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SYNTHESIS AND COMPLEXATION OF NEW SUBSTITUTED DIBENZODIAZA MACROCYCLIC DIESTER COMPOUNDS

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ABSTRACT

The synthesis of some new precursors that contain substituted benzo units and their use in the preparation of azamacrocyclic diester compounds are reported. These precursors and ligands were characterized by Elemental analysis, ¹H and ¹³C NMR spectroscopy, and IR spectroscopy. The complexation constants K_e and ΔG° values for the diesters with several transition metal cations (Ag^+ , Zn^{2+} and Cu^{2+}) in a dioxan–water system using a conductometric method at 25°C are also reported.

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Key Words: Diazacrowns; Dibenzodiazacrowns; Oligoethylene glycols; Derivatives; Synthesis; Complexation constant; Conductometry

INTRODUCTION

There is a great interest in the synthesis of azacrown compounds.^[1,2] Macrocyclic ligands have demonstrated potential for use in many industrial and chemical processes where cation selectivity and/or solubility in nonpolar solvents are required.^[3] For this reason, the synthesis of simple, inexpensive macrocycles with various cation selectivities is desirable.

The first macrocyclic compound prepared from a diacid was dimeric ethylene succinate reported by Vorlander in 1894.^[4] Subsequently, very little work was done with macrocyclic diesters until the 1930s when Carothers and his coworkers commenced a study of polyesters including the macrocyclic monomeric and dimeric carbonates, oxalates, etc.^[5] The main interest in macrocyclic diester compounds involved their use in the preparation of perfumes.^[6] Drewes et al. prepared a number of macrocyclic di- and tetraesters from phthalic^[7,8] and maleic acids^[9] and from aliphatic diacids but using the *o*-xylene moiety as a rigid steric factor.^[10] Bradshaw and coworkers reviewed some of the synthesis and used macrocyclic diester compounds derived from dibasic acids in 1978.^[11]

In this study, we have synthesized two new precursors and two new azacrown ethers, precursors which contain the ester linkages in the cyclic molecule (shown in Figure 1). *N,N'*-bis-[2-carboxy-4-nitrophenyl]-1,2-diaminoethane (**1**) and *N,N'*-bis-[2-carboxy-4,6-dinitrophenyl]-1,2-diaminoethane (**2**) are important intermediates for the synthesis of cryptands, nitrogen-pivot lariat crown ethers and other species.^[12-15] The esters are 1,18-diaza-2,3:16,17-bis[4-nitro benzene]-5,8,11,14-tetraoxa-cycloeicosane-4,15-dione (**3**) and 1,18-diaza-2,3:16,17-bis-[2,4-dinitro benzene]-5,8,11,14-tetraoxa-cycloeicosane-4,15-dione (**4**).

MATERIALS AND METHODS

All infrared (IR) spectra were obtained on a Perkin-Elmer Model BX-II spectrophotometer. The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were obtained on Bruker-AC 200 MHz and 100 MHz spectrometers, respectively. Elemental analysis was obtained on a Carlo-Erba 1108 Model elemental analysis instrument. The conductances were measured at 25 ± 0.05°C with a Suntex SC-170 Model conductometer. Melting points



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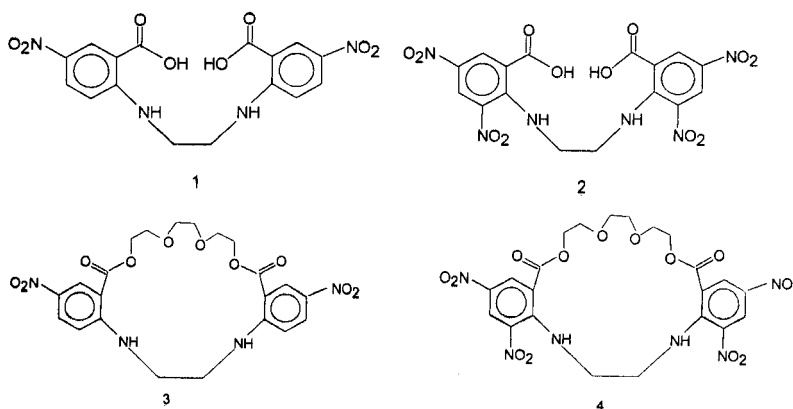


Figure 1. Structures of the precursors and macrocyclic diester ligands.

were determined in open capillary tubes on a Gallenkamp apparatus and are uncorrected.

Reagent grade solvents and chemicals (Fluka and Aldrich) were used without further purification.

EXPERIMENTAL

**Preparation of *N,N'*-Bis-[2-carboxy-4-nitrophenyl]-
1,2-diaminoethane (1)**

0.6 g (10 mmol) K_2CO_3 and 0.125 g (1.57×10^{-3} mmol) CuO were added to a mixture of the 4.03 g (20 mmol) 2-chloro-5-nitrobenzoic acid and 4.8 g (80 mmol) ethylenediamine. The mixture was stirred for 1 h at $40^\circ C$. The excess amine was removed by distillation. 5 g of charcoal was added to the solution and heated for 5 min at boiling point and then filtered. Concentrated HCl was added to the hot solution. The HCl salt of amino acid were obtained and converted to free amino acid by adjustment of pH. The product was crystallized from DMFA.^[16,17] Yield 60%, green solid, m.p. $258\text{--}260^\circ C$; IR (KBr) = 3220 cm^{-1} (ν NH), 2950 cm^{-1} (ν Ar-H), 2800 cm^{-1} (ν CH), 1642 cm^{-1} (ν COOH), 1610, 1581, 1440 cm^{-1} (ν C=C aromatic), $1493, 1322\text{ cm}^{-1}$ (ν NO_2) $1270, 1170\text{ cm}^{-1}$ (ν CH_2).

1H -NMR (DMSO): $\delta = 3.0$ (s, 4H, - NCH_2CH_2N -), 3.71 (s, 2H, NH), 7.07 (d, 2H, $J = 9.49$ Hz, Ar-H), 8.13 (dd, 2H, $J = 7.8$ Hz, $J = 2.48$ Hz, Ar-H), 8.60 (d, 2H, $J = 2.50$ Hz, Ar-H), 9.2 (s, 2H, COOH). ^{13}C NMR (DMSO) $\delta = 38.11, 111.17, 112.55, 129.25, 130.03, 135.99, 155.28, 169.10$.



Analytical Calculated For $C_{16}H_{14}N_4O_8$ (Mw: 390): C, 49.23; H, 3.58; N, 14.35. Found: C, 49.28; H, 3.59; N, 14.43.

Preparation of *N,N'*-Bis-[2-carboxy-4,6-dinitrophenyl]-1,2-diaminoethane (2)

4.93 g, (20 mmol) 2-Chloro-3,5-dinitrobenzoic acid, 4.80 g (80 mmol) ethylene diamine, 0.60 g (10 mmol) K_2CO_3 and 1.57×10^{-3} g (1.57×10^{-3} mmol) CuO were used. The same procedure was followed. The precipitate was crystallized from DMFA, Yield 62%, yellow solid, m.p. 268–270°C; IR (KBr) = 3222 cm^{-1} (ν NH), 3070 cm^{-1} (ν CH aromatic), 2933, 2868 cm^{-1} (ν CH), 1694 cm^{-1} (ν COOH), 1607, 1455 cm^{-1} (ν C=C aromatic), 1515, 1323 cm^{-1} (ν NO₂), 1225, 1165 cm^{-1} (ν CH₂).

¹H-NMR (CDCl₃ + DMSO): δ = 2.91 (s, 4H, -NCH₂CH₂N-), 3.35 (s, 2H, NH), 8.78 (d, 2H, J = 3.2 Hz, Ar-H), 8.91 (d, 2H, J = 3.2 Hz, Ar-H), 9.58 (s, 2H, COOH). ¹³C NMR (CDCl₃ + DMSO) δ = 46.48, 116.29, 126.48, 134.11, 135.04, 148.65, 167.59, COOH has not been observed.

Analytical calculated for $C_{16}H_{12}N_6O_{12}$ (Mw: 480): C, 40.00; H, 2.50; N, 17.50. Found: C, 39.79; H, 2.70; N, 17.30.

1,18-Diaza-2,3:16,17-bis-[4-nitrobenzene]-5,8,11,14-tetraoxacycloicosane-4,15-dion (NTET) (3)

120 ml of benzene was placed into a 250 ml one necked flask, and then 0.38 g (2.5 mmol) triethyleneglycol and 0.975 g (2.5 mmol) (1) were added. The flask was equipped with a Dean-Stark apparatus and the reaction mixture was stirred at reflux temperature for 24 h. After the reaction was complete, the reaction mixture was cooled to room temperature and consequently evaporated to dryness under reduced pressure.

The product was obtained as light yellow oil, which was chromatographed on silica gel from ethyl acetate to yield 47%; IR (KBr) = 3438 cm^{-1} (ν NH), 3080, 3040, 3030 cm^{-1} (ν CH aromatic), 2855, 2850 cm^{-1} (ν CH), 1740, 1710 cm^{-1} (ν CO ester), 1670, 1630, 1570 cm^{-1} (ν C=C aromatic), 1535, 1365 cm^{-1} (ν NO₂).

¹H-NMR (DMSO): δ = 4.45 (s, 2H, -NH-); 5.12 (s, 4H, -OCH₂CH₂O-); 5.80 (s, 4H, -NCH₂CH₂N-); 4.79–5.87 (m, 8H, -COOCH₂CH₂O-); 7.00 (d, 2H, J = 9.40 Hz, ArH), 7.55–7.80 (dd, 2H, J = 7.80 Hz, J = 2.45 Hz, ArH); 8.20 (d, 2H, J = 2.48 Hz, ArH). ¹³C NMR (DMSO) δ = 55.0, 67.1, 69.4, 70.1, 112.9, 115.2, 127.0, 129.1, 135.8, 157.6, 169.6.



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Analytical calculated for $C_{22}H_{24}N_4O_{10}$ (Mw: 504): C, 52.41; H, 4.76; N, 11.11. Found: C, 52.33; H, 4.93; N, 11.09.

1,18-Diaza-2,3:16,17-bis-[2,4-dinitrobenzene]-5,8,11,14-tetraoxacycloicosane-4,15-dion (DNTE) (4)

0.38 g triethylene glycol (2.5 mmol) and 1.217 g (2.5 mmol) (**2**) were used. The same procedure was followed. Removal of the solvent in vacuo left a yellow solid, which was crystallized from ether/ $CHCl_3$ (1 : 1) to yield 70%, m.p. 218.5°C; IR (KBr) = 3440 (ν NH), 3110, 3025 (ν CH aromatic), 1745 (ν CO ester), 1640, 1615, 1585, 1485 (ν -C=C aromatic), 1530, 1415 (ν NO₂).

¹H-NMR ($CDCl_3$ + DMSO): δ = 4.60 (s, 2H, -NH-); 5.00 (s, 4H, -OCH₂CH₂O-); 5.77 (s, 4H, -NCH₂CH₂N-); 4.83–5.71 (m, 8H, -COOCH₂CH₂O-); 8.85 (d, 2H, J = 3.00 Hz, ArH); 8.92 (d, 2H, J = 3.02 Hz, ArH). ¹³C NMR ($CDCl_3$ + DMSO) δ = 53.0, 65.7, 69.8, 72.2, 117.8, 125.2, 133.0, 135.1, 138.7, 150.9, 168.8.

Analytical calculated for $C_{22}H_{22}N_6O_{14}$ (Mw: 594): C, 44.46; H, 3.70; N, 14.14. Found: C, 44.12; H, 3.85; N, 14.08.

COMPLEXATION STUDIES AND THE DETERMINATION OF THE STABILITY CONSTANT (K_e)

Stability constants of $AgNO_3$, $ZnCl_2$ and $Cu(NO_3)_2$ complexes with compound (**3**) and (**4**) were measured by means of a conductometric method.^[18,19]

Anhydrous the solutions were prepared at a constant 1 : 1 ratio of metal salt to diesters (NTET and DNTE) in a 80% dioxan–water mixture. Water used in the conductometric studies was redistilled from alkaline permanganate. Dioxan was dried over sodium metal. The cell constants were determined as 0.769 cm^{-1} at 25°C, by measuring the conductivity of aqueous KCl solutions at different concentrations. Results are reported as the average and standard deviation from the average of 4–6 independent experimental determinations.

RESULTS AND DISCUSSION

Generally, macrocyclic polyether–diester compounds do not complex metal cations as strongly as the crown ethers.^[20,21] Compounds (**3**) and (**4**)



Table 1. Log Ke (dm^3/mol) and $-\Delta G^\circ$ (kJ/mol) Values for the Interaction of NTET and DNTE Macrocyclic Diester Ligands with Ag^+ , Zn^{2+} and Cu^{2+} Metal Ions in an 80% Dioxan–Water Mixture at 25°C

Ligand	Value	Ag^+	Zn^{2+}	Cu^{2+}
NTET	log Ke	–	3.51 ± 0.03	3.09 ± 0.01
	$-\Delta G^\circ$	–	4780.06 ± 0.5	4208.50 ± 0.20
DNTE	log Ke	–	5.59 ± 0.06	2.78 ± 0.02
	$-\Delta G^\circ$	–	7620.71 ± 0.2	788.94 ± 0.40

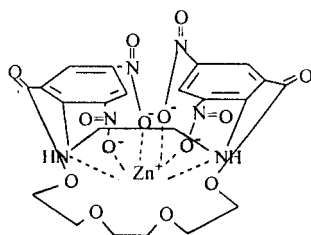


Figure 2. The conjectural complexation of Zn^{2+} with DNTE ligand.

form significantly stable complexes with Zn^{2+} and Cu^{2+} cations and are relatively easy and inexpensive to prepare compared to most of the crown ether compounds.^[22] Formation of complexes by these diester ligands with metal cations in an equimolar mixture of two reactants in dioxane–water binary systems was observed for Zn^{2+} and Cu^{2+} cations but not for the Ag^+ . The complexation constants (log Ke) and free energy ($-\Delta G^\circ$) values were given in Table 1 and Figures 3–5.

The Zn^{2+} ion was complexed to NTET and DNTE ligands more strongly than the Cu^{2+} ion. The conjectural structure of the Zn^{2+} complex with DNTE was shown in Figure 2. It is believed that the Zn^{2+} ion would be bonding outside of the cavity in DNTE.^[22,23] A possible explanation is that the oxygens of the nitro groups as electron donors were accompanied with the other oxygens of the crown ring. Thus, the whole ring would surround the metal cation. Just as this complexation occurs, the planarity of the nitro groups substituted on the benzene ring was deformed, and the oxygens in the structure of nitro groups with a partial negative charge were stabilized by the formation of an electrostatic attraction with the cation. Otherwise, owing to the electron withdrawing effect of the nitro groups on the benzene ring, the basicity of the nitrogen donor atoms in the crown ring



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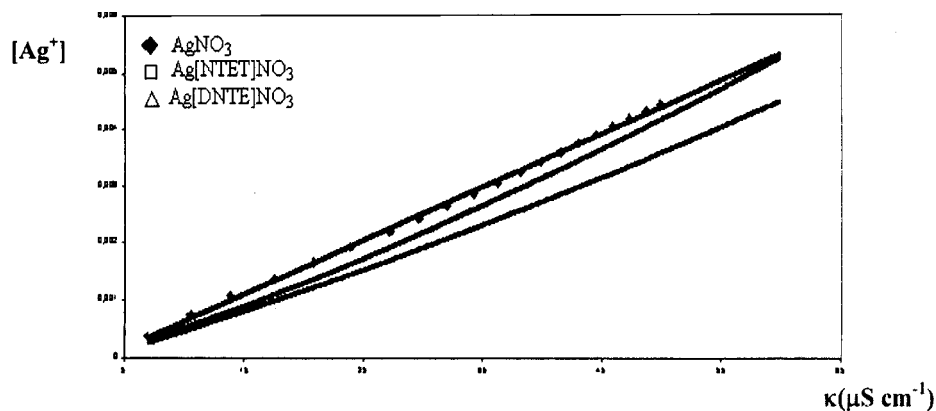


Figure 3. The plot of $[Ag^+]$ (mol L^{-1}) versus observed conductivity of $AgNO_3$ with NTET and DNTET in 80% dioxan–water mixtures at 25°C .

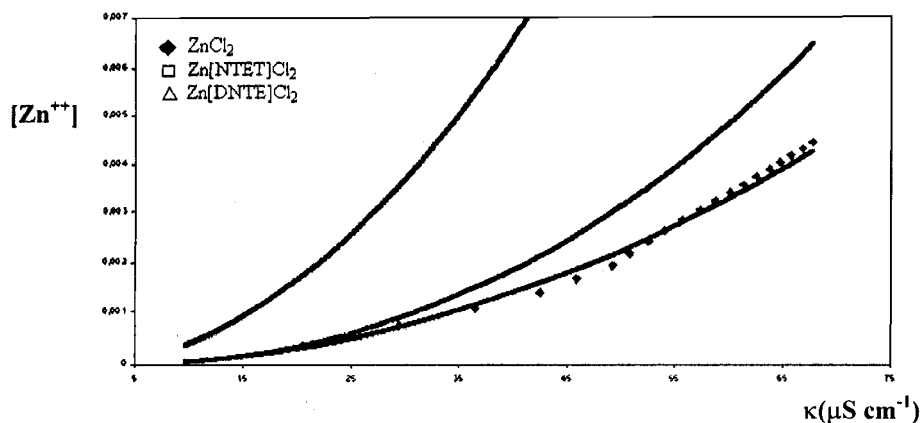


Figure 4. The plot of $[Zn^{2+}]$ (mol L^{-1}) versus observed conductivity of $ZnCl_2$ with NTET and DNTET in 80% dioxan–water mixtures at 25°C .

would be reduced and, under these circumstances, the nitro groups on the benzene ring should reduce the interactions between the macrocyclic ligands and the metal ions. However, it is surprising that complex formation for the dinitro substituted ligand was greater than the mononitro derivative.

The $-\Delta G^\circ$ values where the molar ratio of crown to salt, C:S, 1:1 can be equated to the free energy for an equilibrium of the metal salt from one

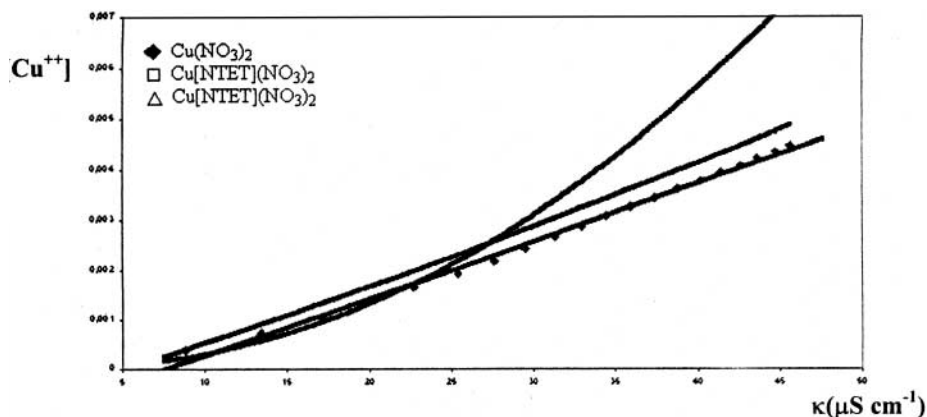


Figure 5. The plot of $[\text{Cu}^{2+}]$ (mol L^{-1}) versus observed conductivity of $\text{Cu}(\text{NO}_3)_2$ with NTET and DNTE in 80% dioxan/water mixtures at 25°C .

face of the ligand to the other face with both dissociative and ring-inversion components.^[24–26]

The $-\Delta G^\circ$ values are the measure of the kinetic stabilities of the complexes. As studied in the literature, a stability constant of $\log K_e = 5.31 \text{ dm}^3/\text{mol}$ of Zn^{2+} -complexes with similar ligands, which do not contain any nitro and carbonyl group, was found for complexation in H_2O .^[26]

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