Stoichiometric Complexes of Some Main Group Metal Ions with Noncyclic Synthetic Polyethers

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ABSTRACT

The stoichiometric complexes of Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+} and Sr^{2+} salts were isolated using some noncyclic synthetic polyethers. Magnesium picrate and magnesium dinitrophenolate form complexes with di- and monobutyl ether derivatives of diethylene glycol (A & B). Sodium, barium and strontium picrates formed the complexes with the acyclic cryptand tris (2- (2 methoxy ethoxy) ethyl amine (C). Potassium failed to form complexes with these ligands. The isolated complexes were characterised by m.p. and spectral data. Metal estimation showed that Mg^{2+} forms 1 : 2 complexes with ligands A & B while ligand C form complexes of 1 : 1 stoichiometry.

INTRODUCTION

Macrocyclic polyethers have drawn attention in both chemistry and biology for selective complexation of main group metal cations /1/. In order to understand biological processes, chemists often design abiotic systems that mimick the features of these processes. This goal can only be achieved if some insight is gained into the structural recognition occurring through multiple site complexation. Henceforth the current interest is in lipophilic ion complexing agents of relatively low molar mass. Open chain analogues of crown ethers have attracted increasing atttention due to availability, fairly high effectiveness and the possibility of wide scale regulation of their complex forming properties by altering their structure /2/.

With these considerations, we are reporting here the isolation and characterisation of stoichiometric complexes of Na^+, K^+, Ca^{2+}, Mg^{2+}, Ba^{2+} and Sr^{2+} picrates (Pic), dinitrophenolates (Dnp) and orthonitrophenolates (Onp)with noncyclic synthetic ligands, i.e., diethylene glycol dibutyl ether (A), diethylene glycol monobutyl ether (B) and an open chain cryptand, tris (2- (2 methoxy)) ethyl amine (C) (Fig. 1).

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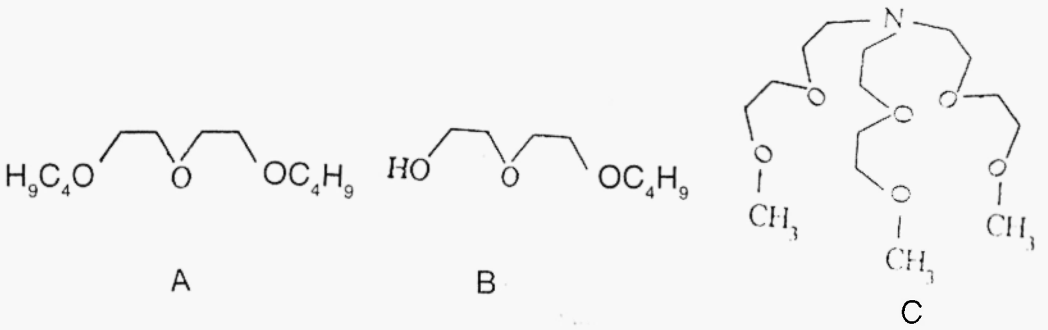

Fig. 1: The ligands used in the present study.

RESULTS AND DISCUSSION

All isolation studies were performed in duplicate to check reproducibility. Results are listed in Tables 1-6. Spectroscopic results show that no (acidic) salts /3/ of the polyethers are formed but that the complexes exhibit crown ether complex properties.

Metal estimation results (Table 1) showed that Mg^{2+} form 1:2 MX-ligand complexes with ligands A and B. But in the case of ligand C, all the three MX-C complexes are of 1 : 1 stoichiometry. The results are independant of proportion of reactants because complexes with 1 : 1 stoichiometry were obtained in the case of barium and strontium picrates from 1 : 2 reaction mixtures.

FTIR spectra of the complexes were recorded using KBr pellets and the shifts in peaks for Mg^{2+} complexes of ligands A and B when Pic$^-$ and Dnp$^-$ were the anions are tabulated in Tables 2 and 3. Table 4 tabulates the shifts in peaks for Na$^+$, Ba^{2+} and Sr^{2+} complexes of ligand C when Pic$^-$ was the anion.

It is observed that peaks in ligand molecule A at 1070, 1122 cm^{-1} ($-CH_2-O-CH_2-$), 2869, 2931 cm^{-1} ($-CH_3$, $-CH_2$) are shifted in the complexes. Similarly in the complexes of ligand B, besides the shifts in the peaks of $-O-CH_2-$, $-CH_3$ and-CH_2-, a shift at 3431 cm^{-1} (-OH) was observed indicating the change in conformation of ligand during complexation. Aromatic protons appeared in the range 1435 - 1645 cm^{-1}, indicating the presence of anion in the complexes of ligands A &B. The ion - dipole interaction between metal ion and donor sites of the tripodand C is clearly indicated by the shifts in IR peaks, i.e., 1089 - 1197 cm^{-1} ($-O-CH_2-$), 2817 - 2945 cm^{-1} ($-OCH_3$), 1197 - 1247 cm^{-1} (N-CH2-). From the IR spectra, it is seen that water molecules are present in all three complexes of ligand C.

PMR studies performed in CDC13 / DMSO with TMS internal standard at 400 MHz show shifts of the characteristic peaks of ligand B in its complexes. In Mg $(Pic)_2$-B and Mg $(Dnp)_2$-B complexes there are no changes in chemical shifts of protons at δ0.74,δ1.16 and δ1.36 (of $-CH_3$, $-CH_2$, $-CH_2$) whereas downfield shifts are observed in the case of protons at δ3.30, δ3.50, i.e. for -OH and $-OCH_2$- respectively (Table 5). This indicates the absence of interaction between the $-C_4H_9$ moiety of ligand B and Mg $(Pic)_2$ and Mg $(Dnp)_2$ salts during complexation. The downfield shift to δ4.7 and the presence of peaks at δ6.5 - d8.7 show the presence of anion in the complex.

PMR spectra of the ligand C and the ligand metal complexes at 300 MHz reveal that signals for the protons at δ3.508 - 3.570 ($-O-CH_2-$) and δ3.277 ($-OCH_3$) in the ligand are shifted downfield in the complexes

Table 1

Properties of isolated complexes of alkali and alkaline earth metal salts with various ligands

	Ligand	Salt used	Solvent	M.P.	Stoichiometry M:L	Elemental analysis (%)*			
						C	H	N	M
1	A	$Mg(Pic)_2$	Methanol	182°C	1:2	47.09 (47.16)	6.18 (6.11)	9.12 (9.17)	2.66 (2.62)
2	A	$Mg\ (Dnp)_2$	Acetonitrile	220°C	1:2	52.50 (52.30)	7.00 (7.02)	6.74 (6.78)	2.88 (2.90)
3.	B	$Mg(Pic)_2$	Methanol	170°C	1:2	41.75 (41.79)	4.92 (4.98)	10.41 (10.45)	2.95 (2.99)
4.	B	$Mg(Dnp)_2$	Methanol	200°C	1:2	47.00 (47.06)	5.83 (5.88)	7.85 (7.84)	3.41 (3.36)
5	C	NaPic	Methanol	180°C	1:1	43.87 (43.90)	6.00 (6.10)	9.70 (9.76)	3.98 (4.01)
6.	C	$Ba(Pic)_2$	Methanol	160°C	1:1	35.40 (35.37)	4.00 (4.04)	10.65 (10.70)	14.93 (14.97)
7.	C	$Sr(Pic)_2$	Methanol	125°C	1:1	37.41 (37.37)	4.31 (4.27)	11.33 (11.30)	10.20 (10.15)

* Calculated values given in parenthesis

Table 2

IR spectroscopic data of ligand A and its complexes

$\bar{\upsilon}$, cm^{-1}			
Groups	Ligand A	Mg (Pic)$_2$ - A complex	Mg (Dnp)$_2$ - A complex
$-CH_2-O-CH_2-$	1070, 1122	1080, 1161	1062, 1145
$(CH_3, -CH_2)$	2869, 2931	2824, 3086	2870, 2962
Ar. group		1439 - 1633	1427 - 1614

Table3

IR spectroscopic data of ligand B and its complexes

$\bar{\upsilon}$, cm^{-1}			
Groups	Ligand B	Mg (Pic)$_2$ - B complex	Mg (Dnp)$_2$ - B complex
CH_2-O-CH_2	1070, 1122	1080, 1161	1057, 1136
$(-CH_3, -CH_2)$	2869, 2931	2824	2393
(-OH)	3431	3566	3474
(Ar. Group)		1435 - 1645	1433 - 1655

Table 4

IR spectroscopic data of ligand C and its complexes

$\bar{\upsilon}$, cm^{-1}				
Groups	Ligand C	Na Pic-C complex	Ba(Pic)$_2$-C complex	Sr (Pic)$_2$-C complex
CH_2-O-CH_2	1089, 1197	1095, 1199	1080, 1161	1080,1159
$(-OCH_3)$	2817, 2945	2899	2887, 3091	2839, 2889
$(>N-CH_2-)$	1197, 1247	1199, 1269	120, 1271	1199, 1271
(Ar. group)		1438 - 1633	1438 - 1635	1440 - 1637

Table 5

NMR spectroscopic data of ligand B and its complexes

δ values			
Groups	Ligand B	Mg (Pic)$_2$- B complex	Mg(Dnp)$_2$ -B complex
(-CH$_3$)	0.74	No change	No change
(-CH$_2$-)	1.16	No change	No change
(-CH$_2$-)	1.36	No change	No change
(-OH)	3.38	4.7	4.7
(-OCH$_2$-)	3.5		
(Ar.Proton)		8.62	6.54, 8.68

Table 6

NMR spectroscopic data of ligand C and its complexes

δ values			
Groups	Ligand C	Na (Pic) -C complex	Ba(Pic)$_2$ -C complex
(-O-CH$_2$-)	3.508-3.570	3.531-3.571	3.534-3.567
(>N-CH$_2$-)	2.697 -2.737	2.692-2.732	2.738-2.776
(-O-CH$_3$-)	3.277	3.282	3.282
(Ar.Proton)		8.787	8.853

(Table 6). The protons at the C adjacent to N (δ2.697) are shifted upfield by 0.005 ppm in the NaPic - C complex, whereas they are shifted downfield by 0.041 ppm in the Ba (Pic)$_2$-C complex. The shifting and splitting of the signal for -OCH$_2$- into multiplets indicates the change in conformation of the ligand during complexation. The splitting of the -OCH$_2$-signal is greater in Ba(Pic)$_2$-C complex than in NaPic-C complex, indicating greater extent of complexation in the former. The presence of anion is indicated by the presence of proton signals at δ8.787 and δ8.853 in the complexes (Fig. 2) and has also been detected spectrophotometrically.

C, H, N and metal analyses confirm the formation of 1 : 2 complexes between ligand A and B with Mg (Pic)$_2$ and Mg (Dnp)$_2$ as well as 1 : 1 complexes between ligand C and the metal picrate salts of sodium,

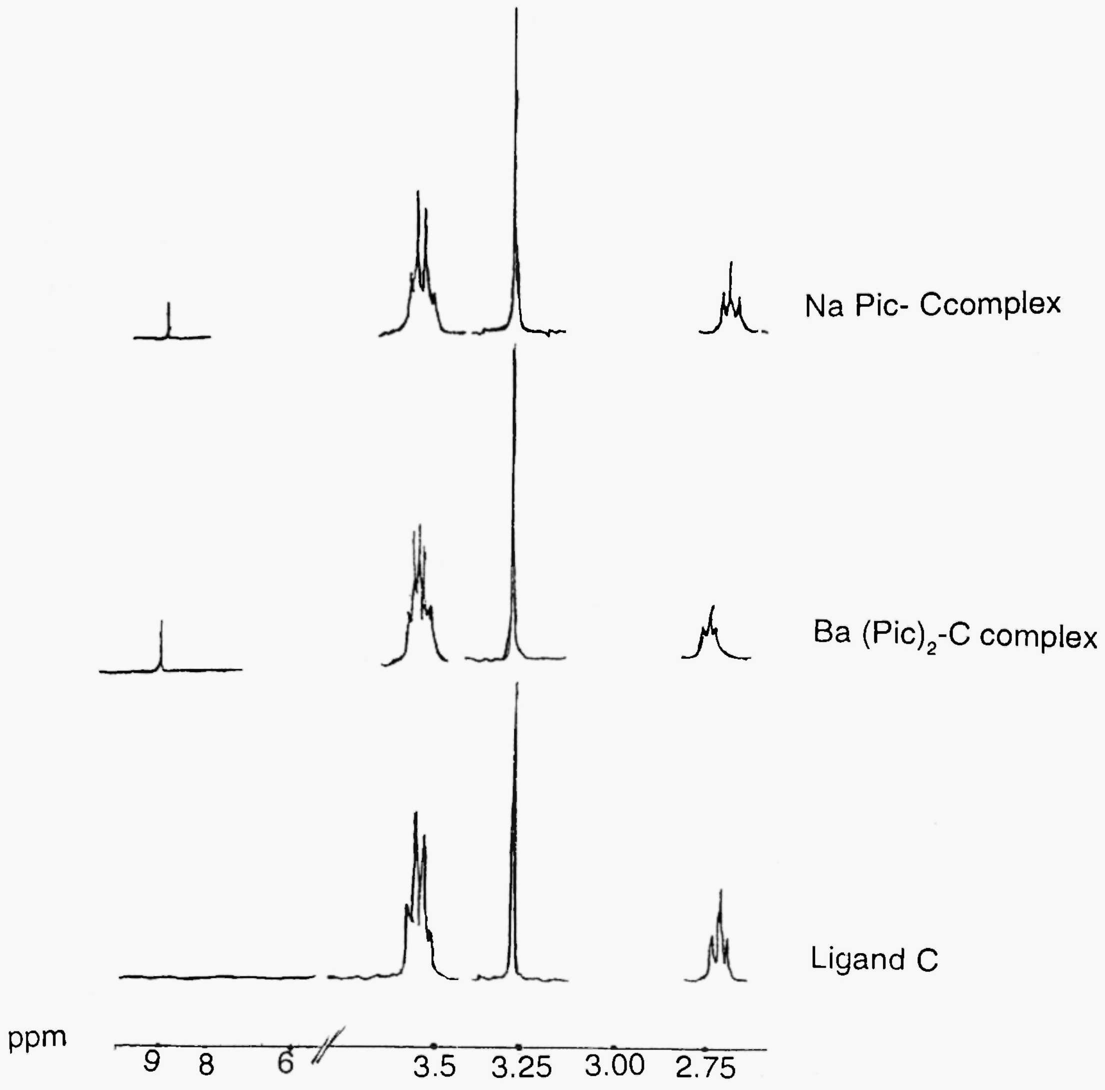

Fig. 2: ^{1}HTNMR spectra (sections) of the free ligand C and some of their complexes. Shift in peaks of the groups - OCH_2, NCH_2 -, -O-CH_3 and peaks for the aromatic protons are shown.

barium and strontium. Divalent ions possess smaller size and much higher charge density than monovalent cations and this promises stronger interaction with donor oxygen atoms of ligand molecules. X-ray studies of crystalline complexes /4/ formed by podands indicate that, as the number of donor oxygen atoms increases, ligand wraps round the metal ion in a helical way. The whole ligand skeleton is held in the podate conformation only by the cation - donor atom interactions /5/. In the case of ligand C the three - OCH_3 terminal groups may have participated in co-ordination of the metal ions (Na^+, Ba^{2+} and Sr^{2+}) located at the centre of the pseudocavity /2/. All the complexes of ligand C contain water in stoichiometric proportions, as revealed by the appearance of more or less sharp -OH bonds in the IR spectra. The question whether the H_2O molecules are in co-ordinational contact with the complexed cation or exist as free water of crystallization in the crystal lattice /6/ will only be conclusively settled by X-ray structure studies.

On comparing our results with the isolation studies with diethyleneglycol dibenzoate /7/ (D), it is observed that all the three ligands (A, B & D) are inefficient in forming complexes with large sized K^+ ions. Smaller chain lengths of A, B and D are unable to form complexes with larger sized K^+ ion and the effect is compounded by the steric hinderance caused by the bulky end groups.

EXPERIMENTAL

Chemicals

Diethylene glycol dibutyl ether (Merck), Diethylene glycol monobutyl ether and tris (2-(2methoxy ethoxy)) ethylamine were obtained from Fluka. Analytical grade solvents and chemicals were used for all experiments. Metal picrates, dinitrophenolates and orthonitrophenolates were prepared as reported earlier /8/.

Instruments

Scientific Instruments Co. Ltd Boss 165 melting point apparatus was used. Elemental analysis, IR and NMR studies were performed at CDRI, Lucknow.

Isolation Method

The isolation of metal ligand complexes involved mixing of the metal salts and the ligand in 1 : 1 ratio in the case of alkali metal salts and in 1 : 2 ratio in the case of alkaline earth metal salts in a suitable organic solvent /9/. The mixture was heated on a water bath to about 95 ± 2°C,thus reduced and then allowed to crystallize at room temperature. Crystallization generally occurs within 1 to 3 days. The crystals were vacuum filtered and recrystallised from the pure solvent from which they were isolated. The solvents used for isolation were methanol, ethylacetate, isopropanol and acetonitrile. The complexes were identified by determining their m.p and characterized by element detection and spectral analysis. The stoichiometry of the complexes was determined by metal estimation on atomic absorption spectrophotometer.

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