Inorganic Esters of Ethylene Glycol as Macrocyclic Ligands

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Abstract. Six different inorganic esters of ethylene glycol: $B(OR)_3$, $P(OR)_3$, $OS(OR)_2$, $OP(OR)_3$, $OPH(OR)_2$ and $As(OR)_3$, where $R = CH_2CH_2OCH_3$ were obtained. Their structures were studied by multinuclear NMR. These compounds can complex metal cations and behave like macrocyclic ligands. The influence of metal cation complexation on spectra were investigated by ^1H, ^{13}C, ^{17}O, ^{11}B, ^7Li, ^{87}Rb and ^{31}P NMR.

**Key words:** supramolecular chemistry, inorganic esters of ethylene glycol, macrocyclic ligands

1. Introduction

Polyethylene glycols (**1**) and their derivatives – polyethylene glycols ethers (**2**) are characterized by a CH_2CH_2O fragment. From the supramolecular chemistry point of view these compounds are very similar to open chain-like derivatives of crown ethers (**3**) or fragments of cryptands (**4**), because of the characteristic carbon- carbon- heteroatom fragment (Scheme 1).

For many years extensive studies [1–3] of different kinds of podands have been carried out. From non-cyclic, pentaethylene glycol dimethyl ether to much more complicated open-chain like derivatives and virtually crown ethers or cryptands (tripod ligands) there are very interesting compounds because of cyclization and complexation processes. One of the most important things in these studies is the "end-group" concept relative to the structure and stability of the complex state formed.

If the one of the chains in cryptand is open, the compound with the lariat ether structure (**5**) can be obtained. These compounds can have three identical (**6**) or different (**7**) substituents. In these two examples (**6**) and (**7**) the additional chain is connected to the nitrogen atom. Complexes of these with a variety of cations, including barium, potassium and others were studied by Saenger and his associates [4]. He called these systems "three-legged octopus" molecules and "tripodands", while Vögtle as "non-cyclic cryptands" [1]. There are also known some examples with the oxygen atom in these kinds of compounds (Scheme 2).

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(1)   **(2)**   **(3)**   **(4)**

Scheme 1.

(5)   **(6)**   **(7)**
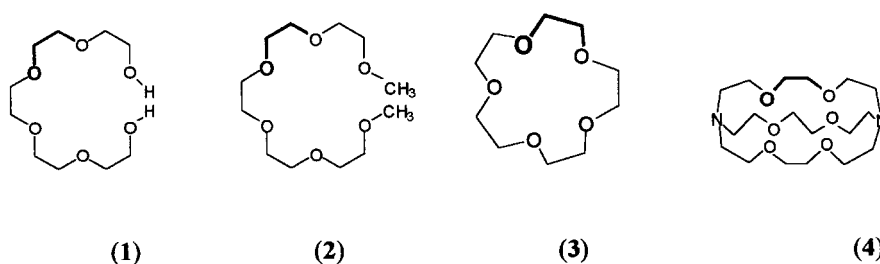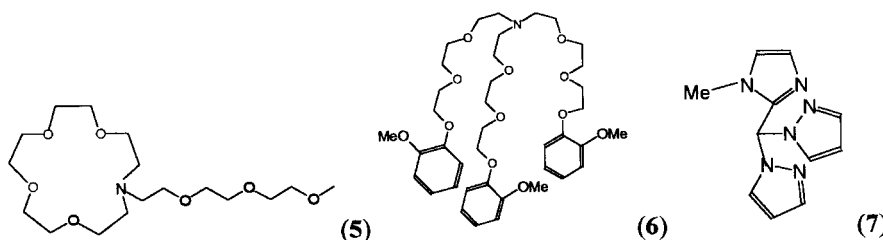
Scheme 2.

Crowns and cryptands have used donor atoms to stabilize cations or other dipolar species when the complexation process occurred and were capable of considerable structural adjustment.

The complexation reaction between acyclic ligands and different alkali metal salts was studied by Landini [5]. They obtained many interesting results. The stability of complexes decrease according to a decrease of the chain length. These results were used during studies on f.e. phase-transfer catalysis, much better than open-chain compounds.

In this paper we present the synthesis and multinuclear NMR studies of new inorganic esters of ethylene glycol as macrocyclic ligands and discuss the complexation process between cations and ligands (Scheme 3).

2. Experimental

Borate (B2) was obtained in the reaction of boric (III) acid (1 mol) with anhydrous ethyleneglycolmonomethylether (3.3 mol). The benzene solutions of these compounds were prepared and heated for about 20 hours in the Dean-Stark apparatus. After removing the solvent, the oily product was distilled under reduced pressure. The yield of this reaction was 65%. B.p. 179–180 °C/20 mm Hg.

Sulphur ester (OS2) was obtained in the reaction between cooled (-10 °C) thionyl chloride (SOCl$_2$) (1 mol) and anhydrous ethyleneglycolmonomethylether (2.2 mol) lasting 10 hours. The mixture was mixed for 5 hours. The obtained products (yield = 93%) were distilled under reduced pressure. B.p. = 182–182 °C/ 2 mm Hg.
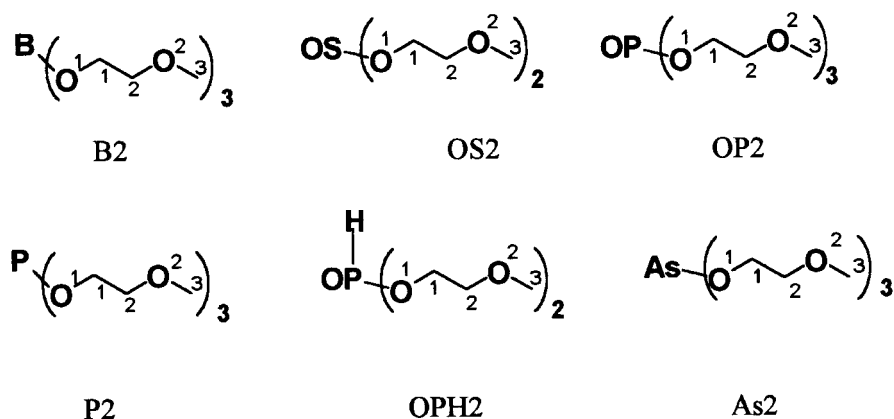
Scheme 3.

Trialkylphosphate (V) (OP2) – under reduced pressure (200 mm Hg) the mixture (anhydrous ethyleneglycolmonomethylether (1.3 mol) and 250 mL xylene) was cooled to -10 °C and phosphorus oxychloride (POCl$_3$) (0.33 mol) was dropped. Afterwards the mixture was heated to 50 °C for 1 hour. The obtained product (yield = 80%) was distilled under pressure. B.p. = 160–163 °C/0.04 mm Hg.

Dialkylphosphate (V) (OPH2) was obtained in the reaction between anhydrous ethyleneglycolmonomethylether (1 mol) and phosphorus trichloride (PCl$_3$) in 250 mL benzene at 0 °C lasting 3 hours. The obtained mixture was heated to boiling for 2 hours (500 mm Hg). Benzene was evaporated, the obtained products were distilled in vacuum. B.p. = 130–132 °C/0.1 mm Hg. Yield = 87%.

Trialkoxyphosphine (III) (P2) was obtained in the reaction between piperidine (1.2 mol) and anhydrous ethyleneglycolmonomethylether (1.2 mol) in 1 L ethyl ether. At -30 °C drop-by-drop addition of phosphorus trichloride (PCl$_3$) (0.33 mol) in 250 mL ethyl ether was started. The obtained mixture was heated to boiling for 2 hours (500 mm Hg). After it the deposit of piperidine hydrochloride was filtered. The ethyl ether was evaporated and the obtained products were distilled in vacuum. B.p. =150–151 °C/0.08. Yield = 95%.

The ester of arsenic acid (III) was obtained in the reaction between arsenic trioxide (0.1 mol) and anhydrous ethylene glycol monomethyl ether (0.32 mol) in 250 mL benzene (about 250 hours). The benzene was distilled. The obtained product was distilled in vacuum and stored in an argon atmosphere. B.p. = 190–192 °C/0.02 mm Hg. Yield = 95%.

2.1. PREPARATIONS OF COMPLEXES

The $1:1$ mixtures of complexes for NMR studies were prepared by dissolving equimolar amounts of the corresponding ligands and anhydrous salts $(0.1 \text{ mol dm}^{-3})$.

2.2. SPECTROSCOPIC MEASUREMENTS

The NMR spectra were recorded using a Varian Gemini 300. All ^{1}H NMR measurements were carried out at operating frequency sfrq = 300.075 MHz; pw = 45°; sw = 4500 Hz; at = 2.0 s; T = 293.0 K and TMS as the internal standard in CD_3OD.

^{13}C NMR spectra were recorded at operating frequency sfrq = 75.454 MHz; pw = 60°; sw = 19000 Hz; at =1.8 s (for complexes of Co^{2+}, Cu^{2+} and Ni^{2+} at = 0.03 s); T = 293.0 K and TMS.

For ^{17}O NMR the following parameters were used: 0.5 M D_2O in CD_3CN, as external standard ($\delta = 0.00$ ppm), 2-butanone as internal standard ($\delta = 558.00$ ppm), sfrq = 40.680 MHz; pw = 85°; sw = 100 kHz; at = 0.03 s; 100 000 scans, T = 348.0 K. The spectra were recorded with sample spinning and without lock.

All ^{11}B NMR measurements were carried out at operating frequency sfrq = 96.276 MHz; pw = 45°; sw = 100 kHz; at = 0.1 s; T = 293.0 K and BF_3*Et_2O in $CDCl_3$ (1 M) as the internal standard in CD_3OD.

For ^{7}Li NMR the following parameters were used: LiCl in D_2O (1 M) as external standard, sfrq = 116.621 MHz; pw = 25°; sw = 20 000 Hz; at = 1.0 s; T = 293.0 K.

For [87]Rb NMR the following parameters were used: $RbBPh_4$ in D_2O (1 M) as external standard, sfrq = 98.181 MHz; pw = 40°; sw = 100 000 Hz; at = 0.02 s; T = 293.0 K.

For ^{31}P NMR the following parameters were used: 85% H_3PO_4 as external standard, sfrq = 121.472, pw = 60°, sw = 50 000 Hz, at = 2 s, T = 293.0 K.

3. Results and Discussion

Multinuclear NMR is employed to define structures and to obtain stability constant of complexes of macrocyclic compounds with metal cations and neutral molecules [6]. Thanks to the properties of many different nuclei (H, C, N, P, B, O) this technique allows us to observe changes taking place not only in ligands, but also changes in the metal nuclei (Li, K., Rb, Cu, Co) during the complexation process.

We used multinuclear NMR to study the complexing-properties of the new ligands: inorganic esters of ethylene glycol. Six different inorganic esters of ethylene glycol: $B(OR)_3$, $P(OR)_3$, $OS(OR)_2$, $OP(OR)_3$, $OPH(OR)_2$ and $As(OR)_3$, where R = $CH_2CH_2OCH_3$ were obtained. The ^{1}H, ^{13}C, ^{17}O, ^{11}B, and ^{31}P NMR spectra for the obtained ligands and complexes were recorded. The NMR results for the ligands and complexes are given in Tables I–VIII.

Table I. ^{1}H NMR chemical shifts (ppm) for ligands

Ligands	C[1]H	C[2]H	C[3]H	P-H
B2	3.64(t)	3.45(t)	3.35(s)	
OS2	4.11(t)	3.60(t)	3.36(s)	
OP2	4.09(m)	3.55(m)	3.32(s)	
P2	3.98(m)	3.56(m)	3.39(s)	
OPH2	4.22(m)	3.61(m)	3.39(s)	6.91(d) J = 712.5 Hz
As2	4.03(m)	3.51(m)	3.44(m)	

Table II. ^{13}C NMR chemical shifts (ppm) for esters and their complexes

Compounds	^{13}C NMR chemical shifts (ppm)		
	C[1]	C[2]	C[3]
B2	62.03	75.11	59.08
B2 + CoCl$_2$	69.65	84.24	64.70
OS2	62.51	71.90	59.10
OS2 + CoCl$_2$	69.80	82.12	68.18
OP2	68.07(d) J^2_{P-C} = 7.2 Hz	72.60(d) J^3_{P-C} = 5.7 Hz	59.54(s)
OP2 + CoCl$_2$	Single very broad line ∼95 ppm		
P2	62.33(d) J^2_{P-C} = 8.2 Hz	72.26(d) J^3_{P-C} = 5.5 Hz	58.82(s)
P2+ CoCl$_2$	Single very broad line ∼100 ppm		
OPH2	63.72(d) J^2_{P-C} = 5.7 Hz	70.54(d) J^3_{P-C} = 5.7 Hz	57.85(s)
OPH2 + CoCl$_2$	Single very broad line ∼95 ppm		
As2	61.3(s)	72.7(s)	57.7(s)
As2 + CoCl$_2$	Very broad line with 2 maxima ∼90 ppm and ∼100 ppm		

Table III. ^{7}Li NMR chemical shifts (ppm) for the lithium salt and its complex with B2 borate

Compounds	^{7}Li NMR chemical shifts (ppm)
LiCl	+0.102
B2 + LiCl	−0.026

Table IV. ^{23}Na NMR chemical shifts (ppm) for the sodium salt and its complex with B2 borate

Compounds	^{23}Na NMR chemical shifts (ppm)
NaBPh$_4$	−2.988
B2 +NaBPh$_4$	−3.812

Table V. [87]Rb NMR chemical shifts (ppm) for the rubidium salt and its complex with B2 borate

Compounds	[87]Rb NMR chemical shifts (ppm)
RbBPh$_4$	−16.9
B2 + RbBPh$_4$	−13.9

According to the ligand structure in ^{1}H NMR spectra we could observe a considerable influence of the hydrogen atom (C^3 carbon atom) on the chemical shift. In ^{13}C NMR spectra for the C^3 carbon atom the chemical shift is in the range from 57 to 59 ppm, while for the C^1 carbon atom it is 61–69 ppm and as in the ^{1}H NMR spectra this situation depends on the ligand structure. The influence of the complex formation between ligands and CoCl$_2$ on the carbon atoms chemical shifts were studied.

We could observe that the obtained complexes moved signals to higher values of chemical shifts and this process applied to all carbon atoms. During the complexation we could also note the self-organization process, all ligand chains surrounding the metal cation could create 4–6 bonds between the oxygen atoms and the metal cation. For example the obtained boron ligand is characterized by strong complexing properties related to the alkali metal cations (Li$^+$, Na$^+$, Rb$^+$). Together with

Table VI. ^{17}O NMR chemical shifts (ppm) for ligands and theirs complexes with CoCl$_2$

Compounds	^{17}O NMR chemical shifts (ppm)		
	O^1.	O^2	O = S
B2	35.4	−29.4	
B2 + CoCl$_2$	−11.2	−59.5	
OS2	140.4	−26.4	178.8
OS2 + CoCl$_2$	136.8	−5.9	211.8

Table VII. ^{11}B NMR chemical shifts (ppm) for B2 borate and its complex with CoCl$_2$

Compounds	^{11}B NMR chemical shifts (ppm)
B2	19.274
B2 + CoCl$_2$	39.371

Table VIII. [31]P chemical shifts (ppm) for ligands and their complexes with CoCl$_2$

Compounds	^{31}P NMR chemical shifts (ppm)
OP2	-0.063(spsp) $^3J_{P-H} = 7.5$, $^4J_{P-H} = 1.6$
OP2 + CoCl$_2$	Signal for ^{31}P was not observed
P2	132.5 (septet) $J^3_{P-H} = 8.4$ Hz
P2 + CoCl$_2$	Signal for ^{31}P was not observed
OPH2	9.30 (dq) $J^1_{P-H} = 712.1$ Hz, $J^2_{P-H} = 9.2$ Hz
OPH2 + CoCl$_2$	Signal for ^{31}P was not observed

increasing of the cation radius we observed higher values of chemical shift changes for the metal cation. This fact indicates an increase of the stability constant of the complexes.

^{17}O NMR is very useful during complexation studies because this technique refers to the heteroatom that is responsible for the formation of chemical bonds with the metal cation. This process was studied for the B2 and OS2 (Table VI). We observed that in the complex B2-Co^{2+} two oxygen atoms (number 1 and 2) were involved in complex formation, while in the complex OS2-Co^{2+} only oxygen atom number 2 and the O=S oxygen atom were responsible for this process. ^{11}B NMR spectra showed a strong influence of the metal ion for the nucleus of the boron atom.

Phosphorus compounds and their complexes are very popular and play a very important part in biochemistry processes. The obtained ligands are characterized with abilities to complex formation with atoms of transition elements. However we could not study this process by ^{31}P NMR, because as a result of the paramagnetic nucleus the resonance signal of ^{31}P could not be observed.

The obtained inorganic esters could complex metal cations and behave like macrocyclic ligands with 4–6 oxygen atoms capable of chemical bond formation.

Acknowledgment

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