

the charge-transfer absorption was greatly diminished in pyridine solution as was the RR intensity of the Fe-N-Fe band. Likewise for $(\text{FeTPP})_2\text{N}^+$, we find broad absorption in the B-band region, suggesting a contribution from a charge-transfer transition. The B band narrows considerably in pyridine, suggesting that the charge-transfer band has shifted out of the region; as in the case of $(\text{FeTPP})_2\text{N}$, the RR intensity of the Fe-N-Fe band markedly decreases (Figure 2). In the case of $(\text{FeTPP})_2\text{C}$, however, the B band is narrow in methylene chloride, while pyridine produces a high-energy shoulder on this band. The Fe-C-Fe band intensity increases substantially in pyridine (Figure 1), suggesting additional enhancement via a new charge-transfer transition. In the absence of such a transition, however, the RR enhancement is much greater for $(\text{FeTPP})_2\text{C}$ (in methylene chloride) than for $(\text{FeTPP})_2\text{N}^+$ or $(\text{FeTPP})_2\text{N}$ (in pyridine). This intrinsic enhancement is attributable to direct coupling to the porphyrin $\pi-\pi^*$ transition, made effective by the large extent of C-Fe π bonding. Stretching of the C-Fe bond modulates the Fe-porphyrin π interaction and provides a coupling mechanism. The situation is analogous to that found in oxyhemoglobin, for which the high frequency of the Fe-O₂ stretch²⁷ gives evidence for substantial π bonding. The excitation profile for the Fe-O₂ stretch shows no evidence for charge-transfer enhancement but simply follows the porphyrin absorption spectrum. This is consistent with direct coupling to the porphyrin $\pi-\pi^*$ transition.²⁸

For $(\text{FeTPP})_2\text{C}$ and $(\text{FeTPP})_2\text{N}^+$, the highest filled orbital is an e_g nonbonding orbital made up of the Fe d_{π} orbitals.⁹ $(\text{FeTPP})_2\text{N}$, however, has an extra electron that is predicted to go into an a_{1g} antibonding orbital with mainly d_z character.⁹ Analysis of the EPR spectrum of $(\text{FeTPP})_2\text{N}$ confirms that the unpaired electron resides in an a_{1g} orbital with mostly Fe character.^{11a} Curiously, however, the Fe-X bond distance is nearly the same for $(\text{FeTPP})_2\text{C}$ as for $(\text{FeTPP})_2\text{N}$, despite the antibonding electron of the latter. It may be that the electron is largely localized on the side of the Fe atoms away from the bridge (presumably by mixing in of iron $4p_z$ orbital character). Consistent with this is the absence of pyridine adduct formation^{11b} in the case of $(\text{FeTPP})_2\text{N}$. When the latter is dissolved in pyridine, the excited state is influenced, as evidenced by the diminution of the charge-transfer band intensity,¹³ but there is no perturbation of the ground state. The Fe-N-Fe stretching band, although much weaker, is unshifted in frequency. In contrast, both $(\text{FeTPP})_2\text{C}$ and $(\text{FeTPP})_2\text{N}^+$ do form well-defined adducts,^{5,6} and the lowering in frequency of the Fe-X-Fe stretch reflects appreciable weakening of the Fe-X bonds, as discussed above.

Acknowledgment. This work was supported by NIH Grants HL12526 (T.G.S.), HL25934 (K.S.S.), and HL13652 (D. N.H.) and by the American Heart Association (K.S.S.; Grant 83923). We thank Prof. D. F. Bocian for a preprint of his related study, and Dr. R. Czernuszewicz for help with the force constant calculations.

Registry No. $(\text{FeTPP})_2\text{C}$, 75249-87-5; $(^{54}\text{FeTPP})_2\text{C}$, 92669-36-8; $[(\text{FeTPP})_2\text{N}]\text{ClO}_4$, 83967-78-6; $[(^{54}\text{FeTPP})_2\text{N}]\text{ClO}_4$, 92669-38-0; $(\text{FeTPP})_2\text{N}^+$, 78591-88-5.

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Solvent Effects in the Complexation of Dibenzo-14-crown-4 and Its Analogues with Lithium Ion

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Received October 17, 1983

The lithium-7 NMR spectroscopic results for the complexation of lithium ion with the crown ether dibenzo-14-crown-4 (DB14C4) and its methyl (Me-DB14C4), *tert*-butyl (*t*-Bu-DB14C4), and *di-tert*-butyl (*t*-Bu₂-DB14C4) derivatives in acetonitrile (ACN), propylene carbonate (PC), acetone (AC), tetrahydrofuran (THF), pyridine (py), dimethyl sulfoxide (Me₂SO), and dimethylformamide (DMF) are discussed. In solvents of medium or low donor number the 1:1 complex was formed, and there was no clear-cut evidence for the existence of 2:1 complexes. The formation of complexes is strongly influenced by the solvent, and the stability of these complexes varies inversely with the donor number of solvents. Different substituent groups on the benzene ring of the crown ethers can also influence the stability of the complexes, and the stability sequence is Me-DB14C4 > *t*-Bu-DB14C4 > *t*-Bu₂-DB14C4 > DB14C4. The substituent effect on the reaction has also been found to be quite significant along with the solvent effect.

Introduction

Since Pedersen first synthesized macrocyclic polyethers¹ (crown ethers) as very effective complexing agents for the alkali-metal and alkaline-earth-metal cations,² there has been considerable interest shown in the chemical and physical properties of these compounds. There are many parameters^{2,3} that determine the stability and the selectivity of crown ether

complexation with metal ions, such as cavity size of the ligand, cation diameter, spatial distribution of ring binding sites, the character of the heteroatoms, the presence of additional binding sites, and the type of solvent. Although it is already known that the substituent effect is very significant for por-

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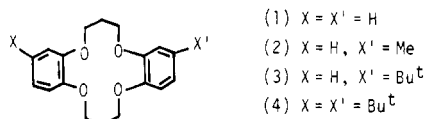


Figure 1. Macrocyclic ligands used in this investigation: DB14C4 (1); Me-DB14C4 (2); *t*-Bu-DB14C4 (3); *t*-Bu₂-DB14C4 (4).

phyrin complexes in biological systems,⁴ only a few studies⁵⁻⁷ of the variation of stability constants of metal ions with crown ethers bearing different substituents have been reported. It has been found that aromatic substituents have a pronounced effect on the complexation and selectivity of crown ethers to cations.

Recently, Popov,⁸ Dye,⁹ Lehn,¹⁰ and their co-workers have used NMR spectroscopy to study the different properties of the complexes of cations with crown ethers in nonaqueous solvents, where the usual electrochemical techniques (potentiometry, conductance, and polarography) often become very difficult. However, no systematic investigations of the complexation of lithium ion by DB14C4 and its analogues in various solvents had been undertaken. The object of this paper is to use lithium-7 NMR to study the complexation reaction of lithium ion with four crown ethers that carry different substituent groups, i.e. dibenzo-14-crown-4 (DB14C4), 4-methyl-dibenzo-14-crown-4 (Me-DB14C4), 4-*tert*-butyldibenzo-14-crown-4 (*t*-Bu-DB14C4), and di-*tert*-butyldibenzo-14-crown-4 (*t*-Bu₂-DB14C4) (Figure 1), in several nonaqueous solvents covering a broad range of dielectric constants and donor abilities.

Experimental Section

Reagents and Solvents. Lithium perchlorate used in this study was of reagent grade quality (Fluka) and had been dried at 150 °C for several days before use.

Macrocyclic polyethers of DB14C4 (1), Me-DB14C4 (2), *t*-Bu-DB14C4 (3), and *t*-Bu₂-DB14C4 (4) were synthesized in our laboratory and have been reported in previous work.¹¹⁻¹⁴

Tetrahydrofuran (Ferah Berlin), acetonitrile (Ferah Berlin), propylene carbonate (Tokyo Kasei), and acetone (Union Chemical Works, ROC) were refluxed over calcium hydride for about 18 h and then fractionally distilled. Pyridine (Merck) was refluxed over calcium hydride and distilled under reduced pressure. Dimethyl sulfoxide (Sigma) was dried over molecular sieves for 24 h and then refluxed over calcium hydride for 16 h; it was then carefully distilled under reduced pressure. Dimethylformamide (Ferah Berlin) was vacuum distilled from phosphorus oxide.

Analysis of water in solvents was carried out by using an automatic Karl Fischer titrator. The water content in acetone was analyzed by gas chromatography. The water content of all purified solvents was found to be less than 100 ppm.

NMR Measurements and Data Treatment. All solutions were prepared and the NMR tubes were filled in a glovebox under a dry nitrogen atmosphere. Lithium-7 NMR spectra were obtained by using a pulsed Fourier transform FT-80A (Varian) NMR spectrometer operating at 28.6625 MHz. All ⁷Li chemical shift measurements are referenced to an external aqueous 2.0 M LiClO₄ solution contained in a 1-mm capillary and are corrected for differences in bulk diamagnetic susceptibility of the solvents.¹⁵ A negative value of the

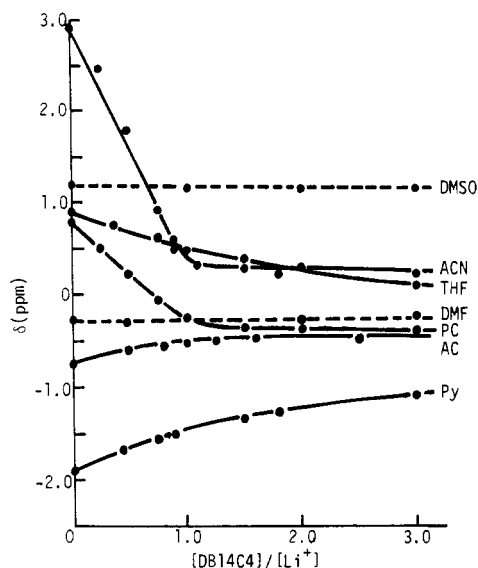


Figure 2. Variation of the Li chemical shift as a function of ligand:Li⁺ mole ratio in nonaqueous solvents. (Solid lines represent the least-squares fits of the calculated chemical shift, based on the assumption of formation of only 1:1 complexes.)

chemical shift δ represents an upfield shift. All measurements were made at ambient temperature (26 °C) in 5-mm o.d. Wilmad spinning NMR tubes. The data were treated by a nonlinear least-squares curve-fitting program, based on the equation described by Popov and Roach,¹⁶ to compute the two unknown quantities δ_c and K .

Results and Discussion

Owing to its lability, lithium ion undergoes a rapid exchange between its solvated and complexed species. This means that the ⁷Li NMR detects an averaged signal of these species. Typical variations of lithium-7 chemical shifts in different solvents as a function of ligand:Li⁺ mole ratio are shown in Figure 2. The features of the curves in Figure 2 can be approximately divided into three categories:

1. Those curves with chemical shifts that do not change with increasing ligand concentration, which include those cases for which Me₂SO and DMF were used as solvents, indicate that no complexation reactions occurred in such solvents.

2. Those curves with chemical shifts that are gradually moving either upfield or downfield with increasing ligand concentration and finally reach a limiting value, which include the ligand/Li⁺ systems in AC, PC, THF, and py, indicate the formation of lithium crown ether complexes.

3. The curve has an inflection point at the 1:1 ligand:Li⁺ mole ratio and then reaches a constant value in ACN solvent, which indicates the formation of a stable 1:1 complex.

In the second category, we assume that only 1:1 complexes instead of both 1:1 and 2:1 complexes are formed because the data were not fitted at all by four parameters, K_1 , K_2 , and two limiting chemical shifts (presumably because K_2 is too small to be determined). The same phenomenon for DCC/Cs⁺ was also observed by Dye¹⁷ et al. This may be attributed to the fact that the cavity size of DB14C4, 1.2–1.5 Å,¹⁸ matches well with that of lithium ion, 1.3–1.5 Å.^{19,20}

From Figure 2, the ⁷Li chemical shifts (δ_f) for free lithium ion in various solvents are in good agreement with those re-

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Table I. Formation Constants and Limiting ⁷Li Chemical Shifts of Li⁺/Crown Ether Complexes in Various Solvents

solvent	Me-DB14C4		<i>t</i> -Bu-DB14C4		<i>t</i> -Bu ₂ -DB14C4		DB14C4		12C4 ^a log K _f
	log K _f	δ _{lim}	log K _f	δ _{lim}	log K _f	δ _{lim}	log K _f	δ _{lim}	
ACN ^b	~5.0 ^b	+0.22	~5.0 ^b	+0.26	~4.7 ^b	+0.24	~4.5 ^b	+0.26	4.25 ± 0.46
PC ^c	4.40 ± 0.24	-0.45	4.25 ± 0.25	-0.41	4.25 ± 0.20	-0.41	3.60 ± 0.04	-0.40	
AC ^c	4.06 ± 0.03	-0.42	3.97 ± 0.05	-0.47	3.72 ± 0.02	-0.47	3.15 ± 0.01	-0.48	1.62 ± 0.03
THF ^c	2.28 ± 0.02	-0.33	2.18 ± 0.01	-0.22	2.00 ± 0.04	-0.04	1.85 ± 0.03	-0.07	
Me ₂ SO	~0		~0		~0		~0		~0
DMF	~0		~0		~0		~0		~0
py ^c	2.16 ± 0.06	-0.59	2.04 ± 0.04	-0.71	2.02 ± 0.03	-0.65	1.97 ± 0.05	-0.07	0.70 ± 0.05

^a Reference 24. ^b The computer-calculated log K_f will be less accurate when it is greater than 4. The numerical data presented here are only to show a general tendency of the formation constant of the complex. ^c It is possible that both 1:1 and 2:1 complexes form with ligands in these solvents. However, a good fit of the data is obtained by assuming formation of only the 1:1 complex.

ported by Maciel et al.²¹ and Popov et al.²² No correlation was found between δ_f in different solvents, and the Gutmann donor numbers of these solvents. Variations in δ_f with solvent are attributed to the different electronic environments of Li⁺ surrounded by various solvent molecules. The variation of chemical shifts in different solvents with L:M mole ratios approaching one another and reaching finite values at high ligand:Li⁺ mole ratios, as shown in Figure 2, strongly suggests the occurrence of a complexation reaction and that these complexes probably have similar configurations. The minor differences in configuration of these complexes, as observed by the different δ_{lim} values, were associated with the character of solvents that coordinate closely below and/or above the 1:1 Li⁺·DB14C4 complex.²⁰ This is contrary to the Li⁺·C211 cryptate system in which the Li⁺ ion is insulated completely by the three-dimensional ligand from the surrounding solvent, which leads to the same δ_{lim} in various solvents.²³ From Table I, in ACN, PC, and AC solutions the δ_{lim} does not change significantly with the different substituent group on the DB14C4, while it does change in THF and py solvents. A reason for this is that in the latter solvents there is formation of ion pairs of Li⁺·DB14C4 with perchlorate ions,²⁴ causing the perchlorate ion to interact somewhat differently with the various substituents on the benzene ring of DB14C4, which does not occur in the former solvents.

From Table I, the K_f's of DB14C4 and its analogues with Li⁺ are found to be larger than that of 12C4. Obviously, the cavity size is a significant factor affecting the stability of these complexes. The solvent properties also play an important role in K_f values; for example, the log K_f values change from ~5.0 in ACN to 2.16 in py. No clear correlation was found between the dielectric constant of the solvents and the formation constant of complexes. However, an inverse correlation between solvent donor numbers, as expressed by the Gutmann donor numbers,²⁵ and the complex formation constants was found, with an exception in the py solutions. A likely explanation²⁶ may be that pyridine, being a nitrogen donor or a "soft base", does not strongly solvate a "hard acid" such as Li⁺ ion. A parallel reason is due to the formation of the lithium-perchlorate ion pair²⁴ in which the K_f value cannot be correctly calculated.

Inspection of Table I reveals that formation constants, K_f, of Li⁺ complexes with DB14C4 ligands show a pronounced

dependence on the nature of the 4-substituent on the benzene rings; i.e., the K_f's of complexes with the attached electron-releasing group are greater than those of complexes with the unattached one in ACN, PC, AC, THF, and py solutions. Such behavior is consistent with the observation by Smid et al.⁶ The extent of interaction of the lithium ion with a crown ether depends on the basicity of the etherate oxygen on the polyether (pK_a), which is somewhat affected by the electronic nature of the attached substituent group. However, an anomalous substituent effect on K_f values was found in our study; i.e., the magnitude of K_f value varies according to methyl > *tert*-butyl > *di-tert*-butyl. This trend is not consistent with the so-called "normal electrostatic order" of the substituent group, but it might be explained by the Baker-Nathan effect.²⁷

On the basis of the observation of invariance in the δ_{lim} of the complexes of Li⁺ with crown ethers 1, 2, 3, and 4 in PC as solvent, the configuration entropies, ΔS's, of the reactions are approximately the same (TΔS for 1 and 2 are 1.87 and 1.95 kcal mol⁻¹, respectively).²⁸ Meanwhile, the values of the heat of desolvation, ΔH_{des}, can also be expected to be the same and are less than 9.51 kcal mol⁻¹,²⁹ the heat of solution of LiClO₄ in PC. Therefore, the relative increment of heat of complexation, ΔΔH_c, can be reasonably calculated from the corresponding K_f value at room temperature (26 ± 1 °C) as -1.10, -0.90, and -0.90 kcal mol⁻¹ for the methyl, *tert*-butyl, and *di-tert*-butyl derivatives as compared to DB14C4, respectively. Recently, we measured the heats of formation of lithium ion with four crown ethers in PC solvent which were -4.09, -3.69, -3.59, and -3.06 kcal mol⁻¹ for the methyl, *tert*-butyl, and *di-tert*-butyl derivatives of DB14C4 and for DB14C4, respectively.²⁸ Therefore, the heat of complexation, -ΔH_c = ΔH_{des} - ΔH_f, of Li⁺·DB14C4 in PC was believed to be less than 9.51 + 3.06 = 12.57 kcal mol⁻¹. Thus, the relative increment of heat of complexation, ΔΔH_c, from the substituent effect should be no less than -(0.9-1.1)/-12.57 = 7.2-8.8%. We therefore wish to emphasize that, besides the solvent, the substituent group on the benzene ring of DB14C4 has a substantial effect on the complexation reaction with the lithium ion.

Acknowledgment. The authors are deeply indebted to the Institute of Nuclear Energy Research for their support of this research. They also thank Dr. Z. T. Tsai for helpful discussions and comments and Dr. C. L. Wang for help in computer programming.

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