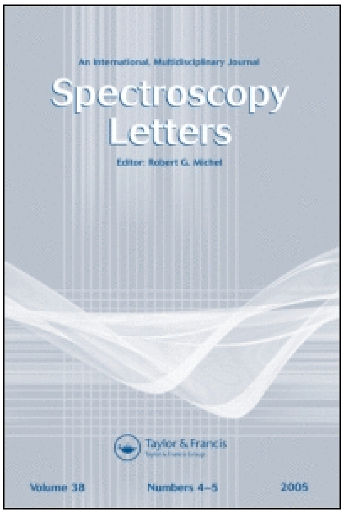

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Hamdi Temel[a]; Halil Hosgören[b]; Mustafa Boybay[c]
[a] Department of Chemistry, Faculty of Education, University of Dicle, Diyarbakir, Turkey
[b] Department of Chemistry, Faculty of Arts and Sciences, University of Dicle, Diyarbakir, Turkey
[c] Department of Chemistry, Faculty of Arts and Sciences, University of Firat, Elazig, Turkey

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SYNTHESIS AND CHARACTERIZATION OF Na^+, K^+, Ca^{2+}, Ba^{2+}, Sr^{2+}, AND Pb^{2+} COMPLEXES WITH SOME LIPOPHILIC DIAZA-18-CROWN-6 DERIVATIVES

Hamdi Temel,[1] Halil Hosgören,[2] and Mustafa Boybay[3]

[1]Department of Chemistry, Faculty of Education, and
[2]Department of Chemistry, Faculty of Arts and
Sciences, University of Dicle, Diyarbakir
[3]Department of Chemistry, Faculty of Arts and
Sciences, University of Firat, Elazig, Turkey

ABSTRACT

In this study, the complexes of 7,16-Dibenzyl-4,7,10,13-tetraoxa-7,16-diazacyclooctadecane; 7,16-Dihexzyl-4,7,10,13-tetraoxa-7,16-diazacyclooctadecane; 7,16-Diheptyl-4,7,10,13-tetraoxa-7,16-diazacyclooctadecane; 7,16-Dioctyl-4,7,10,13-tetraoxa-7,16-diazacyclooctadecane; 7,16-Dinonyl-4,7,10,13-tetraoxa-7,16-diazacyclooctadecane; 7,16-Didodecyl 4,7,10,13-tetraoxa-7,16-diazacyclooctadecane with Na^+, K^+, Ca^{2+}, Ba^{2+}, Sr^{2+} and Pb^{2+} were prepared by using perchlorates salts. Their complexes were produced by adding the solution of metal salts in ethyl alcohol to the solution of ligand in ethyl alcohol. The complexes obtained were filtered and washed with ethyl alcohol and recrystallizied in ethyl alcohol and dried in vacuum. Their complexes were investigated by using Elemental Analysis, and infrared (IR). Observed ^1H NMR,

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^{13}C NMR, and ^{13}C chemical shifts are discussed in terms of conformational changes of the macrocycle.

Key Words: IR; $^{1}H/^{13}C$ NMR diazamacrocycles; Metal complexes

INTRODUCTION

The coordination chemistry of alkali metals is an important, growing branch of inorganic and organometallic chemistry. Although a few examples of cyclic polyethers had been known in the literature before the work of Pedersen, it was he who synthesized numerous compounds of this type and showed their ability to complex cations, both alkali metals and others[1,2]. Hundreds of alkali metal cation complexes of macrocyclic polyethers and related ligands have been synthesized and thoughly investigated over the last two decades[3]. The complexation of alkali or alkaline earth ions by dibenzo-crown ether compounds has been largely described as well as the factors affecting the formation[4]. Since alkali metal and alkaline-earth metal cations play an important role in biological systems, a detailed study of the complexation of alkaline-earth ions appears to be promising[5].

After metal-diazapolyoxa macrocycle complexes optained by Lehn[6] the azacrown compounds have received considerable attention because of their ability to complex a variety of metal and organic cations and anions[7,8]. In general preferential complexation results when the relative sizes of the cation and ligand cavities are matched[9–13]. In addition, the azacrown are important intermediates for the synthesis of the criptands and the nitrogen pivot lariat crown ethers[14]. They have important uses as synthetic receptors in molecular recognition processes, as catalysts in nucleophilic substitution and oxidation reactions[15,16] and in design of chromogenic reagents which are sensitive to alkali and alkaline earth cations. In addition, they have anion complexation properties which are similar to those found in certain biological systems[17].

The aim of our study is to synthesize metal complexes of crown ethers with Na^{+}, K^{+}, Ca^{2+} , Ba^{2+}, Sr^{2+} and Pb^{2+} cations.

EXPERIMENTAL

The chemicals were obtained from FLUKA unless otherwise cited. Ligands were recently synthesis by Hosgören[18]. A solution of $M^{+n}(ClO_4)_n$ (0.50 mmol) in ethyl alcohol (2 mL) added dropwise to solution of diazacrown (0.50 mmol) in ethyl alcohol (2 mL). The mixture was stirred at room

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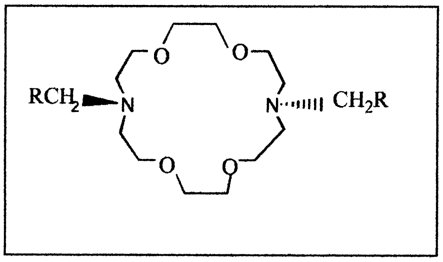
temperature over 24 h. The precipitated solid complex was filtered, washed with ethyl alcohol and recrystallized from ethyl alcohol and then dried in vacuum. Structural data of complexes with the elemental analyses performed on a Carlo Erba model 1200 instrument are given as Structure I and Table 1.



Comp	R
I	C_6H_5
II	C_5H_{11}
III	C_6H_{13}
IV	C_7H_{15}
V	C_8H_{17}
VI	$C_{11}H_{23}$

Structure I.

The melting points are uncorrected. IR spectra of the complexes were recorded with a Midac 1700 instrument in KBr pellets. ^1H and ^{13}C NMR spectra at 200 MHz and 50.2 MHz respectively as well as the 2D spectra and decoupling experiments of the free and complexed macrocycles were recorded on a BRUKER-AC spectrometer in $CDCl_3$ and reported in ppm (δ) from internal TMS. The elemental analyses were conducted on Carlo Erba instrument.

RESULTS AND DISCUSSION

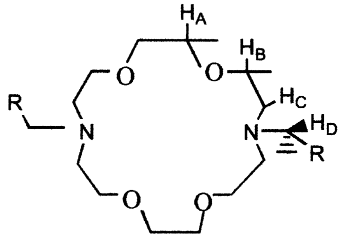
The IR spectra of the complexes clearly demonstrated that the COC and CCO stretching vibrations are altered compared to ligands due to conformational changes[19]. The ν(R-O-R) absorption is shifted to lower wave numbers in complexes providing another evidence of complexing[20]. IR spectra of the complexes of 3300–3400, 1650–1660 and 560–570 cm^{-1} regions are due to ν(OH), δ(HOH) and ρ(HOH), respectively, indicating the coordinated water molecules[21]. Accordingly, the IR bonds due to (ClO_4^-) is found at 620–630 cm^{-1}. The band at 1110 cm^{-1} due to $\nu(ClO_4)^-_{asym}$ overlaps the ν(COC) which is found at roughly the same frequency[22], Structure II and Table 2.

Table 1. Structural Data of Metal-Diazamacrocycles Complexes

	Complex Formula	M.p.°C	Yield	Calculated/ C%	Found H%	%N
I	$C_{26}H_{40}N_2O_9ClNa$	102–104	88	53.56	6.89	4.83
				53.59	6.88	4.81
I	$C_{26}H_{38}N_2O_8ClK$	118–120	10	53.75	6.55	4.82
				53.78	6.60	4.75
I	$C_{26}H_{40}N_2O_{13}Cl_2Ba$	265–270*	64	39.19	5.06	3.52
				39.20	4.99	3.57
I	$C_{26}H_{42}N_2O_{14}Cl_2Ca$	225–230*	36	43.75	6.45	3.92
				43.80	6.42	3.90
I	$C_{78}H_{124}N_2O_{25}Cl_2Pb$	104–106	36	50.87	6.85	4.57
				50.85	6.81	4.60
II	$C_{24}H_{50}N_2O_4Cl_2Ba$	215–217	23	35.59	6.57	3.65
				35.63	6.50	3.60
III	$C_{26}H_{54}N_2O_4Cl_2Ba$	162–163	62	38.42	6.89	3.44
				38.45	6.92	3.43
IV	$C_{28}H_{60}N_2O_{13}Cl_2Ba$	158–160	65	40.00	7.14	3.33
				40.09	7.16	3.30
IV	$C_{28}H_{60}N_2O_9ClNa$	26–28	24	53.63	9.58	4.47
				53.66	9.60	4.50
V	$C_{30}H_{64}N_2O_{13}Cl_2Ba$	104–106	24	41.47	7.37	3.22
				41.51	7.40	3.20
VI	$C_{36}H_{76}N_2O_9ClNa$	88–89	87	58.49	10.29	3.79
				58.48	10.34	3.75
VI	$C_{38}H_{74}N_4O_4S_2K_2$	66–67	10	57.57	9.34	7.07
				57.52	9.38	7.02
VI	$C_{36}H_{76}N_2O_{13}Cl_2Ba$	171–173	43	45.37	10.98	2.94
				45.37	10.99	2.97
VI	$C_{36}H_{74}N_2O_{12}Cl_2Ca$	67–70	11	50.52	8.89	3.27
				50.55	8.87	3.28
VI	$C_{36}H_{74}N_2O_{12}Cl_2Pb$	25–27	40	53.93	9.24	3.49
				53.90	9.28	3.45

*Decompose [I]7,16-Dibenzyl-4,7,10,13-tetraoxa-7,16-diazacyclooctadecane, [II]7,16-di hexzyl-4,7-,10,13-tetraoxa-7,16-diazacyclooctadecane, [III]7,16-Diheptyl-4,7,10,13-tetraoxa-7,16-iazacyclo-octadecane, [IV]7,16-Dioctyl-4,7,10,13-tetraoxa-7, 16-diazacyclo-octadecane, [V]7,16-Dinonyl-4,7,10,13-tetraoxa-7,16-diazacyclooctadecane, [VI]7,16-Dido-decyl-4,7,10-,13-tetraoxa-7,16-diazacyclooctadecane.

In the NMR spectroscopy of the macrocycles and N-substituted methylene protons in alkyl chains were assigned by means of selective heteronuclear decoupling experiments and 2D-HETCOR spectroscopy, Tables 3 and 4.



Structure II.

Table 2. Stretching Vibrations of COC(asym) and CCO(sym) in Metal Complexes

Crown	Salt	COC_{asim}	CCO_{asim}	COC_{sim}	CCO_{sim}
I		1121.5	1105.3	994.8	939.28
I	$NaClO_4{\cdot}H_2O$	1102.2	1036.1	975.16	935.2
$\Delta\nu(cm^{-1})$		19.3	69.2	19.64	4.08
I	$Ba(ClO_4)_2{\cdot}H_2O$	1093.5	1063.5	981.7	917.09
$\Delta\nu(cm^{-1})$		28	41.8	13.1	22.09
I	$Pb(ClO_4)_2{\cdot}3\ H_2O$	1097.9	1036.6	973.03	934.77
$\Delta\nu(cm^{-1})$		23.5	68.7	21.77	4.51
II		1127.7	1078.6	995.24	921.92
II	$Ba(ClO_4)_2{\cdot}H_2O$	1103.2	1035.7	961.45	903.32
$\Delta\nu(cm^{-1})$		24.5	42.9	33.79	18.6
III		1127.7	1078.6	995.24	921.92
III	$Ba(ClO_4)_2{\cdot}H_2O$	1103.2	1035.7	961.45	903.32
$\Delta\nu(cm^{-1})$		24.5	42.9	33.79	18.6
IV		1127.8	1074.1	989.22	932.18
IV	$Ba(ClO_4)_2{\cdot}H_2O$	1109.9	1051.1	955.19	931.6
$\Delta\nu(cm^{-1})$		17.9	23	34.04	0.58
IV	$NaClO_4{\cdot}H_2O$	1106.25	1028	975.21	928.67
$\Delta\nu(cm^{-1})$		21.25	46.1	14.01	3.51
IV	$Ca(ClO_4)_2{\cdot}H_2O$	1104.1	1000	962.51	912.27
$\Delta\nu(cm^{-1})$		23.7	74.1	26.77	19.91
V		1127.8	1074.1	989.22	932.18
V	$Ba(ClO_4)_2{\cdot}H_2O$	1096.4	1000	960.49	894.21
$\Delta\nu(cm^{-1})$		31.4	74.1	28.73	37.97
VI		1120.8	1096.7	980.57	945.65
VI	$NaClO_4{\cdot}H_2O$	1099.3	1042	967.64	936.68
$\Delta\nu(cm^{-1})$		21.5	54.7	12.93	8.97
VI	$Ba(ClO_4)_2{\cdot}H_2O$	1099.1	1063	972.49	944.27
$\Delta\nu(cm^{-1})$		21.7	33.7	8.08	1.38
VI	$Pb(ClO_4)_2{\cdot}3H_2O$	1101.2	1040.8	967.49	937.9
$\Delta\nu(cm^{-1})$		19.6	55.9	13.02	7.75

Table 3. Proton Chemical Shifts (δ) of the Free Diazamacrocycles and with NaClO$_4$ in ppm

	Ligand		Complex		Δδ	
Proton	I	VI	I	VI	I	VI
H$_D$	2.84	2.76	2.71	2.67	−0.13	−0.09
H$_B$	3.64	3.60	3.60	3.58	−0.04	−0.02
H$_A$	3.62	3.61	3.50	3.68	−0.12	+0.07
H$_C$	3.70	2.47	3.62	2.53	−0.08	+0.06
Ph	7.39–7.23	–	7.28–7.08	–	−0.11/0.15	–

Table 4. ^{13}C Chemical Shifts (δ) of Diazamacrocycles and Complexes in ppm in CDCl$_3$

	Ligand		NaClO$_4$ Complex		Δδ		Ligand	BaClO$_4$·H$_2$O Complex	Δδ
	I	VI	I	VI	I	VI	IV	IV	IV
C-1	72.75	72.75	70.61	70.56	−2.14	−2.19	72.67	72.00	−0.67
C-2	72.11	72.06	69.22	68.83	−2.89	−3.23	71.98	70.45	−1.53
C-3	62.03	59.00	60.75	56.04	−1.28	−2.96	57.97	53.56	−4.41
C-4	55.86	55.86	54.42	54.62	−1.44	−1.24	55.91	53.49	−2.42

The ^{1}H NMR spectra of Diazamacrocyclic in CDCl$_3$ consist of multiplet, in the ether region at about 2.5–3.5 ppm down field from Me$_4$Si and another multiplet due to aromatic protons at about 7.2–7.3 ppm down field from Me$_4$Si(for I). In I and VI, methylene proton resonances are shifted higher field by 0.01–0.10 ppm in metal complexes. Likewise, the aromatic proton signals of I are shifted higher field by up to 0.11–.15 ppm, only at VI shift the resonance of H$_A$ and H$_C$ to lower field. The ^{1}H NMR behaviour is best interpreted in terms of an electric field effect. The field effect is observed not only on the methylene protons but also on all aryl protons(for I). In the shift changes depend on the distance of each proton from the complexation site, again supporting this conclusion[23,24].

The ^{13}C chemical shifts should be more useful for deducing conformational variations during metal complexation owing to their more characteristic dependence on stereochemistry[25,26]. The ^{13}C chemical shifts involving the conformational changes due to complexing are moved to higher fields.

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