

## Multinuclear Nmr Study of Some Alkali and of Thallium Complexes with 1,10-Diaza-18-crown-6 in Nonaqueous Solutions

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*Complexes of 1,10-diaza-18-crown-6 macrocycle with  $Tl^+$ ,  $Li^+$ ,  $Na^+$  and  $Cs^+$  ions were investigated by multinuclear NMR technique in a number of nonaqueous solvents. With the exception of pyridine solutions the stabilities of the complexes varied inversely with the Gutmann donicity of the solvents. In a given solvent, the complexity constants decreased in the order  $Tl^+ > Li^+ > Na^+ > Cs^+$ . A somewhat different order is observed for the analogous polyether 18-crown-6, where it is,  $Tl^+ > Cs^+ > Na^+ > Li^+$ .*

### Introduction

The macrocycle 1,10-diaza-18-crown-6 (I, DA18C6) was first synthesized by Dietrich *et al.* in the course of synthesis of a diazamacrobicyclic ligand (cryptand 2.2.2) [1]. The complexing ability of this ligand with the  $K^+$  and  $Ag^+$  ions was studied by Frensdorff [2] in methanol and in aqueous solutions respectively. The logarithms of the formation constants for the two complexes were found to be 2.04 and 7.8. Since in general the stabilities of macrocyclic complexes are significantly enhanced in methanol solutions, it is evident that the silver complex in either solvent should be much more stable than the potassium complex. On the other hand, the respective complexes with the macrocycle 18-crown-6 (II, 18C6) the stabilities are reversed, and the  $\log K_f$  values of  $18C6 \cdot K^+$  and  $18C6 \cdot Ag^+$  complexes in aqueous solutions are 2.03 and 1.50 [3] respectively. Thus it is evident that the substitution of the two

oxygen atoms by two -NH groups drastically alters the complexing ability of the ligand.

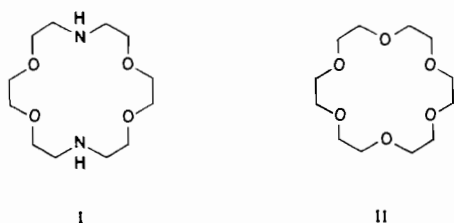
Solutions of DA18C6 and of some of its complexes have been studied by proton magnetic resonance [4, 5] and the crystal structures of the copper(II) [6] and of the potassium [7] complexes have been determined. The enthalpy and the entropy of complexation of some alkali earth and transition metal ions of this ligand in aqueous solutions, have been reported by Anderegg [8].

The present studies were undertaken to investigate the influence of solvent properties on the stabilities of lithium, sodium, cesium and thallium complexes of DA18C6 and to compare the stabilities of these complexes in nonaqueous solvents with those of 18C6. Multinuclear NMR seemed to be particularly suitable for such studies since in principle this technique can be applied to any solvent system. However, while the NMR technique is very useful for the determination of stability constants for weak and intermediate strength complexes [9], it fails when  $K_f > 10^5$ .

### Experimental

The ligand, 1,10-diaza-18-crown-6 (Merck) was recrystallized from reagent grade n-heptane and vacuum dried for 72 hours. 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. Cesium thiocyanate (Pfaltz and Bauer) was recrystallized from reagent grade methanol and dried under vacuum for several days. Thallium(I) perchlorate (K and K) was recrystallized from water and dried at 110 °C for 24 hours.

Acetone (Ac), acetonitrile (AN), dimethylformamide (DMF), dimethylsulfoxide (DMSO), nitromethane (NM), propylene carbonate (PC), pyridine (Py), and tetramethylguanidine (TMG) were purified and dried by previously described techniques [10]. Trimethylene oxide (TMO) was dried over activated molecular sieves for 48 hours. Water content of the solvents was determined by the Karl Fischer titra-



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TABLE I. Experimental Conditions.

Nucleus	Resonance Frequency (MHz)	External Reference Solution	Chemical Shift Reference
${}^7\text{Li}^{\text{a}}$	23.32	4.0 M LiClO <sub>4</sub> in H <sub>2</sub> O	4.0 M LiClO <sub>4</sub> in H <sub>2</sub> O
${}^{23}\text{Na}$	15.87	3.0 M NaCl in H <sub>2</sub> O	Infinitely dilute Na <sup>+</sup> in H <sub>2</sub> O
${}^{133}\text{Cs}$	7.87	0.5 M CsBr in H <sub>2</sub> O	Infinitely dilute Cs <sup>+</sup> in H <sub>2</sub> O
${}^{205}\text{Tl}$	34.61	0.3 M TlNO <sub>3</sub> in H <sub>2</sub> O	Infinitely dilute Tl <sup>+</sup> in H <sub>2</sub> O

<sup>a</sup>Lithium-7 chemical shift for aqueous LiClO<sub>4</sub> solutions is essentially independent of concentration.

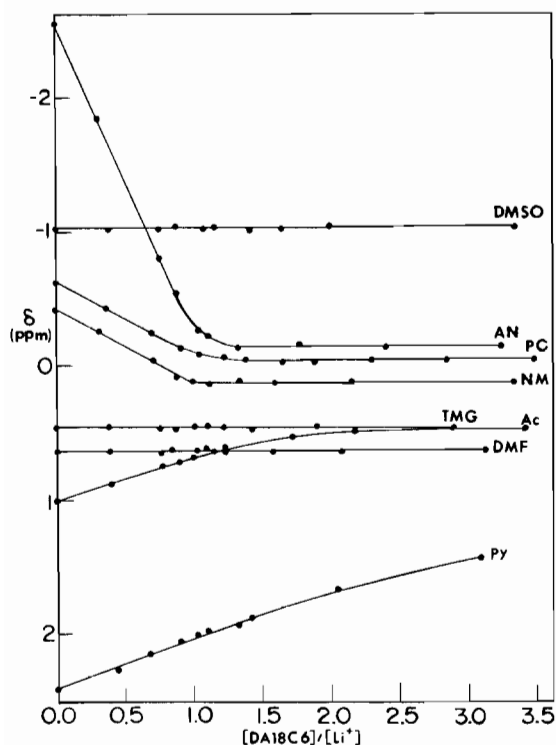


Fig. 1. Lithium-7 chemical shifts as a function of diaza-18-C-6/Li<sup>+</sup> mol ratio in various solvents.

tion. In all cases it was found to be less than 100 ppm.

Nuclear magnetic resonance measurements were carried out on a Varian Associate DA-60 spectrometer, equipped with a wide-band probe and an external proton lock at a field of 14.09 kgauss in a pulsed Fourier transfer mode. The experimental conditions are given in Table I. Downfield (paramagnetic) chemical shifts from the reference are indicated as *positive*. The concentration of the salt solutions were as follows: Li<sup>+</sup> 0.025 M; Na<sup>+</sup> 0.025 M; Cs<sup>+</sup> 0.005 M; and Tl<sup>+</sup> 0.005 M.

### Results and Discussion

Lithium-7, sodium-23, cesium-133, and thallium-205 chemical shifts were determined as a function of

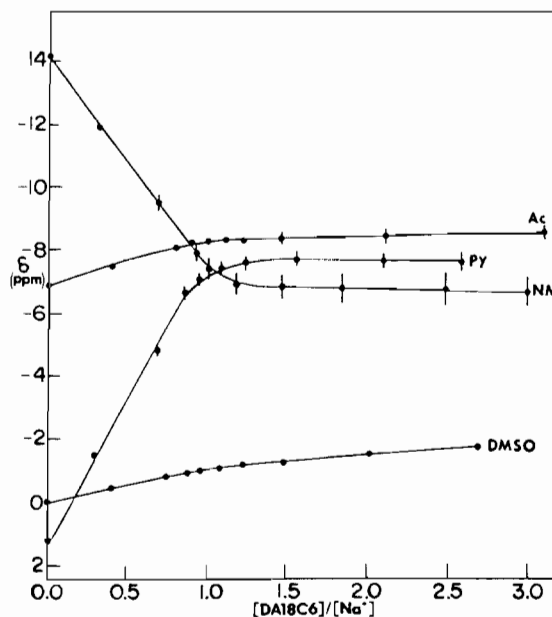


Fig. 2. Sodium-23 chemical shifts as a function of diaza-18-C-6/Na<sup>+</sup> mol ratio in various solvents.

DA18C6/metal ion mole ratio in various solvents, and the results are shown in Figures 1–4. In all cases only one population average resonance of the metal ion was observed, indicating that the exchange of the metal ion between the two sites (*i.e.* the solvated cation and the complex) is fast.

As seen in Figures 1–4, in solvents of high solvating ability, such as DMSO and DMF, the metal resonance is almost independent of the ligand/metal ion mol ratio. This behavior indicates that in these solvents, the immediate environment of the metal ion is not changed significantly upon the addition of the ligand and, at best, only a very weak complex is formed. It is possible but quite unlikely that the cationic chemical shift is the same for the solutions and complexed cation. In such case the measurement would not give any information on the complexation reaction.

In solvents of low and medium donicity (as defined by Gutmann [11]), such as nitromethane, acetonitrile, propylene carbonate, and acetone, the reso-

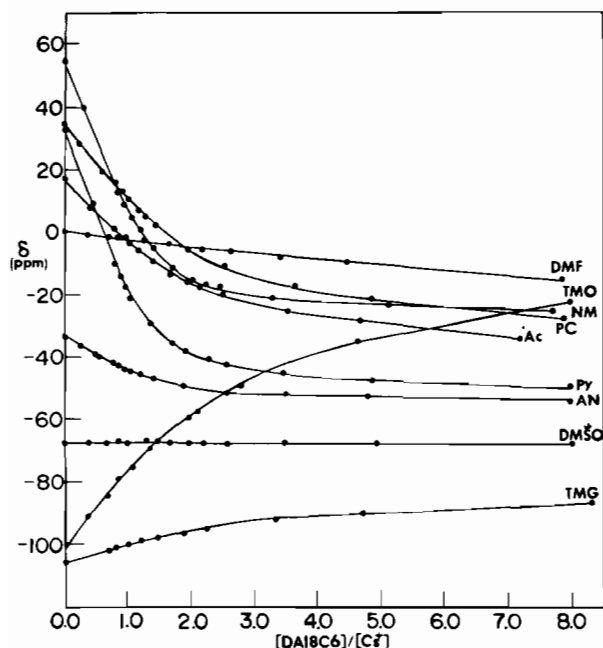


Fig. 3. Cesium-133 chemical shifts as a function of diaza-18-C-6/ $Cs^+$  mol ratio in various solvents.

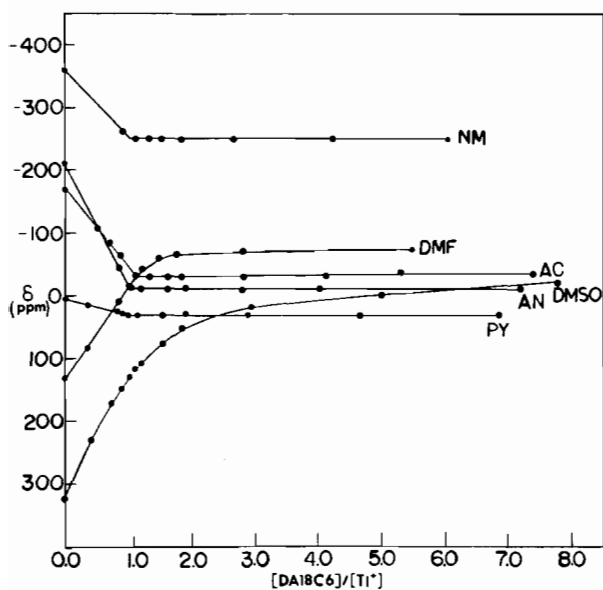


Fig. 4. Thallium-205 chemical shifts as a function of diaza-18-C-6/ $Tl^+$  mol ratio in various solvents.

nances of lithium-7, sodium-23 and thallium-205 nuclei are significantly affected by the addition of the ligand. The paramagnetic or diamagnetic shifts begin to level off at a mol ratio of about 1 indicating the formation of a 1:1 complex. Addition of the ligand to the cesium ion solution, however, produces a large but a gradual paramagnetic or diamagnetic shift of the cesium-133 resonance (Fig. 3) and in all

TABLE II. Formation Constants of  $Li^+$ ,  $Na^+$ ,  $Cs^+$  and  $Tl^+$  Ion Complexes of 1,10-Diaza-18-Crown-6 and 18-Crown-6 in Various Solvents.

Solvent	DN <sup>a</sup>	Log $K_f$	1,10-Diaza-18-Crown-6				18-Crown-6		
			$Tl^+$	$Li^+$	$Na^+$	$Cs^+$	$Tl^+$ <sup>b</sup>	$Li^+$ <sup>c</sup>	$Na^+$ <sup>d</sup>
NM	2.7	>5	>5	3.37 ± 0.13	2.79 ± 0.02	>5	>4	>4	>4
AN	14.1	>5	4.39 ± 0.41	2.26 ± 0.02 <sup>g</sup>	2.26 ± 0.02 <sup>g</sup>	>5	2.34 ± 0.04	3.80 ± 0.20	>4
PC	15.1	>5	3.67 ± 0.25	1.95 ± 0.02	1.95 ± 0.02	>5	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	0.61 ± 0.07	0.61 ± 0.07	3.35 ± 0.06	2.23 ± 0.04	2.23 ± 0.04	3.90 ± 0.15
DMSO	29.8	2.13 ± 0.03	~0.0	1.19 ± 0.08	0.0	1.92 ± 0.01	1.41 ± 0.07	1.41 ± 0.07	3.04 ± 0.04
TMO			~0.0	1.94 ± 0.02	1.94 ± 0.02		~0.0		
TMG			~0.0	1.55 ± 0.02	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
H <sub>2</sub> O						2.27 <sup>f</sup>	0.8 <sup>f</sup>	0.8 <sup>f</sup>	0.99 <sup>f</sup>

<sup>a</sup>Ref. 12. <sup>b</sup>Ref. 20. <sup>c</sup>Ref. 21. <sup>d</sup>Ref. 22. <sup>e</sup>Ref. 23. <sup>f</sup>Ref. 3. <sup>g</sup>Log  $K_f$  value of 2.48 was recently obtained by Kulstad and Malmsten, ref. 14.

solvents used in this work the chemical shifts of the complexed cesium ion did not reach a limiting value. The results seem to indicate the formation of a weak 1:1 complex between the cesium ion and the ligand. There is no evidence of the formation of a 1:2 (metal to ligand) complex, such as that reported by Mei *et al.* for the 18C6·Cs<sup>+</sup> system [12].

The formation constants of the complexes were obtained by computer fitting of the mol ratio data to an equation which relates the observed chemical shift to the formation constant as described in a previous publication [13]. The results, along with the corresponding literature values for the 18-crown-6 complexes, are shown in Table II. The comparison of our result for the Na<sup>+</sup>·DA18C6 complex in acetonitrile solution with the value determined recently by electrical conductance measurements [14] shows satisfactory agreement.

It is immediately obvious that for a given cation the stabilities of the complexes are very much dependent on the nature of the solvent. In all solvents, except pyridine, there is an inverse relationship between the stability of the complexes and the donicity of the solvents as expressed by the Gutmann donor number. It has been pointed out previously, that pyridine is a relatively 'soft' base and, therefore, it does not solvate strongly a 'hard acid' ion such as sodium or cesium [15]. Consequently, in this solvent DA18C6 forms stable complexes with the sodium and cesium ions.

In a given solvent the stability of the DA18C6 complexes decreases in the order TI<sup>+</sup> > Li<sup>+</sup> > Na<sup>+</sup> > Cs<sup>+</sup>. Obviously, the consonance between the ionic size and the size of the macrocyclic ring is an important factor in determining the stability of the macrocyclic complexes. According to Ladd [16] the ionic diameters of the Li<sup>+</sup>, Na<sup>+</sup>, Cs<sup>+</sup> and TI<sup>+</sup> ions are 1.72, 2.24, 3.68 and 3.08 Å respectively. The ring sizes of crown ethers are not known precisely but on the basis of molecular models the ring size of 18C6 has been estimated to be 2.6–3.2 Å. It should be very nearly the same for the DA18C6.

On the basis of size considerations alone, we would expect that other factors being constant, the stability order should be TI<sup>+</sup> > Na<sup>+</sup> > Li<sup>+</sup> ~ Cs<sup>+</sup>. (It seems difficult to predict *a priori* the relative stabilities of the last two complexes). It is seen from Table II, however, that for DA18C6 in general, the order is TI<sup>+</sup> > Li<sup>+</sup> > Na<sup>+</sup> > Cs<sup>+</sup>, while for 18C6 it is usually TI<sup>+</sup> > Cs<sup>+</sup> > Na<sup>+</sup> > Li<sup>+</sup> but it does vary somewhat with the solvent.

The substitution of two oxygen atoms by two nitrogens in the 18C6 macrocyclic ring significantly decreases the stability of the sodium and cesium complexes. Similar results were obtained by Frensdorff [2]. The effect is most pronounced in the case of the cesium complex (decrease of ~two orders of magnitude in the K<sub>f</sub> values, Table II). Again these

results are not unexpected since Cs<sup>+</sup> ion is a 'harder' acid than Na<sup>+</sup> and would interact less strongly with the nitrogen atoms of the ring.

On the other hand, this substitution increases the stability of the thallium(I) and lithium complexes (except for Li<sup>+</sup> in pyridine solution). Once again it seems that here we have an example of 'soft-soft' interaction which increases the interaction energy, although in the case of the lithium ion the strength of the resulting complex is somewhat surprising in view of the small size of the cation.

The above results strongly emphasize the variability of factors which affect the stability of a macrocyclic complex. While the relative sizes of the cation and of the macrocyclic cavity play an important role, they are certainly not the unique, and not always the most important, factors which determine the stabilities of macrocyclic complexes. The relative donor abilities of the heteroatoms of the macrocyclic rings are of considerable importance. The 'hard-soft' character of the ions and of the solvents also play an important role.

The importance of the solvent properties on the stability of the macrocyclic complexes is very evident from the data shown in Table II. In general, but not without exceptions, the complexes are much more stable in nonaqueous solvents than in water. Thus, for example, Na<sup>+</sup>·18C6 complex has log K<sub>f</sub> of greater than 4 in nitromethane and only 0.8 in water. On the other hand it is only slightly more stable in DMSO than in water. The solvating abilities of the two solvents, however, are not too different [11]. The formation constant of the Li<sup>+</sup>·DA18C6 complex in nitromethane is more than five orders of magnitude larger than in dimethylformamide, dimethylsulfoxide or tetramethylguanidine solutions. Nitromethane, however, despite its polar nature (D = 35.87 at 30 °C, μ = 3.56 Debyes), has a very low solvating ability [11].

It seems obvious that particularly in nonaqueous solutions, we should consider not only the solvent-cation, but also the solvent-ligand interactions as important factors in the complexation reactions. Yet such information seems to be largely unavailable. We can judge about the influence of solvent-macrocyclic ligand interactions from the fact that (a) 18C6 forms a relatively stable 1:1 solid complex with acetonitrile [17] and (b) the transfer enthalpy of cryptand C222 from water to methanol is +13.9 kcal mol<sup>-1</sup> [18].

Our previous studies have shown that the formation of macrocyclic complexes in nonaqueous solutions is enthalpy stabilized [19] but entropy destabilized, and that this behavior seems to be strongly related to the change in the conformational entropy of the ligand upon complexation which, in turn, is related to its interaction with the solvent.

At this point the data are too meager to allow useful speculations. It seems rather certain that

further studies of the various conditions which govern the stabilities of macrocyclic complexes will eventually elucidate the macrocyclic effect and will improve the ability to predict the extent of ligand-cation interactions.

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