



Competitive ^7Li NMR study of complexation of different metal ions with tetraethyleneglycol-bis(8-quinolyl) ether in acetonitrile–dimethylsulfoxide and nitromethane–dimethylsulfoxide binary mixtures

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ABSTRACT

^7Li NMR spectroscopy was used to determine the stoichiometry and stability of the Li^+ ion complex with tetraethyleneglycol-bis(8-quinolyl) ether (**L**) in acetonitrile–dimethylsulfoxide (97.2:2.8, w/w) and nitromethane–dimethylsulfoxide (97.2:2.8, w/w) binary mixtures. A competitive ^7Li NMR spectroscopy was also employed to probe the complexation of Na^+ , Ag^+ , Ca^{2+} , Mg^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} and UO_2^{2+} ions with **L** in the same solvent systems. The ^7Li chemical shift data indicated that all studied cations form 1:1 complexes with the ligand and all the resulting 1:1 complexes in nitromethane–dimethylsulfoxide are more stable than those in acetonitrile–dimethylsulfoxide solution. In both solvent systems, the stability of the resulting complexes was found to vary in the order $\text{Ag}^+ > \text{Pb}^{2+} > \text{Na}^+ > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Li}^+ > \text{Ca}^{2+} > \text{UO}_2^{2+} > \text{Mg}^{2+}$.

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1. Introduction

Since the first work of Moore and Pressman on the transport of potassium ions through the mitochondrial membrane by the antibiotic valinomycin [1], a wide range of studies has been focused on the ion carrier ability of other naturally occurring [2] and synthetic ligands, including crown ethers [3] and cryptands [4], in transport of ions through biological and artificial membranes [5,6]. Meanwhile, due to similarities of open-chain polyethylene glycols in many respects to naturally occurring and synthetic antibiotics, there has been a continuous interest in coordination chemistry of these ligands and their metal ion complexes in the past two decades [7–16]. It has been found that the oxyethylene chain of common glymes can form complexes with cations, although with lower stabilities compared with the corresponding cyclic ones.

Vögtle and his coworkers introduced a group of open chain polyether compounds with rigid aromatic end-groups attaching to the oligo(ethylene glycol) backbone, and studied the influence of aromatic donor end groups on thermodynamics and kinetics of their complex formation with alkali metal ions in methanol solution [17,18]. 1,13-Bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (**L**, Scheme 1) is an open-chain polyether bearing quinoline end groups,

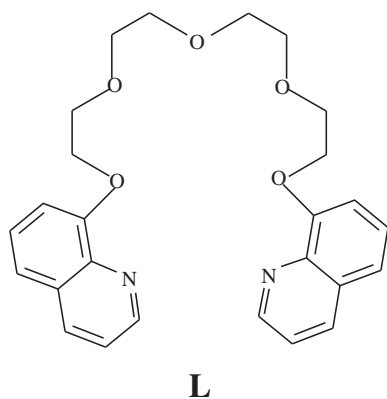
which can be considered as a key podand due to its attractive characteristics. It has an intermediate affinity for alkali metal ions and neutral molecules in solution and solid states [18], and can form a stable complex with Ag^+ in solution [19,20] and solid state [21]. We have previously reported the thermodynamics of complexation of **L** with some alkali [22] and transition and heavy metal ions [23,24] in nonaqueous solvents.

It has been clearly shown that nuclear magnetic resonance spectroscopy offers a very sensitive technique for the study of changes in the immediate chemical environment of metal ions in solution, which make it a very suitable probe for the study of thermodynamics and kinetics of metal ion complexation with macromolecule ligands [25]. In the past decade, we have used proton and alkali NMR techniques to study the thermodynamics and kinetics of metal ion complexation with some macrocyclic and acyclic ligands [26–40]. However, some cations including alkaline earth and transition metal ions suffer from unsuitable NMR properties such as low receptivity, high quadrupole moment, insensitive chemical shifts, etc. [41]. Thus, in order to overcome this problem, we have employed a competitive NMR spectroscopy technique to investigate the thermodynamics of complexation of variety macrocycle-metal ion systems [42–45].

In this work, we have studied the influences of the nature and size of cations and solvent properties on the stoichiometry and stability of the Li^+ , Na^+ , Ca^{2+} , Mg^{2+} , Ag^+ , Cd^{2+} , Pb^{2+} , Zn^{2+} and UO_2^{2+} complexes with **L** in acetonitrile–dimethylsulfoxide (97.2:2.8, w/w)

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Scheme 1. Structure of 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (**L**).

and in nitromethane–dimethylsulfoxide (97.2:2.8, w/w) solvent mixtures using competitive ^7Li NMR as a very sensitive probe. As mentioned above, the alkaline earth, transition and heavy metal ions used possess unsuitable NMR properties, which make their use in such NMR studies practically impossible.

2. Experimental

Reagent grade 1,13-bis(8-quinolyl)-1,4,7,10,13-pentaoxatridecane (**L**, >99.0%), acetonitrile (AN), deuterated acetonitrile, nitromethane (NM), deuterated nitromethane and dimethylsulfoxide (DMSO) were purchased from Merck chemical company and used as received. The analytical grade nitrate salts of all cations used were of the highest purity available from Fluka and used without any further purification except for vacuum drying. AN–DMSO and NM–DMSO (97.2:2.8, w/w) mixtures were prepared by weight and found to properly dissolve all the salts used. The concentration of all cations used was 0.005 M.

All ^7Li NMR measurements were made on a Bruker Avance 300 MHz FT-NMR spectrometer with the processing software XWIN-NMR version 3.1, equipped with a dedicated 5-mm QNP probe head using 500 μL of samples. The field strength of the spectrometer was 70.49 kG. At this field, lithium-7 resonates at 116.64 MHz. An aqueous 4.0 M LiCl solution was used as the external reference and the reported lithium-7 chemical shifts were referenced to this solution. The paramagnetic (downfield) shift from the reference is designated as being positive. The chemical shift measurements were carried out at a probe temperature of 25.0 ± 0.1 °C. A 90° pulse of 9.52 s was used in the ^7Li NMR recording. The acquisition time was 7.03 s, corresponding to a sweep width of 2.33 kHz. The relaxation time was 1.0 s. Typically, the number of scans applied was 16. All shifts were accurate to ± 0.01 ppm and the temperature was measured to a precision of ± 0.1 °C.

3. Results and discussion

The lithium-7 chemical shifts were measured as a function of the ligand **L** to lithium ion mole ratio in AN–DMSO and NM–DMSO solutions (97.2:2.8, w/w), in the absence and presence of equimolar concentrations of different ions used. It should be noted that a least amount of DMSO (i.e., 2.8 wt.%) was added to pure AN and NM in order to make the dissolution of the ligand and nitrate salts of different cations used, at the desired concentrations, appropriately possible. In all cases, only one population-averaged resonance was observed, indicating that the exchange rate of lithium ion between the bulk solution and the complexed sites is fast on the NMR time scale. Sample lithium-7 NMR spectra of a 0.005 M LiNO_3 in NM–DMSO (97.2:2.8 w/w) mixture at various $[\text{L}]/[\text{Li}^+]$ mole ratios in the absence and presence of equimolar concentrations of Ag^+ ion are shown in Fig. 1.

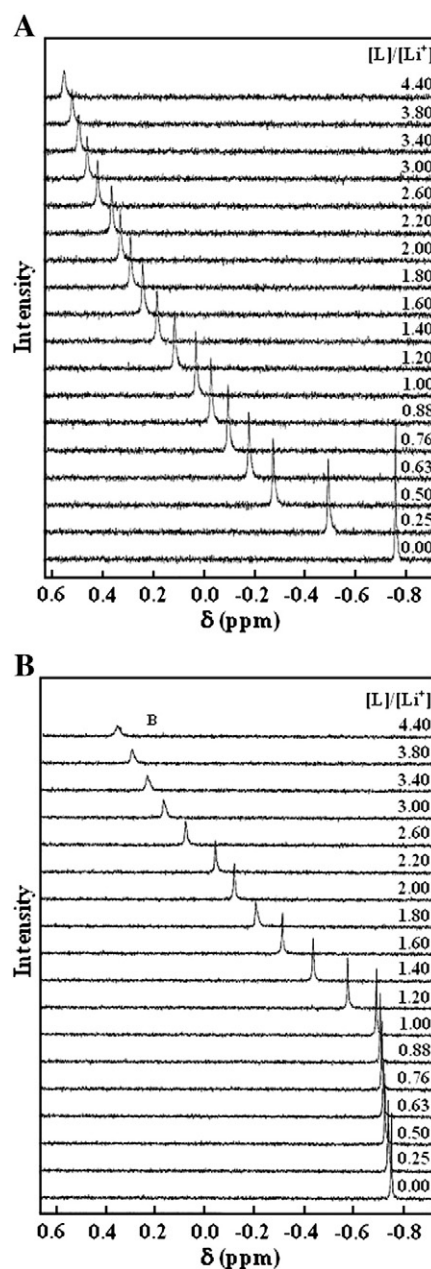


Fig. 1. Lithium-7 NMR spectra of 0.005 M LiNO_3 in NM–DMSO (97.2:2.8 w/w) at various $[\text{L}]/[\text{Li}^+]$ mole ratios in the absence (A) and presence of equimolar concentration of Ag^+ ion (B).

The resulting chemical shift– $[\text{L}]/[\text{Li}^+]$ mole ratio plots, in the absence of any other metal ion, in both NM–DMSO and AN–DMSO mixtures are illustrated in Fig. 2. As can be seen, in the absence of other metal ions, the addition of ligand **L** to the lithium ion solution causes a gradual paramagnetic shift, which tends to level off at mole ratios greater than unity. As seen, the slope of the resulting mole ratio plots changes significantly at the point where the ligand-to-cation mole ratio is equal to one, indicating the formation of relatively stable 1:1 complexes. It is interesting to note that the inflection point of the mole ratio plot in NM–DMSO solution is clearly sharper than that in AN–DMSO solution, emphasizing the higher stability of the resulting complex in the former solvent mixture.

The variations of lithium-7 chemical shift with $[\text{L}]/[\text{Li}^+]$ mole ratio were used to evaluate the formation constants of the 1:1 Li^+ complexes with **L** in both solvent mixtures used. Assuming that only a 1:1 complex is formed in solution and fast exchange kinetics is

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