22 30.75 27.37 25.41 24.86 24.24 24.15 24.07	60.86 53.01 44.79 36.86 32.54 29.49 27.05 26.27 25.72 25.02 24.95	63.38 54.75 46.12 38.51 34.59 31.13 28.78 28.07 27.06 26.67 26.27	64.39 56.08 48.16 40.00 36.23 33.72 30.82 30.04 28.47 27.14 26.90	65.81 57.57 49.33 42.59 38.58 35.68 33.02 31.92 30.27 28.55 28.00
Solven	t: Aceto	nitrile				
DB21C7	/Cs ⁺		Temperatu	are, °C		
	20	30	40	50	60	75
0.00 0.35 0.64 0.82 0.92 1.04 1.22 1.33 1.50 1.83 2.52 3.21	$\begin{array}{r} -33.24 \\ -25.96 \\ -19.99 \\ -16.33 \\ -14.32 \\ -12.30 \\ -9.98 \\ -9.74 \\ -9.67 \\ -9.45 \\ -9.20 \\ -9.14 \end{array}$	-31.93 -24.79 -19.06 -15.49 -13.47 -11.76 -9.47 -9.36 -9.05 -8.74 -8.52 -8.40	$\begin{array}{r} -30.05 \\ -23.02 \\ -17.74 \\ -14.63 \\ -12.64 \\ -11.00 \\ -8.73 \\ -8.27 \\ -8.05 \\ -7.73 \\ -7.42 \\ -7.18 \end{array}$	$\begin{array}{r} -28.44 \\ -21.86 \\ -16.72 \\ -13.70 \\ -12.23 \\ -10.76 \\ -8.35 \\ -7.80 \\ -7.49 \\ -7.11 \\ -6.41 \\ -6.15 \end{array}$	-27.43 -20.91 -16.02 -13.34 -11.53 -10.14 -7.83 -7.42 -6.96 -6.25 -5.64 -5.27	-24.91 -19.13 -14.79 -12.47 -11.15 -9.98 -7.57 -7.19 -6.49 -5.71 -5.00 -4.30

Table 31. Cesium-133 Chemical Shifts of 0.005M Cs⁺ Ion in the Presence of DB21C7 at Various Temperatures.

Table 31. Continued.

Solvent	: Aceto 'Cs ⁺	ne				
			Temperat	ure, °C		
	10	20	30	40	55	······
0.00 0.30 0.56 0.79 0.89 1.03 1.12 1.20 1.43 1.90 2.37 3.16 Solvent	16.67 13.83 11.10 9.02 8.01 7.00 6.37 6.15 6.06 6.00 5.98 5.96	17.86 14.98 12.43 10.26 9.40 8.32 7.54 7.54 7.39 7.23 7.07 7.03 6.99	19.48 16.46 13.82 11.65 10.72 9.67 8.94 8.78 8.42 8.24 8.20 8.10	21.26 18.16 15.60 13.35 12.58 11.34 10.80 10.65 10.13 9.67 9.45 9.35	22.74 19.56 17.16 15.22 14.06 13.36 12.58 12.35 11.73 11.42 11.27 10.90	
DB21C7/	'Cs'	i	Temperatu	re, °C		
	20	30	40	50	60	
0.00 0.30 0.54 0.68 0.90 1.03 1.14 1.28 1.46 1.85 2.42 3.04	45.43 38.13 31.85 28.60 23.17 21.00 20.30 19.45 19.00 18.83 18.60 18.53	46.97 39.53 32.86 29.92 24.64 22.40 21.55 20.62 19.90 19.66 19.53 19.34	48.76 41.01 34.34 31.07 26.66 24.65 23.40 22.16 21.39 20.82 20.45 20.30	49.92 41.85 35.65 32.55 27.75 25.81 24.88 23.32 22.47 21.70 21.23 21.00	50.50 42.55 36.82 33.86 29.60 27.82 26.82 25.26 24.33 23.10 22.80 22.40	

Solvent DB21C7/	: Pyrid 'Cs ⁺	ine		0.0		
	30	40	Temperat	ure, °C 60	75	90
0.00 0.17 0.50 0.77 0.91 0.99 1.14 1.29 1.51 1.88 2.37 2.97	24.53 19.80 11.12 3.91 -0.67 -2.30 -5.47 -5.63 -5.78 -5.78 -5.82 -5.94 -6.05	27.08 22.44 12.83 5.61 1.03 -0.60 -3.77 -3.93 -4.63 -5.06 -5.16 -5.32	29.18 24.77 15.07 7.24 2.43 0.49 -2.68 -3.39 -3.93 -4.50 -4.72 -4.96	31.9027.1817.409.104.142.89 $-0.75-1.60-2.30-2.69-3.07-3.40$	34.92 30.20 20.19 12.20 7.39 5.54 1.55 0.95 -0.36 -1.07 -1.36 -2.03	38.50 31.97 23.06 14.00 10.93 8.49 6.00 3.44 1.66 1.04 0.15 -0.61



Figure 26. Cesium-133 Chemical Shifts <u>vs</u>. [DB21C7]/[Cs⁺] Mole Ratio in Nitromethane at Different Temperatures.



Figure 27. Cesium-133 Chemical Shifts <u>vs</u>. [DB21C7]/[Cs⁺] Mole Ratio in Acetonitrile at Different Temperatures.



Figure 28. Cesium-133 Chemical Shifts vs. [DB21C7]/[Cs⁺] Mole Ratio in Acetone at Different Temperatures.



Figure 29. Cesium-133 Chemical Shifts vs. [DB21C7]/[Cs⁺] Mole Ratio in Methanol at Different Temperatures.



Figure 30. Cesium-133 Chemical Shifts <u>vs</u>. [DB21C7]/[Cs⁺] Mole Ratio in Pyridine at Different Temperatures.

Solvent	Temp. (°C)	Log K _f
Nitromethane	90	3.21±0.03
	75	3.39±0.05
	60	3.66±0.04
	45	3.81±0.05
	30	4.14±0.07
	. 15	4.40±0.10
Acetonitrile	75	3.15±0.05
	60	3.41±0.03
	40	3.73±0.05
	30	3.95±0.04
	20	4.11±0.05
Acetone	55	3.36±0.06
	40	3.64±0.03
	30	3.93±0.06
	20	4.19±0.04
	10	4.52±0.04
Methanol	60	3.54±0.04
	50	3.68±0.02
	40	3.83±0.02
	30	3.96±0.06
	20	4.14±0.02
Pyridine	90	3.39±0.05
	75	3.57±0.07
	60	3.78±0.05
	50	3.89±0.04
	40	4.07±0.05
	30	4.27±0.07

Table 32. Formation Constants of DB21C7.Cs⁺ Complex in Nonaqueous Solvents at Various Temperatures.

Plots of $ln \ K_f \ vs.$ 1/T for the five systems are shown in Figure 31. The enthalpies and the entropies of the complexation were obtained in the usual manner from the slopes and the intercepts of the plots and the results are listed in Table 33. As is seen, in all cases the complexes are enthalpy stabilized but entropy destabilized. The enthalpy and entropy values vary very significantly with the solvent, but in all cases they compensate each other resulting in a nearly identical free energy for the complexation. The sequence of the increase in the entropy change in different solvents is acetone < acetonitrile < nitromethane < pyridine < methanol.

4.5. DISCUSSION

A deeper understanding of the thermodynamics of the complexation of the metal ions with macrocyclic crown ethers can be provided by the evaluation of the enthalpy and the entropy changes of the reaction. The magnitudes of enthalpy values are indicative of the metal ion-ligand interaction providing information about the type and the number of binding sites. The magnitude of the entropy values are indicative of the solvent-solute interactions. It can supply information about the relative degrees of solvation of the particles involved (<u>i.e.</u>, the metal ion, the ligand, and the complex), the less of degrees of freedom of the ligand upon complexation, and the charge



Figure 31. Van't Hoff Plots for Complexation of Cs⁺ Ion by Dibenzo-21-Crown-7 in Various Solvents.

Solvent	∆G°(30°C) (kcal/mole)	∆H° (kcal/mole)	∆S° (cal/mole °K)
Nitromethane	-5.75±0.10	-7.61±0.25	-6.25±0.78
Acetonitrile	-5.49±0.05	-8.24±0.20	-9.19±0.66
Acetone	-5.46±0.08	-11.13±0.41	-18.64±1.35
Methanol	-5.50±0.08	-6.61±0.14	-3.54±0.44
Pyridine	-5.93±0.10	-7.22±0.18	-4.38±0.56
Methanol Pyridine	-5.50±0.08 -5.93±0.10	-6.61±0.14 -7.22±0.18	-3.54±0.44 -4.38±0.56

Table 33. Thermodynamic Parameters for the Complexation of Cs⁺ Ion by DB21C7 in Nonaqueous Solvents at Different Temperatures.

types involved in the reaction.

In all three complexation reactions studied in this thesis, <u>i.e.</u>, complexation of the cesium ion with DB30Cl0, DB24C8, and DB21C7, the contributions of the metal ion solvation and its charge type to the entropy changes in the same solvants are the same. Whereas, because of the difference in the size and in the number of the binding sites of the ligands, the contributions of the conformational change of the ligand and of the solvation of the ligand and the complex to the entropy changes are different. Thus in order to interpret the thermodynamic data, these factors must be considered.

In all cases studied, the complexes are enthalpy stabilized but entropy destabilized. The entropies of the complexation of the cesium ion with DB30C10, DB24C8, and DB21C7 in various solvents are compared in Table 34. The solvation of the free and of the complexed cesium ion could be very different so that the complexation can influence the structure of the solvent which could contribute to the entropy of the complexation. Since the solvents we worked with are less structured than water, the contribution of this factor to the entropy would not be very important. However, at the present time we have no knowledge about the extent of solvation of either the ligands or the complexes.

A more important contribution to the negative entropy

		∆S°(cal/mole	°K)
Solvent	DB30Cl0·Cs ⁺	DB24C8·Cs ⁺	DB21C7·Cs ⁺
Nitromethane	-6.66±1.25	-1.79±0.34	-6.25±0.78
Acetonitrile	-1.53±0.89	-8.66±0.48	-9.19±0.66
Acetone	-26.19±1.69	-20.08±1.71	-18.64±1.35
Methanol	-22.82±1.11	-16.10±1.49	-3.54±0.44
Pyridine	-7.94±0.36	-5.93±1.13	-4.38±0.56

Table 34. Entropies of the Complexation of Cesium Ion by DB30C10, DB24C8, and DB21C7 in Various Solvents.

values would be the change in conformation of the ligands. from a flexible structure in the free state to a more rigid form, upon complexation. It is interesting to note that, with the exception of acetonitrile, in all solvents used, first, the entropy values of the DB24C8·Cs⁺ complex are about 4 to 6 e.u. less negative than those for DB30Cl0.Cs⁺ complex, and second, the sequence of the solvent effect on the entropy values is the same for both complexes. According to these results, it seems reasonable to assume that among the various factors contributing to the negative entropies of the complexation of the cesium ion with DB30Cl0 and DB24C8, the decrease in the conformational entropy of the ligand upon complexation is the dominant one. Large macrocyclic ligands such as DB30Cl0 and DB24C8 are rather flexible in free state. The degree of flexibility would vary with the size of the ligands and with the solvent (i.e., with the extent of ligand-solvent interaction). DB30Cl0 is more flexible than DB24C8 in free state because of its larger size, and also $DB30C10 \cdot Cs^+$ complex is probably more rigid than $DB24C8 \cdot Cs^+$ complex because of its complete "wrap around" structure (Chapter 3). Therefore, the more negative entropy values for DB30C10.Cs⁺ complex than those for DB24C8·Cs⁺ are not unexpected. Acetonitrile as solvent, however, is an exceptional case probably because it can form a complex with the ligands, such as that reported with 18-crown-6 (135), and, therefore, can deviate the



results from the expected trend.

On the other hand, in the case of the complexation of the cesium ion with DB21C7, neither the sequence of the solvent effect on the entropy values nor the trend of the entropy values, i.e., decreasing the entropy with increasing the size of the ligand, agree with the DB30C10 and DB24C8 cases. Since the cesium ion, with diameter of 3.68 Å (128), has a very close size to that of DB21C7 cavity, with the size of 3.4-4.3 Å (23), it seems reasonable to assume that the DB21C7·Cs⁺ complex has a two-dimensional structure. Therefore the large conformation changes involving the ligand "wrapping around" the cation such as one observed of DB30Cl0 are not expected in this ligand. Thus, unlike the cases of DB30Cl0 and DB24C8, the conformational change of the ligand upon complexation is not necessarily the dominant factor in this case. Such an example can be found in the literature. Dibenzo-30-crown-10 (32) and 18-crown-6 (62) form complexes with the potassium ion in methanol solution with about the same entropy values of -17.7 e.u. and -17.3 e.u. respectively. If the decreased conformational change of the ligand upon complexation was the dominant contribution to the entropy values in both cases, we would expect the dibenzo-30-crown-10·Cs⁺ complex to have a much more negative entropy value than 18-crown-6·Cs⁺. It has been shown that potassium ion forms a three-dimensional "wrap around" complex with dibenzo-30-crown-10 (26,33) but a two-dimensional one with 18-crown-6 (136).

CHAPTER 5

LITHIUM-7, SODIUM-23, CESIUM-133, AND THALLIUM-205 NMR STUDY OF Li⁺, Na⁺, Cs⁺, and Tl⁺ ION COMPLEXES WITH 1,10-DIAZA-18-CROWN-6 IN VARIOUS NONAQUEOUS

SOLVENTS

5.1. INTRODUCTION

The macrocycle 1,10-diaza-18-crown-6 was first synthesized by Dietrich <u>et al</u>. (137).



1.10-DIAZA-18-CROWN-6

Frensdorff (4) has shown that the substitution of two nitrogens for two oxygens in 18-crown-6 reduces the affinity of the ligand for alkali metal ions while enhancing the stability of the complexes of transition metal ions of the same size. Thermodynamic parameters for the complexation of some alkali earth and transition metal ions with this ligand in aqueous solution have been reported by Andereg (138) who used pH-metric titration for the measurements.

Structural properties of some metal ion complexes with l,10-diaza-18-crown-6 in solution have been studied by proton NMR (139,140) and the crystalline structure of the isolated complexes of the ligand with copper (II) and potassium ions have been determined (141,142). Copper (II) was shown to be located inside the cavity of the macrocycle and it is bonded to the two nitrogen atoms and to the two oxygen atoms. The potassium is bonded to the four oxygen atoms of the ring in the same plane and to the two

nitrogen atoms from the top and the bottom of the macrocycle plane.

The present work was undertaken to determine the stoichiometry and the formation constants of 1,10-diaza-18-crown-6 complexes of Li⁺, Na⁺, Cs⁺, and Tl⁺ ions in various nonaqueous solvents.

5.2. RESULTS

Lithium-7, sodium-23, cesium-133, and thallium-205 chemical shifts were measured as a function of the ligand/metal ion mole ratio in various solvents and the results are given in Tables 35-38. In all cases only one population average resonance of the metal ion was observed. Generally, this is only possible if a fast exchange exists between the two sites (<u>i.e.</u>, free and complexed ion) whose rate is larger than $\sqrt{2}/\pi\Delta\nu$ ($\Delta\nu$ is the difference between the resonance frequency of each site). The chemical shiftmole ratio plots for different metal ions are shown in Figures 32-35.

5.2.1. 1,10-Diaza-18-Crown-6 Complexes with Li⁺

The frequency of the lithium-7 resonance in DMF, DMSO, and TMG was found to be independent of the ligand/lithium ion mole ratio (Figure 32). This behavior shows that the immediate environment of Lithium ion is not changed upon

N	M	A	N	P	С	Ac	2
L/L1 ⁺	δ(ppm)	L/Li ⁺	δ(ppm)	L/Li ⁺	^δ (ppm)	L/Li ⁺	δ(ppm)
0.00 0.31 0.69 0.88 1.00 1.10 1.33 1.60 2.14 3.36	0.43 0.28 0.06 -0.07 -0.10 -0.12 -0.10 -0.11 -0.11 -0.11	0.00 0.31 0.76 0.88 1.02 1.11 1.33 1.77 2.41 3.24	2.56 1.84 0.81 0.56 0.27 0.20 0.16 0.18 0.16 0.16	0.00 0.35 0.69 1.04 1.23 1.38 1.66 1.88 2.31 2.85 3.44	0.63 0.43 0.26 0.12 0.09 0.08 0.05 0.05 0.05 0.05 0.05	0.00 0.39 0.77 0.90 0.99 1.14 1.23 1.73 2.18 3.43	-1.00 -0.87 -0.73 -0.69 -0.67 -0.64 -0.62 -0.52 -0.48 =0.45
D	MF	DM	ISO	T	MG	F	у
L/Li ⁺	δ _(ppm)	L/Li ⁺	δ _(ppm)	L/Li ⁺	δ _(ppm)	L/Li ⁺	δ _(ppm)
0.00 0.38 0.75 0.86 1.02 1.11 1.22 1.57 2.07 3.13	-0.63 -0.62 -0.64 -0.62 -0.63 -0.62 -0.63 -0.64 -0.63 -0.64	0.00 0.38 0.75 0.87 1.08 1.16 1.40 1.66 1.99 3.35	1.03 1.04 1.04 1.06 1.04 1.06 1.03 1.05 1.05 1.05	0.00 0.38 0.75 0.88 1.00 1.11 1.23 1.43 1.90 2.90	$\begin{array}{c} -0.45 \\ -0.44 \\ -0.46 \\ -0.47 \\ -0.45 \\ -0.44 \\ -0.46 \\ -0.46 \\ -0.44 \\ -0.45 \end{array}$	0.00 0.44 0.67 0.91 1.02 1.10 1.32 1.43 2.05 3.10	-2.41 -2.24 -2.16 -2.06 -2.01 -1.98 -1.93 -1.88 -1.66 -1.43

Table 35. Mole Ratio Study of 1,10-Diaza-18-Crown-6 Complex with 0.02<u>M</u> LiClO₄ in Various Solvents at 30°C.



	NM			Ac	
L/Na ⁺	δ(ppm)	$\Delta v_{1/2}(Hz)$	L/Na ⁺	δ(ppm)	Δν _{1/2} (Hz)
0.00 0.32 0.70 0.91 1.02 1.19 1.47 1.84 2.48 2.97	14.21 11.97 9.46 7.89 7.31 6.69 6.88 6.83 6.79 6.75	13 114 201 260 273 268 274 276 276 298	0.00 0.41 0.80 0.90 1.00 1.11 1.22 1.46 2.11 3.10	6.93 7.52 8.14 8.26 8.29 8.32 8.32 8.32 8.35 8.40 8.56	18 41 67 68 73 76 79 83 85 93
	DMSO			Ру	
L/Na ⁺	δ(ppm)	$\Delta v_{1/2}(Hz)$	L/Na ⁺	δ _(ppm)	Δν _{1/2} (Hz)
0.00 0.40 0.75 0.88 0.96 1.09 1.23 1.49 2.02 2.68	0.04 0.54 0.86 0.90 1.02 1.11 1.20 1.26 1.50 1.81	46 55 68 67 74 74 78 80 96 105	0.00 0.29 0.70 0.86 0.94 1.09 1.23 1.55 2.09 2.57	-1.15 1.43 4.81 6.70 7.08 7.44 7.62 7.70 7.66 7.67	21 55 104 121 137 135 137 146 144 155

Table 36. Mole Ratio Study of 1,10-Diaza-18-Crown-6 Complex with 0.05M NaBPh₄ in Various Solvents at 30°C.

Various	
ln	
Ion	
+ 8	
о Ч	
wit	
Complex	
Study of 1,10-Diaza-18-Crown-6	t 30°C.
Ratio	nts at
Mole	Solve
37.	
le	
Tab.	

_

NN	Ча	AN	la	PC	Ja	Ш	O ^a
L/Cs ⁺	و (ppm)	L/Cs ⁺	(bpm)	L/Cs ⁺	(ppm)	L/Cs ⁺	(ppm)
0.00	54.95	0.00	-33.41	0.00	34.26	00.0	-100.63
0.32	40.37	0.26	-36.13	0.22	29.24	0.34	-92.17
0.85	12.92	0.49	-39.46	0.59	19.70	0.67	-84.04
0.95	8.65	0.52	-39.62	0.76	15.94	0.85	-78.84
1.05	4.62	0.78	-42.33	0.88	12.81	1.05	-75.27
1.20	2.06	0.82	-42.72	0.98	10.10	1.35	-69.22
1.40	-5.15	0.96	-43.75	1.16	6.91	1.47	-67.06
1.69	-11.12	1.06	-44.74	1.28	4.82	1.94	-59.48
1.96	-14.69	1.20	-45.66	1.43	2.25	2.13	-57.75
2.23	-15.47	1.43	-47.29	1.96	-4.	2.80	-48.83
2.48	-16.71	1.88	-49.07	2.52	-10.28	4.63	-35.03
3.54	-20.66	2.57	-50.70	3.62	-17.21	7.88	-23.24
5.09	-23.14	3.50	-51.94	4.86	-21.70		
7.70	-25.08	4.80	-52.87	7.85	-26.82		
		7.97	-54.19				

Ac ^b DMFa DMSOa TMGa TMGa Py ^b L/cs^{+} δ (ppm) L/cs^{+} L/cs^{+} L/cs^{+} L										
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	A	cb	Ŋ	ſ Ба	DIN	1SO ^a	É	4G ^a	P3	d,
0.00 15.89 0.00 -0.13 0.00 -68.25 0.00 -106.18 0.00 33. 0.43 8.18 0.35 -0.67 0.40 -67.48 0.38 -104.53 0.44 9. 0.77 1.11 0.70 -1.36 0.67 -67.70 0.71 -102.22 0.80 -9. 0.88 -1.68 0.84 -1.67 0.86 -67.39 0.82 -101.82 0.88 -12. 0.99 -3.30 0.95 -2.06 1.01 -67.34 1.18 -00.12 1.04 -21. 1.18 -5.63 1.25 -3.07 1.16 -67.34 1.18 -100.12 1.04 -21. 1.18 -9.28 1.166 -47.34 1.18 -100.12 1.04 -21. 1.198 -12.76 1.96 -47.69 1.91 -67.69 1.90 -97.02 1.71 -35. 1.98 -12.76 1.98 -67.69 1.90 -97.02 1.71 -36. 1.98 -14.93 2.19 2.67<	L/Cs ⁺	(mqq) ^ð	L/Cs ⁺	(mqq) ⁸	L/Cs ⁺	(mqq) ⁸	L/Cs ⁺	(mpm) ⁸	L/Cs ⁺	(mqq) ⁸
0.43 8.18 0.35 -0.67 0.40 -67.48 0.38 -104.53 0.44 9. 0.77 1.11 0.70 -1.36 0.67 -67.70 0.71 -102.22 0.80 -9. 0.88 -1.66 0.84 -1.67 0.86 -67.39 0.82 -101.82 0.80 -9. 0.99 -3.30 0.95 -2.06 1.01 -67.34 0.99 -100.81 0.98 -12. 1.18 -5.63 1.25 -3.07 1.16 -67.34 1.18 -100.12 1.04 -21. 1.18 -5.63 1.25 -3.07 1.16 -67.24 1.50 -98.57 1.38 -28. 1.68 -12.76 1.96 -67.65 1.90 -97.02 1.71 -37. 1.68 -14.28 1.68 -67.65 2.24 -95.18 1.96 -37. 1.98 -14.93 2.16 -167.65 2.24 -92.99 2.27 -40. 2.51 -16.32 2.67 -67.70 4.75 -92.99	0.00	15.89	0.00	-0.13	00.00	-68.25	0.00	-106.18	00.0	33.07
0.77 1.11 0.70 -1.36 0.67 -67.70 0.71 -102.22 0.80 -9. 0.88 -1.67 0.84 -1.67 0.86 -67.39 0.82 -101.82 0.88 -12. 0.99 -3.30 0.95 -2.06 1.01 -67.34 0.99 -100.81 0.98 -17. 1.18 -5.63 1.25 -3.07 1.16 -67.34 1.18 -100.12 1.04 -21. 1.39 -9.28 1.66 -3.53 1.31 -67.24 1.50 -98.57 1.38 -28. 1.98 -114.93 2.15 -44.28 1.66 -57.65 2.24 -95.18 1.96 -37. 1.98 -114.93 2.15 -44.78 2.00 -67.65 2.24 -95.18 1.96 -37. 2.14 -16.32 2.13 -67.65 2.24 -90.19 2.59 -40. 2.51 -18.97 3.49 -67.65 8.29 -86.94 3.45 -40. 2.51 -18.97 4.92	0.43	8.18	0.35	-0.67	0,40	-67.48	0.38	-104.53	0.44	9.18
0.88 -1.68 0.84 -1.67 0.86 -67.39 0.82 -101.82 0.88 -17. 0.99 -3.30 0.95 -2.06 1.01 -67.34 0.99 -100.81 0.98 -17. 1.18 -5.63 1.25 -3.07 1.16 -67.34 1.18 -100.12 1.04 -21. 1.39 -9.28 1.66 -3.53 1.31 -67.24 1.50 -98.57 1.38 -28. 1.68 -12.76 1.96 -4.28 1.68 -67.69 1.90 -97.02 1.71 -35. 1.68 -16.75 2.17 -67.65 2.24 -97.02 1.71 -35. 1.98 -14.93 2.15 -44.78 2.00 -67.65 2.24 -90.19 2.27 -40. 2.51 -16.32 2.53 -6.02 2.17 -67.65 2.24 -92.99 2.27 -40. 2.51 -16.33 3.49 -7.65 2.57 -67.70 4.75 -90.19 2.59 -45. 2.51 -1	0.77	11.1	0.70	-1.36	0.67	-67.70	17.0	-102.22	0.80	-9.58
0.99 -3.30 0.95 -2.06 1.01 -67.34 0.99 -100.81 0.98 -17. 1.18 -5.63 1.25 -3.07 1.16 -67.34 1.18 -100.12 1.04 -21. 1.39 -9.28 1.66 -3.53 1.31 -67.24 1.50 -98.57 1.38 -28. 1.68 -12.76 1.96 -4.28 1.68 -67.69 1.90 -97.02 1.71 -35. 1.68 -14.93 2.15 -4.78 1.68 -67.65 2.24 -95.18 1.96 -37. 2.14 -16.32 2.15 -4.78 2.00 -67.65 2.24 -95.18 1.96 -37. 2.14 -16.32 2.15 -4.78 2.07 -40.5 2.27 -40.5 2.51 -18.97 3.40 -7.65 2.57 -67.70 4.75 -90.19 2.59 -42. 3.52 -24.86 4.46 -9.59 3.49 -67.71 4.95 4.00 4.67 -28.66 7.83 -14.	0.88	-1.68	0.84	-1.67	0.86	-67.39	0.82	-101.82	0.88	-12.84
1.18 -5.63 1.25 -3.07 1.16 -67.34 1.18 -100.12 1.04 -21. 1.39 -9.28 1.66 -3.53 1.31 -67.24 1.50 98.57 1.38 -28. 1.68 -12.76 1.96 -4.28 1.68 -67.69 1.90 -97.02 1.71 -35. 1.98 -14.93 2.15 -4.78 2.00 -67.65 2.24 -92.99 2.77 -40. 2.14 -16.32 2.63 -6.02 2.17 -67.65 2.24 -92.99 2.77 -40. 2.51 -18.97 3.40 -7.65 2.57 -67.70 4.75 -90.19 2.59 -42. 2.51 -18.97 3.40 -7.65 2.57 -67.71 4.75 -90.19 2.59 -45. 2.51 -24.86 4.446 -9.59 3.45 -45. 4.66 -47. 2.18 -33.48 -14.47 4.92 -67.71 4.75 -90.19 2.77 -40. 7.18 -33.48 -	0.99	-3.30	0.95	-2.06	1.01	-67.34	0.99	-100.81	0.98	-17.03
1.39 -9.28 1.66 -3.53 1.31 -67.24 1.50 -98.57 1.38 -28. 1.68 -12.76 1.96 -4.28 1.68 -67.69 1.90 -97.02 1.71 -35. 1.98 -14.93 2.15 -4.78 2.00 -67.65 2.24 -95.18 1.96 -37. 2.14 -16.32 2.63 -6.02 2.17 -67.65 2.24 -95.18 1.96 -37. 2.51 -18.97 3.40 -7.65 2.57 -67.70 4.75 -90.19 2.59 -42. 3.52 -24.86 4.46 -9.59 3.49 -67.55 8.29 -86.94 3.45 -45. 4.67 -28.66 7.83 -14.47 4.92 -67.71 4.75 -90.19 2.57 -45. 7.18 -33.48 -14.47 4.92 -67.72 7.97 -49. 7.18 -33.48 -14.47 4.92 -67.22 7.97 -49. 3.01M CSSCN. b.0.01M CSBPh. b.0.1M CSBPh. -97.22	1.18	-5.63	1.25	-3.07	1.16	-67.34	1.18	-100.12	1.04	-21.37
1.68 -12.76 1.96 -4.28 1.68 -67.69 1.90 -97.02 1.71 -35. 1.98 -14.93 2.15 -4.78 2.00 -67.65 2.24 -95.18 1.96 -37. 2.14 -16.32 2.63 -6.02 2.17 -67.63 3.34 -92.99 2.27 -40. 2.51 -18.97 3.40 -7.65 2.57 -67.70 4.75 -90.19 2.59 -42. 2.51 -18.97 3.40 -7.65 2.57 -67.70 4.75 -90.19 2.59 -45. 3.52 -24.86 4.46 -9.59 3.49 -67.71 4.75 -90.19 2.59 -45. 4.67 -28.66 7.83 -14.47 4.92 -67.71 4.88 -47. 7.18 -33.48 -33.48 -3.00.19 2.57 -40. 7.97 -49. a.0.01M csSCN. b.0.01M csBPh. -9.02.22 7.02 7.97 -49.	1.39	-9.28	1.66	-3.53	1.31	-67.24	1.50	98.57	1.38	-28.74
1.98 -14.93 2.15 -4.78 2.00 -67.65 2.24 -95.18 1.96 -37. 2.14 -16.32 2.63 -6.02 2.17 -67.63 3.34 -92.99 2.27 -40. 2.51 -18.97 3.40 -7.65 2.57 -67.70 4.75 -90.19 2.59 -42. 3.52 -24.86 4.46 -9.59 3.49 -67.55 8.29 -86.94 3.45 -45. 4.67 -28.66 7.83 -14.47 4.92 -67.71 4.88 -47. 4.67 -28.66 7.83 -14.47 4.92 -67.71 4.88 -47. 7.18 -33.48 8.00 -67.22 7.07 4.9. 3.001M CsSCN. ^b 0.01M CsBPh_{1. 8.00 -67.22 7.97 7.97 -49.	1.68	-12.76	1.96	-4.28	1.68	-67.69	1.90	-97.02	1.71	-35.02
2.14 -16.32 2.63 -6.02 2.17 -67.63 3.34 -92.99 2.27 -40. 2.51 -18.97 3.40 -7.65 2.57 -67.70 4.75 -90.19 2.59 -42. 3.52 -24.86 4.46 -9.59 3.49 -67.55 8.29 -86.94 3.45 -45. 4.67 -28.66 7.83 -14.47 4.92 -67.71 4.98 -47. 7.18 -33.48 8.00 -67.22 7.97 -49.	1.98	-14.93	2.15	-4.78	2.00	-67.65	2.24	-95.18	1.96	-37.50
2.51 -18.97 3.40 -7.65 2.57 -67.70 4.75 -90.19 2.59 -42. 3.52 -24.86 4.46 -9.59 3.49 -67.55 8.29 -86.94 3.45 -45. 4.67 -28.66 7.83 -14.47 4.92 -67.71 4.88 -47. 7.18 -33.48 8.00 -67.22 7.97 -49.	2.14	-16.32	2.63	-6.02	2.17	-67.63	3.34	-92.99	2.27	-40.29
3.52 -24.86 4.46 -9.59 3.49 -67.55 8.29 -86.94 3.45 -45. 4.67 -28.66 7.83 -14.47 4.92 -67.71 4.88 -47. 7.18 -33.48 8.00 -67.22 7.97 -49. ^a 0.01M CSSCN. ^b 0.01M CSBPh _i .	2.51	-18.97	3.40	-7.65	2.57	-67.70	4.75	-90.19	2.59	-42.00
4.67 -28.66 7.83 -14.47 4.92 -67.71 4.88 -47. 7.18 -33.48 8.00 -67.22 7.97 -49. ^a 0.01M CsSCN. ^b 0.01M CSBPh _i .	3.52	-24.86	4.46	-9.59	3.49	-67.55	8.29	-86.94	3.45	-45.10
7.18 -33.48 8.00 -67.22 7.97 -49. ^a 0.01M CsSCN. ^b 0.01M CsBPh _i .	4.67	-28.66	7.83	-14.47	4.92	-67.71			4.88	-47.58
^a 0.01M CsSCN. ^b 0.01M CsBPh _h .	7.18	-33.48			8.00	-67.22			7.97	-49.60
1	80.01M	CsSCN.	MI0.0 ^d	CsBPh ₄ .						

Table 37. Continued.

	NMa	A	N ^b	Ad	ca
L/T1 ⁺	δ _(ppm)	L/T1 ⁺	δ _(ppm)	l/Tl ⁺	δ(ppm)
0.00 0.93 1.12 1.36 1.52 1.86 2.67 4.26 6.05	364.9 273.6 251.8 252.9 251.3 251.9 251.8 251.2 251.9	0.00 0.85 1.05 1.19 1.60 1.91 2.81 4.03 7.17	213.6 45.1 12.0 12.2 12.8 12.4 12.8 12.4	0.00 0.50 0.70 0.88 1.12 1.32 1.62 1.85 2.82 4.15 7.41	171.3 112.8 83.4 66.8 32.4 31.9 32.0 32.1 31.9 32.4 32.4 32.6
	DMF ^b	DMSO ^b		Py ^b	
L/T1 ⁺	δ(ppm)	L/T1 ⁺	δ _(ppm)	L/T1 ⁺	δ(ppm)
0.00 0.36 0.84 1.00 1.21 1.48 1.74 2.80 5.48	-129.9 -85.1 -10.9 14.4 40.1 60.1 66.0 71.3 72.7	0.00 0.41 0.72 0.88 1.00 1.09 1.20 1.55 1.85 2.94 5.29 7.80	-324.1 -230.8 -172.2 -147.5 -130.9 -114.7 -108.7 -77.0 -53.2 -19.0 13.1 21.4	0.00 0.36 0.83 0.91 1.01 1.10 1.16 1.56 1.89 2.90 4.67 6.58	-4.9 -13.1 -25.4 -27.0 -29.4 -30.6 -30.8 -31.7 -31.8 -31.6 -31.3 -30.9

Table 38. Mole Ratio Study of 1,10-Diaza-18-Crown-6 Complexes with T1⁺ Ion in Various Solvents at 30°C.

a0.01<u>M</u> T1C104.

^b0.02<u>м</u> тісіо₄.



Figure 32. Lithium-7 Chemical Shifts vs. [DA18C6]/[Li⁺] Mole Ratio in Different Solvents.



Figure 33. Sodium-23 Chemical Shifts vs. [DA18C6]/[Na⁺] Mole Ratio in Different Solvents.



Figure 34. Cesium-133 Chemical Shifts <u>vs</u>. [DA18C6]/[Cs⁺] Mole Ratio in Different Solvents.



Figure 35. Thallium-205 Chemical Shifts <u>vs.</u> [DA18C6]/[T1⁺] Mole Ratio in Different Solvents.

addition of the ligand, evidence of formation of a very weak complex at the best. These are solvents with high donicities and strong solvating abilities and, therefore can compete with the ligand for the lithium ion.

On the other hand, in solvents of weak and medium donor ability such as nitromethane, acetonitrile, propylene carbonate, and acetone (with respective Gutmann donor numbers of 2.7, 14.1, 15.1, and 17.0) the lithium-7 chemical shift is strongly affected by addition of the ligand, indicating existence of an interaction between the lithium ion and the ligand. As is seen in Figure 32, the lithium-7 resonance has a linear paramagnetic shift in nitromethane, acetonitrile, and propylene carbonate (diamagnetic in acetone) upon addition of the ligand which begins to level off at mole ratio of about 1, indicating formation of a complex with 1:1 stoichiometry between the lithium ion and the ligand. A gradual diamagnetic shift was observed in pyridine solutions which could be attributed to the formation of a weak complex. The limiting chemical shifts and the formation constants of the complexes were obtained by computer fitting the chemical shift-mole ratio data to an equation (discussed in Chapter 3) which relates the observed chemical shift to the complex formation constant using KINFIT program. The results are given in Table 39.

While the cavity size of the macrocycle is larger than the size of the lithium ion, the resulting complexes seem

Table 39. Formation Constants and the Limiting Chemical Shifts of 1,10-Diaza-18-Crown-6.Li⁺ Complexes in Various Solvents.

Solvent	Log K _f	δ _{lim} (ppm)
Nitromethane	>5	-0.11±0.02
Acetonitrile	4.39±0.41	0.16±0.00
Propylenecarbonate	3.67±0.25	0.05±0.00
Acetone	2.13±0.08	-0.36±0.02
Dimethylformamide	~0.0	
Dimethylsulfoxide	~0.0	
Tetramethylguanidine	~0.0	
Pyridine	0.43±0.08	0.6±0.3

.

unexpectedly strong, particularly in the solvents with low donicity. The formation constants are even greater than those reported for 18-crown- $6 \cdot \text{Li}^+$ complex in the same solvents (81). The stability of the complexes in different solvents decreases in the order of nitromethane > acetonitrile > propylene carbonate > acetone > pyridine which is the order of increase in Gutmann donor number of the solvents. Despite the close range of the limiting chemical shifts in nitromethane, acetonitrile, propylene carbonate, and acetone, chemical shift of the complexed lithium ion is solvent dependent, indicating incomplete insulation of the cation from the solvent by complexation.

5.2.2. 1,10-Diaza-18-Crown-6 Complexes with Na⁺

Sodium-23 NMR study of the sodium ion complexes with the ligand in a number of solvents such as propylene carbonate and DMF was limited by the quadropolar broadening of the ²³Na resonance ($\Delta v_{1/2}$)500 Hz) which makes the precise measurements of the chemical shift impossible. The change in ²³Na chemical shift upon addition of the ligand to the sodium salt solution in acetonitrile was found to be less than 0.5 ppm which is in the range of the error of the chemical shift measurement and, therefore, cannot be used in such studies. Thus, the complexation of sodium ion with the ligand was studied only in nitromethane, acetone, DMSO, and pyridine solutions, where the linewidths
are narrow enough to measure the chemical shifts accurately.

The addition of the ligand to the sodium tetraphenylborate solution in the above four solvents results in an upfield or a downfield chemical shift which begins to level off at mole ratio of about 1 indicating formation of a 1:1 complex between the cation and the ligand. The formation constants and the limiting chemical shifts for the complexes are shown in Table 40. The limiting chemical shifts of the complex in nitromethane, acetone, and pyridine are close to each other which possibly indicates that the cation is mostly covered by the ligand. In DMSO solutions, however, the complex seems to be more solvent dependent. It should be noted that DMSO has a strong solvating ability and, therefore, can compete with the ligand for the cation.

With the exception of pyridine, the complex formation constant increases with decreasing Gutmann donor number of the solvents. The results in pyridine are even unexpected because it should be a good solvating solvent as indicated by the magnitude of its sodium-23 chemical shift (143) and the high Gutmann donor number of 33.1. This is possibly because of existence of nitrogen atom as a soft donor which cannot strongly solvate a hard ion such as sodium. The sodium ion complexes with 1,10-diaza-18crown-6 are much weaker than those with 18-crown-6 in the same solvents (144) because of the introduction of two nitrogen atoms into the 18-crown-6 ring. According to the

Table 40. Formation Constants and the Limiting Chemical Shifts of 1,10-Diaza-18-Crown-6.Na⁺ Complexes in Various Solvents.

Solvent	Log K _f	δ _{lim} (ppm)
Nitromethane	3.37±0.13	6.74±0.02
Acetone	1.96±0.18	8.83±0.09
Dimethylsulfoxide	1.19±0.08	2.86±0.21
Pyridine	4.12±0.30	7.69±0.02

Pearsons Hard-Soft-Acid-Base (HSAB) theory (145), the interaction of the sodium ion as a hard acid with the nitrogen atom as a soft base should be weaker than that with the oxygen atom as a hard base.

Another interesting point to note is that the line width of the sodium-23 resonance at half height $(\Delta v_{1/2})$ increases almost linearly with increasing the ligand to sodium ion mole ratio, indicating creation of a more unsymmetric environment of ²³Na nucleus because of the complexation, and begins to level off after mole ratio of 1, showing a 1:1 stoichiometry for the complex (Table 36).

5.2.3. 1,10-Diaza-18-Crown-6 Complexes with Cs⁺

In all solvents used, with the exception of DMSO, the addition of the ligand to the cesium ion solution produces a large but gradual paramagnetic or diamagnetic shift of the cesium-133 resonance (Figure 34). In none of the solvents used does the chemical shift of the complexed cesium ion reach a limiting value even at ligand to metal ion mole ratio of about eight. The results seem to indicate formation of a weak 1:1 complex between the cesium ion and the ligand.

Using cesium-133 NMR, Mei <u>et al</u>. (94) have shown that cesium ion forms both 1:1 and 2:1 (ligand to metal) complexes with 18-crown-6. In pyridine, acetone, DMF, and

PC solutions they observed a downfield shift of ¹³³Cs resonance followed by a relatively sharp break at the mole ratio of 1 and an upfield shift which gradually approaches a limiting value. This behavior was explained by formation of a 1:1 complex followed by addition of a second molecule of the ligand to form a 2:1 sandwich complex. It is reasonable to assume that the large cesium ion will also form 1:1 and 2:1 complexes with 1,10-diaza-18-crown-6 which has a cavity of about the same size as 18-crown-6. However, no clear evidence of the formation of a 2:1 complex between cesium ion and 1,10-diaza-18crown-6 was observed in this study.

The formation constant and the limiting chemical shifts for 1:1 complexes of the cesium ion with the ligand in different solvents are given in Table 41. A large difference in the limiting chemical shifts of the complexes (about 65 ppm) in different solvents clearly indicates that the cesium ion is too large to fit into the ligand's cavity, therefore the cation mostly remains under the influence of the solvent. The complexes are much weaker than the 1:1 cesium ion complex of 18-crown-6 reported by Mei <u>et al.</u> (94). This is simply because of the existence of the two nitrogen atoms as a soft base in the ligand which cannot strongly interact with the cesium ion, known as a hard acid (145). Therefore, the resulting complex should be weaker than that with 18-crown-6. This instability

Solvent	Log K _f	δ _{lim} (ppm)
Nitromethane	2.79±0.02	-28.06±0.11
Acetonitrile	2.26±0.02 ^a	-55.93±0.08
Acetonitrile	2.30±0.01 ^b	-56.50±0.02
Propylene Carbonate	1.95±0.02	-36.76±0.36
Acetone	1.89±0.01 ^a	-43.88±0.19
Acetone	1.92±0.01 ^c	-45.56±0.17
Dimethylformamide	0.61±0.07	-61.0 ±8.6
Dimethylsulfoxide	~0.0	
Trimethyleneoxide	1.94±0.02	1.91±0.72
Tetramethylguanidine	1.55±0.02	-79.82±0.38
Pyridine	2.62±0.01	-52.42±0.06
Dimethylsulfoxide Trimethyleneoxide Tetramethylguanidine Pyridine	~0.0 1.94±0.02 1.55±0.02 2.62±0.01	 1.91±0.72 -79.82±0.38 -52.42±0.06

Table 41. Formation Constants and the Limiting Chemical Shifts of 1,10-Diaza-18-Crown-6.Cs⁺ Complexes in Various Solvents.

a0.01<u>M</u> CsSCN.

^b0.03<u>M</u> CsSCN.

°0.01<u>M</u> CsBPh₄.

indicates that if the 2:1 complexes are formed, the second formation constant would be $<<K_1$ and, therefore, probably would not show up on the mole ratio plots.

It is seen that the complex stability is not affected either by a change in the concentration of the salt, in acetonitrile solutions, or by changing the anion, in acetone solutions. It is evident therefore, that at low concentrations of the cesium salts, used in this study, the formation of the complex is unaffected by ion pairing. It is also interesting to note that, with the exception of pyridine solution, the stability of 1,10-diaza-18-crown- $6 \cdot Cs^+$ complex increases by decreasing the donicity of the solvent.

5.2.4. 1,10-Diaza-18-Crown-6 Complexes with T1⁺

In nitromethane, acetonitrile, acetone, and pyridine solutions the thallium-205 resonance shifts nearly linearly with the ligand to metal ion mole ratio until a mole ratio of 1 is reached. Further addition of the ligand does not have any further effect on the 205 Tl resonance (Figure 35). This behavior indicates formation of a strong complex ($K_f > 10^5$) between Tl⁺ ion and the ligand in the above solvents. On the other hand, in DMSO and DMF, solvents with high donicity, a gradual diamagnetic shift of the thallium-205 resonance was observed upon addition of the ligand which tends to level off after the mole ratio of 1, indicating formation of weaker complexes in these solvents.

The formation constants and the limiting chemical shifts for the complex in various solvents are shown in Table 42. The formation constants of the complexes in nitromethane, acetonitrile, acetone, and pyridine are greater than 10^5 and their precise values could not be determined by our technique. In DMSO and DMF, solvents with high donor ability, the stability of the complex is still significant. The scattered values of the complex limiting chemical shifts shows that the solvent molecules can still interact with the complexed thallium ion, possibly from the top and the bottom of the ligand's plane.

5.3. DISCUSSION

The formation constants of Li⁺, Na⁺, Cs⁺, and Tl⁺ ion complexes of 1,10-diaza-18-crown-6 and 18-crown-6 in various solvents are compared in Table 43. The most probable ionic diameters, calculated by using a combination of deduction from r_0 values and experimental electron density maps by Ladd (128), for the above cations are 1.72 Å, 2.24 Å, 3.68 Å, and 3.08 Å, respectively. The cavity size of the ligand is about 2.6-3.2 Å (23). The stabilities of the 1,10-diaza-18-crown-6 complexes decreases in the following order Tl⁺ > Li⁺ > Na⁺ > Cs⁺. Among the various factors contributing to the complex stability, the two following

Solvent	Log K _f	δ _{lim} (ppm)
Nitromethane	>5	251.8
Acetonitrile	>5	12.4
Acetone	>5	32.4
Dimethylformamide	3.22±0.08	74.0±0.3
Dimethylsulfoxide	2.13±0.03	40.6±1.1
Pyridine	>5	-31.5

Table 42. Formation Constants and the Limiting Chemical Shifts of 1,10-Diaza-18-Crown-6.Tl+ Complexes in Various Solvents.

						Log K _f			
			1,10-Diaza	-18-Crown-6			18- Cr(0 ~u~ 0	
Solvent	NQ	r1+	+11	Na ⁺	Cs+	T1 ⁺⁸	r1 ^{+p}	Na ^{+c}	Cs ^{+d}
MN	2.7	>5	>5	3.37±0.13	2.79±0.02	>5	>4	74	
AN	14.1	>5	4.39±0.41		2.26±0.02	>5	2.34±0.04	3.80±0.20	>4
PC	15.1		3.67±0.25		1.95±0.02		2.69±0.11	4 <	4.14±0.19
AC	17.0	>5	2.13±0.08	1.96±0.18	1.89±0.01	>5	1.50±0.02	4 <	>5
DMF	26.6	3.22±0.08	0.0	ļ	0.61±0.07	3. 35±0.06		2.23±0.04	3.9±0.15
DMSO	29.8	2.13±0.03	0.0	1.19±0.08	0.0	1.92±0.01	0.0~	1.41±0.07	3.04±0.04
OMI				8	1.94±0.02		1		8
JIMG		8	0.0		1.55±0.02		0.0		
Py	33.1	>5	0.43±0.08	4.12±0.30	2.62±0.01	>5	0.62±0.07	>4	>5
^a Referei	ice 147.	b _{Refer}	ence 81.	^c Reference	144. ^d Rı	eference 94	•		

 Table 43.
 Formation Constants of Li⁺, Na⁺, Cs⁺ and Tl⁺ Ion Complexes of 1,10-Diaza-18-Crown-6 and

factors are especially important: first, the relative sizes of the cation and the ligand, and second, the strength of the interaction between the cation and the coordination sites of the ligand. In order to interprete the data, these factors should be considered.

In the case of the cesium ion both factors are against the complexation. Cesium ion is a hard acid (145) which cannot strongly interact with the soft nitrogen atoms of the ligand. It is also too large to fit inside the ligand's cavity. Therefore, the cesium ion complex in different solvents is the weakest one in the series. Despite the hard character of the sodium ion and consequently its weak interaction with the soft nitrogen atoms of the macrocycle ring, this cation has a suitable size for the ligand. Thus it is not surprising that 1,10-diaza-18-crown-6 forms stronger complex with sodium ion than that with cesium Although the size of the lithium ion is a little ion. smaller than that of the sodium ion for the ligand and it is harder than the sodium ion, it forms an unexpectedly more stable complex with the ligand than sodium ion. Among the alkali metal ions, lithium ion is known to have a great tendency toward covalent bond formation because of its great polarization power (146). Therefore, the existence of such covalent bond in the lithium ion complex with the ligand could possibly result in such a great stability of the complex. In the case of the thallium (I)

ion both factors are in the favor of the complexation and, therefore, the thallium (I) ion complex is the strongest among the series.

The substitution of two nitrogen atoms for two oxygen atoms in 18-crown-6 greatly influences the complexation of the ligands with the metal ions, as shown by the data in Table 43. The sodium and the cesium ion complexes are weakened appreciably by the nitrogen substitution. This is just as expected: as the negative charge on the coordination sites drops by the substitution, the electrostatic interaction between the ligand and the cation would diminish and the resulting complex would be weaker. The effect is more pronounced in the case of the cesium complex (i.e., weakening of the complex by about two orders of magnitude) than that of the sodium complex. This is simply because the cesium ion is a harder acid than the sodium ion which results in a weaker interaction between the substituted nitrogen atoms, as a soft base, and the cesium ion than that with the sodium ion.

The effect of the nitrogen substitution on the lithium ion complex is exactly the opposite: the stability of the complex is greatly increased. Because of its small size and large polarizability, lithium is known to have some chemical behavior that resembles the chemistry of magnesium (146). Because of this unusual behavior, lithium ion has a great ability to form covalent bond. It is

evident, therefore, that the increased stability of the lithium ion complex upon the substitution is because of the existence of both electrostatic and covalent bonding, in contrast with the cesium and the sodium ion cases where the bonding is only electrostatic in nature. In the case of the thallium (I) ion complex, in most of the solvents used the stability of the complexes are not exactly calculated and, therefore, they cannot be compared. We can expect, however, the thallium (I) ion complex with 1,10diaza-18-crown-6 to be more stable than that with 18-crown-6, such as that observed in DMSO solution. This is because the interaction of the soft thallium (I) ion with the soft nitrogen atoms of the ring is quite strong.

CHAPTER 6

A STUDY OF DYNAMICS OF CESIUM ION COMPLEXES WITH DIBENZO-30-CROWN-10, DIBENZO-24-CROWN-8, AND DIBENZO-21-CROWN-7 IN ACETONE AND METHANOL

6.1. INTRODUCTION

While there are several scientific reports available in the literature on the study of thermodynamics of the complexation of alkali ions by crown ethers, the complexation kinetics of the cyclic polyethers have received less attention. Kinetic studies of alkali metal complexation with crown ethers are usually impeded by several factors: complexes are not usually strong enough and therefore must be studied at high metal ion concentrations; the reaction rates are usually high and experimental difficulties are encountered especially if work at high concentrations is required; and finally, the complexes are usually colorless, so that spectrophotometric measurements of rates are rarely possible.

In an early sodium-23 NMR study of complexation of sodium ion by dibenzo-18-crown-6 in DMF solution, Shchori $\underline{et \ al}$. (87) concluded that the strong ionic strength dependence of the kinetics indicates that the dynamic equilibrium involves interaction of solvated sodium ion with uncoordinated ligand rather than a simple bimolecular exchange equilibrium.

The same authors (88) studied the effect of solvents and aromatic ring substituents on the kinetics of complexation of sodium ion by dibenzo-18-crown-6. They used the sodium-23 NMR technique and worked with DMF, methanol,

and dimethoxyethane solvents. They found that the activation energy for decomplexation of sodium ion by dibenzo-18-crown-6 is the same in all solvents (\sim 12.6 kcal/mole) but is considerably less (8.3 kcal/mole) for dicyclohexyl-18-crown-6 in methanol. Shporer and Luz (93) have used ³⁹K and ⁸⁷Rb NMR to determine the rate constants for potassium and rubidium ion decomplexation by dibenzo-18-crown-6 in methanol solution at low temperatures. They found that the decomplexation of rubidium is much faster than of potassium ion.

Using spectrophotometric measurements, Chock (32) determined the rate constants for complexation of several monovalent cations by dibenzo-30-crown-10 in methanol solution. From the resulting data he suggested the existence of a fast crown ether conformational transition preceding the complexation reaction:

in which CR_1 and CR_2 denote different conformations of the uncomplexed ligand.

Eyring and coworkers (148,149) have determined the rate constants for cation decomplexation by 15-crown-5 and 18-crown-6 in aqueous solutions by ultrasonic

absorption method. They concluded that the slow decomplexation of 18-crown-6·Cs⁺ complex is the reason for the high selectivity of 18-crown-6 for potassium ion over the other alkali ions.

The purpose of the work described in this chapter is to study the kinetics of the complexation of the cesium ion by DB30Cl0, DB24C8, and DB21C7 in acetone and methanol solutions by cesium-133 NMR lineshape analysis at various temperatures.

6.2. DETERMINATION AND INTERPRETATION OF THE LINESHAPES

The modified Block equations proposed by McConnell (150) which describe the motion of the X and Y components of magnetization in the rotating frame are shown as follows:

$$\frac{\mathrm{d}G_{\mathrm{A}}}{\mathrm{d}t} + \alpha_{\mathrm{A}}G_{\mathrm{A}} = -i\gamma H_{\mathrm{1}}M_{\mathrm{OA}} + \tau_{\mathrm{B}}^{-1}G_{\mathrm{B}} - \tau_{\mathrm{A}}^{-1}G_{\mathrm{A}} \qquad (1)$$

$$\frac{dG_{B}}{dt} + \alpha_{B}G_{B} = -i\gamma H_{1}M_{OB} + \tau_{A}^{-1}G_{A} - \tau_{B}^{-1}G_{B}$$
(2)

where

$$\alpha_{A} = 1/T_{2A} - i(\omega_{A} - \omega)$$
 and $\alpha_{B} = 1/T_{2B} - i(\omega_{B} - \omega)$

$$G = u + iv \tag{3}$$

u and v are the transverse components (<u>i.e.</u>, absorption and dispersion mode lineshapes) of magnetization along and perpendicular to the rotating field, H_1 .

The solutions of Equations (1) and (2) appropriate for slow passage are obtained by

$$\frac{\mathrm{dG}_{\mathrm{A}}}{\mathrm{dt}} = \frac{\mathrm{dG}_{\mathrm{B}}}{\mathrm{dt}} = 0 \tag{4}$$

The equations can be solved for ${\tt G}_{A}$ and ${\tt G}_{B}.$ Noting that

$$M_{OA} = P_A M_O$$
 and $M_{OB} = P_B M_O$ (5)

the total complex moment is

$$G = G_{A} + G_{B} = -i\gamma H_{1}M_{0} \frac{\tau_{A} + \tau_{B} + \tau_{A}\tau_{B}(\alpha_{A}P_{A} + \alpha_{B}P_{B})}{(1 + \alpha_{A}\tau_{A})(1 + \alpha_{B}\tau_{B}) - 1}$$
(6)

 $\underline{Fast\ Exchange}.$ In the limit of rapid exchange, τ_A and τ_B are small and Equation (6) reduces to

$$G = -i\gamma H_1 M_0 \frac{\tau_A + \tau_B}{\alpha_A \tau_A + \alpha_B \tau_B} = - \frac{i\gamma H_1 M_0}{P_A \alpha_A + P_B \alpha_B}$$
(7)

The imaginary part is

$$v = -\gamma H_{1}M_{0} \frac{T'_{2}}{1 + T'_{2}^{2}(P_{A}\omega_{A} + P_{B}\omega_{B} - \omega)^{2}}$$
(8)

representing a resonance line centered on a mean frequency of

$$\omega_{\text{mean}} = P_A \omega_A + P_B \omega_B \tag{9}$$

with a linewidth given by

$$\frac{1}{T_2'} = \frac{P_A}{T_{2A}} + \frac{P_B}{T_{2B}}$$
(10)

If the exchange is not quite rapid enough to give complete collapse, the central signal centered on ω_{mean} will appear to have a larger width than that given by Eq. (10). A corrected form of Equation (10) can be obtained by putting $\omega = \omega_{mean}$ in Equation (6) and expanding in powers of τ . This gives an effective transverse relaxation time

$$\frac{1}{T_{2}} = \frac{P_{A}}{T_{2A}} + \frac{P_{B}}{T_{2B}} + P_{A}^{2}P_{B}^{2}(\omega_{A} - \omega_{B})^{2}(\tau_{A} + \tau_{B})$$
(11)

where P_A and P_B are relative populations at sites A and B, respectively, the quantities ω_A and ω_B are the resonance frequencies at the two sites at a given temperature in the absence of exchange, and T_{2A} and T_{2B} are the respective relaxation times at each site at a given temperature. The lifetime of interaction is defined as

$$\tau = \frac{\tau_A \tau_B}{\tau_A + \tau_B}$$
(12)

If at a given temperature the τ value is greater than $\frac{\sqrt{2}}{\pi\Delta\omega}$, where $\Delta\omega = |\omega_A - \omega_B|$, two separate resonance lines are observed for the two respective sites. If the τ value is less than $\frac{\sqrt{2}}{\pi\Delta\omega}$, only one population average resonance is observed.

In some cases such as ${}^{13}C$ and ${}^{1}H$ NMR, where the transverse relaxation times are long enough, the following assumption has been made (151-153):

$$\frac{1}{T_{2A}} = \frac{1}{T_{2B}} = 0$$
(13)

Since cesium-133 is a nuclei with narrow natural linewidth of about 1 Hz (quadrupole moment of \mathbf{q} = 0.003 barns) and consequently long enough transverse relaxation time, it seems reasonable to assume that the above assumption is also valid for ¹³³Cs NMR case.

In all cases studied, the ligand to cesium ion mole ratio was 0.5 and also the formation constants of the complexes were greater than 10^3 (Chapter 3). Therefore

$$P_{A} = P_{B} = 1/2$$
 (14)

The relationship between the frequency in radians per second, ω , and that in cycles per second, ν , is defined

as

$$\omega = 2\pi\nu \tag{15}$$

In general the relaxation time is given by (154):

$$\frac{1}{\tau_{i}} = \frac{\text{rate of removal of molecule from i}^{\text{th}} \text{ state by exchange}}{\text{number of molecules in the i}^{\text{th}} \text{ state}}$$
(16)

If we consider the following complexation reaction

$$M + L \stackrel{k_{f}}{\leftarrow} ML \qquad (17)$$

then

$$\frac{1}{\tau_{\rm B}} = \frac{d_{\rm ML}/dt}{C_{\rm ML}}$$
(18)

$$\frac{1}{\tau_{A}} = \frac{d_{M}/dt}{C_{M}}$$
(19)

Since

$$-\frac{d_{\rm ML}}{dt} = k_{\rm b} C_{\rm ML}$$
(20)

$$-\frac{d_{M}}{dt} = k_{f} C_{M}C_{L}$$
(21)

Therefore

$$\frac{1}{\tau_{\rm B}} = k_{\rm b} \tag{22}$$

.

$$\frac{1}{\tau_{\rm A}} = -k_{\rm f} C_{\rm L} \tag{23}$$

we have

$$\tau = P_A \tau_A = P_B \tau_B = 1/2\tau_A = 1/2\tau_B$$
(24)

with Equation (23)

$$\tau = \frac{P_A}{k_b}$$
(25)

For equal population that we used; Equation (14)

$$\tau = \frac{1}{2k_{\rm b}} \tag{26}$$

By substitution of Equations (12), (14), (15), (24), and (26) in Equation (11) we will come out with the following equation:

$$\frac{1}{T_{2}} = \frac{\pi^{2}(v_{A} - v_{B})}{2k_{b}}$$
(27)

It is known that

$$\frac{1}{T_2'} = \pi W \tag{28}$$

where W is the linewidth at half height. By substitution of Equation (28) in Equation (27) we have

$$k_{\rm b} = \frac{\pi (v_{\rm A} - v_{\rm B})^2}{2W}$$
(28)

where v_A and v_B are the resonance frequencies of the two sites in the absence of exchange, and $W = \Delta v_{1/2}^{obs} - \Delta v_{1/2}^{ref}$. The $\Delta v_{1/2}^{obs}$ and $\Delta v_{1/2}^{ref}$ are the linewidths at half height in the presence and absence of exchange, respectively.

Thus above the coalescence temperature, the linewidth of the sample solution (with the ligand/cesium ion mole ratio of 0.5) was measured and corrected for natural broadening by subtracting the linewidth of the resonance signal of a solution of pure cesium salt in the same solvent at the same temperature from it. The resonance frequencies of the solutions containing free and complexed cesium ion, v_A and v_B , respectively, in the same solvent at the same temperature were also measured. The k_b value at each temperature was then calculated from Equation (29).

Slow Exchange. If the lifetimes τ_A and τ_B are sufficiently large compared with the inverse of the separation $(\omega_A - \omega_B)^{-1}$, the spectrum will consist of two distinct signals in the vicinity of the ω_A and ω_B frequencies. For example, if the frequency of ω is close to ω_A , and thus far

away from ω_B , G_B is effectively zero and the solutions of Equations (1) and (2) become

$$G \approx G_A \approx i\gamma H_1 M_0 \frac{P_A \tau_A}{1 + \alpha_A \tau_A}$$
 (31)

The imaginary part is

$$v = -i\gamma H_{1}M_{0} \frac{P_{A}T_{2A}}{1 + (T_{2A})^{2}(\omega_{A} - \omega_{B})^{2}}$$
(32)

A broadened signal centered at $\boldsymbol{\omega}_A$ with width given by parameter

$$T_{2A}^{-1} = T_{2A}^{-1} + \tau_{A}^{-1}$$
(33)

There will be a corresponding signal centered on $\omega_{\rm B}$. This shows that the exchange leads to an additional broadening of the individual signals. If $T_{2\rm A}^{-1}$ is known, measurements of the width of these broadened signals provide a means of estimating $\tau_{\rm A}$.

Thus below the coalescence temperature the ${\bf k}_{\rm b}$ value can be calculated from

$$k_{b} = \pi W \tag{34}$$

where W is the corrected linewidth of the resonance signals, <u>i.e.</u>, $W = \Delta v_{1/2}^{obs} - \Delta v_{1/2}^{ref}$. The Arrhenius activation energy, E_a , is given by

$$\left(\frac{\partial \ln k_{b}}{\partial T}\right)_{V \text{ or } P} = E_{a}/RT^{2}$$
(35)

or

$$\ln k_{\rm b} = A - \frac{E_{\rm a}}{RT} \tag{36}$$

The activation energy was obtained from the slopes of the activation plots, (<u>i.e.</u>, $\ln k_b vs. 1/T$) by using a linear least squares program. The thermodynamic parameters of activation were calculated from the following equations:

$$\Delta H_{O}^{\neq} = E_{a} - RT \qquad (37)$$

-

$$\Delta S_{O}^{\neq} = R \ln k_{D} - R \ln \frac{k_{T}}{h} + \frac{\Delta H_{O}^{\neq}}{T}$$
(38)

$$\Delta G_{O}^{\neq} = \Delta H_{O}^{\neq} - T\Delta S_{O}^{\neq}$$
(39)

where ΔG_0^{\neq} , ΔH_0^{\neq} , and ΔS_0^{\neq} are the standard free energy of activation, the standard enthalpy of activation, and the standard entropy of activation, respectively, and k and h are Boltzmann and Planck constants, respectively. The rate constants for the forward reactions (<u>i.e.</u>, complexation)

were calculated from the following equation:

$$k_{f} = K k_{b} \tag{40}$$

where K is the complex stability constant at 25°C.

6.3. RESULTS AND DISCUSSION

In order to study the kinetics of the complexation reactions between cesium ion and dibenzo-21-crown-7, dibenzo-24-crown-8, and dibenzo-30-crown-10 in acetone and methanol solutions, the cesium-133 NMR spectra of the cesium thiocyanate in the presence of the ligands (with a ligand/Cs⁺ mole ratio of 0.5) at various temperatures were obtained. The results are shown in Figures 36-41. The required information in the absence of exchange (<u>i.e.</u> v_A , v_B , and $\Delta v_{1/2}^{\text{ref}}$) was obtained by lineshape analyses of the cesium-133 NMR spectra of the solutions of salt (site A) and of the completely complexed cesium ion (site B), collected at exactly the same conditions as the exchange case.

The rate constants for the release of the cesium ion from the complexes, k_b , at temperatures above coalescence were calculated from Equation (29), below the coalescence temperature from Equation (34). The data are listed in Table 44. The Arrhenius plots, log $k_b \underline{vs}$. 1/T are shown in Figure 42. Activation energies (E_a), rate constants (k_b), and values of $\Delta H_o^{\not=}$, $\Delta S_o^{\not=}$, and $\Delta G_o^{\not=}$ for the release of



Figure 36. Cesium-133 NMR Spectra of 0.02 <u>M</u> CsSCN, 0.01 <u>M</u> DB21C7 Solution in Acetone at Various Temperatures.



Figure 37. Cesium-133 NMR Spectra of 0.04 M CsSCN, 0.02 M DB21C7 Solution in Methanol at Various Temperatures.



Figure 38. Cesium-133 NMR Spectra of 0.02 <u>M</u> CsSCN, 0.01 <u>M</u> DB24C8 Solution in Acetone at Various Temperatures.



Figure 39. Cesium-133 NMR Spectra of 0.02 <u>M</u> CsSCN, 0.01 <u>M</u> DB24C8 Solution in Methanol at Various Temperatures.



Figure 40. Cesium-133 NMR Spectra of 0.01 M CsSCN, 0.005 M DB30Cl0 Solution in Acetone at Various Temperatures.

$$\frac{c_{s}c^{*}}{W_{w}} + \frac{c_{s}^{*}}{W_{w}} + \frac{c_{s}}{W_{w}} + \frac$$

Figure 41. Cesium-133 NMR Spectra of 0.01 M CsSCN, 0.005 M DB30Cl0 Solution in Methanol at Various Temperatures.

Ligand	Solvent	Temp. (°C)	log k _b
DB21C7	Acetone	- 82 *	0.93
		-76*	1.24
		-70*	a
		- 64 *	а
		- 57	2.18
		-50	2.48
		-42	2.77
	Methanol	<u>-84*</u>	1.66
		- 72 *	2.07
		- 65 *	2.32
		-61	2.45
		-48	2.85
		-27	3.43
DB24C8	Acetone	- 98 *	0.76
		-88*	1.36
		- 77 *	1.84
		- 67 *	a
		-54	2.84
		-40	3.30
		-28	3.73
	Methanol	-92	1.93
		-84	2.24
		-78	2.47
		-73	2.62
		- 55	3.32

Table 44. Temperature Dependence of the Rate Constants for the Release of Cs⁺ Ion from DB21C7·Cs⁺, DB24C8·Cs⁺, and DB30C10·Cs⁺ Complexes in Acetone and Methanol.

Table 44. Continued.

Ligand	Solvent	Temp. (°C)	log k _b
DB30C10	Acetone	-80	1.84
		-68	2.32
		-56	2.66
		<u>-</u> 41	3.12
		-28	3.28
	Methanol	-90*	a
		- 80 *	a
		-64	2.95
		- 55	3.14
		-49	3.34
		-45	3.42
		-42	3.50
		-30	3.77

*Below the coalesence temperature.

^aThe k_{b} values are not calculated.



Figure 42. Arrhenius Plots of log k_b <u>vs</u>. 1/T for the Release of Cs⁺ Ion in Acetone and Methanol with Large Crown Ethers. A-DB30Cl0·Cs⁺ in Methanol, B-DB24C8·Cs⁺ in Methanol, C-DB30Cl0·Cs⁺ in Acetone, D-DB21C7·Cs⁺ in Methanol, E-DB24C8·Cs⁺ in Acetone, F-DB21C7·Cs⁺ in Acetone.

the cesium ion from the complexes, as well as the rate constants for the complexation reactions (k_{f}) are given in Table 45.

It is immediately obvious that the nature of the solvent plays an important role in the kinetics of the complexation reactions. In all cases, the energy of activation for the release of the cesium ion from the complex in methanol is less than that in acetone. It should be noted that methanol is a solvent with higher donicity than acetone as expressed by their respective Gutmann donor number of 25.7 and 17.0 (106). The same effect was observed by Cahen et al. (78) for the release of lithium ion from cryptate C211.Li⁺ in pyridine, water, DMSO, DMF, and formamide solutions. By contrast Shchori et al. (88) found that the activation energy for decomplexation of sodium ion by dibenzo-18crown-6 is the same in methanol, DMF, and dimethoxyethane. However, two of these solvents, i.e., DMF and methanol, have about the same donicity, while the donicity of dimethoxyethane is not known.

The activation energy for the release of the cesium ion from the complex is also dependent on the size of the ligand. In the same solvent, there is an inverse relationship between the activation energy for decomplexation of the cesium ion by the ligand and the size of the ligand (Table 45). These results seem to indicate that the major barrier to removal of the cesium ion by the complexes is the

+ Ion from Some	
ິຊີ	
of	
or Release	•
Parameters f	and Methanol
Exchange Rates and Thermodynamic	Large Crown Complexes in Acetone
Table 45.	

Solvent	DN ^a	Ligand	E _a kcal/mole	k _b x10 ⁻⁴ sec-1	k _f xl0 ⁻⁸ M ⁻¹ sec ⁻¹	∆H ≠ o kcal/mole	ΔS [≠] kcal/mole	∆G [≠] (298°K) kcal/mole
Acetone	17.0	DB21C7 DB24C8 DB30C10	9.3(0.8) ^b 8.2(0.6) 6.1(0.5)	5.9(1.1) 10.3(1.7) 2.1(0.4)	7.1(1.5) 6.7(1.8) 3.0(0.8)	8.7(0.7) 7.6(0.6) 5.5(0.5)	-7.5(2.5) -10.1(2.2) -20.3(1.9)	10.9(0.1) 10.6(0.1) 11.5(0.1)
Methanol	25.7	DB21C7 DB24C8 DB30C10	6.7(0.5) 6.3(0.6) 5.2(0.4)	2.8(0.5) 8.7(1.7) 3.5(0.6)	3.2(0.6) 4.4(1.0) 7.5(1.6)	6.1(0.5) 5.7(0.6) 4.6(0.4)	-17.7(1.4) -16.8(2.2) -22.3(1.6)	11.4(0.1) 10.7(0.1) 11.2(0.1)

^aGutmann donor number.

^bStandard deviation.

•
energy required to affect a conformational rearrangement. The lower activation energy for the release of the cesium ion from the larger crowns would then be a result of the greater flexibility of the ligand.

In both solvents, the rate constants for decomplexation of the cesium ion by DB24C8, k_{h} , is greater than those for the release of the cation by DB30Cl0 and DB21C7. The rate constants for the decomplexation reactions seem to be determined by the rigidity of the resulted complexes. Cesium ion with diameter of 3.68 Å (128) has a convenient size for the cavity of DB21C7 with the size of 3.4-4.3 Å (23) to form a firm "cation in the hole" complex. We have already shown (Chapter 3) that DB30C10 is large enough to form a rigid "wrap around" complex with the cesium ion, while due to differences in the sizes of DB24C8 cavity and of the cesium ion either a complete "wrap around" or a "cation in the hole" complex. The rate constants for both complexation and decomplexation of the cesium ion by DB30C10, <u>i.e.</u>, $k_f = 7.5 \times 10^8 M^{-1} sec^{-1}$ and $k_h = 3.5 \times 10^4$ sec⁻¹, are in a satisfactory agreement with the values reported by Chock (32), <u>i.e.</u>, $k_f = 8 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ and $k_{\rm b} = 4.7 \times 10^4 \, {\rm M}^{-1} \, {\rm sec}^{-1}$.

As is seen in Table 45, while the enthalpy and the entropy of activation for the release of the cesium ion from the ligands are very sensitive to the solvent and to the size of the ligand, the free energies of activation

207

in all cases are about the same. Such a compensation of the enthalpy with the entropy is not an uncommon occurrence (155). It is interesting to note that the entropy of activation for decomplexation of the cesium ion by large crowns (Table 45) are in opposite direction with the corresponding overall entropies (Table 34, Chapter 4). This is in contrast with the entropy values reported for the release of the cesium ion from cryptate C222 in DMF solution by Mei et al. (95), where the activation and the overall entropies have the same sign and are close in value. From the results the authors concluded that the activated complex should resemble the final state, i.e., the solvated cesium ion and the free cryptand. The opposite sign for ΔS_{O}^{\neq} and ΔS° values for decomplexation of the cesium ion by large crowns, however, suggests that the conformational entropy changes may play an important role (156).

Since the activation energy for decomplexation of the cesium ion by the ligands increases with increasing the donicity of the solvent, the transition state must involve a substantial ionic solvation. A sample entropy profile for decomplexation of the cesium ion by DB30Cl0 in acetone is shown in Figure 43. It clearly shows that the transition state must be more ordered than both the initial and the final states, <u>i.e.</u>, the solvated complex and the solvated cesium and the free ligand. Thus the possible

208



Figure 43. Entropy Profile for the Release of Cs⁺ Ion From DB30C10.Cs⁺ Complex in Acetone.

mechanism for the release of the cesium ion from the complex can be shown by

DB30C10·Cs⁺
$$\xrightarrow{\Delta S^{\neq}}$$
 (DB30C10·Cs⁺) ^{\neq} $\xrightarrow{\Delta S^{\neq}}$ DB30C10 + Cs⁺
-20.3e.u. -46.5e.u.

where the overall entropy is $\Delta S^{\circ} = 26.2 \text{ e.u.}$

APPENDICES

.

APPENDIX I

DETERMINATION OF COMPLEX FORMATION CONSTANTS BY THE NMR TECHNIQUE, DESCRIPTION OF COMPUTER PROGRAM KINFIT AND SUBROUTINE EQUATION Let's consider the following equilibrium for a one to one complex,

$$M + L \stackrel{*}{\downarrow} ML \tag{1}$$

with the concentration formation constant K

$$K = C_{ML} / C_{M} \cdot C_{L}$$
 (2)

C, stands for concentration.

The observed chemical shift of M (δ_{obs}) is a mass average of the characteristic chemical shift of M at each site (M in the bulk solution, and M complexed), assuming that a fast exchange occurs between these two sites with respect to the NMR time scale.

$$\delta_{\text{obs}} = X_{\text{M}} \delta_{\text{M}} + X_{\text{ML}} \delta_{\text{ML}}$$
(3)

Where: $\delta_{\rm M}$ is the characteristic chemical shift for M in the bulk solution, $\delta_{\rm ML}$ is the characteristic chemical shift for M complexed (ML), $X_{\rm M}$ is the fraction of M ($C_{\rm M}$ / ($C_{\rm M} + C_{\rm ML}$)), $X_{\rm ML}$ is the fraction of ML ($C_{\rm ML}/(C_{\rm M} + C_{\rm ML})$), then

$$\delta_{obs} = X_{M} \delta_{M} + (1 - X_{M}) \delta_{ML}$$

$$\delta_{obs} = X_{M} (\delta_{M} - \delta_{ML}) + \delta_{ML}$$
(4)

$$C_{M}^{t} = C_{M} + C_{ML}$$
 (the analytical concentration of M) (5)

$$\delta_{\text{obs}} = \frac{C_{M}}{C_{M}^{5}} \left(\delta_{M} - \delta_{ML} \right) + \delta_{ML}$$
(6)

 $C_{L}^{t} = C_{ML} + C_{L}$ (the analytical concentration of L) (7)

$$C_{L} = C_{L}^{t} - C_{ML}$$

using (5) and (7),
$$C_L = C_L^t - (C_M^t - C_M)$$

$$K = \frac{C_{M}^{t} - C_{M}}{(C_{M})(C_{L}^{t} = C_{M}^{t} + C_{M})}$$
(8)

+KC^tM

 C_{M} is solved in (8)

.

$$C_{M}(C_{L}^{t} - C_{M}^{t} + C_{M})K = C_{M}^{t} - C_{M}$$

$$KC_{M}^{2} + (KC_{L}^{t} - KC_{M}^{t} + 1)C_{m} - C_{M}^{t} = 0$$

$$C_{M} = \frac{-(KC_{L}^{t} - KC_{M}^{t} + 1) \pm \sqrt{(KC_{L}^{t} - KC_{M}^{t} + 1)^{2} + 4}}{2K}$$

the positive root is

$$C_{M} = \frac{(KC_{M}^{t} - KC_{L}^{t} - 1) + \sqrt{K^{2}C_{L}^{t^{2}} + K^{2}C_{M}^{t^{2}} - 2K^{2}C_{L}^{t}C_{M}^{t} + 2KC_{L}^{t} + 2KC_{M}^{t} + 1}{2K}}{2K}$$
(9)

Substitution of C_M from (9) in Equation (6)

$$\delta_{obs} = \left[\left[(KC_{M}^{t} - KC_{L}^{t} - 1) + \sqrt{K^{2}c_{L}^{t^{2}} + K^{2}c_{M}^{t^{2}} - 2K^{2}c_{L}^{t}c_{M}^{t} + 2Kc_{L}^{t} + 2Kc_{M}^{t} + 1} \right] \right]$$

$$\left[(\delta_{M} - \delta_{ML})/2c^{t}K \right] + \delta_{ML}$$
(10)

We assume a constant value for $\delta_{\rm M}$ and that $\delta_{\rm ML}$ and K are unknown. In order to fit the calculated shift (the right hand side of Equation (10) to the observed chemical shift, the program may vary the values of $\delta_{\rm ML}$ and K. Hence, the number of unknowns, NOUNK, equals two as does the number of variables, NOVAR.

The first card contains the number of experimental points (columns 1-5 (F.15)), the maximum number of iterations allowed (columns 10-15 (F.15)), the number of constants (columns 36-40 (F.15)) and the maximum value of (Δ parameter/parameter) for convergence to be assumed (0.0001 works well) in columns 41-50 (F10.6). The second data card contains any title the user desires. The third

data card contains the value of CONST(1) (C_M^t) columns 1-10 (F10.6) in <u>M</u>, CONST(2) (δ_{M}) columns 11-20 (F10.6) other constants can be listed on columns 21-30, 31-40, etc. The fourth data card contains the initial estimates of the unknowns U(1) = δ_{ML} and U(2) = K, in columns 1-10 and 11-20 (F10.6), respectively. The fifth through N data cards contain XX(1) = C_{M}^{t} in columns 1-10 (F10.6) variances on XX(1) in columns 11-20, XX(2) = the chemical shift at XX(1)in columns 31-40 (F10.6) followed by the same parameters for the next data point. Each card may contain two data If no further data are to be analyzed the next points. card after the last data point(s) should be a blank card followed by a 6789 card. If more data sets are to be analyzed, the next card after the last data point(s) is the first data card of the next set.

citAcolifine EGN cfr control the EGN if control the EGN cfr control the EGN if control the EGN cfr control the EGN if control the EGN cfr con

APPENDIX II

DETERMINATION OF COMPLEX FORMATION CONSTANT WITH ION PAIR FORMATION BY THE NMR METHOD Definition of symbols,

$$[M] = \text{cation}$$

$$[A] = \text{anion}$$

$$[L] = \text{ligand}$$

$$[MA] = \text{ion pair}$$

$$[ML] = \text{metal complex}$$

$$C_M = \text{analytical concentration of metal ion}$$

$$C_L = \text{analytical concentration of ligand}$$

$$K_{ip} == \text{ion pair equilibrium constant}$$

$$K_f = \text{formation constant of complex}$$

Ion pair equilibrium,

[M] + [A] ^Kip ≵ [MA]

$$K_{ip} = \frac{[MA]}{[M][A]}$$
(11)

Complexation equilibrium,

$$K_{f} = \frac{[ML]}{[M][L]}$$
(12)

$$C_{L} = [ML] + [L]$$
(13)

$$C_{M} = [ML] + [M] + [MA]$$
(14)

$$C_{M} = [MA] + [A]$$
(15)

From (11),

$$[MA] = K_{ip} [M][A]$$
(16)

From (12),

$$[ML] = K_{f}[M][L]$$
(17)

Substitute in (13)

$$C_{L} = K[M][L] + [L] = [L](K_{f}[M] + 1)$$

$$\cdot \cdot [L] = \frac{C_{L}}{K_{f}[M] + 1}$$
(18)

Substitute in (14),

$$C_{M} = K_{f}[M][L] + [M] + K_{ip}[M][A]$$
 (19)

Substitute in (15),

$$C_{M} = [A] + K_{ip}[M][A] = [A](1 + K_{ip}[M])$$

$$. .[A] = \frac{C_{M}}{1 + K_{ip}[M]}$$
(20)

•

Substitute (18) and (20) in (19),

$$C_{M} = \frac{K_{f}[M]C_{L}}{K_{f}[M] + 1} + [M] + \frac{K_{ip}[M]C_{M}}{1 + K_{ip}[M]}$$
(21)

Multiply (21) across by $(1 + K_{f}[M])(1 + K_{ip}[M])$,

$$C_{M}(1 + K_{f}[M])(1 + K_{ip}[M]) = K_{f}C_{L}[M](1 + K_{ip}[M])$$

+ [M](1 + K_{f}[M])(1 + K_{ip}[M]) + K_{ip}C_{M}[M](1 + K_{f}[M]) (22)

$$c_{M} + \kappa_{ip}c_{M}[M] + \kappa_{f}c_{M}[M] + \kappa_{f}\kappa_{ip}c_{M}[M]^{2}$$

= $\kappa_{f}c_{L}[M] + \kappa_{f}\kappa_{ip}c_{L}[M]^{2} + [M] + \kappa_{ip}[M]^{2}$
+ $\kappa_{f}[M]^{2} + \kappa_{f}\kappa_{ip}[M]^{3} + \kappa_{ip}c_{M}[M] + \kappa_{f}\kappa_{ip}c_{M}[M]^{2}$ (23)

Collecting terms,

$$\kappa_{f}\kappa_{ip}[M]^{3} + (\kappa_{f}\kappa_{ip}C_{L} + \kappa_{ip} + \kappa_{f})[M]^{2}$$

+ ($\kappa_{f}C_{L} + 1 - \kappa_{f}C_{M}$)[M] - $C_{M} = 0$ (24)

$$[M]^{3} + \frac{(K_{f}K_{ip}C_{L} + K_{ip} + K_{f})}{L_{f}K_{ip}} [M]^{2}$$

$$+ \frac{(K_{f}C_{L} + 1 - K_{f}C_{M})}{K_{f}K_{ip}} [M] - \frac{C_{M}}{K_{f}K_{ip}} = 0$$
(25)

Solution to cubic equation,

$$y^{3} + py^{2} + qy + r = 0$$
$$p = \frac{(K_{f}K_{ip}C_{L} + K_{ip} + K_{f})}{K_{f}K_{ip}}$$

$$q = \frac{(K_f C_L + 1 - K_f C_M)}{K_f K_{ip}}$$

$$r = \frac{-C_{M}}{K_{f}K_{ip}}$$

$$y = x - \frac{p}{3}$$

$$x^{3} + ax + b = 0$$

$$a = (3q - p^2)/3$$

$$b = (2p^3 - 9pq + 27r)/27$$

$$A = \sqrt{3} - \frac{b}{2} + \sqrt{\frac{b^2}{4} + \frac{a^3}{27}}$$

$$B = \sqrt[3]{-\frac{b}{2}} - \sqrt{\frac{b^2}{4} + \frac{a^3}{27}}$$

Case I
$$\frac{b^2}{4} + \frac{a^3}{27} > 0 \Rightarrow 1 \text{ real root}$$

II
$$\frac{b^2}{4} + \frac{a^3}{27} = 0 \Rightarrow 3 \text{ real roots}$$

III
$$\frac{b^2}{4} + \frac{a^3}{27} < 0 \rightarrow 3$$
 real roots

Case I, x = A + BCase II and III, use trigonometric form

$$\cos\phi = -\frac{b}{2} \div \sqrt{\left(-\frac{a^3}{27}\right)}$$

$$x = 2\sqrt{-\frac{a}{3}}\cos\frac{\phi}{3}$$

$$2\sqrt{-\frac{a}{3}}\cos\left(\frac{\phi}{3} + 120^\circ\right)$$

$$2\sqrt{-\frac{a}{3}}\cos\left(\frac{\phi}{3} + 240^\circ\right)$$

Now, solve for [M] in (25).

Then substitute in following equations,

$$[ML] = \frac{K_{f}C_{L}[M]}{K_{f}[M] + 1}$$
(26)

$$[MA] = \frac{K_{ip}C_{M}[M]}{K_{ip}[M] + 1}$$
(27)

$$\delta_{\text{obs}} = x_{\text{M}} \delta_{\text{M}} + x_{\text{ML}} \delta_{\text{ML}} + x_{\text{MA}} \delta_{\text{MA}}$$
(28)

$$\delta_{\text{obs}} = \frac{[M]}{C_{\text{L}}} \delta_{\text{M}} + \frac{[ML]}{C_{\text{M}}} \delta_{\text{ML}} + \frac{[ML]}{C_{\text{M}}} \delta_{\text{MA}}$$
(29)

Use final form of $\delta_{\rm obs}$ in EQN subroutine. Coding symbols in EQN,

$$a = AA$$
 $p = PP$ $b = BB$ $q = QQ$ $A = AAA$ $r = RR$ $B = BBB$ $\phi = FE$ $y = R$ $Cos \phi = CFE$ $CONST(1) = K_{1p}$ $CONST(2) = C_M$ $CONST(2) = C_M$ $CONST(3) = \delta_{1p}$ $CONST(4) = \delta_M$ $U(1) = \delta_{ML}$ $XX(1) = C_L$ $U(2) = K_f$ $XX(2) = \delta_{obs}$

. .

С С С С GD TO 30 THE TO GONOMETRIC FORM OF THE SOLUTION IS USED MER 31 FLAGEC. RLU=2.*ACOS(-1.) ANGLE=RAD/3. CFE=(-HR/2.)/(SORT(ARS((-AA*3)/27.))) CHECK FOR VALIDITY OF COSINE TERM IF((CFE.LT.-1.).OR.(CFE.GT.1.)) GO TO 40 FEEPAD-ACOS(CFF) 14 50=2.*(SQRT(AAS(-AA/3.)))*COS(FE/3.*ANGLE*FLAG) DEMP-(PP/3.) CHECK FOR VALIDITY OF THE CALCULATED METAL CONC TF(R)13.13.30 41 WRITE(JTAPE.2) 22 FUMMAT(* COSINE OF FEE ONTSIDE OF *1 AND -1*) GO BACK AND FIND ANOTHER ROOT 13 FLAGEFLAGE1. 14 (3.-FLAG)15.15.14 15 WRITE(JTAPE.2) С С С С 21 FORWAT(* ALL THREE ROOTS FLUNKED*) STOP SUBSTITUTE CALCULATED METAL CONC. IN ORIGINAL FOUATION 30 DLLTA*(D*CONST(4)*IU(2)*******(1)*U(1))/(1**U(2)**)*(CONST(1)*P*CONS 11(2)*CONST(3))/(1**CONST(1)**)/CONST(2) RCTUBN 3 CONTINUE 2 ETUEN 3 CONTINUE 3 CONTINUE 4 CUNTINUE 1 F(THETM*VE*-1) GO TO 20 RETURN 20 CONTINUE 9 CONTINUE 10 CONTINUE 11 CONTINUE 12 CONTINUE 13 CONTINUE 14 CONTINUE 14 CONTINUE 15 CONTINUE 16 CONTINUE 17 CONTINUE 18 CONTINUE 19 CONTINUE 10 CONTINUE 10 CONTINUE 11 CONTINUE 12 CONTINUE 13 CONTINUE 14 CONTINUE 14 CONTINUE 15 CONTINUE 16 CONTINUE 17 CONTINUE 18 CONTINUE 19 CONTINUE 10 CONTINUE 10 CONTINUE 10 CONTINUE 11 CONTINUE 12 CONTINUE 12 CONTINUE 14 CONTINUE 15 CONTINUE 16 CONTINUE 17 CONTINUE 18 CONTINUE 19 CONTINUE 10 CONTINUE 10 CONTINUE 10 CONTINUE 10 CONTINUE 11 CONTINUE 12 CONTINUE 13 CONTINUE 14 CONTINUE 14 CONTINUE 15 CONTINUE 16 CONTINUE 17 CONTINUE 18 CONTINUE 19 CONTINUE 10 CONTINUE 10 CONTINUE 10 CONTINUE 10 CONTINUE 10 CONTINUE 11 CONTINUE 11 CONTINUE 12 CONTINUE 13 CONTINUE 14 CONTINUE 14 CONTINUE 15 CONTINUE 16 CONTINUE 17 CONTINUE 18 CONTINU С

REFERENCES

REFERENCES

- 1. C. J. Pedersen, <u>J. Amer. Chem. Soc.</u>, <u>89</u>, 7017 (1967).
- 2. "Structure and Bonding", Vol. 16, Springer-Verlag, New York, NY, 1963
- 3. A. I. Popov and J. M. Lehn, in "Chemistry of Macrocyclic Compounds", G. A. Melson, Ed., Plenum Press, New York, New York, in press, Chapter 9.
- 4. H. K. Frensdorff, <u>J. Amer. Chem. Soc.</u>, <u>93</u>, 600 (1971).
- 5. J. J. Christensen, J. O. Hill, and R. M. Izatt, Science, <u>174</u>, 45a (1971).
- 6. J.-M. Lehn and J. P. Sauvage, <u>J. Amer. Chem. Soc.</u>, <u>97</u>, 6700 (1975).
- N. K. Dalley, J. S. Smith, S. B. Larson, K. L. Matheson, J. J. Christensen, and R. M. Izatt, <u>J. Chem</u>. Soc. Chem. Commun., 84 (1975).
- 8. D. J. Cram et al., Pure Appl. Chem., 43, 327 (1975).
- 9. K. H. Pannel, W. Yee, G. S. Lewandos, and D. C. Hambrick, J. Amer. Chem. Soc., 99, 145 (1977).
- 10. R. Ungaro, B. El Haj, and J. Smid, <u>J. Amer. Chem</u>. <u>Soc.</u>, <u>98</u>, 5198 (1976).
- 11. S. C. Shah, K. Kopolow, and J. Smid, <u>J. Polym. Sci</u>. <u>14</u>, 2023 (1976).
- 12. W. Steinmann and T. A. Kaden, <u>Helv. Chim. Acta</u>, <u>58</u>, 1358 (1975).
- 13. B. E. Jepson and R. Dewitt, <u>J. Inorg. Nucl. Chem.</u>, <u>38</u>, 1175 (1976).
- 14. N. Matsura <u>et al.</u>, <u>Bull. Chem. Soc. Japn.</u>, <u>49</u>, 1246 (1976).
- 15. E. M. Arnett and T. C. Moriarity, <u>J. Amer. Chem. Soc.</u>, <u>93</u>, 4908, (1971).

- 16. T. H. Ryan, J. Koryta, A. Hofmanova-Matejkova, and
 M. Brezina, <u>Anal. Letters</u>, 1, 335 (1974).
- 17. C. J. Pedersen and H. K. Frensdorff, <u>Angew. Chem</u>. <u>Internal. Edit.</u>, <u>11</u>, 16 (1972).
- 18. J. J. Christensen, D. J. Eatough, and R. M. Izatt, <u>Chem. Rev.</u>, <u>74</u>, 351 (1974).
- 19. I. M. Kolthoff, <u>Anal. Chem.</u>, <u>51</u>, 1R (1979).
- 20. C. J. Pedersen, Fed. Proc., Fed. Amer. Soc. Exp. Biol., 27, 1305 (1968).
- 21. D. C. Tosteson, <u>Fed. Proc., Fed. Amer. Soc. Exp.</u> <u>Biol., 27</u>, 1269 (1968).
- 22. H. Lardy, Fed. Proc., Fed. Amer. Soc. Exp. Biol., 27, 1278 (1968).
- 23. C. J. Pedersen, J. Amer. Chem. Soc., 92, 386 (1970).
- 24. N. S. Poonia and M. R. Truter, <u>J. Chem. Soc. Dalton</u>, 2062 (1973).
- 25. D. G. Parsons, M. R. Truter, and J. N. Wingfield, Inorg. Chim. Acta, 14, 45 (1975).
- 26. M. A. Bush and M. R. Truter, <u>J. Chem. Soc. Perkin</u> <u>II</u>, 345 (1972).
- 27. M. Mercer and M. R. Truter, <u>J. Chem. Soc. Dalton</u>, 2469 (1973).
- 28. D. E. Fenton, M. Mercer, N. S. Poonia, and M. R. Truter, J. Chem. Soc. Chem. Commun., 66 (1972).
- 29. J. D. Owen and M. R. Truter, <u>J. Chem. Soc. Dalton</u>, accepted for publication.
- 30. M. Pinkerton, L. K. Steinrauf, and P. Dawkins, <u>Bio-Chem. Biophys. Res. Commun.</u>, <u>35</u>, 512 (1969).
- 31. G. A. Rechnitz and E. Eyal, <u>Anal. Chem.</u>, <u>44</u>, 370 (1972).
- 32. P. B. Chock, <u>Proc. Nat. Acad. Sci. USA</u>, <u>69</u>, 1939 (1972).
- 33. D. Live and S. I. Chan, <u>J. Amer. Chem. Soc.</u>, <u>98</u>, 3769 (1976).

- 34. R. M. Izatt, R. E. Terry, D. P. Nelson, Y. Chan, D. J. Eatough, J. S. Bradshow, L. D. Hansen, and J. J. Christensen, <u>J. Amer. Chem. Soc</u>., <u>98</u>, 7626 (1976).
- 35. A. Hofmanova, J. Koryta, M. Berzina, and M. L. Mittal, <u>Inorg. Chim. Acta</u>, <u>28</u>, 73 (1978).
- 36. J.-M. Lehn, P. Vierling, and R. C. Hayward, <u>J. Chem.</u> Soc. Chem. Commun., <u>296</u> (1979).
- 37. M. Ciampolini, P. Paoletti, and L. Sacconi, <u>J. Chem</u>. <u>Soc</u>., 2994 (1961).
- 38. L. Sacconi, P. Paoletti, and M. Ciampolini, <u>J. Chem</u>. <u>Soc</u>., 5115 (1961).
- 39. P. Paoletti and A. Vacca, <u>J. Chem. Soc.</u>, 5051 (1964).
- 40. L. Sacconi, P. Paoletti, and M. Ciampolini, <u>J. Chem</u>. <u>Soc</u>., 5046 (1964).
- 41. G. Schwarzenbach, <u>Advan. Inorg. Chem. Radiochem.</u>, <u>3</u>, 257 (1961).
- 42. G. Anderegg, Helv. Chim. Acta, 48, 1718 (1965).
- 43. G. Anderegg, <u>Helv. Chim. Acta</u>, <u>46</u>, 1833 (1963).
- 44. G. Anderegg, Proc. 8th I. C. C. C. (Vienna) 34 (1964).
- 45. G. Anderegg, <u>Helv. Chim. Acta</u>, <u>47</u>, 1801 (1964).
- 46. D. K. Cabbiness and D. W. Margerum, <u>J. Amer. Chem.</u> <u>Soc.</u>, <u>91</u>, 6540 (1969).
- 47. P. Paoletti, L. Fabbrizzi, and R. Barbucci, <u>Inorg</u>. <u>Chem.</u>, <u>12</u>, 1961 (1973).
- 48. R. P. Hinz and D. W. Margerum, <u>Inorg. Chem.</u>, <u>13</u>, 2941 (1974).
- 49. A. Dei, and R. Gori, <u>Inorg. Chim. Acta</u>, <u>14</u>, 157 (1975).
- 50. M. Kodama and E. Kimura, <u>J. Chem. Soc. Chem. Commun</u>., 326 (1975).
- 51. M. Kodoma and E. Kimura, <u>J. Chem. Soc. Dalton</u>, 116 (1976).

- 52. F. Arnaud-neu, M. J. Schwing-weill, J. Juillard, R. Louis, and R. Weiss, Inorg. Nucl. Chem. Letters, 14, 367 (1978).
- 53. R. M. Izatt, J. H. Rytting, D. P. Nelson, B. L. Haymore, and J. J. Christensen, <u>Science</u>, 164, 443 (1969).
- 54. R. M. Izatt, D. P. Nelson, J. H. Rytting, B. L. Haymore, and J. J. Christensen, <u>J. Amer. Chem. Soc.</u>, <u>93</u>, 1619 (1971).
- 55. P. U. Fruh, J. T. Clerc, and W. Simon, <u>Helv. Chim</u>. Acta, <u>54</u>, 1445 (1971).
- 56. W. K. Lutz, P. U. Fruh, and W. Simon, <u>Helv. Chim</u>. <u>Acta</u>, <u>54</u>, 2767 (1971).
- 57. C. U. Zust, P. U. Fruh, and W. Simon, <u>Helv. Chim</u>. <u>Acta</u>, <u>56</u>, 495 (1973).
- 58. E. Schori and J. Jagur-Grodzinski, Isr. <u>J. Chem.</u>, <u>11</u>, 243 (1973).
- 59. T. E. Hogen-Esch and J. Smid, <u>J. Phys. Chem.</u>, <u>79</u>, 233 (1975).
- 60. R. M. Izatt, R. E. Terry, B. L. Haymore, L. D. Hansen, N. K. Dalley, A. G. Avondet, and J. J. Christensen, J. Amer. Chem. Soc., 98, 7620 (1976).
- 61. R. M. Izatt, J. D. Lamb, R. E. Asay, G. E. Maas, J. S. Bradshow, and J. J. Christensen, <u>J. Amer</u>. Chem. Soc., 99, 6134 (1977).
- 62. R. M. Izatt, J. D. Lamb, G. E. Maas, R. E. Asay, J. S. Bradshow, and J. J. Christensen, J. Amer. Chem. Soc., 99, 2365 (1977).
- 63. E. Mei, J. L. Dye, and A. I. Popov, <u>J. Amer. Chem.</u> <u>Soc.</u>, <u>98</u>, 1619 (1976).
- 64. E. Mei, J. L. Dye, and A. I. Popov, <u>J. Amer. Chem.</u> <u>Soc.</u>, <u>99</u>, 5308 (1977.
- 65. R. M. Izatt, N. E. Izatt, B. E. Rossiter, and J. J. Christensen, Science, 199, 994 (1978).
- 66. R. M. Izatt, J. D. Lamb, B. E. Rossiter, N. E. Izatt, and J. J. Christensen, <u>J. Chem. Soc. Chem. Commun</u>., 386 (1978).

- 67. R. M. Izatt, R. E. Terry, L. D. Hansen, A. G. Avondet, J. S. Bradshow, N. K. Dalley, T. E. Jensen, and J. J. Christensen, <u>Inorg. Chim. Acta</u>, <u>30</u>, 1 (1978).
- 68. F. Bloch, Phys. Rev., 70, 460 (1946).
- 69. F. Bloch, W. W. Hansen, and M. Packard, <u>Phys. Rev.</u>, <u>69</u>, 37 (1945).
- 70. N. F. Ramsey, Phys. Rev., 77, 567 (1950).
- 71. N. F. Ramsey, Phys. Rev., 78, 699 (1950).
- 72. N. F. Ramsey, Phys. Rev., 86, 243 (1952).
- 73. J. Kondo and J. Hamashita, <u>J. Phys. Chem. Solids</u>, <u>10</u>, 245 (1959).
- 74. C. Deverell and R. E. Richards, <u>Mol. Phys.</u>, <u>10</u>, 551 (1966).
- 75. R. G. Barnes and W. V. Smith, <u>Phys. Rev</u>., <u>93</u>, 95 (1954).
- 76. B. Ditrich, J.-M. Lehn, and P. Sauvage, <u>Tetrahed</u>. Letts, 2885 (1969).
- 77. E. T. Roach, P. R. Handy, and A. I. Popov, <u>Inorg</u>. Nucl. Chem. Letters, <u>9</u>, 359 (1973).
- 78. Y. M. Cahen, J. L. Dye, and A. I. Popov, <u>J. Phys.</u> <u>Chem.</u>, <u>79</u>, 1289 (1975).
- 79. Y. M. Cahen, J. L. Dye, and A. I. Popov, <u>J. Phys.</u> <u>Chem.</u>, <u>79</u>, 1292 (1975).
- 80. A. Hourdakis and A. I. Popov, <u>J. Solution Chem</u>., 6, 299 (1977).
- 81. A. J. Smetana, Ph.D. Thesis, Michigan State University, East Lansing, MI (1979).
- 82. D. H. Haynes, B. C. Pressman, and A. Kowalsky, <u>Bio-</u> <u>chem.</u>, <u>10</u>, 852 (1971).
- 83. R. Bodner, M. S. Greenberg, and A. I. Popov, <u>Spect</u>. Letts. <u>5</u>, 489 (1972).
- 84. A. M. Grotens, J. Smid, and E. deBoer, <u>J. Chem. Soc.</u> Chem. Commun., 759 (1971).

- 85. R. H. Erlich, E. Roach, and A. I. Popov, <u>J. Amer</u>. Chem. Soc., <u>92</u>, 4989 (1970).
- 86. J. Grandjean, P. Laszlo, F. Vogtle, and H. Sieger, Angew. Chem. Internal. Ed., <u>17</u>, 856 (1978).
- 87. E. Shchori, J. Jagur-Grodzinski, Z. Luz, and M. Shporer, <u>J. Amer. Chem. Soc</u>., <u>93</u>, 7133 (1971).
- 88. E. Shchori, J. Jagur-Grodzinski, and M. Shporer, J. Amer. Chem. Soc., <u>95</u>, 3842 (1973).
- 89. J. M. Ceraso and J. L. Dye, <u>J. Amer. Chem. Soc.</u>, <u>95</u>, 4432 (1973).
- 90. J. P. Kintzinger and J.-M. Lehn, <u>J. Amer. Chem. Soc.</u>, <u>96</u>, 3313 (1974).
- 91. J. M. Ceraso, P. B. Smith, J. S. Landers, and J. L. Dye, <u>J. Phys. Chem.</u>, <u>81</u>, 760 (1977).
- 92. J. S. Shih, Ph.D. Thesis, Michigan State University, East Lansing, MI (1978).
- 93. M. Shporer and Z. Luz, <u>J. Amer. Chem. Soc.</u>, <u>97</u>, 665 (1975).
- 94. E. Mei, A. I. Popov, and J. L. Dye, <u>J. Phys. Chem.</u>, <u>81</u>, 1677 (1977).
- 95. E. Mei, A. I. Popov, and J. L. Dye, <u>J. Amer. Chem</u>. <u>Soc.</u>, <u>99</u>, 6532 (1977).
- 96. E. Mei, L. Liu, J. L. Dye, and A. I. Popov, <u>J. Solu-</u> <u>tion Chem.</u>, <u>6</u>, 771 (1977).
- 97. F. J. Kayne and J. Reuben, <u>J. Amer. Chem. Soc.</u>, <u>92</u>, 220 (1970).
- 98. C. Srivanavit, J. I. Zink, and J. J. Dechter, <u>J. Amer.</u> <u>Chem. Soc.</u>, <u>99</u>, 5876 (1977).
- 99. R. W. Briggs and J. F. Hinton, <u>J. Mag. Res.</u>, <u>33</u>, 363 (1979).
- 100. A. E. Martell, <u>Adv. Chem. Ser.</u>, <u>62</u>, 272 (1967).
- 101. D. D. Traficante, J. A. Simms, and M. Mulcay, <u>J. Mag.</u> <u>Res.</u>, <u>15</u>, 484 (1974).
- 102. D. A. Wright and M. T. Rogers, <u>Rev. Sci. Instrum.</u>, <u>44</u>, 1189 (1973).

- 103. J. W. Cooper, "An Introduction to Fourier Transform NMR and the Nicolet 1080 Data System", Nicolet Instrument Corp., Madison, WI, 1972.
- 104. D. H. Live and S. I. Chan, <u>Anal. Chem</u>., <u>42</u>, 791 (1972).
- 105. G. Foex, G. L. Gorter, and L. J. Smits, "Constantes Selectionees, Diamagnetisme et Paramagnetisme, Relaxation Paramagnetique", Massoy and Cie Editeurs, Patis, 1957.
- 106. (a) V. Gutmann and E. Wychera, <u>Inorg. Nucl. Chem</u>. <u>Letts</u>, <u>2</u>, 257 (1966);

(b) V. Gutmann, "Coordination Chemistry in Nonaqueous Solvents", Springer-Verlag, Vienna, 1968.

- 107. M. S. Greenberg, Ph.D. Thesis, Michigan State University, East Lansing, MI (1974).
- 108. J. L. Dye and V. A. Nicely, <u>J. Chem. Educ.</u>, <u>48</u>, 443 (1971).
- 109. A. I. Popov, Pure Appl. Chem., 51, 101 (1979).
- 110. Y. M. Cahen, Ph.D. Thesis, Michigan State University, East Lansing, MI (1975).
- 111. W. J. Dewitte, Ph.D. Thesis, Michigan State University, East Lansing, MI (1975).
- 112. E. Mei, Ph.D. Thesis, Michigan State University, East Lansing, MI (1977).
- 113. E. G. Bloor and R. G. Kidd, <u>Can. J. Chem.</u>, <u>46</u>, 3425 (1968).
- 114. C. Deverell and R. E. Richards, <u>Mol. Phys.</u>, <u>16</u>, 421 (1969).
- 115. A. L. Van Geet, <u>J. Amer. Chem. Soc.</u>, <u>94</u>, 5583 (1972).
- 116. J. J. Dechter and J. I. Zink, <u>J. Amer. Chem. Soc.</u>, <u>97</u>, 2937 (1975).
- 117. R. W. Briggs and J. F. Jinton, <u>J. Solution Chem.</u>, <u>7</u>, 1 (1978).

1

118. A. I. Popov, Chapter 13 in "Solute-Solvent Interactions", J. F. Coetzee and C. D. Richhie Editors, M. Dekker Inc., New York, NY, Vol. , 1976, page 271.

- 119. J.-M. Lehn and J. Simon, <u>Helv. Chim. Acta</u>, <u>60</u>, 141 (1977).
- 120. J. F. Hinton and R. W. Briggs, <u>J. Mag. Res.</u>, <u>25</u>, 379 (1977).
- 121. G. E. Maciel, et al., Inorg. Chem., 5, 554 (1966).
- 122. R. H. Cox and H. W. Terry, <u>J. Mag. Res.</u>, <u>14</u>, 317 (1974).
- 123. R. H. Erlich and A. I. Popov, <u>J. Amer. Chem. Soc.</u>, <u>93</u>, 5620 (1971).
- 124. M. S. Greenberg, R. L. Bodner, and A. I. Popov, <u>J</u>. <u>Phys. Chem.</u>, <u>77</u>, 2449 (1973).
- 125. R. Freeman, <u>et al.</u>, <u>Mol. Phys</u>., <u>2</u>, 75 (1959).
- 126. W. J. DeWitte, <u>et al.</u>, <u>J. Solution Chem</u>., <u>6</u>, 337 (1977).
- 127. A. G. Lee, <u>Coord. Chem. Rev.</u>, <u>8</u>, 289 (1972).
- 128. M. F. C. Ladd, <u>Theoret. Chim. Acta</u>, <u>12</u>, 333 (1968).
- 129. J.-M. Lehn, Struct. Bonding (Berlin), 16, 1 (1973).
- 130. N. Ahmad and M. C. Day, <u>J. Amer. Chem. Soc.</u>, <u>99</u>, 941 (1977).
- 131. M. Shamsipur and A. I. Popov, <u>J. Amer. Chem. Soc.</u>, <u>101</u>, 4051 (1979).
- 132. J.-M. Lehn, J. P. Sauvage, and B. Deitrich, <u>J. Amer</u>. Chem. Soc., <u>92</u>, 2916 (1970).
- 133. A. Hourdakis, Ph.D. Thesis, Michigan State University, East Lansing, MI (1978).
- 134. E. Kauffmann, J.-M. Lehn, and J. P. Sauvage, <u>Helv</u>. <u>Chim. Acta</u>, <u>59</u>, 1099 (1976).
- 135. D. J. Cram, <u>J. Org. Chem.</u>, <u>39</u>, 2445 (1974).
- 136. M. R. Truter, <u>Struct. Bonding</u>, <u>16</u>, 71 (1973).
- 137. B. Dietrich, J.-M. Lehn, and J. P. Sauvage, <u>Tetrahed</u>. Letts., <u>34</u>, 2885 (1969).
- 138. G. Anderegg, <u>Helv. Chim. Acta</u>, <u>58</u>, 1218 (1975).

- 139. B. Dietrich, J.-M. Lehn, and J. P. Sauvage, <u>Tetra-hedron</u>, <u>29</u>, 1647 (1973).
- 140. A. Knochel, J. Oehler, G. Rudolph, and V. Sinnwell, <u>Tetrahedron</u>, <u>33</u>, 119 (1977).
- 141. M. Herceg and R. Weiss, <u>Inorg. Nucl. Chem. Letts</u>, <u>6</u>, 435 (1970).
- 142. D. Moras, B. Metz, M. Herceg, and R. Weiss, <u>Bull</u>. Soc. Chim. France, 551 (1972).
- 143. M. S. Greenberg and A. I. Popov, <u>J. Solution Chem</u>., <u>4</u>, 599 (1975).
- 144. J. D. Lin and A. I. Popov, to be published.
- 145. (a) R. G. Pearson, <u>J. Amer. Chem. Soc</u>., <u>85</u>, 3533 (1963).
 - (b) R. G. Pearson, <u>J. Chem. Educ.</u>, <u>45</u>, 643 (1968).
- 146. F. A. Cotton and G. Wilkinson, "Advances in Inorganic Chemistry", Third Edition, Interscience Publisher, New York, NY, 1972, page 190.
- 147. G. Rounaghi and A. I. Popov, to be published.
- 148. G. W. Liesegang, M. M. Farrow, N. Purdie, and E. M. Eyring, <u>J. Amer. Chem. Soc.</u>, <u>98</u>, 6905 (1976).
- 149. G. W. Liesegang, M. M. Farrow, F. A. Vazquez, N. Purdie, and E. M. Eyring, <u>J. Amer. Chem. Soc.</u>, <u>99</u>, 3240 (1977).
- 150. H. M. McConnell, J. Chem. Phys., 28, 430 (1958).
- 151. F. A. L. Anet, J. Amer. Chem. Soc., 86, 458 (1964).
- 152. J. E. Anderson and J.-M. Lehn, <u>J. Amer. Chem. Soc.</u>, <u>89</u>, 81 (1967).
- 153. F. A. L. Anet and A. J. R. Bourn, <u>J. Amer. Chem. Soc.</u>, <u>89</u>, 760 (1967).
- 154. Amdur and Hammes, "Chemical Kinetics Principles and Selected Topics", McGraw Hill Co., New York, NY, 1966, page 147.
- 155. K. U. Laider, "Chemical Kinetics", McGraw Hill Co., New York, NY, 1965, page 251.

156. J. L. Dye, "Progress in Macrocyclic Chemistry", Vol. 1, R. M. Izatt and J. J. Christensen, Editors, Wiley-Interscience, New York, NY, 1979, page 63.