Complexation Studies of Some Newly Synthesized Precursors for Substituted Dibenzo and Dibenzodiaza Crown Ethers

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ABSTRACT: This study represents the synthesis of dibenzo and dibenzodiaza crown ether precursors with various functional groups in good yield by employing four different methods using polar protic and aprotic solvents with high boiling points. Also the complexation abilities of all synthesized ligands with Cu^{2+}, Zn^{2+}, and Ag^+ were studied by conductometry; thus the conductometric behavior of $Cu(NO_3)_2$, $ZnCl_2$, and $AgNO_3$ in 80% dioxane–water mixture was investigated in the presence of these ligands. The order of formation constant for complexes of the ligands with Cu^{2+}, Zn^{2+}, and Ag^+ ions was found to be: $Cu^{2+} > Zn^{2+} > Ag^+$ for the ligands of **VI**, **VII**, **XI**, and **XII**; $Cu^{2+} > Ag^+ > Zn^{2+}$ for the ligands of **III** and **VIII**; and $Zn^{2+} > Cu^{2+} > Ag^+$ for the ligands of **I**, **II**, **IV**, **V**, **IX**, and **X**. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2497–2501, 2004

Key words: diazacrowns; dibenzodiazacrowns; oligoethylene glycol derivatives; conductometry; complex formation

INTRODUCTION

There has been a great interest in synthesis of crown ether precursors. These compounds are important intermediates for the synthesis of cryptands,[1] nitrogen-pivot lariat crown ethers,[2] and other species requiring one or two nitrogens in the macroring.[3] Most of the simple oligoethylene glycols, other diols, amino alcohols, amino phenols, diamines, and phenylene diamines used for the synthesis of macrocyclic compounds are commercially available. This study represented some new precursors that contain substituted benzo units. Some of them, alkyl nitro phenols derivatives, have been shown to be effective as insecticides[4] and selective weed killers[5] and the others, some aromatic ethers, contain carboxaldehyde, carboxyl, and halogen groups bound to the ring.[6,7]

So far there have been only a limited number of methods to prepare precursors used in the synthesis of benzocrown ethers that also show differences in terms of synthetic application. To investigate this, Cram and coworkers[8,9] prepared a series of *o*-aminophenol derivatives to be used in the synthesis of benzoaza crown ethers. For the same reason, *o*-aminophenol and *o*-phenylene diamine derivatives were used by Lockhort et al.[10] Some representative *o*-aminophenol derivatives as precursors are presented as follows.[9,11] Besides diazido-substituted ethers,[12–14] their derivatives

obtained by reduction were reported in the literature for these purposes.[15]

This work represents a relatively simple way of preparing azocrown ether precursors, bis(phenoxy)ethane, and *N*,*N*′-diphenyldiaminoethane derivatives, where the benzene ring bears carboxyl, alkyl, halogen, or aldehyde groups. Although some of these precursors were previously reported in the literature, our study focused on synthesis of azacrown ether precursors bearing more than one substituent on the rings. Furthermore, in this study we report the conductometric measurement of complexation constant K_e and Gibbs free enthalpies values $\Delta G°$ for the all synthesized ligands with $Cu(NO_3)_2$, $AgNO_3$, and $ZnCl_2$ salts in 80% dioxane–water at 25°C.

The ability of macrocyclicpolyethers (crown ethers) to form stable complexes with several cations, mainly with alkali and alkaline earth cations, has spurred interest in these compounds.[16] Conductance measurements of an electrolyte solution in the presence of a convenient ligand provide two valuable pieces of information. The first is detection of complexation between the ligands and the cations constituting the electrolyte. Furthermore, the stability constant of the ligand–cation complex can be determined from the conductance data. The second useful piece of information relates to the transport phenomena of the ligand–electrolyte complex in the solution. Studies recorded in the literature were related with conductometric measurement of some electrolytes in nonaqueous solvents.[17–21] In this study we used binary dioxane aqueous solution. This system owes its popularity largely

to the possibility of attaining a large range of dielectric constant (D = 10–80 Debye).[22]

EXPERIMENTAL

Apparatus and chemicals

All chemicals were grade reagent and purchased from Merck, unless otherwise specified. Infrared spectra were recorded on a Midac FTIR Model 1700 spectrophotometer. Elemental analyses were obtained with a Carlo-Erba Model 1108 apparatus. Melting points were recorded on a Gallenkamp model apparatus with open capillaries. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a Bruker DPX-400 high-performance digital FT-NMR spectrometer (Bruker Instruments, Billerica, MA). The ligands (**I–XIII**, Fig. 1, Tables I and II) were used for complexation studies. Water used in conductometric studies was redistilled from alkaline permanganate. Dioxane, used as solvent, was dried over sodium metal.

Conductometric measurements

Stability constants were measured by means of the conductometric method. The solutions were prepared at constant 1 : 1 ratio of metal salt to ligand in 80% dioxane–water mixture. All solutions were prepared in a dry box and transferred to the dry conductivity cell. The conductances were measured at 25 ± 0.05°C.

The measuring equipment consisted of a glass vessel (type Ingold) with an external jacket. At the same time, the system was connected to a thermostatted water bath (25 ± 0.05°C) and a conductivity cell (Cole Parmer 19050-66) with a conductometer (Suntex Model SC-170).

The cell constant was determined as 0.769 cm^{-1} at 25°C, by measuring the conductivity of aqueous potassium chloride solutions of various concentrations.[22] Values of log K_e and $-\Delta G°$ for the reaction of the ligands with cations were determined by the conductometric procedure outlined previously.[22] Results are reported as the average and standard deviation from the average of four to six independent experimental determinations.

Synthesizing methods

Method a

A mixture of appropriate glycol ditosylate (50 mmol), and phenol derivatives (l00 mmol) and K$_2$CO$_3$ (25 g) in DMFA (200 mL) a 500-mL flask was refluxed for 14–16 h. The hot mixture was filtered and then evaporated. Crude product was crystallized from benzene.[6,9]

Method b

A mixture of sodium nitro phenolate (100 mmol), 1,2-dibromo ethane (50 mmol) in ethylene glycol (50
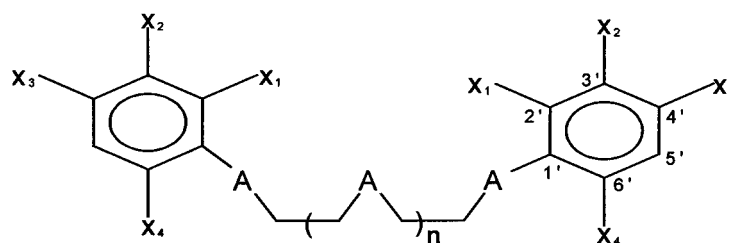

Figure 1 General structures of dibenzo and dibenzodiaza precursors.

TABLE I
Structures of Prepared Compounds and Methods Used in the Synthesis

Compound	Method	A	n	X_1	X_2	X_3	X_4
I	b	O	0	NO$_2$	H	H	H
II	b	O	0	Cl	H	H	H
III	a	O	0	CHO	H	H	H
IV	b	O	0	H	H	NO$_2$	H
V	b	O	0	H	NO$_2$	H	H
VI	—	O	0	NH$_2$	H	H	H
VII	—	O	0	H	H	NH$_2$	H
VIII	a	O	1	CHO	H	H	H
IX	a	O	1	NO$_2$	H	H	H
X	b	O	0	CI	H	NO$_2$	H
XI	b	O	0	NO$_2$	H	C(CH$_3$)$_3$	H
XII	c	N	0	COOH	H	NO$_2$	H
XIII	c	N	0	COOH	H	NO$_2$	NO$_2$

TABLE II
Elemental Analysis of the Compounds

Compound	Name of compound	Formula (MW)	Melting point (°C)	Elemental analysis (Calcd/Found)		
				C%	H%	N%
I	1,2-bis-(o-nitro phenoxy)ethane	$C_{14}H_{12}N_2O_6$ (304)	166–167			
II	1,2-bis-(o-chloro phenoxy)ethane	$C_{14}H_{12}O_2Cl_2$ (283)	100–101	59.36	4.24	—
				59.37	4.16	—
III	1,2-bis-(o-carboxaldehyde phenoxy) ethane	$C_{16}H_{14}O_4$ (270)	130–131			
IV	1,2-bis-(p-nitro phenoxy) ethane	$C_{14}H_{12}N_2O_6$ (304)	165–166			
V	1,2-bis-(m-nitro phenoxy) ethane	$C_{14}H_{12}N_2O_6$ (304)	142–144	55.26	3.94	9.21
				55.30	3.91	9.29
VI	1,2-bis-(o-amino phenoxy) ethane	$C_{14}H_{16}N_2O_2$ (244)	130–131			
VII		$C_{14}H_{16}N_2O_2$ (244)	170–175			
VIII	3-oxa-1,5-bis-(o-carboxaldehydephenoxy) pentane	$C_{18}H_{18}O_5$ (314)	76–78			
IX	3-oxa-1,5,-bis-(o-nitro phenoxy) pentane	$C_{16}H_{16}N_2O_7$ (348)	68–69			
X	1,2-bis-(2-chloro-4-nitro phenoxy) ethane	$C_{14}H_{10}N_2O_6Cl_2$ (373)	230–231	45.04	2.68	7.50
				45.18	2.65	7.83
XI	1,2-bis-(4-*tert* butyl-2-nitro phenoxy)ethane	$C_{22}H_{28}N_2O_6$ (416)	112–114	63.46	6.73	6.73
				63.51	6.87	6.38
XII	*N,N'*-bis-(2-carboxy-4-nitrophenyl)-1,2-diamino ethane	$C_{16}H_{14}N_4O_8$ (390)	258–260	49.23	3.58	14.35
				49.28	3.69	14.43
XIII	*N,N'*-bis-(2-carboxy-4,6-dinitrophenyl)-1,2-diamino ethane	$C_{16}H_{12}N_6O_{12}$ (480)	268–270	40.00	2.50	17.50
				39.89	2.59	17.42

mL) was placed in a 250-mL flask and stirred for 3–4 h at 150–155°C in an oil bath. The mixture was stirred for a further 2 h at room temperature. Water (50–60 mL) was added to the mixture and kept for 2 h at −10°C. The precipitate was filtered and crystallized from acetonitrile or ethylacetate.[23]

Method c

To a mixture of *o*-chlorobenzoic acid (20 mmol), ethylene diamine (40 mmol), either diamino ether or ω,ω′–diaminoalkane, K_2CO_3 (10 mmol), and CuO (125 mg) were added and the mixture was stirred for 1 h at 40°C. The excess amine was removed by distillation. Active coal (5 g) was added to the solution and heated for 5 min at the boiling point and filtered. Conc. HCl was added to the hot solution for adjustment of pH to precipitate amino acid, after which the residue was filtered off. The product was crystallized from water–acetonitrile–ethylacetate (1 : 1 : 1) mixture or DMFA.[24]

General procedure for reduction of dinitro compound to amine

A mixture of ω,ω′-bis(nitrophenoxy) alkane and raney nickel (2–3 g) in absolute ethanol (120 mL) was replaced in a sealed system and H_2 gas was passed through the system for 7–10 h at 3–4 atm. The solid was removed by filtration and treated with ether in a Soxhlet apparatus for a few times with small portions. These extracts were combined with ethanol solution and the solvent was

evaporated and then the residue distilled *in vacuo* and crystallized from absolute ethanol.[23]

1,2-Bis-(o-nitro phenoxy)ethane (*I*). Yield 70%, white solid from acetonitrile, mp 166–167°C. (reported as mp 167.5–168°C, yield 73% in the literature[9]).

1,2-Bis-(o-chloro phenoxy)ethane (*II*). Yield 82%, white solid from acetonitrile, mp 100–101°C. IR (KBr) ν cm^{-1} = 3052.5, 3015.5 (Ar—H), 2965, 2947, 2882 (CH), 1588.7, 1487.5, 1443 (C=C aromatic), 1377.6, 1296.5, 1276, 1254.8 (Ar—OC), 1071.7, 1039, 945, 930, 740 (CH aromatic). ^{1}H-NMR (CDCl$_3$) δ = 4.46 (s, 4H), 6.96 (td, 2H), 7.25 (td, 2H), 7.08–7.10 (dd, 2H), 7.39–7.41 (dd, 2H). ^{13}C-NMR (CDCl$_3$) δ = 68.40, 114.99, 122.51, 123.85, 128.18, 130.79, 154.75.

1,2-Bis-(o-carboxaldehyde phenoxy) ethane (*III*). Yield 78%, white solid from benzene, mp 130–131°C.[6]

1,2-Bis-(p-nitro phenoxy) ethane (*IV*). Yield 88%, white solid from ethyl acetate, mp 145–146°C.[25]

1,2-Bis-(m-nitro phenoxy) ethane (*V*). Yield 80%, white solid from ethyl acetate, mp 142–144°C. IR (KBr) v cm^{-1} = 3096.80 (ArH), 2959, 2927, 2878 (CH), 1628, 1578, 1481, 1453 (C=C aromatic), 1530, 1344 (NO$_2$), 1282, 1245.50, (ArOC), 1098, 1056 (COC), 997, 967, 890, 859, 738 (ArH, *m*-substitute). ^{1}H-NMR (CDCl$_3$ + DMSO) δ = 4.33 (s, 4H), 7.16–7.36 (dd, 2H), 7.34 (td, 2H), 7.66–7.72 (m, 4H). ^{13}C-NMR (CDCl$_3$) δ = 67.34, 109.35, 116.52, 122.08, 130.48, 149.48, 159.33.

1,2-Bis-(o-amino phenoxy)ethane (*VI*). Yield 85%, white solid absolute alcohol, mp 130–131°C (reported as mp 131–132°C in the literature[23]).

*1,2-Bis-(p-amino phenoxy)ethane (**VII**).* Yield 90%, white solid absolute alcohol, mp 173–175°C.[25]

3-Oxa-1,5-bis(o-carboxaldehyde phenoxy) pentane (viii). Yield 81%, white solid from benzene, mp 76–78°C.[6]

*3-Oxa-1,5-bis(o-nitro phenoxy) pentane (**IX**).* Yield 83%, white solid from benzene, mp 68–69°C (reported as mp 68–69°C, yield 77% in the literature[9]).

*1,2-Bis(2-chloro-4-nitro phenoxy)ethane (**X**).* Yield 83%, brown solid from acetonitrile, mp 230–231°C. IR (KBr) ν cm^{-1} = 3109 (Ar—H), 2987, 2897 (CH), 1603, 1582, 1472 (C═C aromatic), 1511, 1346 (NO$_2$), 1275 (Ar—OC), 1144, 1127, 1058 (COC), 1025, 895, 848, 818, (CH aromatic). ^{1}H-NMR (DMSO): δ = 4 0.60 (s, 4H), 7.30 (d, 2H), 7.90 (dd, 2H), 8.30 (d, 2H). ^{13}C-NMR (DMSO + CDCI$_3$): δ = 69.04, 114.54, 125.13, 129.50, 141.82, 152.12, 159.81.

*1,2-Bis(4-tert butyl-2-nitro phenoxy)ethane (**XI**).* Yield 74%, clear yellow solid from ethyl acetate, mp 112–114°C. IR (KBr) ν cm^{-1} = 3053 (ArH), 2966.30, 2881.40 (CH), 1618.90, 1453.90 (C═C aromatic), 1529.10, 1349.50 (NO$_2$), 1264.90 (ArOC), 1176, 1087, 1069 (COC), 944, 903, 833, 725 (ArH, *o*- and *m*-substitute). ^{1}H-NMR (CDCl$_3$) δ = 1.33 (s, 18H), 4.51 (s, 4H), 7.28 (d, J = 8.78 Hz, 2H), 7.58 (dd, 2H), 7.82 (d, J = 2.48 Hz, 2H). ^{13}C-NMR (CDCl$_3$) δ = 31.52, 34.79, 69.36, 116.28, 122.67, 131.74, 140.00, 145.34, 150.12.

N,N′-*Bis(2-carboxy-4-nitrophenyl)-1,2-diamino ethane (**XII**).* Yield 90%, green solid from DMFA and water–acetonitrile–ethyl acetate mixture (1 : 1 : 1) mp 258–260°C. IR (KBr) ν cm^{-1} = 3220 (NH), 3050 (Ar—H), 2800 (CH), 1642 (COOH), 1610, 1581, 1440, 1360 (C═C aromatic), 1493, 1322 (NO$_2$) 1270, 1170 (CH$_2$). ^{1}H-NMR (DMSO) δ = 3.0 (s, 4H), 3.71 (s, 2H), 7.07 (d, 2H, J = 9.49 Hz), 8.13 (dd, 2H, J = 7.80 Hz, J = 2.48 Hz), 8.60 (d, 2H, J = 2.50 Hz), 9.2 (s, 2H). ^{13}C-NMR (DMSO) δ = 38.11, 111.17, 112.55, 129.25, 130.03, 135.99, 155.28, 169.10.

N,N′-*Bis(2-carboxy-4,6-dinitrophenyl)-1,2-diamino ethane (**XIII**).* Yield 88%, yellow solid from DMFA, mp 268–270°C. IR (KBr) ν cm^{-1} = 3222 (NH), 3070 (Ar—H), 2933, 2868 (CH), 1694 (COOH), 1607, 1455 (C═C aromatic), 1515, 1323 (NO$_2$), 1225, 1165 (CH$_2$). ^{1}H-NMR (CDCl$_3$ + DMSO) δ = 2.91 (s, 4H), 3.35 (s, 2H), 8.78 (d, 2H, J = 3.2 Hz), 8.91 (d, 2H, J = 3.2 Hz), 9.58 (s, 2H). ^{13}C-NMR (CDCl$_3$ + DMSO) δ = 46.48, 116.29, 126.48, 134.11, 135.04, 148.65, 167.59. COOH was not observed.

RESULTS AND DISCUSSION

The versatile building blocks of crown ethers with various functional groups were prepared in good yield by using methods different from those recorded in the literature.[6,9,10,11,16,23,24] Spectroscopic data and elemental analysis results of some ligands were not provided because they were previously reported in the literature.[6,9,10,23,25] Ligands **II** and **V** were synthe-

sized in high yields compared with the literature.[9,26] Ligands **X**, **XI**, **XII**, and **XIII** are new. Ligands **XII** and **XIII** that possess COOH groups were previously used to synthesize macrocyclic diesters.[27] The advantage of our procedure compared to procedures reported in the literature is summarized as follows: In method a, we obtained similar product yields without vacuum distillation and inert atmosphere. In method c, the reaction was carried out at a mild temperature, within a short time, and with reasonably very good yield. In the reduction of dinitro compounds to amines, Pd/C and NH$_2$NH$_2$ were also used and the overall yield was good in this procedure compared to that of raney nickel/H$_2$.

The conductometry measurements were carried out with high precision at optimal concentrations in 80% dioxane–water mixtures at 25°C. The complex formation constant, $K_e = (\Lambda_M^{m+} - \Lambda)/\{(\Lambda - \Lambda_{ML}^{m+})\ [L]\}$ for ligand–cation complexes in dioxane–water mixtures were estimated from conductance parameters (κ, λ, and α). Molar conductivities Λ_M (Ω^{-1} cm^2 mol^{-1}) were calculated from the infinite frequency electrolytic conductances κ after correcting for the pure solvent conductance (i.e., $\Lambda_M = 1000\kappa/C_{MX}$ where C_{MX} is total concentration of the metal salt). The association constants (K_e) and Gibbs free enthalpy values ($-\Delta G°$) of synthesized ligands with Cu^2, Ag$^+$, and Zn^{2+} ions were measured by means of a conductometric method[22] in 80% dioxane–water mixtures at 25°C.

The $-\Delta G°$ values where the molar ratio of ligand to salt L : S, 1 : 1 can be equated to the free energy for an equilibrium of the metal salt from one face of the ligand to the other face with both dissociative and half ring-inversion components.[28–30]

The $-\Delta G°$ values are measure of kinetics stabilities of the complexes. This binary solvent mixture is among those that enhance the ligand–cation interactions.[18,19,21,22,28,31–35] The experimental molar conductance equations and all calculations for stability constants and Gibbs free enthalpy values were published in a previous work.[22]

All of the synthesized ligands were complexed with Cu^{2+}, Zn^{2+}, and Ag$^+$ ions in 80% dioxane–water mixture; Table III shows the systematic decrease in values of K_e in the following order:

For Cu(NO$_3$)$_2$: **VII** > **VI** > **III** > **VIII** > **XI** > **IV** > **XIII** > **II** > **I** > **X** > **IX** > **V** > **XII**

For ZnCl$_2$: **V** > **IV** > **II** > **X** > **I** > **VII** > **IX** > **VI** > **XI** > **VIII** > **III** > **XIII** > **XII**

For AgNO$_3$: **VI** > **VIII** > **IV** > **XI** > **III** > **X** > **VII** > **II** > **I**, **V**, **IX**, **XII**, **XIII**

The decreasing order of the best complexing ability of the different cations for (**I**, **II**, **IV**, **V**, **IX**, and **X**), (**VI**, **VII**, **XI**, and **XIII**), and (**III** and **VIII**) ligand series was

TABLE III
Log K_e and $-\Delta G°$ (kcal/mol) Values for the Interaction of the Ligands with $Cu(NO_3)_2$, $AgNO_3$, and $ZnCl_2$ in a 80% Dioxan–Water Mixture at 25°C by Conductometric Study

Ligand	Value	Cu^{2+}	Zn^{2+}	Ag^+
I	$\log K_e$	1.76	3.20	—
	$-\Delta G°$	2398.11	4363.96	—
II	$\log K_e$	2.52	3.47	1.48
	$-\Delta G°$	3434.33	4725.16	2013.22
III	$\log K_e$	3.89	2.22	2.32
	$-\Delta G°$	5299.52	3025.76	3161.95
IV	$\log K_e$	3.07	3.71	2.51
	$-\Delta G°$	4180.41	5056.75	3422.48
V	$\log K_e$	—	4.01	—
	$-\Delta G°$	—	5465.32	—
VI	$\log K_e$	4.00	2.91	2.63
	$-\Delta G°$	5453.48	3967.24	3582.36
VII	$\log K_e$	4.11	3.15	2.14
	$-\Delta G°$	5601.51	4292.91	2913.26
VIII	$\log K_e$	3.28	2.51	2.60
	$-\Delta G°$	4470.55	3422.48	3540.91
IX	$\log K_e$	1.11	2.98	—
	$-\Delta G°$	1509.92	4061.98	—
X	$\log K_e$	1.50	3.21	2.31
	$-\Delta G°$	2042.83	4375.81	3150.11
XI	$\log K_e$	3.24	2.84	2.35
	$-\Delta G°$	4417.26	3872.51	3203.40
XII	$\log K_e$	—	—	—
	$-\Delta G°$	—	—	—
XIII	$\log K_e$	3.01	1.37	—
	$-\Delta G°$	4103.43	1865.19	—

generally found as follows: $Zn^{2+} > Cu^{2+} > Ag^+$; $Cu^{2+} > Zn^{2+} > Ag^+$ and $Cu^{2+} > Ag^+ > Zn^{2+}$, respectively.

It has been established that benzo substitution affects the complexation properties of the ligands.[36] The complex abilities of ligands were thus evaluated in terms of structural and functional modification. These results were in concert with our previous work.[27]

Conductometry measurements showed that when the functional groups was either NH_2, CHO, or COOH, the complexation ability of Cu^{2+} was greater than that of Zn^{2+} and Ag^+. On the other hand, when the functional group was NO_2, the complexation ability of Zn^{2+} was especially favorable. As seen in Table III, ligand **V** including the NO_2 group exhibited the best complexation value only to Zn^{2+} ion; ligand **VII**, which has the NH_2 group, showed a higher complexation stability constant to Cu^{2+} ion than that of all the other synthesized ligands. In general the structural modification and functional groups on ligands affect the complexation abilities of ions.

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