

NMR STUDY OF BENZO-15-CROWN-5 COMPLEXES WITH ${}^7\text{Li}^+$ and ${}^{133}\text{Cs}^+$ IONS IN NONAQUEOUS SOLVENTS

M. Shamsipur*

M. K. Amini

Department of Chemistry, Shiraz University, Shiraz, Iran.

(Received 20th Nov. 1989)

(Approved 28th May 1990)

ABSTRACT

Complexes of benzo-15-crown-5 macrocycle with Li^+ and Cs^+ ions were investigated by ${}^7\text{Li}$ and ${}^{133}\text{Cs}$ NMR in a number of non-aqueous solutions. The resulting 1:1 complex with Li^+ ion was found to be much more stable than that with Cs^+ ion. With the exception of pyridine solutions the stabilities of the complexes varied inversely with the Gutmann donor number of the solvents. Some indirect evidence for the formation of very weak 2:1 CsL_2^+ complexes was observed.

INTRODUCTION

From investigations, on many macrocyclic crown ether it has been well recognized that the relative size of the metal ion and the cavity formed by the ligand plays a very fundamental role on the ligand selectivity and of course the stability of the resulting complexes [1-4]. According to the so called "ion-in-the-hole" model [1], the maximum stability could be predicted for the ion-macrocyclic complex, when the cation to macrocycle relative size approaches unity. On the other hand, when the ionic size is

either too large or too small for the macrocycle's cavity, the stability of the resulting complex will decrease drastically [3].

In this work we undertook investigating the effects of the relative size and solvent properties on the stoichiometry and stability of benzo-15-crown-5 complexes with Li^+ and Cs^+ ions.

EXPERIMENTAL

Benzo-15-crown-5 (B15C5) was synthesized by a slight modification of Pedersen's method [5]. The product

*Corresponding author

was recrystallized from n-heptane and vacuum dried. Reagent grade lithium perchlorate (Alfa) was dried at 180°C for several days. Cesium thiocyanate (Pfaltz and Bauer, reagent quality) was dried under vacuum at 60°C for 72 h.

Nitromethane (NM, Aldrich), acetonitrile (AN, Baker), acetone (AC, Fisher), propylene carbonate (PC, Aldrich), dimethylformamide (DMF, Fisher), dimethylsulfoxide (DMSO, Fisher) and pyridine (PY, Aldrich) were purified and dried using the previously reported methods [6]. The water content of the solvent after drying was found to be less than 100 ppm as measured by Karl Fischer titrations.

Lithium-7 and cesium-133 NMR measurements were carried out on a

Bruker WH-180 Spectrometer operating at a Field of 42.27 KG. The measurements were made at 65.591 MHz for ^7Li and 23.63 MHz for ^{133}Cs nuclei using a 4 M aqueous solution of a lithium perchlorate and 0.5 M aqueous solution of cesium bromide, respectively, as external references. The following salt concentrations were used: Li^+ , 0.02 M and Cs^+ , 0.005 M.

RESULTS AND DISCUSSION

The variation of lithium-7 and cesium-133 resonance frequencies were measured in different solvents as a function of ligand/metal ion mole ratio and the results are shown in Figures 1 and 2. In all cases only one population average signal was

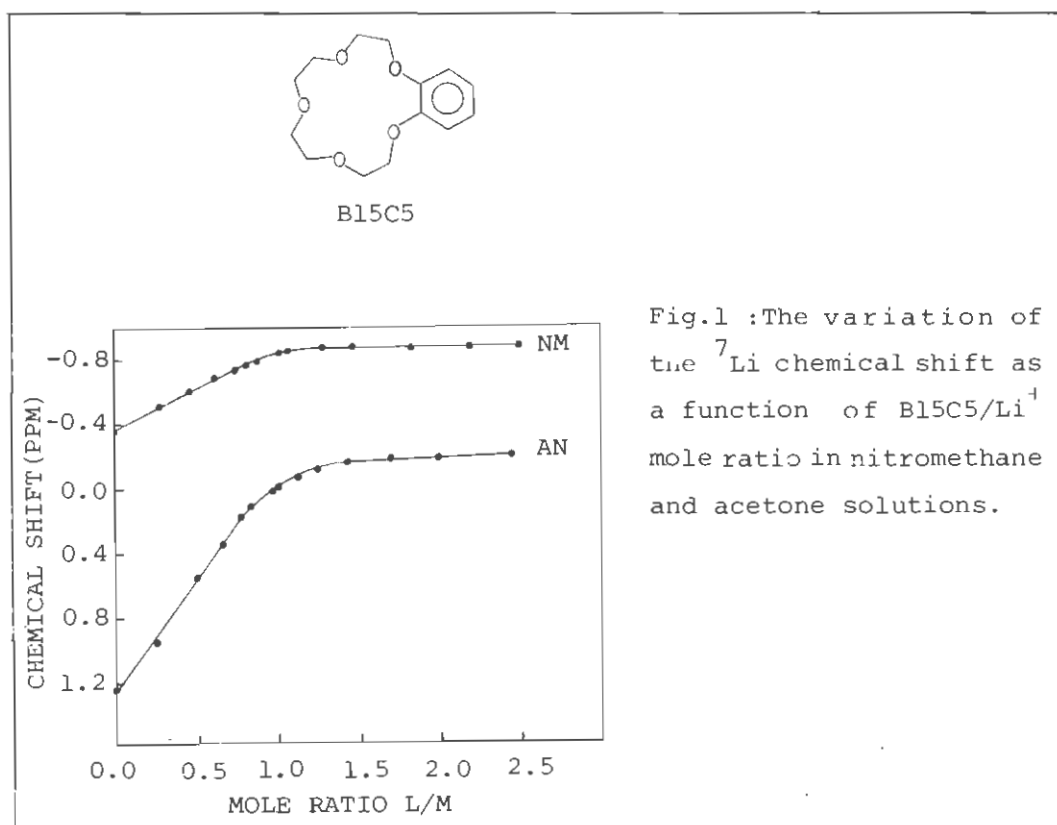


Fig.1 :The variation of the ^7Li chemical shift as a function of B15C5/ Li^+ mole ratio in nitromethane and acetone solutions.

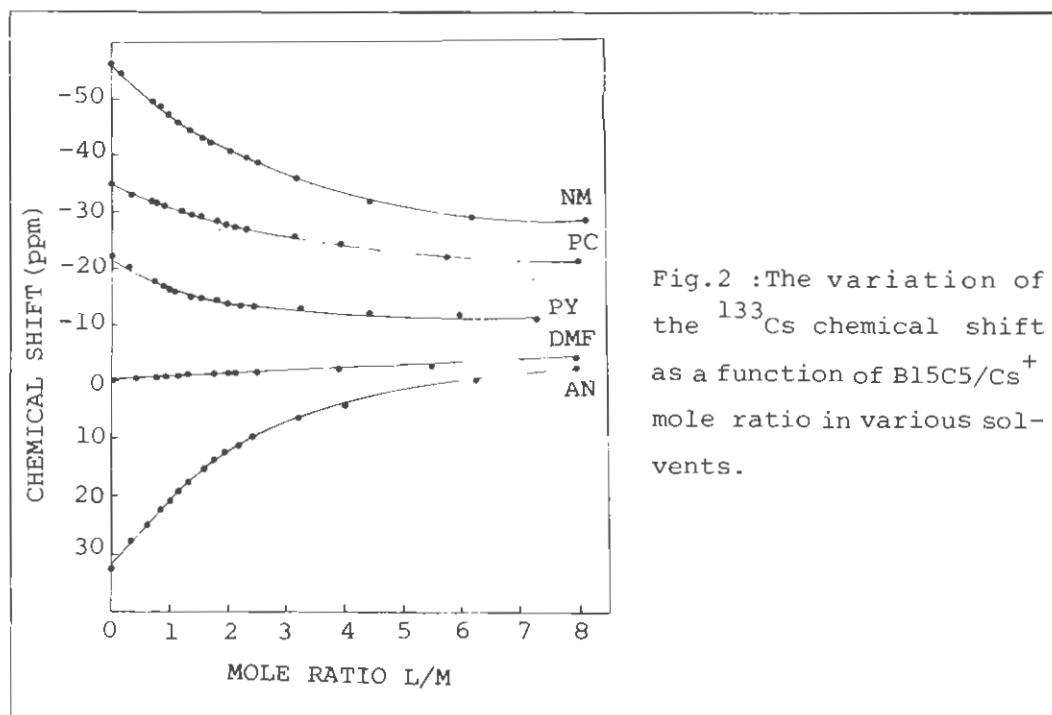


Fig.2 :The variation of the ^{133}Cs chemical shift as a function of $\text{B15C5}/\text{Cs}^+$ mole ratio in various solvents.

observed, indicating that the exchange of the metal ion between the solvated and complexed sites is faster than the NMR time scale. In the case of Li^+ ion, the chemical shift varied upfield linearly with the mole ratio until the mole ratio of 1 is reached. Further addition of the ligand does not change the resonance frequency. Such a behavior indicates the formation of a stable 1:1 complex. This is not unexpected, since Li^+ ion with ionic size of 1.56 \AA [7] has a suitable dimension to fit inside the cavity of B15C5 with a size of $1.7\text{-}2.2 \text{ \AA}$ [8].

The mole ratio plots in Fig.2, show that an increase in the ligand concentration gradually shifts the ^{133}Cs resonance downfield (upfield in AN solution) and the chemical shift does not seem to reach a limiting

value even at fairly high values of the mole ratio of about 8. The results seem to indicate the formation of a weak 1:1 complex between Cs^+ ion and B15C5. Cesium ion with ionic size of 3.30 \AA [7] is too large for the cavity of the ligand so that it can only partially penetrate inside the ligand's cavity, resulting in a very weak ion-macrocyclic interaction. Although the large size of the Cs^+ ion provides a good situation for the formation of a 2:1 (ligand to metal) "sandwich" complex, no clear-cut evidence was observed in the ^{133}Cs NMR studies. However, such a direct evidence for the formation of the 2:1 complexes has been reported previously from the multinuclear NMR mole ratio studies for 18-crown-6 . Cs^+ [9,10] and 15-crown-5. Na^+ [11] sys-

tems.

The formation constants of the complexes were obtained by computer fitting of the NMR mole ratio data to an equation which relates the observed chemical shift to the formation constant as previously reported[12]. A sample computer fit of the

mole ratio data is shown in Fig. 3. The results along with the corresponding literature values for 15-crown-5. Cs^+ complex are listed in Table 1. It is immediately obvious that for a given cation the stabilities of the complexes are very much dependent on the nature of the sol-

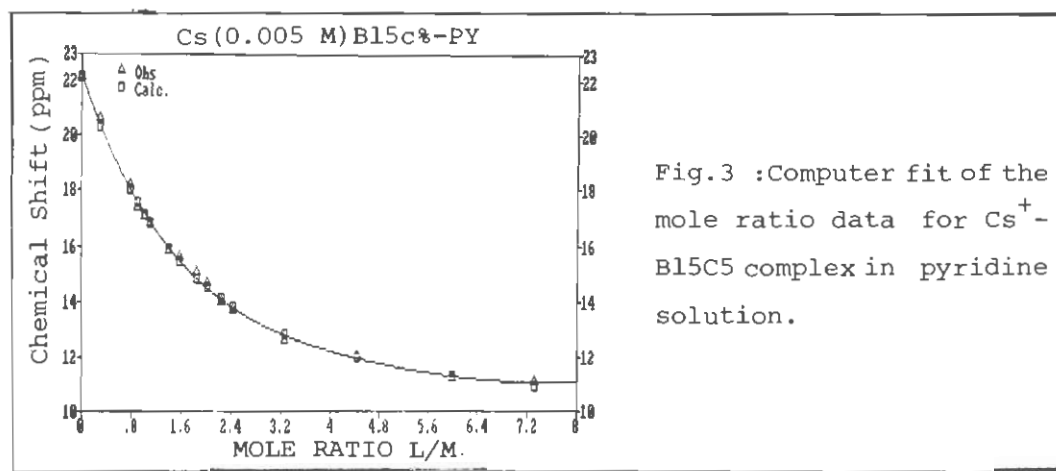


Fig.3 :Computer fit of the mole ratio data for Cs^+ -B15C5 complex in pyridine solution.

Table 1. Formation Constants and Limiting Chemical Shifts of Li^+ and Cs^+ Complexes in Various Solvents

Cation	Solvent	DN ^a	B15C5		15C5
			$\log K_f^b$	δ_{lim}^c	$\log K_f$
Li^+	NM	2.7	3.59	0.87	4 ^d
	AC	17.0	3.27	0.21	3.59 ^d
Cs^+	NM	2.7	2.35	16.70	-
	AN	14.1	2.04	11.13	-
	PC	15.1	1.59	11.01	2.69 ^e
	DMF	26.6	1.04	11.70	-
	DMSO	29.8	1	-	-
	PY	33.1	1.31	9.24	-

^a Donor number, Ref[13].

^b Standard deviation ± 0.05 .

^c Standard deviation ± 0.03 .

^d Ref[20].

^e Ref[21].

vent. With the exception of pyridine, in all other solvents there is an inverse relationship between the stability of the complexes and the Gutmann donicity of the solvents [13]. Such a relationship has also been observed previously for the complexation of various crown ether-metal ion complexes in a wide variety of solvents [11,14-17]. It is interesting to note that despite the high donor number of the pyridine, the stability of the Cs^+ ion complex is comparable with that in the low donicity solvents such as nitromethane. It has been assumed that pyridine as a relatively "soft" base only weakly solvates Cs^+ ion as a "hard" acid and, therefore, it offers only weak competition to the ligand [14].

From Table 1, it is obvious that for all cases, where the data are reported, the Cs^+ ion forms a more stable complex with 15-crown-5 (15C5) than that with benzo-15-crown-5. This is not surprising, since the introduction of an electron withdrawing benzo group reduces the donicity of the five oxygen atoms in the ring and hence reduces the cation-macrocycle interaction. Such a substituent effect has already been reported for some 18-crown-6 complexes [17].

Although the mole ratio plots (Fig. 2) would not reveal any clear-cut evidence for the formation of a 2:1 (2B15C5. Cs^+) complex, the values

obtained from the computer fitting of the data for the limiting chemical shifts δ_{lim} of the complexed cesium ion (Table 1) provide some evidences for the formation of a very weak sandwich complex in solution. It is interesting to note that while the chemical shifts of the solvated cesium ion in different solvents are quite scattered through a range of about 90 ppm (Fig. 2), the limiting chemical shifts of the complexed cation fall in a much more narrow range of about 7 ppm. These observations indicate that at high Cs^+ /B15C5 mole ratios, the cesium ion is largely isolated from the solution. This is possible only if the cation is trapped between at least two bulky ligand molecules which could largely isolate the metal ion from the solution. Similar evidence has been previously used to confirm the formation of a "wrap around" structure for dibenzo-30-crown-10. Cs^+ complex in solution [18,19].

REFERENCES

1. R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamb, J.J. Christensen and D. Sen, *Chem. Rev.* **85**, 271 (1985).
2. J.M. Lehn, *Struct. Bonding (Berlin)* **16**, 1 (1973).
3. J.D. Lamb, R.M. Izatt, J.J. Christensen and D.J. Eatough, In *"Coordination Chemistry of Macrocyclic compounds"*; G.A. Melson, Ed.; Plenum

- Press:New York,pp 145-218(1979).
4. N.S.Poonia and A.V.Bajaj, *Chem.Rev.* 79,389(1979).
 5. C.J.Pedersen, *J.Am.Chem.Soc.* 89, 7017(1967).
 6. M.S. Greenberg and A.I. Popov, *Spectrochim.Acta* 31A,697(1975).
 7. D.F.C.Morris, *Struc.Bonding(Berlin)* 4,63(1968).
 8. C.J.Pedersen, *J.Am.Chem.Soc.* 92, 386 (1970).
 9. E.Meij, J.L.Dye and A.I. Popov, *J. Am Chem. Soc.* 99,5318(1979).
 10. S.Khazaeli, J.L.Dye and A.I. Popov *J. Phys. Chem.* 87,183(1983).
 11. J.D.Lin and A.I. Popov, *J. Am. Chem. Soc.* 103,3773(1981).
 12. V.M.Cahen, R.F.Beisel and A.I. Popov, *J. Inorg. Nucl. Chem. Supplement* . 209 (1976).
 13. V.Gutmann and E.Wyehera, *Inorg. Nucl.Chem.Lett.* 2,257(1966).
 14. M.Shamsipur and A.I. Popov, *Inorg. Chim.Acta* 43,243(1980).
 15. H.Shamsipur, G.Rounaghi and A.I. Popov, *J. Solution Chem.* 9,701(1980).
 16. M.B.Gholivand, S.Kashanian and M. Shamsipur, *Polyhedron* 6,535(1987).
 17. S.Kashanian and M.Shamsipur, *Inorg. Chim.Acta* 155,203(1989).
 18. M.Shamsipur and A.I. Popov, *J. Am. Chem. Soc.* 101,4051(1979).
 19. M.Shamsipur and A.I. Popov, *J. Phys. Chem.* 92,147(1988).
 20. A.J.Smetana and A.I. Popov, *J. Solution, Chem.* 9,183(1980).
 21. Y.Takeda, H.Yano, M. Ishibashi and H. Isozumi, *Bull. Chem. Soc. Jpn.* 53, 72 (1980).