

# Isolation and Structural Characterization of Alkali and Alkaline Earth Metal Salts with Synthetic Non Cyclic Ionophores

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## Abstract

In the present study, an investigation on the complex formation between mono- and divalent metal ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$  and  $\text{Mg}^{2+}$ ) in the form of salt with different podands using various solvents has been carried out. Isolated complexes were characterized by different spectroscopic techniques *viz.* IR, NMR and elemental analysis. On the basis of the obtained data, it was observed that number of donor sites, ionic potential, size fit concept in pseudocyclic cavity *etc.* are the deciding factors for complexation which make it differ between solid and solution complexation using ionophores.

**Keywords:** Podands; Complexation; Pseudocyclic cavity.

## Introduction

Molecular informatics field is related to the molecular storage and the supramolecular processing of information. The organizational ability of membranes mimics in the host-guest systems [1]. Podands having donor groups can interact with alkali and alkaline earth metal cations and are known to be effective host molecules. Variation in the structure leads to variation in cation binding strengths and selectivities and works on the basis of the cooperative coordination through interaction between host and guest in pseudocyclic cavity of ionophore.

Certain polyethers, particularly those containing 5-10 oxygen atoms each separated from the next by two carbon atoms were shown to form crystalline complexes of alkali [2] and alkaline earth metal salts. It was reported that the stoichiometry of these complexes may

be 1:1, 2:1 or 3:1 [metal ion(s): poly- ether] regardless of valency of metal.

## Materials and Methods

The complexes [3, 4] were prepared by mixing different proportions of alkali and alkaline earth metal salts with ionophores ( $\text{P}_1$ - $\text{P}_3$ ) (Figures 1-3) in different solvents like methanol, ethyl acetate, (Methanol+ ethyl acetate), (isopropanol+ethyl acetate) and acetonitrile. The mixture was heated on a water bath, thus reduced and then allowed to crystallize at room temperature. Crystallisation generally occurs within two or three days. The crystals were vacuum filtered and recrystallised from the same solvent from which they were isolated.

The characterization of isolated complexes was carried out by melting point determination and confirmed by elemental and spectral analysis (C,H,N analysis, IR and  $^1\text{H}$  NMR). The stoichiometry of the complexes was

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Figure 1. Dipropylenglycoldibenzoate  $[(C_6H_5CO_2C_3H_6)_2O]$  [P<sub>1</sub>]

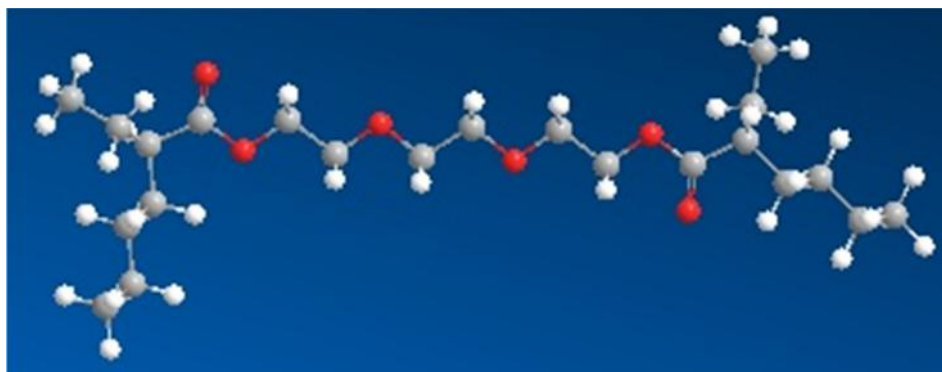


Figure 2. Triethyleneglycolbis(2-ethylhexanoate)  $[C_{22}H_{42}O_6]$  [P<sub>2</sub>]

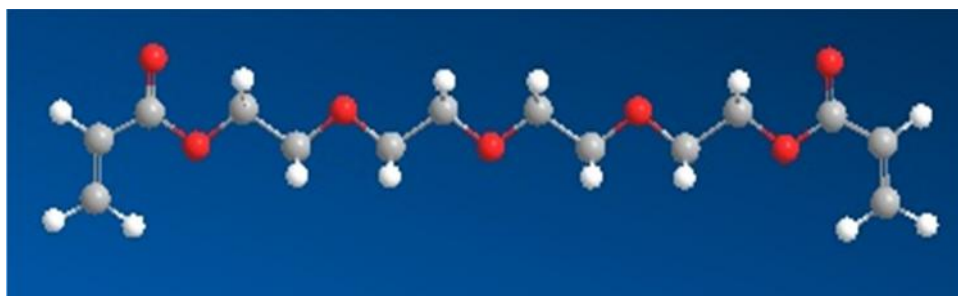


Figure 3. Tetraethyleneglycoldiacrylate  $[C_{14}H_{22}O_7]$  [P<sub>3</sub>]

determined by metal estimation on digital flame photometer (Systronics 128) and atomic absorption spectrophotometer (Shimadzu 6300).

### Results and Discussion

The isolation studies of metal salts with ionophores (P<sub>1</sub>-P<sub>3</sub>) have been carried out and it is observed that P<sub>1</sub>, P<sub>2</sub> and P<sub>3</sub> form complexes with metal salts and the

characterization of complexes are summarized in Tables 1-3.

In the formation of complexes the solvation of metal ion and solvation of the ligand are two deciding factors. Complexes were isolated in ethyl acetate and methanol.

Almost all complexes were isolated with  $M(\text{Pic})_x$  and  $M(\text{Dnp})_x$  salts while  $M(\text{Onp})_x$  salts were failed to complex with non cyclic ligands.

**Table 1.** Properties of isolated complexes of alkali and alkaline earth metal salts with podands P<sub>1</sub>, P<sub>2</sub> and P<sub>3</sub>

S.No.	Metal Salt	Ionophore	Solvent	Stoichiometry M:L	M.P. (°C)	Molecular formula	Elemental Analysis (%)				
							C	H	N	M	
1	NaPic	P <sub>1</sub>	CH <sub>3</sub> COO C <sub>2</sub> H <sub>5</sub>	1:1	245	C <sub>26</sub> H <sub>24</sub> O <sub>12</sub> N <sub>3</sub> Na	C	52.58	4.04	7.08	3.88
							F	52.56	4.01	7.11	3.92
2	KPic	P <sub>1</sub>	CH <sub>3</sub> COO C <sub>2</sub> H <sub>5</sub>	1:1	255	C <sub>26</sub> H <sub>24</sub> O <sub>12</sub> N <sub>3</sub> K	C	51.20	3.94	6.89	6.40
							F	51.13	3.92	6.90	6.37
3	LiDnp	P <sub>1</sub>	CH <sub>3</sub> OH	1:1	101	C <sub>26</sub> H <sub>25</sub> O <sub>10</sub> N <sub>2</sub> Li	C	58.61	4.70	5.26	1.30
							F	58.40	4.74	5.18	1.35
4	KPic	P <sub>2</sub>	CH <sub>3</sub> OH	1:1	257	C <sub>28</sub> H <sub>44</sub> O <sub>13</sub> N <sub>3</sub> K	C	50.18	6.57	6.27	5.82
							F	50.15	6.52	6.31	5.79
5	NaPic	P <sub>2</sub>	CH <sub>3</sub> OH	1:1	260	C <sub>28</sub> H <sub>44</sub> O <sub>13</sub> N <sub>3</sub> Na	C	51.41	6.73	6.43	3.52
							F	51.45	6.74	6.40	3.49
6	LiDnp	P <sub>2</sub>	CH <sub>3</sub> OH	1:1	91	C <sub>28</sub> H <sub>45</sub> O <sub>11</sub> N <sub>2</sub> Li	C	56.71	7.59	4.72	1.17
							F	56.65	7.57	4.79	1.21
7	Mg(Dnp) <sub>2</sub>	P <sub>2</sub>	CH <sub>3</sub> OH	1:1	73	C <sub>34</sub> H <sub>48</sub> O <sub>16</sub> N <sub>4</sub> Mg	C	51.48	6.06	7.06	3.03
							F	51.37	6.12	7.11	2.99
8	Mg(Dnp) <sub>2</sub>	P <sub>3</sub>	CH <sub>3</sub> OH	1:1	63	C <sub>26</sub> H <sub>28</sub> O <sub>17</sub> N <sub>4</sub> Mg	C	45.06	4.04	8.09	3.47
							F	45.14	3.99	8.15	3.42

**Table 2.** IR spectral data of alkali and alkaline earth metal complexes with podands P<sub>1</sub>, P<sub>2</sub> and P<sub>3</sub>

Ionophore	Complex	Selected IR absorption bands in ionophore and respective shift in complex (cm <sup>-1</sup> )
		3064.12 (Ar C-H), 1714.36 (C=O), 1584.84(C-C), 1451.52 (C-H in CH <sub>2</sub> ), 1378.43 (C-H in CH <sub>3</sub> ), 1315.17 (C-O in ester), 1176.59 (C-O-C)
P <sub>1</sub>	P <sub>1</sub> .NaPic	3100 (Ar C-H), 1700 (C=O), 1530(C-C), 1436.62 (C-H in CH <sub>2</sub> ), 1370.57 (C-H in CH <sub>3</sub> ), 1279.65 (C-O in ester), 1162.60 (C-O-C)
	P <sub>1</sub> .KPic	3087.57 (Ar C-H), 1869.04 (C=O), 1568.64(C-C), 1430.38 (C-H in CH <sub>2</sub> ), 1372.93 (C-H in CH <sub>3</sub> ), 1278.93 (C-O in ester), 1162.78 (C-O-C)
	P <sub>1</sub> .LiDnp	3109.28 (Ar C-H), 1829.71 (C=O), 1540.06(C-C), 1435.66 (C-H in CH <sub>2</sub> ), 1335.20 (C-H in CH <sub>3</sub> ), 1255.44 (C-O in ester), 1137.04 (C-O-C)
		1734.83 (C=O), 1460.74 (C-H in CH <sub>2</sub> ), 1382.74 (C-H in CH <sub>3</sub> ), 1175.09 (C-O-C)
P <sub>2</sub>	P <sub>2</sub> .KPic	1869.05 (C=O), 1430.43 (C-H in CH <sub>2</sub> ), 1371.98 (C-H in CH <sub>3</sub> ), 1162.95 (C-O-C)
	P <sub>2</sub> .NaPic	1860 (C=O), 1437.41 (C-H in CH <sub>2</sub> ), 1370.09 (C-H in CH <sub>3</sub> ), 1278.72 (C-O-C)
	P <sub>2</sub> .LiDnp	1829.74 (C=O), 1435.66 (C-H in CH <sub>2</sub> ), 1335.91 (C-H in CH <sub>3</sub> ), 1136.80 (C-O-C)
	P <sub>2</sub> .Mg(Dnp) <sub>2</sub>	1800 (C=O), 1435.61 (C-H in CH <sub>2</sub> ), 1336.16 (C-H in CH <sub>3</sub> ), 1183.86 (C-O-C)
P <sub>3</sub>	P <sub>3</sub> .Mg(Dnp) <sub>2</sub>	2873.48 (=C-H), 1730.17 (C=O), 1135.28 (C-O-C), 1453.09 (C-H in CH <sub>2</sub> )
		3109.00 (=C-H), 1829.73 (C=O), 1107.91 (C-O-C), 1435.73 (C-H in CH <sub>2</sub> )

Ionophore P<sub>1</sub> shows complexing ability with Li<sup>+</sup>, Na<sup>+</sup> and K<sup>+</sup>, P<sub>2</sub> with Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup> and Mg<sup>2+</sup> while P<sub>3</sub> with Mg<sup>2+</sup>. It is clear from elemental analysis and metal estimation of isolated complexes that stoichiometric ratio of metal salt and ionophore for P<sub>1</sub>, P<sub>2</sub> and P<sub>3</sub> is 1:1.

From Table 2, It is observed that characteristics IR peaks of the ionophore P<sub>1</sub> at 1714.36 (C=O), 1315.17 (C-O in ester) and 1176.59 (C-O-C) are shifted in the complexes. It shows the participation of these groups in the complexation and slight shift in the case of NaPic

indicates the lesser amount of participation of these groups in complexation which may be attributed to the conformational changes in the non cyclic ionophores.

Ionophore P<sub>1</sub> forms complexes with sodium picrate, potassium picrate and lithium dinitrophenolate (Figure 4). The shifting of the peaks are greater in P<sub>1</sub>.LiDnp complex than P<sub>1</sub>.NaPic and P<sub>1</sub>.KPic. The selectivity of ionophore P<sub>1</sub> for Li<sup>+</sup> can be explained by pseudocyclic cavity fit concept. It may be suggested that the ionic diameter of Li<sup>+</sup> (1.36 Å) matches with pseudocavity

**Table 3.**  $^1\text{H}$  NMR spectral data of alkali and alkaline earth metal complexes with podands  $\text{P}_1$ ,  $\text{P}_2$  and  $\text{P}_3$ 

Ionophore	Complex	Selected NMR absorption bands in ionophore and respective shift in complex ( ppm)
$\text{P}_1$		1.33-1.37 ( $\text{CH}_3$ ), 3.55-3.99 ( $\text{CH}$ ), 4.31-4.48 ( $\text{OCH}_2$ ), 8.00-8.06 ( $\text{ArH}$ )
	$\text{P}_1\cdot\text{NaPic}$	1.27-1.35 ( $\text{CH}_3$ ), 3.47-3.55 ( $\text{CH}$ ), 4.76-4.84 ( $\text{OCH}_2$ ), 8.45-8.49 ( $\text{ArH}$ )
	$\text{P}_1\cdot\text{KPic}$	1.29-1.36 ( $\text{CH}_3$ ), 3.57-3.60 ( $\text{CH}$ ), 4.76-4.84 ( $\text{OCH}_2$ ), 8.59-8.88 ( $\text{ArH}$ )
	$\text{P}_1\cdot\text{LiDnp}$	1.25-1.58 ( $\text{CH}_3$ ), 3.65-3.69 ( $\text{CH}$ ), 4.51-4.53 ( $\text{OCH}_2$ ), 8.45-8.49 ( $\text{ArH}$ )
$\text{P}_2$		1.27-1.31 ( $\text{CH}_2$ ), 3.64-3.69 ( $\text{CH}$ ), 4.23-4.26 ( $\text{OCH}_2$ )
	$\text{P}_2\cdot\text{KPic}$	1.1-1.3 ( $\text{CH}_2$ ), 3.25 ( $\text{CH}$ ), 4.62-4.70 ( $\text{OCH}_2$ ), 8.51-8.52 ( $\text{ArH}$ )
	$\text{P}_2\cdot\text{NaPic}$	1.31-1.39 ( $\text{CH}_2$ ), 3.5-3.7 ( $\text{CH}$ ), 4.62-4.68 ( $\text{OCH}_2$ ), 8.42-8.43 ( $\text{ArH}$ )
	$\text{P}_2\cdot\text{LiDnp}$	1.61 ( $\text{CH}_2$ ), 3.65 ( $\text{CH}$ ), 4.46-4.97 ( $\text{OCH}_2$ ), 8.45-8.49 ( $\text{ArH}$ )
$\text{P}_3$	$\text{P}_2\cdot\text{Mg}(\text{Dnp})_2$	1.60 ( $\text{CH}_2$ ), 3.57-3.65 ( $\text{CH}$ ), 4.47-4.79 ( $\text{OCH}_2$ ), 8.46-8.49 ( $\text{ArH}$ )
	$\text{P}_3\cdot\text{Mg}(\text{Dnp})_2$	1.91 ( $\text{CH}_2$ ), 3.52-3.88 ( $\text{CH}$ ), 4.32-4.46 ( $\text{OCH}_2$ )
		1.92 ( $\text{CH}_2$ ), 3.64 ( $\text{CH}$ ), 4.39-4.47 ( $\text{OCH}_2$ ), 8.35-8.49 ( $\text{ArH}$ )

formed due to ion-dipole interaction.

Ionophore  $\text{P}_2$  forms complexes with NaPic, KPic and LiDnp. The ionophores  $\text{P}_1$ ,  $\text{P}_2$  and  $\text{P}_3$  have donor sites, and frequency lowers in case of LiDnp, KPic and  $\text{Mg}(\text{Dnp})_2$  complexes which indicates the interactions of donor sites of ionophores with  $\text{Li}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{2+}$  due to ion-dipole interactions. The results are further supported by  $^1\text{H}$  NMR spectral data.

$^1\text{H}$ -NMR spectral data of the ionophores ( $\text{P}_1$ ,  $\text{P}_2$  and  $\text{P}_3$ ) and complexes are shown in Table 3. The data in case of  $\text{P}_1$  reveal that the signals for the protons at  $\delta$  1.33-1.37 ( $\text{CH}_3$ ),  $\delta$  4.3-4.4 ( $\text{OCH}_2$ ),  $\delta$  8.45-8.49 ( $\text{ArH}$ ) found to be shifted downfield in the complexes. In case of  $\text{P}_2$  and its complexes with sodium, potassium, lithium and magnesium ions, downfield shifting was observed from  $\delta$  1.27-1.31 ( $\text{CH}_2$ ),  $\delta$  4.23-4.26 ( $\text{OCH}_2$ ) while signals from  $\delta$  1.91 ( $\text{CH}_2$ ),  $\delta$  3.52-3.88 ( $\text{CH}$ ),  $\delta$  4.32-4.46 ( $\text{OCH}_2$ ) also show downfield shifting in case of  $\text{P}_3$  with magnesium as well as the peaks at  $\delta$  8.42-8.52 and  $\delta$  8.35-8.49 indicate the presence of aromatic moiety in

complexes which were absent in  $\text{P}_2$  and  $\text{P}_3$ . Hence, the interaction of the metal ions with ionophores results the formation of complexes. The splitting of the signals into multiplet indicates the change in conformation of the ionophore during complexation.

On the basis of the above characterization, the metal is supposed to be caged in the pseudocyclic cavity of the ligand species made by  $-\text{O}-$  groups of ether and ester.

It is concluded from the spectral data of the complex that there is a prominent role of oxygen donor sites during complexation. The number of donor sites and pseudocavity diameter affect the ion-dipole interaction and hence the cation binding property.

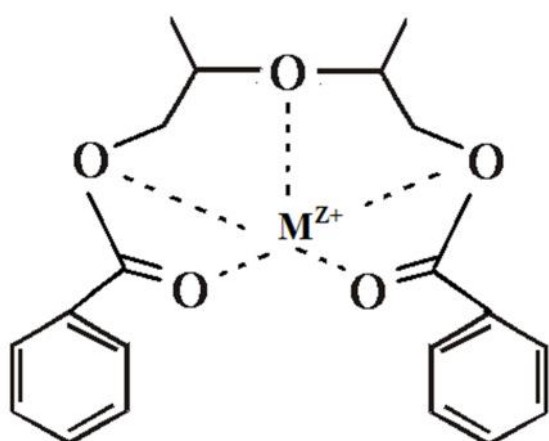
The adoptability of the ionophore according to the size and charge density of the metal ions is an important factor for complexation and for molecular recognition. It was reported among various crown ethers; 12-crown-4, 15-crown-5 and 18-crown-6 are best extractants [5] for lithium, sodium and potassium cations respectively. This supports the approach of adoptability in podands and lariat ethers but the size fit concept does not exist which loss in specificity [6, 7].

From the results, it is concluded that the noncovalent interactions, structural aspects of the ionophore and the factors such as size and charge density of the metal ions are important for the molecular recognition.

Although the above discussion concerns with the complexation in solid phase (isolation studies) but the chemistry involved may qualitatively be extrapolated to the solution state because failure to isolate a complex is not being attributed to its absence of interaction in the solution.

### Conclusions

It was observed that  $\text{Li}^+$  and  $\text{Mg}^{2+}$  show complexation in the solid state with  $\text{P}_1$ ,  $\text{P}_2$  and  $\text{P}_3$  in the isolation studies. But these ionophores fail to extract and transport of these metal ions in the solution state. By considering the charge density of  $\text{M}^{Z+}$ ,



**Figure 4.** Schematic representation of binding of metal ion in pseudocyclic cavity of podand

nucleophilicity of  $X^-$  and the conformational aspects of the ligand, we can predict the complexation behavior of isolated complexes. The stoichiometry of the isolated complexes is found to be 1:1.

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