

Isolation of alkali and alkaline earth metal complexes by diethylene glycol dibenzoate

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Abstract. Complexes of lithium, sodium, potassium, magnesium and calcium were isolated by diethylene glycol dibenzoate in different organic solvents. Picrate, dinitrophenolate and orthonitrophenolate were used as anions. Stoichiometries of isolated complexes are 1:1 for alkali metal and 1:2 for alkaline earth metal complexes. Shifts in the characteristic frequencies of ligand molecule were observed in IR and ^1H NMR spectra of complexes.

Keywords. Isolation of metal complexes; diethylene glycol benzoate; podands; chain length; flexibility.

1. Introduction

Podands are open chain analogues of crown ethers. Glycol derivatives with aromatic end groups were found to possess better complexing abilities in comparison with common glymes (Hiratani *et al* 1986). One of us has reported the isolation of alkali metal cations with tetra and triethylene glycol dibenzoate (Qureshi *et al* 1992). In this communication we report the isolation of Li^+ , Na^+ , K^+ , Cs^+ , Mg^{2+} , Ca^{2+} , complexes by diethylene glycol dibenzoate (figure 1). Picrate, dinitrophenolate, orthonitrophenolate have been used as anions. The aim of the work is to understand the principles and factors that are involved during the complexation of non-cyclic polyethers having aromatic end groups with alkali and alkaline earth metal ions i.e. the anions, stoichiometry of the complexes, chain length of the ligand, size of cation etc.

2. Experimental section

2.1 Chemicals

Diethylene glycol dibenzoate (Aldrich), picric acid, dinitrophenol and orthonitrophenol (Merck) and other chemicals of BDH and Loba were used.

2.2 Apparatus

Instruments employed were the Scientific Instruments Co. Ltd. Boss 165 melting-point apparatus, Perkin Elmer 377 IR spectrometer, Systronics 121 digital flame photometer for estimation of Li^+ , Na^+ , K^+ and Philips atomic absorption spectrophotometer for estimation of Mg^{2+} and Ca^{2+} . Elemental analysis and NMR studies $\text{D}_2\text{O}/\text{CDCl}_3$ were performed at CDRI Lucknow with TMS internal standard at 400 MHz.

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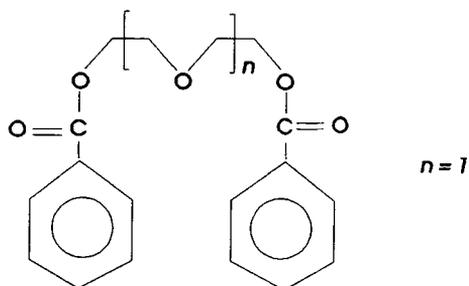


Figure 1. Structure of diethylene glycol dibenzoate.

Alkali and alkaline earth metal picrates (MPic), dinitrophenolates (MDnp) and orthonitrophenolates (MOnp) were prepared by the same procedure as reported earlier (Poonia *et al* 1971). For isolation of the complexes (Qureshi *et al* 1992), the metal salt and ligand were mixed in 1:1 ratio in case of alkali metal salts and 1:2 ratio in case of alkaline earth metal salts in a suitable organic solvent. The mixture was heated on a water bath and thus reduced. The metal ligand complexes were then allowed to crystallize at room temperature. Crystallization generally occurs within 1 to 3 days.

The crystals were vacuum filtered and recrystallized from the same solvent from which they were isolated. The solvents used for isolation were methanol, ethylacetate, isopropanol and acetonitrile. In some cases mixtures of two or more solvents had to be used to obtain the crystals. Complexes were identified by melting points and characterized by IR and NMR.

3. Results and discussions

The properties of isolated complexes are given in table 1. From the elemental analysis and metal estimation of isolated complexes on flame photometer and atomic absorption spectrophotometer it is observed that stoichiometry is 1:1 for alkali metal complexes and 1:2 for alkaline earth metal complexes. It was reported (Ackman *et al* 1955) that a sandwich structure seems the most probable for 1:2 complexes. Bivalent cations have higher charge density and smaller size. They undergo self encapsulation between two molecules of ligand along with anion and these encapsulates are comparable to those obtained from cyclic antibiotics (Dobler *et al* 1969).

The ligand fails to form complexes with K^+ and Cs^+ while it forms complexes with Li^+ and Na^+ . This observation clearly indicates the effect of chain length. The smaller chain length of diethylene glycol dibenzoate is inefficient in forming complexes with larger sized K^+ (1.33 Å) and Cs^+ (1.69 Å) ion, and the effect is compounded by the steric hindrance caused by the bulky end groups.

IR spectra of the ligand were recorded in methanol in a liquid cell between NaCl plates and complexes were recorded using KBr pellets. It is observed that peaks in ligand molecule at $2980\text{--}2880\text{ cm}^{-1}$ (aromatic C-H stretching), $1740\text{--}1730\text{ cm}^{-1}$ (keto C=O), $1180, 1110\text{--}1150, 1070, 1010\text{ cm}^{-1}$ ($CH_2\text{--O--CH}$) are found to be shifted in complexes. NMR spectra of the ligand and complexes reveal that signals for the protons at $\delta 3.9$ ($-\text{OCH}_2$) in ligand are shifted upfield and protons at $\delta 4.53\text{--}4.56$ (ether $-\text{OCH}_2$) and $\delta 8.03\text{--}8.04$ ($-\text{OC}_6\text{H}_5$) in the ligand are shifted downfield in the complexes. Splitting of the signal for $-\text{OCH}_2$ protons into doublets, triplets and ester

Table 1. Properties of isolated complexes of alkali and alkaline earth metal salts by diethyleneglycol dibenzoate.

Complex	Solvent	M.P. [°C]	Yield (%)	Molecular formula	Elemental analysis (%) [*]				
					C	H	N	M	
LiDnp(DEGDB)	Methanol	132	23.93	$C_{24}H_{21}O_{10}N_2Li$	57.12 (57.14)	4.18 (4.16)	5.54 (5.55)	1.37 (1.38)	
NaPic(DEGDB)	Methanol	170	9.62	$C_{24}H_{20}O_{12}N_3Na$	50.95 (50.97)	3.51 (3.53)	7.40 (7.43)	4.04 (4.07)	
Mg(Pic)(DEGDB) ₂	Methanol	118	22.69	$C_{48}H_{40}O_{24}N_6Mg$	51.95 (51.98)	3.60 (3.61)	7.55 (7.58)	2.14 (2.16)	
Mg(Dnp) ₂ (DEGDB) ₂	Acetonitrile	203	3.65	$C_{48}N_4O_{20}H_{42}Mg$	56.55 (56.58)	4.10 (4.12)	5.49 (5.50)	2.36 (2.35)	
Ca(Pic) ₂ (DEGDB) ₂	Methanol	65	1.60	$C_{48}H_{40}O_{24}N_6Ca$	51.22 (51.24)	3.53 (3.55)	7.45 (7.47)	3.54 (3.55)	

^{*}Calculated values given in parenthesis; DEGDB – diethyleneglycol dibenzoate

OCH₂ into multiplets indicates the change in conformation of the ligand during complexation (Vogtle and Weber 1977). The splitting of the signal for ester OCH₂ is greater in the Mg(Pic)₂ (DEGDB) complex than in the (CaPic)₂ (DGEDB) complex and in the NaPic (DEGDB) than in the LiDnp (DEGDB) complex signifying the greater extent of complexation in Mg(Pic)₂ (DEGDB) and NaPic (DEGDB) complexes. In comparison with the higher chain length analogues, lesser number of complexes can be isolated with diethylene glycol dibenzoate. This is due to decrease in number of donor sites and flexibility.

Thus in conclusion the complexation of the polyether dibenzoate depends on the size, charge and density of the cation and on the length of the oxyethylene chain.

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