

# The Syntheses and Characterization of Three Novel Macrocyclic Polyether Ligands and Some of Their Alkaline Metal Complexes

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**ABSTRACT:** The macrocyclic ligands 2,3,5,6-Bis{3'-bromo-5'-tert-butyl benzo-5-phenyl benzo}12C3 ( $L_1$ ), 2,3,5,6-bis{3'-bromo-5'-tert butyl-benzo-5'-phenyl-benzo}15C4 ( $L_2$ ), 2,3,5,6-bis{3'-bromo-5'-tert butyl-benzo-5'-phenyl-benzo}18C5 ( $L_3$ ) have been synthesized and their alkaline metal compounds with  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  and  $\text{KClO}_4$  have been prepared. Chemical formulas of all compounds have been characterized by using elemental analyses and spectroscopic techniques.

**KEY WORDS:** Crown ether, Macrocyclic ligands, Alkaline complex, Spectroscopic technique.

## INTRODUCTION

The importance of crown ether compounds firstly synthesized by Pedersen [1] has been entirely recognized. The usage of the macrocyclic ligands has become widespread as they render alkaline metal salts soluble in an organic solvent, increase the solubility of the salts and activate their anions. The use of macrocyclic ligands for organic syntheses has been continuously increased due to their interaction with alkali metal salts via complexation [2]. For example, macrocyclic ligands have been used as phase transfer catalyst [3-5]. In addition, these macrocycles with the cavity for selective interactions with various charged or neutral guest molecules [6,7] have been very important to host-guest complexation chemistry. Especially, the alkaline and alkaline earth metal ions are more useful than transition metal ions in phase transfer reaction, because the macrocyclic moiety is very poor ligand for transition metal ions [8,9].

Different kinds of crown ethers [10] have been synthesized in order to recognize various molecules such as cubane [11], pentacycloundecane [12], 3-5 disubstituted-4-oxahexacyclo dodecane [13] with superior properties as pervaporation [14] and proper application to various areas. Macrocyclic polyethers are cyclic compounds in which hetero atoms with their numbers ranging from fours to twenty bind to one another with ethylene and propylene linkages. Hetero atoms can be oxygen [15,16], nitrogen [17], sulphur [18] and phosphorus, and the ring can contain one or more such atoms. The capability of separating ionic species by the macrocyclic ligands or macrocyclic ligand polymers has been investigated [19], finding that the thiocyanide salts of Li, Na, K, as well as salts such as KCl, KBr, KI and KSCN [20] can be separated by such macrocycles. On the other hand, the same investigation has been

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performed for the separation of racemate [21,22], these macrocycles can interact with various functional groups, and resembling antibiotics for instance, macro lactones as the natural metabolites. Owing to the rapid increase of the importance of these ligands, we have decided to synthesize the new ligands and their cationic complexes. Three novel macrocyclic ligands the 2,3,5,6-Bis{3'-bromo-5'-tert-butyl benzo-5-phenyl benzo}12C3 ( $L_1$ ), 2,3,5,6-bis{3'-bromo-5'-tert-butyl-benzo-5'-phenyl-benzo}15C4 ( $L_2$ ), 2,3,5,6-bis{3'-bromo-5'-tert-butyl-benzo-5'-phenyl-benzo}18C5 ( $L_3$ ) were synthesized according to reaction condition as shown in Scheme 1. Then, complexes of ( $L_2$ ) with  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  and  $\text{KClO}_4$ ; ( $L_3$ ) with  $\text{KClO}_4$  have been prepared.

## EXPERIMENTAL

Reagents were obtained either from Merck or Fluka and used without further purification. The diethylene, triethylene and tetraethylene glycols were distilled at low pressure in the presence of  $\text{CuSO}_4$ , prior to use. The Ditosylate derivatives and  $L_1$ ,  $L_2$ ,  $L_3$  have been synthesized according to procedures as described in the corresponding literature references as indicated above. Elemental analysis and  $^1\text{H}$  NMR spectroscopic studies were obtained in the TÜBİTAK Research Laboratories (The Scientific and Technological Research Council of Turkey). A Setaram Setys Evolution TGA-DTA/DSC 1750 thermal analysis system was used over the temperature range 0-1100 °C. The samples were placed in Pt crucibles and  $\alpha\text{-Al}_2\text{O}_3$  was used as the reference material. Heating was performed under  $\text{N}_2$  atmosphere at a flow rate of 60 ml/min. The sample weight was limited to 2-8 mg and the heating rate was adjusted to 10 °C/min. IR spectra were recorded on a Pye-Unicam SP 1025 spectrophotometer, in KBr pellets. Melting points were determined in a capillary tube on a Buchi SPM-20 instrument.

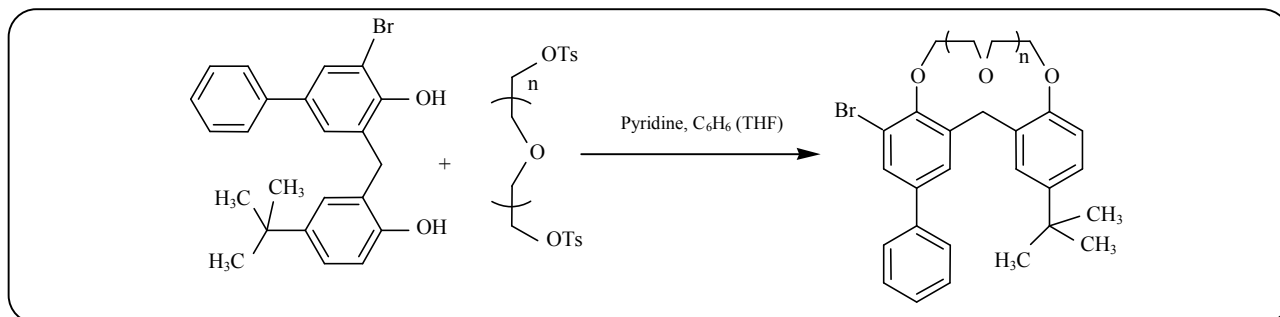
### *Synthesis of Macrocyclic Ligands. "General Procedure"*

A round bottomed five-necked two liter glass flask equipped with two dropping funnels, a reflux condenser, a nitrogen delivery tube and a mechanical stirrer was used as the reaction device. The reflux condenser was equipped with a  $\text{CaCl}_2$  drying tube. One liter of dry benzene (or THF) was transferred into the flask. According to the reaction conditions as shown in Schemes

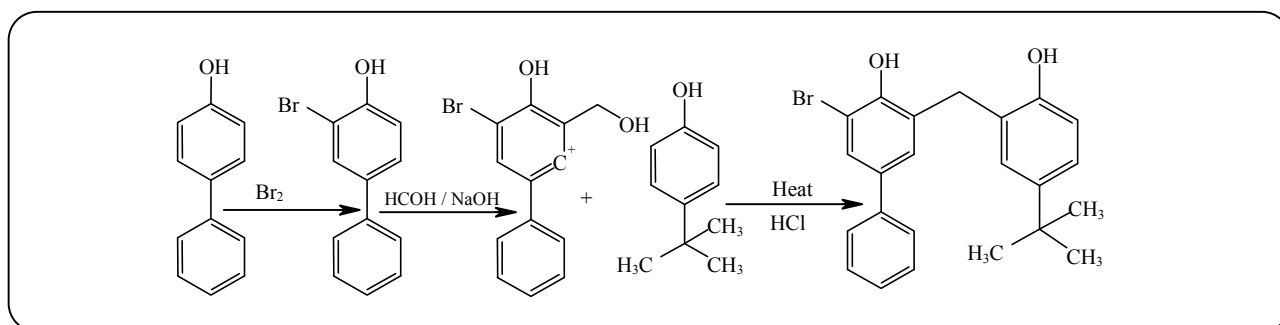
1-3, a stoichiometric amount of pyridine was then added into the flask. The dropping funnels were filled with very dilute solutions of 2,2'-dihydroxy-3-bromo-5-phenyl-5-tert-butyl diphenyl methane (Scheme 2) (**L**) and an appropriate ditosylate derivative of di- tri- or tetra ethylene glycol (Scheme 3) in benzene or THF. The pyridine solution was heated to its boiling point with stirring under nitrogen atmosphere, and the ditosylate derivatives and the dihydroxy compound solutions (at an approximate flow rate of 0.20 mL/min.) were then added to this mixture very slowly. When the additions of the reagent were completed, heating was stopped and the reaction mixture was stirred for two hours. The precipitated pyridine tosylate filtered off, and the excess solvent was removed by a rotary evaporator. The crude macrocyclic product was purified by recrystallization. The obtained characterization data were showed in tables 1, 2, 3 and 4.

### **Synthesis of the 2,2'-dihydroxy-3-bromo-5-phenyl-5-tert-butyl diphenyl methane**

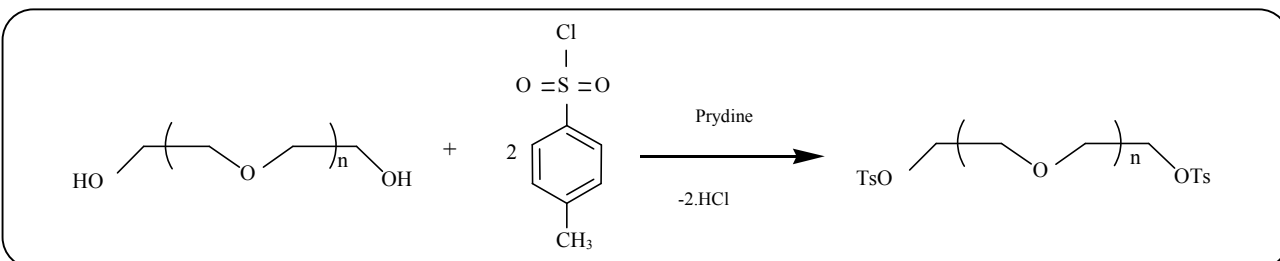
The dihydroxy compound was synthesized according to literature [24]. In the first step, 76.3 g of p-phenyl phenol with 800 mL of chloroform was refluxed at 55-60 °C. To this mixture 27 mL of  $\text{Br}_2$  solution in 30 mL of chloroform were added gradually and resulting solution was boiled, the obtained dark brown solution was then washed with water and dried over  $\text{MgSO}_4$ , excessive chloroform evaporated and white crystals were obtained by addition of petroleum-ether. The isolated crystals of 2-bromo-4-phenyl-phenol was reacted with 100 mL of 20 %  $\text{NaOH}$  and 100 mL of 37 % formaldehyde at 50 °C for 24 hours, then the mixture was precipitated with  $\text{CH}_3\text{COOH}$ . The solid was allowed in the acid solution for several days, then separated and washed with water until no presence of the acidic aroma. The solid product firstly melted at a 100 °C stove and then turned into a glassy form (m.p. 52-55 °C). To 27.9 g (0.1 mol) of this solid of 2-bromo-4-phenyl-6-hydroxy methyl-phenol, 40 g (0.2 mol) of 4-tert-butyl phenol dissolved in 200 mL of xylene were added and heated to 110 °C, 5 mL of  $\text{HCl}$  were added to the boiling solution drop by drop. The mixture was refluxed at 110 °C for a week, the mixture was then cooled to room temperature and dried under air atmosphere; product was obtained as brownish powder. 32 g m.p.



**Scheme 1: Synthesis of the ligands  $L_n$   $n:1,2,3$ .**



**Scheme 2: Synthesis of 2,2'-Dihydroxy-3-Bromo-5-Phenyl-5-Tetra-Butyl Diphenyl Methane (L).**



**Scheme 3: Syntheses of di, tri, and tetraethyleneglycol ditosylate  $Z_n$   $n: 1,2,3$ ; Ts: tosylate.**

120-125 °C,  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.20{s, 9H,  $\text{C}(\text{CH}_3)_3$ }, 3.50 (s, 2H,  $\text{CH}_2$ ), 5.78 (s, 2H, OH), 7.10 (dd, 4H, ArH), 7.36 (m, 5H, ArH), IR (KBr,  $\text{cm}^{-1}$ ): 3250 (C-H ArOH), 2865 ( $\text{CH}_2$ ), 1560 (C=C, Ar), 815 (Br, C-Br). Anal. Calcd. for  $\text{C}_{23}\text{H}_{23}\text{O}_2\text{Br}$ : C 67.16 H 5.64 found C 66.85 H 5.30

#### Synthesis of ligand $L_1$

4.11 g (0.01 mol) of L were dissolved in 400 mL of dry THF in the presence of 2.24 g (0.01 mol) of  $\text{KOC}(\text{CH}_3)_3$  and stirred continuously by the mechanical stirrer and heated to 50 °C, then 4.14 g (0.01 mol) of diethyleneglycol ditosylate Z in 75 mL of THF was dropped to the dihydroxy L solution for two hours. The crude product was crystallized from ethanol with yield of

1.01 g. (Yield 21 %, m.p. 225 °C).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.29{s, 9H,  $\text{C}(\text{CH}_3)_3$ }, 3.75 (s, 2H,  $\text{CH}_2$ ), 3.90 (t, 4H,  $\text{OCH}_2$ ), 4.18 (t, 4H,  $\text{CH}_2\text{OCH}_2$ ), 6.80 (d, 2H Ar), 7.15 (dd, 4H, Ar), 7.36 (t, 3H, Ar), IR(KBr,  $\text{cm}^{-1}$ ): 3015 (CH aryl), 2978 ( $\text{CH}_2\text{CH}_2$ ), 1590 (C=C Ar), 1285 (C-O aryl ether), 1115 (C-O alkyl ether), 790 (C-Br) Anal. Calcd. for  $\text{C}_{27}\text{H}_{29}\text{O}_3\text{Br}$ : C 67.36 H 6.07; found C 66.82 H 5.79.

#### Synthesis of ligand $L_2$

4.11 g (0.01 mol) of L were dissolved in 400 mL of dry THF in the presence of 0.02 mol of  $\text{KOC}(\text{CH}_3)_3$  under similar condition to synthesize  $L_1$ , 4.58 g (0.01 mol) of triethyleneglycol ditosylate  $Z_2$  in 75 mL of THF was then added to the dihydroxy L solution and refluxed for

**Table 1: Characteristic IR Bands of the Ligands and their Complexes as KBr pellets ( $\text{cm}^{-1}$ ).**

Molecular Formula	C-H Aryl	CH <sub>2</sub> -CH <sub>2</sub>	C=C Arom	C-O Aryl ether	C-O	C-Br
C <sub>27</sub> H <sub>29</sub> BrO <sub>3</sub> (L <sub>1</sub> ) (A <sub>1</sub> )	3015	2978	1590	1285	1115	790
C <sub>29</sub> H <sub>33</sub> BrO <sub>4</sub> (L <sub>2</sub> ) (A <sub>2</sub> )	3016	2965	1595	1255	1120	810
C <sub>31</sub> H <sub>37</sub> BrO <sub>5</sub> (L <sub>3</sub> ) (A <sub>3</sub> )	3014	2970	1580	1275	1110	800
Complexes	C-O aryl ether	C-O alkyl ether		ClO <sub>4</sub> <sup>-</sup>	C-Br	
(L <sub>2</sub> )-KClO <sub>4</sub>	1300-1270	1120		1080	800	
(L <sub>2</sub> )-NaClO <sub>4</sub> ·H <sub>2</sub> O	1280	1125		1080	750	
(L <sub>3</sub> )-KClO <sub>4</sub>	1300	1140		1080	720	

**Table 2: Characteristic IR Bands of dihydroxy compound L and ditosylate derivatives Zn ( $\text{cm}^{-1}$ ).**

Compound	Ar-OH	-CH <sub>2</sub> -	-C=C- arom.	C-Br
C <sub>23</sub> H <sub>23</sub> O <sub>2</sub> Br (L)	3250	2865	1560	815
Compound	C-H aryl	-CH <sub>2</sub> -CH <sub>2</sub> -	C=C aryl	C-O alkyl
C <sub>18</sub> H <sub>22</sub> O <sub>7</sub> S <sub>2</sub> (Z <sub>1</sub> )	3040	2980-2930	1550	1150
C <sub>20</sub> H <sub>26</sub> O <sub>8</sub> S <sub>2</sub> (Z <sub>2</sub> )	3040	2970-2930	1550	1110
C <sub>22</sub> H <sub>30</sub> O <sub>9</sub> S <sub>2</sub> (Z <sub>3</sub> )	3035	2980-2940	1500	1135

**Table 3: The colors, yields, melting points and analytical results of the ligands and Three Complexes.**

Molecular Formula	Yield (%)	Color	mp °C	Calc. (Found) %	
				C	H
C <sub>27</sub> H <sub>29</sub> BrO <sub>3</sub> (L <sub>1</sub> )	21	Dark Brown	225	67.36 (66.82)	6.07 (5.79)
C <sub>29</sub> H <sub>33</sub> BrO <sub>4</sub> (L <sub>2</sub> )	27	Brown	220	66.29 (66.09)	6.33 (5.99)
C <sub>31</sub> H <sub>37</sub> BrO <sub>5</sub> (L <sub>3</sub> )	22	Brown	210	65.38 (65.12)	6.55 (6.89)
C <sub>23</sub> H <sub>23</sub> BrO <sub>2</sub> (L)	80	Brown	120	67.16 (66.85)	5.64 (5.30)
C <sub>18</sub> H <sub>22</sub> O <sub>7</sub> S <sub>2</sub> (Z <sub>1</sub> )	59	White	97-98	52.16 (51.85)	5.35 (5.54)
C <sub>20</sub> H <sub>26</sub> O <sub>8</sub> S <sub>2</sub> (Z <sub>2</sub> )	71	White	77-78	52.39 (52.08)	5.31 (5.44)
C <sub>22</sub> H <sub>30</sub> O <sub>9</sub> S <sub>2</sub> (Z <sub>3</sub> )	64	White	65-69	52.52 (51.80)	6.02 (5.90)
C <sub>29</sub> H <sub>33</sub> BrClKO <sub>8</sub> (L <sub>2</sub> )-KClO <sub>4</sub>	36	White	270	52.45 (52.10)	5.01 (4.96)
C <sub>29</sub> H <sub>35</sub> BrClNaO <sub>9</sub> (L <sub>2</sub> )-NaClO <sub>4</sub> ·H <sub>2</sub> O	36	White	285	52.30 (52.15)	5.30 (5.65)
C <sub>31</sub> H <sub>37</sub> BrClKO <sub>9</sub> (L <sub>3</sub> )-KClO <sub>4</sub>	49	White	290	52.58 (52.30)	5.27 (5.10)

**Table 4: <sup>1</sup>H NMR Data for the Ln in CHCl<sub>3</sub>\* n: 1, 2, 3.**

Comp.	C(CH <sub>3</sub> ) <sub>3</sub>	PhCH <sub>2</sub> Ph	PhOCH <sub>2</sub>	CH <sub>2</sub> OCH <sub>2</sub>	H (ArH)	H (ArH)	H (ArH)	ArOH
C <sub>27</sub> H <sub>29</sub> O <sub>3</sub> Br (A <sub>1</sub> )	1.29 s (9H,s)	3.75 s (2H,s)	3.90 t (4H,t)	4.18 t (4H,t)	6.80 d (2H,d)	7.15 dd (4H,dd)	7.36 m (3H,t)	-----
C <sub>29</sub> H <sub>33</sub> O <sub>4</sub> Br (A <sub>2</sub> )	1.25 s (9H,s)	3.65 s (2H,s)	3.90 t (4H,t)	4.10 t (4H,t)	6.85 d (2H,d)	7.10 dd (4H,dd)	7.36 m (3H,m)	-----
C <sub>31</sub> H <sub>37</sub> O <sub>5</sub> Br (A <sub>3</sub> )	1.30 s (9H,s)	3.80 s (2H,s)	3.95 t (4H,t)	4.15 t (4H,t)	6.75 d (2H,d)	7.20 dd (4H,dd)	7.40 m (3H,m)	-----
C <sub>23</sub> H <sub>23</sub> O <sub>2</sub> Br	1.20 s (9H,s)	3.50 s (2H,s)	-----	-----	-----	7.10 dd (4H,dd)	7.36 m (5H,m)	5.78 s (2H,s)

50 hours. The crude product was crystallized from 40 % ethanol-water mixture with yield of 1.40 g. (Yield 26 %, m.p. 220 °C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.25 {s, 9H,  $\text{C}(\text{CH}_3)_3$ }, 3.65 (s, 2H,  $\text{CH}_2$ ), 3.90 (t, 4H,  $\text{OCH}_2$ ), 4.10 (t, 8H,  $\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ ); 6.85 (d, 2H, ArH), 7.15 (dd, 4H, ArH), 7.36 (m, 4H, ArH), IR(KBr,  $\text{cm}^{-1}$ ): 3016 (C-H Aryl), 2965 ( $-\text{CH}_2$ ), 1595 (C=C Ar), 1255 (C-O aryl ether), 1120 (C-O alkyl ether), 810 (C-Br) Anal. calcd for  $\text{C}_{29}\text{H}_{33}\text{O}_4\text{Br}$ : C 66.29; H 6.33 found C 66.02; H 5.99.

### Synthesis of ligand $\text{L}_3$

4.11 g (0.01 mol) of L were dissolved in 400 mL of dry THF in the presence of 2.24 g (0.02 mol) of  $\text{KOC}(\text{CH}_3)_3$ , 5.02 g (0.01 mol) of tetraethylene glycol ditosylate  $\text{Z}_3$  in 75 mL of THF were then added gradually to the dihydroxy L solution and refluxed for 50 hours. The crude product was crystallized from 40 % ethanol-water mixture with 1.25 g (Yield 22 %, m.p. 210 °C,  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 1.30 {s, 9H,  $(\text{CH}_3)_3$ }, 3.80 (s, 2H,  $\text{CH}_2$ ), 3.95 (t, 2H,  $\text{OCH}_2$ ), 4.15 (t, 12H,  $\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2$ ), 7.20 (dd, 4H, ArH), 7.40 (m, 4H, ArH) 6.75 (d, 2H, ArH), IR(KBr,  $\text{cm}^{-1}$ ): 3014 (CH aryl), 2970 ( $\text{CH}_2\text{CH}_2$ ), 1580 (C=C Ar), 1275 (C-O aryl ether), 1110 (CO alkyl ether); 800 (C-Br) Anal. Calcd. for  $\text{C}_{31}\text{H}_{37}\text{O}_5\text{Br}$ : C 65.38 H 6.25 found C 65.12 H 5.89

### Synthesis of diethylene glycol ditosylate $\text{Z}_1$

10.6 g (0.1 mol) of diethylene glycol were added to 80 mL of freshly distilled pyridine and continuously stirred by a mechanical stirrer at -12 °C. 38.2 g (0.2 mol) of p-toluene sulfonyl chloride were then added gradually to the diethylene glycol solution for 4 hours at -7 °C. The crude product Z was washed with ice-water, water-methanol and crystallized from ethanol.

### Synthesis of triethylene glycol ditosylate $\text{Z}_2$

15.0 g (0.1 mol) of triethyleneglycol, 38.2 g (0.2 mol) of the tosylchloride and 100 mL of pyridine were used. This reaction was carried out similar to the synthesis of the  $\text{Z}_1$  and the product  $\text{Z}_2$  was crystallized from ethanol.

### Synthesis of tetraethylene glycol ditosylate $\text{Z}_3$

This compound was synthesized also similar to the synthesis of the  $\text{Z}_1$ . Accordingly, 19.4 g (0.1 mol) of tetraethylene glycol, 38.2 g (0.2 mol) of p-toluene

sulfonyl chloride and 100 mL of pyridine were used for this reaction. Tosyl chloride was added gradually for 4 hours. The product was different from the other ditosylate derivatives, because it is lipoidic. Therefore, the product was crystallized by using a different method from the others. First, the mixture was added to an ice-HCl solution and water phase was then extracted with chloroform. The collected chloroform layers were washed with  $\text{Na}_2\text{CO}_3$  and dried on  $\text{Na}_2\text{SO}_4$ . The chloroform was evaporated and the product  $\text{Z}_3$  was obtained in the form of lipoid.

Preparation of the complex of  $\text{L}_2$  with  $\text{KClO}_4$ :

5 mL of 0.1 M aqueous solution of  $\text{KClO}_4$  and 5 mL of 0.1 M ( $\text{L}_2$ ) in ethanol were mixed. The crystals were filtered and washed with ethanol-water (1:1), then dried in a stove at 75 °C.

Preparation of the complex of  $\text{L}_2$  with  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  :

5 mL of 0.1 M  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  in ethanol and 5 mL of 0.1 M ( $\text{L}_2$ ) in ethanol were mixed. The crystals were filtered, washed with ethanol, and dried in a stove at 100 °C.

Preparation of the complex of  $\text{L}_3$  with  $\text{KClO}_4$  :

5 mL of 0.1 M aqueous solution of  $\text{KClO}_4$  and 5 mL of 0.1 M ( $\text{L}_3$ ) in ethyl acetate were mixed and allowed to stand for three days. The crystals were separated, washed with ethanol, and dried in a stove at 80 °C.

## RESULTS AND DISCUSSION

The macrocyclic ligands ( $\text{L}_1$ ,  $\text{L}_2$ ,  $\text{L}_3$ ) were synthesized according to the Williamson-type ether synthesis. We firstly performed the reaction of diethyleneglycol, triethyleneglycol and tetraethyleneglycol with p-toluene sulfonyl chloride to obtain their corresponding ditosylate derivatives  $\text{Z}_1$ ,  $\text{Z}_2$  and  $\text{Z}_3$  [23]. The 2,2'-dihydroxy-3-bromo-5-phenyl-5-tert-butyl diphenyl methane was used as a dihydroxy compound and synthesized by condensation of 2-bromo-4-phenyl-6 (hydroxyl methyl) phenol and p-tert-butyl phenol in the presence of HCl as a catalyst (m.p. 120-125 °C with decomposition). 2-Bromo-4-phenyl-6(hydroxyl methyl) phenol was synthesized by the reaction of the 2-bromo-4-phenyl phenol with formaldehyde [24].

Polymerization was inhibited by using both highly diluted reagent solutions and longer reaction time. All the reactions were performed under nitrogen atmosphere. Therefore, the yield was increased in comparison to

previously reported procedure [25]. The ability of complexation of the related ligands (**L**<sub>2</sub> and **L**<sub>3</sub>) with NaClO<sub>4</sub>·H<sub>2</sub>O and KClO<sub>4</sub> was then investigated, respectively. It was observed that the studied ligands could form complexes with NaClO<sub>4</sub>·H<sub>2</sub>O and KClO<sub>4</sub>.

The molecular structures of the novel macrocyclic compounds and related alkaline metal complexes were characterized by elemental analyses, IR and <sup>1</sup>H NMR techniques. Characteristic IR bands of these compounds are listed in table 1 and <sup>1</sup>H NMR data are shown in table 4. These values provide supporting evidence for our proposed structures. The molecular formulas, yields, colors, melting points and analytical data of the intermediate ligands and three complexes are shown in table 3.

In this work, attempts have not been made to determine the coordination number, or investigate the stereo chemical properties of the synthesized complexes. The aim of these syntheses was to examine their possible applications to metal-binding processes and we do believe that these polyether derivatives could be successively used in separating racemic mixtures and removal of small quantities of potentially harmful solutes or metal ions. Even though enormous crown ether derivatives and their complexes have been already described, many more interesting systems of this type surely await discovery. These cyclic polyether structures are found to be powerful tools for defining interesting features related to general chemistry and application. The main objective of the present study is to prepare such complexes (**L**<sub>2</sub>, **L**<sub>3</sub> with Na<sup>+</sup>, K<sup>+</sup>), and we believe that the study can be useful for further studies that can deal with the elucidation of main interactions between selected ligands and studied alkali metals, e.g. those in phase-transfer reactions.

The characterization of all compounds is mainly based on <sup>1</sup>H NMR studies. In the <sup>1</sup>H NMR studies, sharp and singlet peaks of the phenolic -OH groups in the starting material **L** are observed at δ 5.78 and this situation supports that the proposed structure for the starting material **L** is corrected as shown in Scheme 2. But the same peaks are not seen around δ 5-5.9 ppm for ligands **L**<sub>1</sub>, **L**<sub>2</sub> and **L**<sub>3</sub>. This situation indicates that proposed molecular formulas of ligands **L**<sub>1</sub>, **L**<sub>2</sub> and **L**<sub>3</sub> are corrected as shown in Scheme 1. At the same time, the proposed structures for ligands **L**<sub>1</sub>, **L**<sub>2</sub> and **L**<sub>3</sub> are also

corrected owing to the new peaks of cyclic ether groups (-OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>O-) around 4-4.5 ppm. Multiplet aromatic C-H protons are observed at 6.75-7.40 ppm for macrocyclic ligands **L**<sub>1</sub>, **L**<sub>2</sub> and **L**<sub>3</sub>, on the other hand singlet protons of tert-butyl and Ph-CH<sub>2</sub>-Ph are seen at 1.20-1.30 ppm and 3.50-3.75 ppm, respectively. Most of the phenolic groups with FeCl<sub>3</sub> form the complex product in blue, red, etc. Applying this test to the ligands **L**<sub>1</sub>, **L**<sub>2</sub> and **L**<sub>3</sub> has yielded no change in color, this situation indicates the absence of phenolic OH groups in the ligands. Then the complexation ability of the selected ligands **L**<sub>2</sub> and **L**<sub>3</sub> with suitable alkaline metal salts is investigated and obtained data are shown in tables 1 and 3.

In the IR spectra, characteristic aliphatic ether stretching band of the ligands **L**<sub>1</sub>, **L**<sub>2</sub> and **L**<sub>3</sub> is seen strongly around 1115-1120 cm<sup>-1</sup>, on the other hand absorptions of the aromatic OH group of compound **L** are assigned between 3200-3250 cm<sup>-1</sup> as broad bands. Especially, no band is observed in the region 3200-3500 cm<sup>-1</sup> attributable to the stretching vibration of the free phenolic hydroxy group for macrocyclic ligands **L**<sub>1</sub>, **L**<sub>2</sub> and **L**<sub>3</sub>, therefore this situation shows that all the phenolic hydroxy group are consumed during reaction. At the same time, characteristic IR band of the (C-Br) bond stretching are also seen around 790-810 cm<sup>-1</sup>. IR spectral data of the complexes are in accordance with IR spectra of the selected ligands, but the ether bands in the complexes are expanded compared to the ligands, it is thought that the expanding of the ether bands resulted from both the ring stretching and ClO<sub>4</sub><sup>-</sup> anion peak at 1090 cm<sup>-1</sup>.

The vibrations at 1090 and 635 cm<sup>-1</sup> of ClO<sub>4</sub><sup>-</sup> anions indicate that the ClO<sub>4</sub><sup>-</sup> anions are not coordinated to the metal cations. On the other hand, this situation is thought to have some relation with the etheric oxygen atoms that have interaction ability with alkali metal to form complexes. Furthermore, the low chemical shifts of the corresponding aromatic protons strongly support the reactions of complexation as stated above. This situation indicates that the oxygen of aliphatic ether groups must be coordinated to the metal ion. On the basis of the elemental analyses of the complexes, it is found that the metal to ligand ratio is 1:1 and the metal cations are inserted in the crown moiety of the ligands as host-guest instead of sandwich type interactions. All these data confirmed the proposed chemical formulas of all

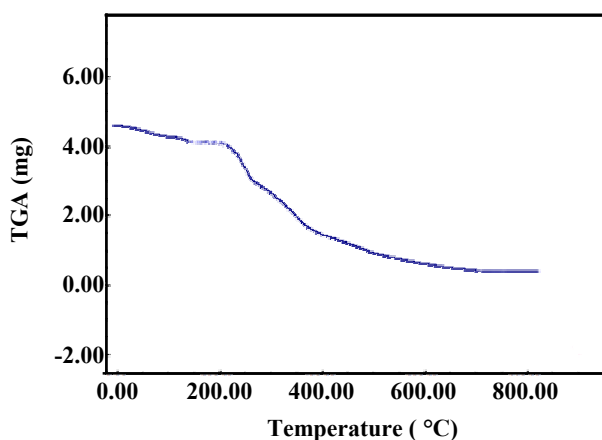


Fig. 1: The TGA curve of the complex of ligand  $L_2$  with  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ .

structures. For the sake of getting more information about the thermal stability of the obtained complexes, DSC-TGA is performed. The thermal decomposition of the complex  $L_2 \cdot \text{NaClO}_4 \cdot \text{H}_2\text{O}$  takes place via two steps (Fig. 1). The first loss, located in the range of 20-140 °C, is attributed to the evolution of water molecules, leading to a total weight loss of about 9.73 % (cacl. 10.11 %). The dehydration processes are interpreted by an endothermic peak in the DSC curve, at the same time, the DSC curve presents a melting process at 288.5 °C by the exothermic peak for the complex of the  $L_2$  with  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$  as shown in Fig. 2. The complex is decomposed completely between 190 and 697 °C. The experimental values for the mass loss in this stage are 70.39 % and 85.58 %, while the calculated values are 73.40 % and 85.42 %, respectively. When the temperature is above 697 °C, the TGA curve presents a platform, implying there is no weight changing in this range.

## CONCLUSIONS

In this work, three new macrocyclic polyethers are synthesized and their appropriate alkaline metal complexes prepared. Chemical formulas of all compounds are established by spectroscopic techniques and elemental analyses. It is thought that this complexation ability of selected ligands with appropriate alkaline metals could be useful, especially in extraction studies, and the cavity of the crown moiety is a crucial aspect for this aim. In the next study, these ligands will be used in an extraction process for selective transfer of alkali and alkaline-earth metal cations at different pH values.

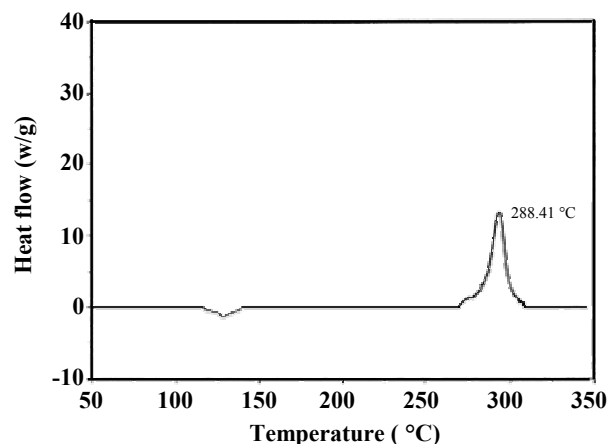


Fig. 2: The DSC curve of the complex of ligand  $L_2$  with  $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ .

**Caution:** Although in these experiments no accidents have occurred, but extreme care should be taken when perchlorates are handled, because they may explode spontaneously and may be sensitive to a shock. The perchlorates should only be prepared in small quantities.

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