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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 (Na^+, K^+, Li^+ and 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 (P_1-P_3) (Figures 1-3) in different solvents like methanol, ethyl acetate, (Methanol+ ethyl acetate), (isopropanol+ethyl acetate) and acetonotrile. 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}H NMR). The stoichiometry of the complexes was

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Figure 1. Dipropyleneglycoldibenzoate [$(C_6H_5CO_2C_3H_6)_2O$] [P_1]

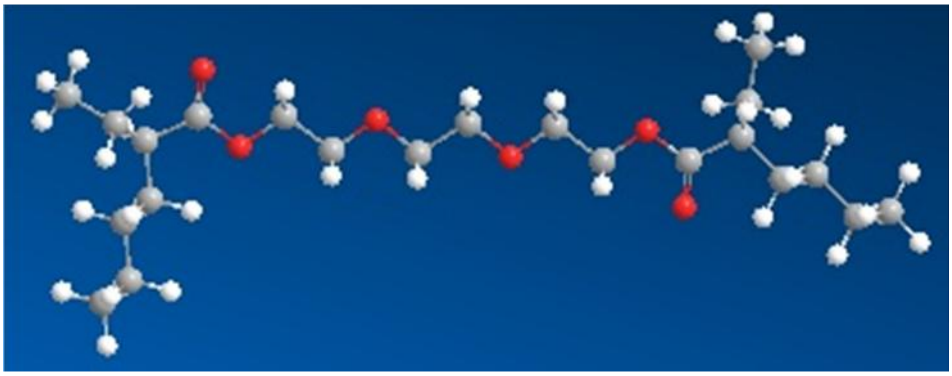

Figure 2. Triethyleneglycolbis(2-ethylhexanoate) [$C_{22}H_{42}O_6$] [P_2]

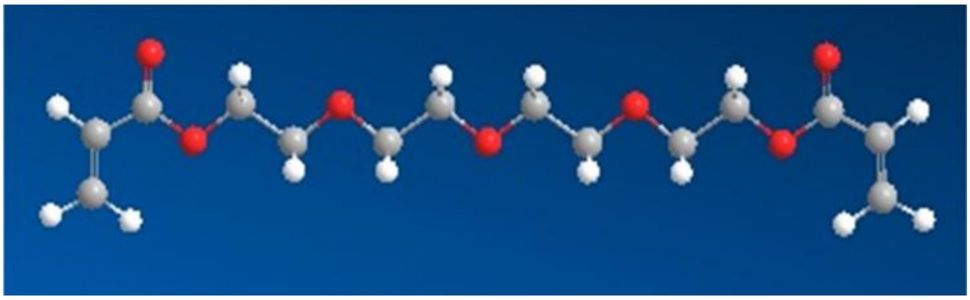

Figure 3. Tetraethyleneglycoldiacrylate [$C_{14}H_{22}O_7$] [P_3]

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_1-P_3) have been carried out and it is observed that P_1, P_2 and P_3 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 $M(Pic)_x$ and $M(Dnp)_x$ salts while $M(Onp)_x$ 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_1, P_2 and P_3

S.No.	Metal Salt	Ionophore	Solvent	Stoichiometry M:L	M.P. (^{0}C)	Molecular formula	Elemental Analysis (%)			
							C	H	N	M
1	NaPic	P_1	$CH_3COOC_2H_5$	1:1	245	$C_{26}H_{24}O_{12}N_3Na$	C 52.58	4.04	7.08	3.88
							F 52.56	4.01	7.11	3.92
2	KPic	P_1	$CH_3COOC_2H_5$	1:1	255	$C_{26}H_{24}O_{12}N_3K$	C 51.20	3.94	6.89	6.40
							F 51.13	3.92	6.90	6.37
3	LiDnp	P_1	CH_3OH	1:1	101	$C_{26}H_{25}O_{10}N_2Li$	C 58.61	4.70	5.26	1.30
							F 58.40	4.74	5.18	1.35
4	KPic	P_2	CH_3OH	1:1	257	$C_{28}H_{44}O_{13}N_3K$	C 50.18	6.57	6.27	5.82
							F 50.15	6.52	6.31	5.79
5	NaPic	P_2	CH_3OH	1:1	260	$C_{28}H_{44}O_{13}N_3Na$	C 51.41	6.73	6.43	3.52
							F 51.45	6.74	6.40	3.49
6	LiDnp	P_2	CH_3OH	1:1	91	$C_{28}H_{45}O_{11}N_2Li$	C 56.71	7.59	4.72	1.17
							F 56.65	7.57	4.79	1.21
7	$Mg(Dnp)_2$	P_2	CH_3OH	1:1	73	$C_{34}H_{48}O_{16}N_4Mg$	C 51.48	6.06	7.06	3.03
							F 51.37	6.12	7.11	2.99
8	$Mg(Dnp)_2$	P_3	CH_3OH	1:1	63	$C_{26}H_{28}O_{17}N_4Mg$	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_1, P_2 and P_3

Ionophore	Complex	Selected IR absorption bands in ionophore and respective shift in complex (cm^{-1})
P_1		3064.12 (Ar C-H), 1714.36 (C=O), 1584.84(C-C), 1451.52 (C-H in CH_2), 1378.43 (C-H in CH_3), 1315.17 (C-O in ester), 1176.59 (C-O-C)
	P_1.NaPic	3100 (Ar C-H), 1700 (C=O), 1530(C-C), 1436.62 (C-H in CH_2), 1370.57 (C-H in CH_3), 1279.65 (C-O in ester), 1162.60 (C-O-C)
	P_1.KPic	3087.57 (Ar C-H), 1869.04 (C=O), 1568.64(C-C), 1430.38 (C-H in CH_2), 1372.93 (C-H in CH_3), 1278.93 (C-O in ester), 1162.78 (C-O-C)
	P_1.LiDnp	3109.28 (Ar C-H), 1829.71 (C=O), 1540.06(C-C), 1435.66 (C-H in CH_2), 1335.20 (C-H in CH_3), 1255.44 (C-O in ester), 1137.04 (C-O-C)
P_2		1734.83 (C=O), 1460.74 (C-H in CH_2), 1382.74 (C-H in CH_3), 1175.09 (C-O-C)
	P_2.KPic	1869.05 (C=O), 1430.43 (C-H in CH_2), 1371.98 (C-H in CH_3), 1162.95 (C-O-C)
	P_2.NaPic	1860 (C=O), 1437.41 (C-H in CH_2), 1370.09 (C-H in CH_3), 1278.72 (C-O-C)
	P_2.LiDnp	1829.74 (C=O), 1435.66 (C-H in CH_2), 1335.91 (C-H in CH_3), 1136.80 (C-O-C)
	P_2.Mg(Dnp)$_2$	1800 (C=O), 1435.61 (C-H in CH_2), 1336.16 (C-H in CH_3), 1183.86 (C-O-C)
P_3		2873.48 (=C-H), 1730.17 (C=O), 1135.28 (C-O-C), 1453.09 (C-H in CH_2)
	P_3.Mg(Dnp)$_2$	3109.00 (=C-H), 1829.73 (C=O), 1107.91 (C-O-C), 1435.73 (C-H in CH_2)

Ionophore P_1 shows complexing ability with Li^+, Na^+ and K^+, P_2 with Li^+, Na^+, K^+ and Mg^{2+} while P_3 with Mg^{2+}. It is clear from elemental analysis and metal estimation of isolated complexes that stoichiometric ratio of metal salt and ionophore for P_1, P_2 and P_3 is 1:1.

From Table 2, It is observed that characteristics IR peaks of the ionophore P_1 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_1 forms complexes with sodium picrate, potassium picrate and lithium dinitrophenolate (Figure 4). The shifting of the peaks are greater in P_1.LiDnp complex than P_1.NaPic and P_1.KPic. The selectivity of ionophore P_1 for Li^+ can be explained by pseudocyclic cavity fit concept. It may be suggested that the ionic diameter of Li^+ (1.36 Å) matches with pseudocavity

Table 3. ^{1}H NMR spectral data of alkali and alkaline earth metal complexes with podands P_1, P_2 and P_3

Ionophore	**Complex**	**Selected NMR absorption bands in ionophore and respective shift in complex (δ ppm)**
P_1		1.33-1.37 (CH_3), 3.55-3.99 (CH), 4.31-4.48 (OCH_2), 8.00-8.06 (ArH)
		1.27-1.35 (CH_3), 3.47-3.55 (CH), 4.76-4.84 (OCH_2), 8.45-8.49 (ArH)
	P_1.NaPic	
	P_1.KPic	1.29-1.36 (CH_3), 3.57-3.60 (CH), 4.76-4.84 (OCH_2), 8.59-8.88 (ArH)
	P_1.LiDnp	1.25-1.58 (CH_3), 3.65-3.69 (CH), 4.51-4.53 (OCH_2), 8.45-8.49 (ArH)
P_2		1.27-1.31 (CH_2), 3.64-3.69 (CH), 4.23-4.26 (OCH_2)
	P_2.KPic	1.1-1.3 (CH_2), 3.25 (CH), 4.62-4.70 (OCH_2), 8.51-8.52 (ArH)
	P_2.NaPic	1.31-1.39 (CH_2), 3.5-3.7 (CH), 4.62-4.68 (OCH_2), 8.42-8.43 (ArH)
	P_2.LiDnp	1.61 (CH_2), 3.65 (CH), 4.46-4.97 (OCH_2), 8.45-8.49 (ArH)
	P_2.Mg(Dnp)$_2$	1.60 (CH_2), 3.57-3.65 (CH), 4.47-4.79 (OCH_2), 8.46-8.49 (ArH)
P_3		1.91 (CH_2), 3.52-3.88 (CH), 4.32-4.46 (OCH_2)
	P_3.Mg(Dnp)$_2$	1.92 (CH_2), 3.64 (CH), 4.39-4.47 (OCH_2), 8.35-8.49 (ArH)

formed due to ion-dipole interaction.

Ionophore P_2 forms complexes with NaPic, KPic and LiDnp. The ionophores P_1, P_2 and P_3 have donor sites, and frequency lowers in case of LiDnp, KPic and Mg(Dnp)$_2$ complexes which indicates the interactions of donor sites of ionophores with Li^+, K^+ and Mg^{2+} due to ion-dipole interactions. The results are further supported by ^{1}H NMR spectral data.

^{1}H-NMR spectral data of the ionophores (P_1, P_2 and P_3) and complexes are shown in Table 3. The data in case of P_1 reveal that the signals for the protons at δ 1.33-1.37 (CH_3), δ 4.3-4.4 (OCH_2), δ 8.45-8.49 (ArH) found to be shifted downfield in the complexes. In case of P_2 and its complexes with sodium, potassium, lithium and magnesium ions, downfield shifting was observed from δ 1.27-1.31 (CH_2), δ 4.23-4.26 (OCH_2) while signals from δ 1.91 (CH_2), δ 3.52-3.88 (CH), δ 4.32-4.46 (OCH_2) also show downfield shifting in case of P_3 with magnesium as well as the peaks at δ 8.42-8.52 and δ 8.35-8.49 indicate the presence of aromatic moiety in complexes which were absent in P_2 and 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.

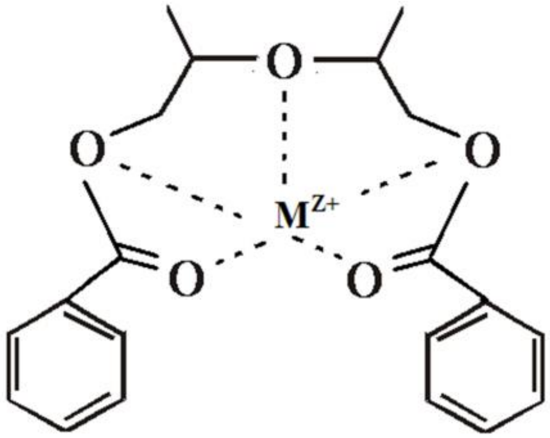

Figure 4. Schematic representation of binding of metal ion in pseudocyclic cavity of podand

On the basis of the above characterization, the metal is supposed to be caged in the pseudocyclic cavity of the ligand species made by –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 Li^+ and Mg^{2+} show complexation in the solid state with P_1, P_2 and 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 M^{Z+}, 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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