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Spectral investigation of the effect of anion on the stability of non covalent assemblies of 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine (benzo-15-crown-5) with sodium halides

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ABSTRACT

A series of complexes of 2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine (benzo-15-crown-5) with sodium halides was synthesized in acetonitrile. The effect of anion on the stability and spectral properties of complexes of benzo-15-crown-5 with sodium halides was investigated. The synthesis of complexes of sodium fluoride and sodium chloride are reported for the first time. Chloroform was used as solvent to study the assembly in solution state by ¹H and ¹³C NMR techniques. Single crystal diffraction studies on the easily crystallizable bromide complex confirmed 1:1 stoichiometry of the complex. IR and Raman studies provided valuable evidence for a water molecule shared between the crown encapsulated cation and the counter ion to give a solvent shared ion pair (SSIP). The fluorescence spectra of the complexes were obtained in chloroform by excitation at 270 nm to study the effect of complexation on the fluorescent properties of benzo-15-crown-5.

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1. Introduction

Alkali metal halides are known to be of biological importance due to their ability to bind to oxygen sites through non covalent bonds. Their role in G-quartet structures in isomeric DNAs is well defined [1]. Crown ether complexes of alkali halides serve as models to study the non covalent interaction between the cation and its binding sites in ion channels [2,3]. Crown ethers are macrocyclic compounds containing hetero atoms which serve as donor atoms when forming complexes with metal ions. The stability constants of these complexes depend on a fine balance between the cavity size of the macrocyclic ring, the size of the metal ion, the rigidity of the ring and the solvent medium [4]. They find applications in the ion chromatographic separations of alkali-metal cations [5], extraction of hazardous metal ions from nuclear waste [6,7], membrane transport [8], anion activation [9,10] and serving as models for studying natural ionophores [11] due to their ion complexation property. Some of these complexes mimic antimicrobial activity [12] of natural ionophores like valinomycin and gramicidin [13]. Induction of a benzo or anthracene unit in the crown ethers further extends their application as sensitive sensors for metal ions [14]. Presently

hybrid compounds containing crown ethers are being designed to be used as sensors for cations as well as anions [15].

Since the synthesis of crown ethers by C. J. Pedersen in 1967 [16], binding ability of crown ethers to transition metal ions [17] and f-block metal ions [18] has been studied by various techniques. Previous studies on transport of Li⁺, Na⁺ and K⁺ in Gramicidin-A channels [19] show that Far-IR region offers important information on cation's interaction with its binding sites. Literature on the synthesis and isolation of complexes of alkali halides with benzo crown ethers is scarce. Isolation reported earlier was either from methanol or chloroform [20,21]. Most of the reported studies involving alkali metal ion complexes of benzo crown ethers were carried out in solution state with large anions like picrates [22], cryptates [23] and butyl thioborates [24].

Alkali halides have limited solubility in acetonitrile. Benzo-15-crown-5, on the other hand, is readily soluble in acetonitrile. In the present study a working molar ratio of benzo-15-crown-5 (**I**) to sodium salts was employed to synthesize these complexes in acetonitrile. The complexes are labeled **Ia**, **Ib**, **Ic** and **Id** for the fluoride, chloride, bromide and iodide salts of sodium, respectively. The complexes were isolated and investigated for spectral variations accompanying complexation. The solid state structure of the easily crystallizable complex of sodium bromide and its packing pattern was ascertained by single crystal studies. The single crystal structure obtained was identical to that reported earlier [20]. However the solution state ¹H and ¹³C NMR studies carried

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out in CDCl_3 in our work showed distinct spectral variations demonstrating the effect of solvent on the conformation of such non covalent assemblies.

2. Experimental

B15C5 was purchased from Sigma-Aldrich and was used as received. Alkali halides were reagent grade hydrated salts obtained from Merck. Acetonitrile was purchased from Sigma-Aldrich. Acetonitrile was refluxed with CaH_2 for 24 h, distilled and used fresh. Acetone was supplied by Fisher. Salts were dried in a vacuum oven at 150 °C for three days before use.

The FTIR spectra of the complexes were collected on KBr pellets and Mid-IR and Far-IR studies were carried out on Bruker FTIR imaging system from Germany, Model: 3000 Hyperion Microscope with Vertex 80 FTIR System. ^1H NMR and ^{13}C spectra of complexes were recorded on Bruker Avance III 400 MHz FT NMR Spectrometer using TMS (Tetramethyl Silane) as an internal standard and CDCl_3 as the solvent. ESI mass spectra were collected on a Waters ZQ-4000 mass spectrometer with a mass range of 20–4000 Da and a resolution of 0.2 Da. Elemental analysis data were recorded on Elementar Vario EL III, STIC-Cochin, India. Raman measurements were made on a Bruker RFS27 stand alone FT-Raman spectrophotometer at SAIF, IITM, Chennai with a resolution of 2 cm^{-1} . The laser source was Nd:YAG 1064 nm. Single crystal X-ray diffraction patterns were collected on Enraf Nonius CAD-4 with Cu ($K\alpha$) source. Fluorescence spectra were recorded on Perkin Elmer LS55 Spectrophotometer with 1 cm quartz cuvette at 2.5 slit width.

2.1. Synthesis

2.1.1. General procedure for preparation of complexes of benzo-15-crown-5 with sodium salts, NaX ($X = \text{F}^-, \text{Cl}^-, \text{Br}^-$ and I^-)

A solution of 0.2 mmol of sodium salt in 3 ml acetonitrile was added dropwise to a 0.2 mmol solution of benzo-15-crown-5 in 4 ml acetonitrile and stirred for 24 h at room temperature. The resulting solution was filtered and left to dry. The solid was extracted with nitromethane to remove unreacted salt, filtered and dried. The excess crown ether was separated from the complex by dichloroethane:petroleum ether mixture (1:0.1 ml). The purity of the complex was checked with TLC (10 parts acetonitrile:1 part acetic acid). The product was again vacuum dried and stored in a vacuum desiccator. The yellow product was recrystallized from acetonitrile.

2.1.1.1. Complex of sodium fluoride with I, $[\text{Na}(\text{benzo-15-crown-5})\text{OH}_2]\text{F}^-$. Mol. Formula $\text{C}_{14}\text{H}_{22}\text{O}_6\text{NaF}$, Yield: 69%, M.pt. 78 °C, ^1H NMR/ppm: (400 MHz, CDCl_3): 6.94–6.36 (d, $J = 2$ Hz, 4 H), 4.19 (t, $J = 4.4$ Hz, $J = 4.4$ Hz, 4 H), 3.96 (t, $J = 4.8$ Hz, $J = 4.0$ Hz, 4 H), 3.81 (s, 4 H); ^{13}C

Table 1

Assignment of selected infrared peaks (cm^{-1}) of benzo-15-crown-5 and its complexes with sodium halides.

Assignment of vibrational modes	I	Ia	Ib	Ic	Id
H_2O : $\bar{\nu}_s \text{OH}_{\text{bound}}$	–	3439	3439	3444	3440
$\bar{\nu}_{\text{as}} \text{CH}_2$		2941	2923	2923	2922
$\bar{\nu}_s \text{CH}_2$		2915	2857	2862	2853
H_2O : $\bar{\nu}_b \text{OH}_{\text{bound}}$	–	1640	1642	1645	1648
$\bar{\nu}_s \text{Ph-O}$		1297	–	–	–
$\bar{\nu}_{\text{as}} \text{Ph-O}$		1258	1257	1254	1252
		1227	1217	1213	1211
$\bar{\nu}_{\text{as}} \text{C-O-C}$		1125	1121	1122	1120
		1105	–	–	–
		1094	–	–	–
		1075	–	–	–
$\bar{\nu}_s \text{C-C-O}$		1043	1036	1046	1042
$\bar{\nu}_s \text{C-O-C}$		980	–	–	–
$\bar{\nu}_s \text{C-C}$		937	937	934	938
$\bar{\nu}_{\text{rocking}} \text{CH}_2$		905	–	–	–

NMR/ppm (100 MHz, CDCl_3): 148.61 (PhC), 121.57 (PhC), 114.51 (PhC), 113.85 (PhC), 70.81 (CH_2), 70.26 (CH_2), 69.21 (CH_2), 68.52 (CH_2); ESI m/z : $[\text{L} + \text{Na}]^+$: 291, calculated 291; IR $\bar{\nu}_{\text{max}}/\text{cm}^{-1}$: 3441(m), 3058(w), 2923(s), 2857(m), 1628(sh), 1588(s), 1257(m), 1217(m), 1121(m), 1036(m), 937(m), 849(w), 749(w), 672(w), 606(w), 506(w), 465(w), 421(w).

2.1.1.2. Complex of sodium chloride with I, $[\text{Na}(\text{benzo-15-crown-5})\text{OH}_2]\text{Cl}^-$. Mol. Formula $\text{C}_{14}\text{H}_{22}\text{O}_6\text{NaCl}$, Yield: 32%, M.pt. 65 °C, ^1H NMR/ppm: (400 MHz, CDCl_3): 6.94 (s, 4 H), 4.15 (t, $J = 5.2$ Hz, $J = 4.4$ Hz, 4 H), 3.88 (t, $J = 5.2$ Hz, 4.0 Hz, 4 H), 3.77 (q, $J = 4.4$ Hz, 3.2 Hz, 2.0 Hz, 4 H), 3.68 (q, $J = 4.4$ Hz, $J = 3.2$ Hz, $J = 2.4$ Hz, $J = 2.0$ Hz, 4 H); ^{13}C NMR/ppm (100 MHz, CDCl_3): 148.69 (PhC), 121.60 (PhC), 114.59 (PhC), 113.87 (PhC), 70.84 (CH_2), 70.28 (CH_2), 69.26 (CH_2), 68.54 (CH_2); ESI m/z : $[\text{L} + \text{Na}]^+$: 291, calculated 291; IR $\bar{\nu}_{\text{max}}/\text{cm}^{-1}$: 3439 (bs), 3062 (w), 2923 (s), 2862 (w), 1628 (sh), 1584 (s), 1502 (m), 1453 (m), 1254 (s), 1213 (w), 1122 (s), 1046 (m), 934 (m), 849 (w), 751 (w), 606 (w), 465 (w).

2.1.1.3. Complex of sodium bromide with I, $[\text{Na}(\text{benzo-15-crown-5})\text{OH}_2]\text{Br}^-$. Mol. Formula $\text{C}_{14}\text{H}_{22}\text{O}_6\text{NaBr}$, Yield: 88%, M.pt. 62 °C, ^1H NMR/ppm (400 MHz, CDCl_3): 6.95–6.88 (m, $J = 3.2$ Hz, $J = 3.2$ Hz, $J = 3.2$ Hz, $J = 3.2$ Hz, $J = 2.8$ Hz, $J = 2.4$ Hz, 4 H), 4.20 (s, 4 H), 4.02 (d, $J = 3.2$ Hz, 4 H), 3.85 (d, $J = 2.8$ Hz, 4 H), 3.77 (d, $J = 2.8$ Hz, 4 H); ^{13}C NMR/ppm (100 MHz, CDCl_3): 148.71 (PhC), 121.61 (PhC), 114.61

Table 2

Crystal structure data and refinement details of $[\text{Na}(\text{benzo-15-crown-5})\text{OH}_2]\text{Br}^-$ crystal.

Formula	$\text{C}_{14}\text{H}_{22}\text{BrNaO}_6$
Formula weight	389.19
Crystal system	Orthorhombic,
Space group (no.)	P212121
a/A	9.4014 (7)
b/A	11.7964 (8) A
c/A	15.4865 (14)
α	90
β	90
γ	90
U/A^3	1717.5 (2)
Z (Calculated density)	4, 1.505 mg/m^3
μ ($\mu\text{-K}\alpha$)/ mm^{-1}	2.442 mm^{-1}
F (000)	800
Total number reflns	21,914
Unique reflns	3384
R_{int}	0.0385
Data/restraints/parameters	3384/3/205
R_1, wR_2 [$I > 2\sigma(I)$] ^b	0.0305, 0.0584
R_1, wR_2 (all data)	0.0544, 0.0657

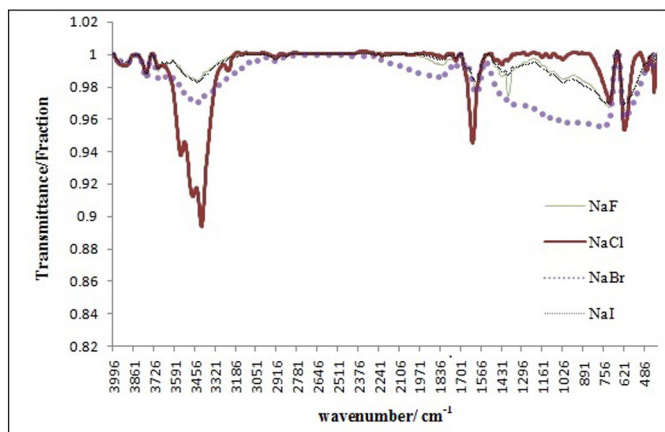


Fig. 1. Mid-IR spectra of NaF, NaCl, NaBr and NaI.

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