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Diaza Crown Ether Complexes of Alkali Metal and Ammonium Cations Paired with Organic Anions

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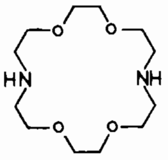
Formation of a series of diaza crown ether complexes of alkali metal and ammonium cations paired with organic anions is reported. Diaza 18-crown-6 (1) forms complexes with potassium, ammonium, and methylammonium 4-nitrophenolate to yield 1:1 colored crystalline compounds. The lowering of energy in the C–O–C frequency absorption band and the solubility of all crown ether complexes in chloroform provided evidence of complex formation. The ^{1}H nmr signal for –NH protons of crown ether is shifted the most in the [K-1] 4-nitrophenolate complex. The polyether (1) also yields *a complex with potassium 2,4-dinitrophenolate but no complex with sodium could be isolated. However, diaza 15-crown-5 (2) yields 1:1 complexes with sodium as well as with potassium and ammonium 4-nitrophenolate salts.*

Introduction

The ability of synthetic macrocyclic polyethers (Crown ethers and Cryptates) to form stable complexes with alkali and alkaline earth metal cations has been well documented in the recent chemical literature [1]. These macrocycles have found many uses in different areas of chemistry: they enhance anion reactivity by shielding the cation [2], are being used as carrier molecules in the study of ion transport through artificial and natural membranes [3], and may be used as reagents for selective extraction procedures [4].

The alkali metal complexes with various crown ethers and cryptates have been isolated, fully characterized and for some, the X-ray crystal structure has been determined. Generally, the alkali metal salts used to form complexes with crown ethers and diaza crown ethers have had the anion of the type Cl^-, Br^-, NO_3^-, ClO_4^- *etc.* There are only a few detailed reports [5] about preparation and isolation of alkali or alkaline earth crown ether complexes where anions have been of the organic type. However, alkali metal picrates have frequently been used in liquid–liquid extraction studies and in crown ether mediated transport studies of cations across a liquid membrane [3].

In our investigations on the effects of organic anions on the carrier facilitated transport of cations [6], we have isolated a series of diaza crown ether complexes with univalent cations paired with organic anions. The complexes of diaza crown ethers *1* and *2* were characterized by recording their infrared, u.v.–visible and n.m.r. spectra. The elemental analyses confirmed the 1:1 stoichiometry of the complexes.



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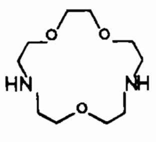

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Experimental

General

Diaza 18-crown-6 was purchased from E. Merck Inc. whereas diaza 15-crown-5 was prepared in our laboratory [7]. Proton NMR spectra were determined on a Bruker WP-100 spectrometer at probe temperature. The solutions were made in $CDCl_3$ and TMS was used as an internal standard. The infrared spectra were recorded as KBr pellets using a Jasco IRA-1 infrared spectrophotometer. UV–visible spectra were taken on either a Unicam SP-800A or Shimadzu UV-240 spectrophotometer. Elemental analyses were carried out on a Carlo Erba model-1106

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TABLE I. Analytical Data.

Complexes	Description	M. Pt. °C	Found (%)			Calc (%)		
			C	H	N	C	H	N
[K-1] 4-NP	Yellow microcrystals	210	49.28	6.83	9.55	49.20	6.83	9.56
[H_4N-1] 4-NP	Light yellow prisms	115–118	51.66	8.13	13.40	51.67	8.13	13.39
[H_3C-NH_3-1] 4-NP	Orange-yellow crystals	156–160	52.78	8.39	12.96	52.77	8.33	12.96
[K-1] 2,4-DNP	Pale yellow crystals	218	44.70	5.98	11.55	44.63	5.99	11.57
[Na-2] 4-NP	Yellow crystals	195–198	50.65	6.86	11.05	50.66	6.86	11.08
[K-2] 4-NP	Yellow microcrystals	205	48.50	6.55	10.69	48.63	6.58	10.63
[H_4N-2] 4-NP	Yellow prims	>154	51.35	8.00	14.95	51.33	8.02	14.97

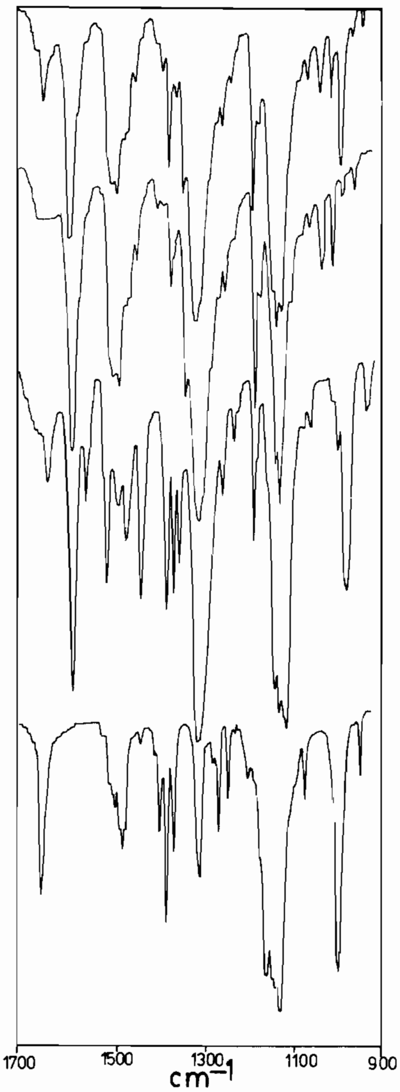

Fig. 1. Infrared spectra of free ligand diaza 18-crown-6 and its complexes with potassium, ammonium and methylammonium 4-nitrophenolate salts, respectively from bottom to top.

Elemental Analyser; melting points were recorded in air using a Thomas Hoover apparatus and are uncorrected.

Preparation of Complexes

Diaza crown ether complexes were prepared by dissolving equimolar amounts of the polyether and the salts in methanol. The solvent was slowly evaporated to reduce the volume, a few drops of ether were added, and on cooling the solution crystals of the crown ether complex were isolated.

Results and Discussion

Complex Formation

Similar procedure and conditions were used to isolate the complexes with both diaza crown ethers and all the salts. Potassium, ammonium and methylammonium 4-nitrophenolate (4-NP) and potassium 2,4-dinitrophenolate (2,4-DNP) salts yielded crystalline 1:1 complexes with diaza 18-crown-6. Table I lists the color, melting points and elemental analyses of these complexes. Four different sodium salts with counterions 4-nitrophenolate, 2-nitrophenolate, 2,4-dinitrophenolate and benzoate were used to form the complex with diaza 18-crown-6, but all attempts to isolate a sodium complex with any of the above mentioned sodium salts were unsuccessful.

Diaza 15-crown-5, having a smaller cavity hole, was then employed and crystalline sodium, potassium, and ammonium 4-nitrophenolate crown complexes were prepared. All complexes were fully characterized and their analytical data is given along with other complexes in Table I.

Spectroscopic Studies

Infrared spectra

IR spectroscopy affords evidence for the complexation of cations by crown ethers. The coordina-

TABLE II. Assignment of Infrared Absorption Bands (cm^{-1}).

Compound	C–O–C linkage	–NO_2 group	
		Asy	Sym
1 & *2*	1122		
K 4-NP	–	1590	1325
[K-1] 4-NP	1106	1578	1296
[H_4N-1] 4-NP	1118	1580	1298
[H_3C-NH_3-1] 4-NP	1105	1580	1296
[K-1] 2,4-DNP	1118	1548, 1535	1280, 1258
[Na-2] 4-NP	1120	1585	1310
[K-2] 4-NP	1121	1583	1309
[H_4N-2] 4-NP	1120	1585	1310

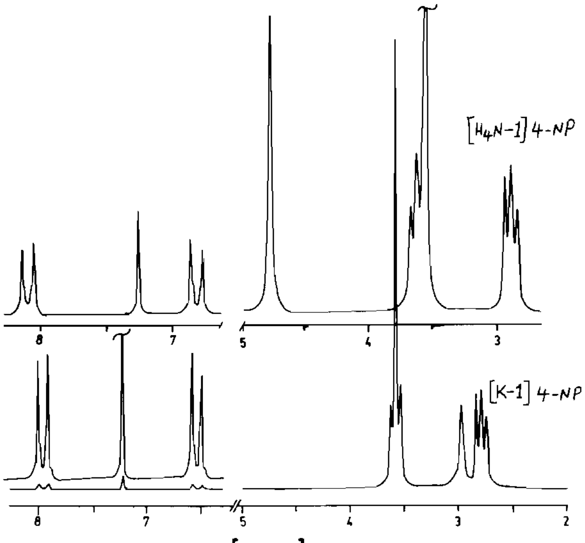

Fig. 2. Proton NMR spectra (in $CDCl_3$) of potassium- and [$NH_4$$^+$-diaza 18-crown-6] 4-nitrophenolate complexes.

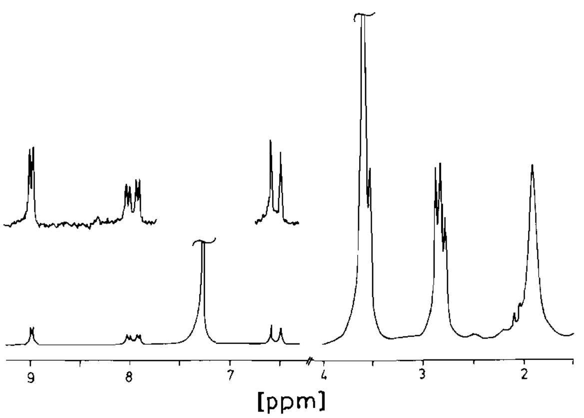

Fig. 3. ^{1}H NMR spectrum (in $CDCl_3$) of [K$^+$-diaza 18-crown-6] 2,4-dinitrophenolate.

tion of crown ether to cations results in shifts to lower energy in the absorptions due to C–O–C stretching vibrations. The C–O–C absorptions bands are found at 1122 cm^{-1} in the spectrum of free diaza 18-c-6 ligand but upon coordination to K$^+$ ion, it is shifted to 1106 cm^{-1}. Infrared spectra of diaza 18-c-6 complexes are recorded in Fig. 1 and Table II lists the frequency of assymmetric and symmetric absorption bands due to –NO_2 group along with the position of C–O–C stretching absorption bands in all the complexes.

NMR spectra

The salts used in this study are insoluble in chloroform but the crown ether complexes of the salts were completely dissolved and all nmr spectra were recorded in $CDCl_3$ without any solubility problem. This was in fact a further indication of the formation of the crown ether complexes. The nmr spectra of potassium and ammonium 4-nitrophenolate and potassium 2,4-dinitrophenolate complexes with diaza 18-c-6 are recorded in Fig.2 and Fig. 3 respectively.

The complex formation caused downfield shifts in all crown ether methylene proton resonances. The –NH proton signal in the spectrum of free ligand *1* (in $CDCl_3$) was recorded at 2.15 ppm, whereas in its complex with potassium 4-nitrophenolate it is found at 3.0 ppm and at 1.91 ppm in the spectrum of the complex made from potassium 2,4-dinitrophenolate. It should be mentioned at this point that both end nitrogens go through pyramidal inversion on formation of a complex [8]. Possibility of chelation by 2,4-dinitrophenolate anion may explain the difference observed in two potassium

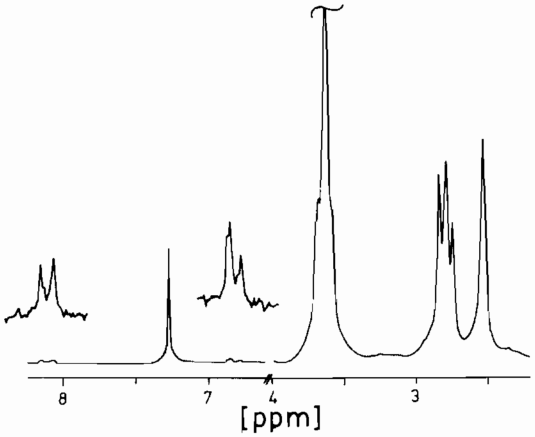

Fig. 4. ^1H NMR spectrum (in $CDCl_3$) of [Na^+-diaza 15-crown-5] 4-nitrophenolate.

diaza 18-c-6 complexes. Similar chelation effects have been noted by other workers upon isolating the dibenzo 18-crown-6 complexes with 2,4-dinitrophenolate salts [5]. The aromatic protons of 4-nitrophenolate moiety experience relatively small shifts in their proton resonances but retain the multiplicity of their signals.

The nmr spectrum of diaza 15-c-5 complex with sodium 4-nitrophenolate is displayed in Fig. 4. It was noted that –NH protons are shifted the most in nmr spectrum of sodium complex among all diaza 15-c-5 complexes prepared in this study.

Absorption spectra

U.V.–visible spectra of the complexes of 4-nitrophenolate salts exhibited a maximum near 410 nm in tetramethylammonium hydroxide solutions and the λ_{max} was not much changed, even after the addition of more than 1:1 molar ratio of crown ether.

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