

Study of Reactivities of Some Synthetic Non-Cyclic Oxo-Crown Ethers with Alkali and Alkaline Earth Metal Ions in Solid State

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Abstract: *One of the Authors has reported earlier about transport properties of alkali and alkaline earth metals using selected synthesized non-cyclic oxo-crown ethers across organic liquid membrane (elsewhere)¹⁻⁵. In present investigation solid state reactivities of these ligands with metal ions is reported. Some complexes are easily formed, while some of them are not formed at all. The solid state screening has demonstrated different tendencies of the cation in governing complex formation under the effect of different anions. It has been demonstrated that favored cation anion interaction can even overcome the negative role played by charge localized orthonitrophenolate ion. The anion contributes to restrict the range of solid complexes while the Picrate anion emerges as the most favored anion.*

Keywords: solid state reactivity, non- cyclic oxo-crown ethers, metal ions

Abbreviations: Onp⁻ (orthonitrophenolate ion), Dnp⁻ (dinitrophenolate ion), Pic⁻ (Picrate ion). Acn (Acetonitrile), Eta (Ethyl acetate), MeOH (methanol)

1. Introduction

The rapid developments in the synthesis of neutral macrocyclic capable of complexing metal and organic ions has stimulated research efforts in many fields of chemistry. The pioneering work of Pedersen on macrocyclic polyethers or crown ethers was chiefly concerned with oxygen containing ring system and produced a series of powerful complexing agents for alkali and alkaline earth cations, as well as for primary alkali ammonium cations⁶⁻⁸. Subsequent investigations led to macrocycles with nitrogen and sulfur atoms as binding sites in addition to oxygen, often as part of a sub heterocyclic structure such as a pyridine, thiophene, and furan ring. More powerful cation complexing ligands became available with the synthesis of macrocycles or cryptands developed by Lehn and his co-workers⁹. An interesting class of neutral acyclic ligands coined "podands" and developed recently by Vogtle and Weber¹⁰ have properties similar to those of crown ethers and cryptands and can also form crystalline alkali ion complexes or extract alkali salts from an aqueous into an organic phase.

The interaction between a cation and a ligand cannot be only monitored in the solution phase but also through a consideration of the solid state synthesis studies. The two approaches are dealt with separately from each other, however in addition to the usual norms of treating them distinct from each other, can also be considered complementary to each other. Logically the cation ligand in the solid state is almost invariably a consequence of that in the solution phase. The cation ligand interaction in solution should be of substantial magnitude so that same may result in the formation of new species (complex), when the conditions conducive to the synthesis studies are applied. Thus there should be a stage of transition from solution phase to solid

state which may not require exact matching of conditions. Interaction between the cation and ligand taking place in solution may not necessarily lead to the formation of the complex in solid state.

The initial emphasis in ligand design was directed at selective complexation of metal cations, notably alkali and alkaline earth cation because of their importance in many chemical and biological processes.

The extensive "host guest" complexation work by Cram and his co-workers¹¹ chiefly focused on the binding of organic molecules endowed with crown ether complexable sites, such as primary ammonium ions, where the hydrogen atoms play a crucial role in the binding process. The properties of the two components of the complex can be manipulated by attaching neutral or ionic moieties in strategic locations. This may either augment or hinder the binding process and affect the ligand selectivity toward various cations. Several other organic cations form complexes with crown ethers, such as diazonium, acylium and guanidinium ions, while solvate and clathrate type complexes have been found with neutral compounds such as acetonitrile and thiourea.

The ion binding properties of crown ethers, cryptands and podands have been actively employed in diverse fields of chemistry. To the synthetic organic chemist the design and synthesis of these materials have been a challenging task, the phenomena exhibited by the often highly structured complexes resemble those underlying important biological processes such as enzyme catalysis and inhibition and material transport¹². The lipophilic character of many of the ligands suggested their use in mediated ion transport through membranes. It also led to their application in the catalysis of many organic reactions by achieving higher concentration of

ionic reactants in the often more reactive, apolar media and/or by anion activation or breakdown of unreactive aggregates through ligand complexation with the counter ion accompanying the ionic reactant. Crystallographers have been able to determine the structure of several crown ether and cryptand salt complexes in the solid state, while ligand interactions with ions and ion pairs in solution as studied by conductance, calorimetry, dipole measurements and spectroscopic techniques have been extensively reviewed¹¹.

2. Experimental

Synthesis of ligands I_a, I_b and I_c.

0.66 mole diethylene glycol was thoroughly mixed with 2 mol of ethyl acetoacetate in a round bottomed flask; and was heated slowly for 4-6 hours at 180°C. During this process a calculated amount of ethanol (0.66 mol) was obtained as distillate. The excess amount of ethyl acetoacetate was removed by the distillation under reduced pressure so as to avoid any possible decomposition at 180°C. A brown oily residue (I_a) in the pure form was recovered from the distillation flask the purity of which was checked by T.L.C. technique and further confirmed by I.R. and P.M.R. spectroscopy. Similar method was utilized for the synthesis of I_b and I_c ligands, using tri and tetra ethylene glycols respectively. (ii) **Synthesis of Ligands II_a, II_b and II_c** Similar procedure was applied for the synthesis of II_a, II_b, and II_c as for that of I_a, I_b, and I_c. 0.66 mol. of polyethylene glycols and 2 ml. of ethyl benzoate was distilled in a round bottomed flask for 4-6 hours at 280°. The excess amount of ethyl acetoacetate was removed by distillation under reduced pressure at 180°C. A viscous oily residue was collected and was characterized by IR and NMR spectral data. **Spectral characterization**-These ligands were characterized by I.R. and N.M.R. spectral data. Because of decomposition of I_b, I_c, II_a, II_b and II_c at elevated temperature exact mass spectral molecular weight determination could not be done. The structures of the ligands used in the present investigations are shown in fig.1 & 2.

Solid state complexes

All the solvents used were freshly distilled twice before use. The solvents used in this work were methanol, ethyl acetate, acetonitrile and ethanol. The nitrophenolate salt and the ligands were prepared as described. 0.5 mmol each of the salt and the ligand were taken in a 100ml beaker and were dissolved in the solvent methanol. To ensure dissolution of both in the solvent, stirring was done and occasionally even some heating was also required when the entire solution become transparent, the system was kept in a refrigerator, Isolation of complex, if any, was monitored after a gap 24 hours. In case no complex was obtained, an extended observation was made after a gap of 48 hours. The entire work was repeated using methanol, ethyl acetate, ethanol and mixtures. The complexes obtained were re-crystallized from methanol and dried in vacuum. Their melting points were determined and they were subjected to elemental and IR analysis.

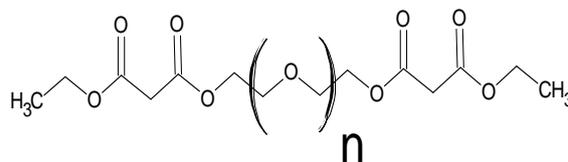


Fig-1
n=1, I_a
n=2, I_b
n=3, I_c

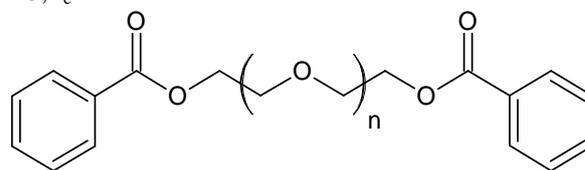


Fig-2
n=1, II_a
n=2, II_b
n=3, II_c

3. Result and Discussion

Perusal of the table 1 and 2 reveals that all the cations form complexes with at least one member of the aliphatic aromatic series. Thus not considering the modification caused in the ligating ability for the members of the series, it appears that the frame work of the ligand is capable of fulfilling some or most of the interactive requirements of the cations. The most interesting case is that of Ca²⁺ which response to all the six ligands, viz, I_a, I_b, I_c, II_a, II_b, II_c, in the presence of all the three types of counter anions viz, Pic⁻, Dnp⁻ and Onp⁻. The other cations which respond to all the six ligands are Na⁺ and K⁺. But neither Na⁺ nor K⁺ succeed in forming a complex with any of these six ligands in the presence of Onp⁻ as the counter anion. Among the three anions Onp⁻ can be considered to be a charged localized anion while picrate anion behaves as charge delocalized anion. Formation of a complex by Ca²⁺ in the presence of Onp⁻ as the counter anion is an unusual feature and reflects the intense interaction of this cation with the concerned ligand, so that even the most deterring anion is unable to prevent isolation of the solid complex.

The cation Ca²⁺ is generally considered to be an anion-philic and in this sense the involvement of this cation with the anion is often of such a high magnitude that this barrier is in general, not easily overcome by the cation ligand interaction. The results for Ca²⁺ are contrary to the general behavior of the cation. A plausible explanation can be that the high charge density of this cation which is commonly pre-occupied with the anionic site(s) present in the counter anion, side has some provision for the favorable electron density disposition through the compatible donor atoms offered by the ligand. It is quite likely that the cation anion involvement may act as insolubilization assisting device, once the cation ligand interaction has taken place. This probably explains that a cation like Ca²⁺ which in general is not the most favored cation by macrocyclic multidentates such crown ethers, is able to "manage" its way through the modest terms and conditions offered by the ligands under investigation. It is interesting to mention that unlike the behavior in the

isolation studies, Ca^{2+} is poorly transported by the same set of ligand. Thus the behavior of the cation to a ligand is not only dependent on the mutual affinity of the two for each other but also on the condition offered by the environment.

Our work helps in further understanding the $\text{Mg}^{2+} / \text{Ca}^{2+}$ discrimination. Unlike Ca^{2+} which is anion-philic, Mg^{2+} is considered to be a solventphilic cation. Indeed in the presence of sulphate ions Mg^{2+} is able to derive sufficient number of H_2O molecule so as to encircle completely through the shell of solvent molecule and the anion is relegated to a secondary position. In our case Mg^{2+} displays a much narrower range of interaction and only picrate permits complex formation, neither Dnp^- nor Onp^- is able to display complex formation. Interestingly Mg^{2+} “refuses” to form solid complex with I_a or II_a .

Among the M^{2+} cations investigated in this work, Ba^{2+} displays the most restricted type of interactions like Mg^{2+} , complex isolation is allowed only when picrate is the counter anion, whereas the ligand fulfilling the requirements of complex isolation turns out to be I_c and II_c . This is contrary to general behavior of Ba^{2+} which enjoys the advantages of self-encapsulation along with the ligand encapsulation. It appears that the interaction of Ba^{2+} with the ligands should be profound in solution but narrowly misses the requirement laid down for the complex formation. The behavior noted for Ba^{2+} in the solid state work is in contrast to that of the same cation in transport studies where it is distinctly preferred over other cations by I_c , II_c .

Among the M^+ cations, Na^+ and K^+ are of course responsive to all the six ligands under investigations. Neither Na^+ nor K^+ is, however, able to overcome the anion involvement imposed by Onp^- . Obviously the range of complexation by both these cations is narrower than one noticed for Ca^{2+} . From the reactivity screening view point none of the six ligands appears to distinguish between Na^+ and K^+ significantly. Usually the cation Na^+ is recognized to be an anionphilic cation whereas K^+ by virtue of its lower charge density, is in general, not able to display anion involvement of the magnitude of Na^+ . From the results of our work, it should not be concluded that the interactive requirements of Na^+ and K^+ are common but an indication has been given that discrimination between Na^+ and K^+ which is otherwise so

conspicuous though many instances can get suppressed by an interplay of varied factors as mentioned in this case. At this juncture it may be mentioned that not only the range of interactions by the cations Na^+ , K^+ and Ca^{2+} is wide enough, but also the rate of formation of a complex is faster than that of analogues systems. Also the complexation for all these three cations is more intense than the general behavior as reflected through high yield of complexes.

None of II_a , II_b and II_c throws light on K^+ - Rb^+ discrimination. The charge density of Rb^+ is marginally lower than that of K^+ and often Rb^+ is either clubbed with K^+ or sometimes with Cs^+ . The ligands I_b and I_c distinguish between the behavior show slow enough by K^+ than that by Rb^+ ; Rb^+ does not form solid complexes with I_a under any conditions whatsoever. On the other hand I_b and I_c demonstrate a sort of parallelism in the behavior of Rb^+ and Cs^+ . In contract to this Cs^+ response to only II_b and II_c unlike Rb^+ which response to II_a , II_b as well as II_c . The cation generate a complex only after a 48 hours of interaction indicating that the negotiation process for this cation and the ligand is slow enough.

Li^+ , similar to Mg^{2+} has some inherent solventphilic characteristics. However this solventphilic tendency of this cation is much lower than that displayed by Mg^{2+} . In this work the range of interaction displayed by Li^+ is lower than that displayed by Mg^{2+} , although both of these cations forms a complex only in the presence of picrate as counter anion. The behavior of Li^+ also indicate that greater availability of donor atoms than the required one is not preferred by this cation and it continues to display a selectivity in the feasibility of solid complex (as well as in transport process). The range of interaction of Li^+ is so narrow that even the low charge density Cs^+ displays a wide range of interaction than this cation. Interestingly I_a forms complex with Li^+ only with picrate as counter anion while II_a forms a complex with Li^+ in presence of Pic- as well Dnp^- .

None of the eight cations studied in this work display isolation when water is employed as an exclusive solvent. The results of MeOH are in general encouraging while all other solvent systems are not able to provide complex friendly environment of that magnitude.

Table 1: Some Properties of isolated alkali metal complexes with non-cyclic Oxo-crowns

S. No.	Complex	Molecular Formula	Solvent System	Colour	Yield %	M.P. (°C)
1	LiPic (I_a)*	$\text{C}_{18}\text{H}_{21}\text{O}_{13}\text{N}_3\text{Li}$	Acn.	Y	52	182
2	NaPic (I_a)	$\text{C}_{18}\text{H}_{21}\text{O}_{13}\text{N}_3\text{Na}$	MeOH	Y	52	190
3	NaDnP (I_a)	$\text{C}_{18}\text{H}_{22}\text{O}_{11}\text{N}_2\text{Na}$	MeOH	Y	49	191
4	KPic (I_a)	$\text{C}_{18}\text{H}_{21}\text{O}_{13}\text{N}_3\text{K}$	MeOH	Y	59	190
5	NaPic (I_b)	$\text{C}_{20}\text{H}_{25}\text{O}_{14}\text{N}_3\text{Na}$	MeOH	Y	62	120
6	NaDnp (I_b)	$\text{C}_{20}\text{H}_{26}\text{O}_{12}\text{N}_2\text{Na}$	Do	Y-O	68	128
7	KPic (I_b)	$\text{C}_{20}\text{H}_{25}\text{O}_{14}\text{N}_3\text{K}$	Do	O	59	172
8	KDnp (I_b)	$\text{C}_{20}\text{H}_{26}\text{O}_{12}\text{N}_2\text{K}$	Do	Y-O	58	178
9	RbPic (I_b)*	$\text{C}_{20}\text{H}_{25}\text{O}_{14}\text{N}_3\text{Rb}$	EtA	Y	32	190
10	RbDnp (I_b)*	$\text{C}_{20}\text{H}_{26}\text{O}_{12}\text{N}_2\text{Rb}$	Do	Y	34	192
11	CsPic (I_b)*	$\text{C}_{20}\text{H}_{25}\text{O}_{14}\text{N}_3\text{Cs}$	Do	B	38	195
12	CsDnp (I_c)	$\text{C}_{20}\text{H}_{26}\text{O}_{12}\text{N}_2\text{Cs}$	Do	Y	37	210
13	NaPic (I_c)	$\text{C}_{22}\text{H}_{30}\text{O}_{13}\text{N}_2\text{Na}$	MeOH	Y	53	180
14	NaDnp (I_c)	$\text{C}_{22}\text{H}_{30}\text{O}_{13}\text{N}_2\text{Na}$	Do	O	53	192
15	KPic (I_c)	$\text{C}_{22}\text{H}_{29}\text{O}_{15}\text{N}_3\text{K}$	Do	Y	59	175
16	KDnp (I_c)	$\text{C}_{22}\text{H}_{30}\text{O}_{13}\text{N}_2\text{K}$	Do	Y	54	138

17	RbPic (I _c)*	C ₂₂ H ₂₉ O ₁₅ N ₃ Rb	Do	B	39	147
18	RbDnp (I _c)*	C ₂₂ H ₃₀ O ₁₃ N ₂ Rb	Do	Y	42	159
19	CsPic (I _c)*	C ₂₂ H ₂₉ O ₁₅ N ₃ Cs	Do	Y	42	182
20	CsDnp (I _c)*	C ₂₂ H ₃₀ O ₁₃ N ₂ Cs	Do	Y	40	202
21	NaPic (II _a)	C ₂₄ H ₂₁ O ₁₁ N ₃ Na	Do	Y-O	56	191
22	NaDnp (II _b)	C ₂₄ H ₂₂ O ₉ N ₂ Na	Do	Y-O	53	195
23	KPic (II _a)	C ₂₄ H ₂₁ O ₁₁ N ₃ K	Do	Y	63	190
24	KDnp (II _a)	C ₂₄ H ₂₂ O ₉ N ₂ K	Do	Y	62	199
25	KbPic (II _a)	*C ₂₄ H ₂₁ O ₁₁ N ₃ Rb	Acn.	Y	58	210
26	RbDnp (II _a)	*C ₂₄ H ₂₂ O ₉ N ₂ Rb	Do	Y	58	205
27	CsPic (II _a)	*C ₂₄ H ₂₁ O ₉ N ₃ Cs	Do	O	60	207
28	NaPic (II _b)	C ₂₆ H ₂₅ O ₁₂ N ₃ Na	MeOH	Y	39	209
29	NaDnp (II _b)	C ₂₆ H ₂₆ O ₁₀ N ₂ Na	Do	Y	64	182
30	KPic (II _b)	C ₂₆ H ₂₅ O ₁₂ N ₃ K	Do	Y	72	173
31	KDnp(II _b)	C ₂₆ H ₂₆ O ₁₀ N ₂ K	Do	Y	58	168
32	RbPic(II _b)	*C ₂₆ H ₂₅ O ₁₂ N ₃ Rb	Do	O	42	175
33	RbDnp(II _b)	*C ₂₆ H ₂₆ O ₁₀ N ₂ Rb	Do	O	46	180
34	CsPic (II _b)	*C ₂₆ H ₂₆ O ₁₀ N ₃ Cs	DO	Y-O	62	194
35	NaPic (II _c)	C ₂₈ H ₂₉ O ₁₃ N ₃ Na	EtA+MeOH	Y	58	198
36	NaDnp (II _c)	C ₂₈ H ₃₀ O ₁₁ N ₂ Na	Do	B	62	201
37	KPic (II _c)	C ₂₈ H ₂₉ O ₁₃ N ₃ K	Do	Y	65	185
38	KDnp(II _c)	C ₂₈ H ₃₀ O ₁₁ N ₂ K	Do	Y	63	173
39	RbPic (II _c)	*C ₂₈ H ₂₉ O ₁₃ N ₃ Rb	Do	Y	49	173
40	RbDnp (II _c)	*C ₂₈ H ₃₀ O ₁₁ N ₂ Rb	Do	Y	47	179
41	CsPic (II _c)	*C ₂₈ H ₃₀ O ₁₁ N ₃ Cs	Do	Y	40	182

Table 2: Some Properties of isolated alkali metal complexes with non-cyclic Oxo-crowns

1	Ca(Pic) ₂ (I _a)	C ₂₄ H ₂₄ O ₁₉ N ₆ Ca	Eta+MeOH	Y	54.10	192
2	Ca (Dnp) ₂ (I _a)	C ₂₄ H ₂₆ O ₁₅ N ₄ Ca	Do	Y	52.00	210
3	Ca (Onp) ₂ (I _a)	C ₂₄ H ₂₈ O ₁₁ N ₂ Ca	Do	Y-O	43.70	220
4	Ca(Pic) ₂ (I _b)	C ₂₆ H ₂₈ O ₂₀ N ₆ Ca	MeOH	B	52.20	192
5	Ca(Dnp) ₂ (I _b)*	C ₂₆ H ₃₀ O ₁₆ N ₄ Ca	Do	B	58.30	199
6	Ca (Onp) ₂ (I _b)*	C ₂₆ H ₃₂ O ₁₂ N ₂ Ca	Do	B	47.20	210
7	Mg (Pic) ₂ (I _b)	C ₂₆ H ₂₈ O ₂₀ N ₆ Mg	Do	Y	39.10	250
8	Ca (Pic) ₂ (I _c)*	C ₂₈ H ₃₂ O ₂₁ N ₆ Ca	MeOH	Y-O	48.90	173
9	Ca(Dnp) ₂ (I _c)*	C ₂₈ H ₃₂ O ₂₁ N ₆ Ca	Do	O	35.70	225
10	Ca (Onp) ₂ (I _c)*	C ₂₈ H ₃₆ O ₁₃ N ₂ Ca	Do	Y	35.80	230
11	Mg (Pic) ₂ (I _c)	C ₂₈ H ₃₂ O ₂₁ N ₆ Mg	Do	Y	32.20	198
12	Ba (Pic) ₂ (I _c)	C ₂₈ H ₃₂ O ₂₁ N ₆ Ba	Do	Y	20.40	197

Y= Yellow, Y-O = Yellow Orange, B = Brown, * = Calculated only

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