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The synthesis and structural studies of a new Kemp's triacid oxaalkyl ester and its complexes with Li^+, Na^+ and K^+ cations

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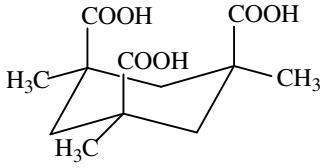
ABSTRACT

A new derivative of Kemp's triacid (KTA) with 2-bromoethyl methyl ether (triester, KTEG1) and its complexes with monovalent cations (Li^+, Na^+ and K^+) have been synthesized and studied by EI MS, multinuclear NMR, FT-IR as well as by the PM5 semiempirical methods. It has been demonstrated that KTEG1 forms stable complexes of 1:1 stoichiometry with the metal cations studied. The mass fragmentation pathways for triester and its complexes are proposed. The FT-IR spectra of the complexes show that in the coordination process no oxygen atoms of the carbonyl groups are involved. The FT-IR and NMR data taken together indicated that the coordination process is realized by the oxygen atoms from the oxaalkyl chains. The structures of the KTEG1 and its complexes with Li^+, Na^+ and K^+ cations are visualized and discussed in detail.

1. Introduction

cis,*cis*-1,3,5-Trimethylcyclohexane-1,3,5-tricarboxylic acid (Kemp's triacid, KTA) was first prepared by Kemp and Petrakis in 1981 year [1] (Scheme 1). Three axially positions of the three carboxylic groups were confirmed by structural studies of some derivatives of KTA [1–3]. Recently, the structures of KTA hydrogen-bonded complexes with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) bases were also investigated by X-ray methods [4,5]. Kemp's triacid was used for selective recognition studies of carboxylate anions [6–9] and its some imide derivatives (*m*-xylenediamine bis(Kemp's triacid imide) as complexones of divalent metal cations such as Zn^{2+}, Co^{2+}, Mg^{2+} [10–18]. KTA complexes with Fe^{+2} were used as models of non-heme iron enzymes [19] and as a porphyrin-linked dicarboxylate ligand in tri-iron complexes [20]. Condensation of Kemp's triacid with aromatic diamines has given new type of ionophore selective toward Hg^{+2} cations [21]. It is interesting to note that crown-ether derivatives of KTA were also investigated as transporters of various metal cations [22,23]. Only a few reports have appeared about triesters of Kemp's triacid. A model substance for the active site of bacteriorhodopsin has been synthesised from Kemp's triacid triethyl ester [24], whereas only tribenzyl ester of KTA has been studied by the X-ray method [25].



Kemp's triacid

Scheme 1. Structure of the Kemp's triacid (KTA).

Our earlier papers have reported formation of complexes between various antibiotics or natural products derivatives containing oxaalkyl moieties and metal cations [26–36]. We have shown that the length of the oxaalkyl chains influences the antibacterial or antifungal activity of the compounds studied [37,38].

In this paper, we report on a new of KTA 2-methoxy-ethyl triester (Scheme 2) synthesized and discuss in detail its structure as well as properties concerning the complexation of Li^+, Na^+ and K^+ cations.

2. Experimental

Kemp's triacid, 2-bromoethyl methyl ether, DBU and respective salts: $LiClO_4$, $NaClO_4$ and $KClO_4$ were commercial product of Aldrich. Because the salts were hydrates it was necessary to dehydrate them by the several evaporations from the mixtures of acetonitrile or benzene with the respective metal salt. CH_3CN and CD_3CN were stored over the 3-Å sieves.

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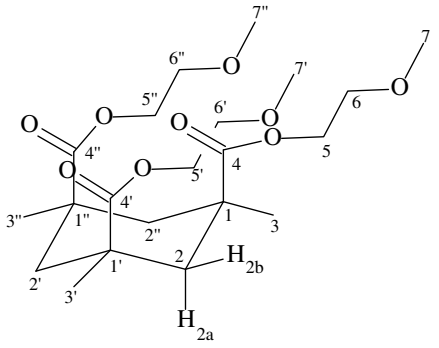


KTEG1

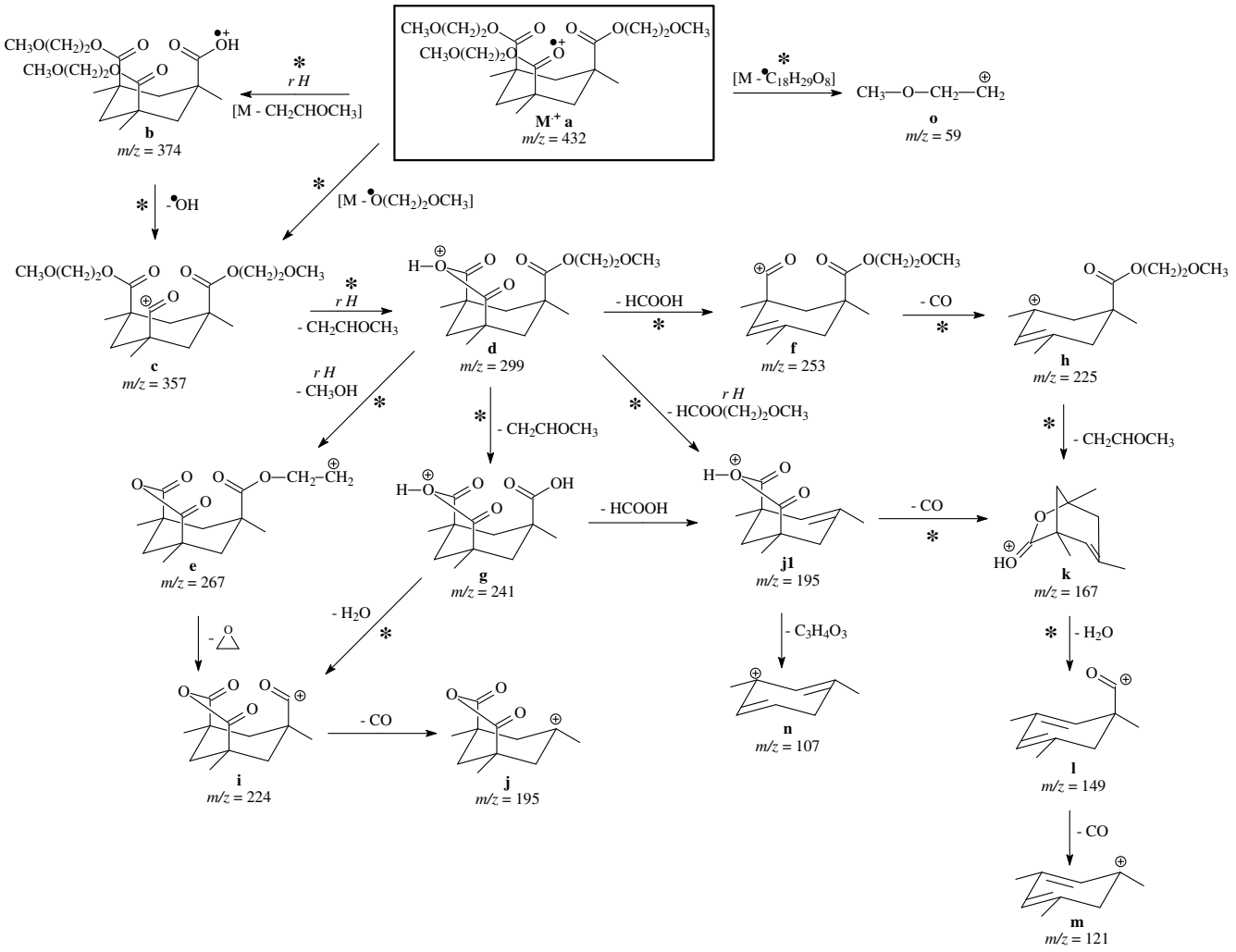
Scheme 2. Structure of a new ester of KTA synthesised.

Table 1
EI MS data of KTEG1

Ion	*m/z*	Relative abundance (%)
M^+ **a**	432	2
b	374	2
c	357	17
d	299	23
e	267	9
f	253	3
g	241	10
h	225	35
i	224	7
j	195	4
j1		
k	167	18
l	149	5
m	121	100
n	107	17
o	59	46

2.1. Synthesis of KTA 2-methoxy-ethyl triester (KTEG1)

The mixture of 2-bromoethyl methyl ether (962 mg; 6,97 mmol), *cic*,*cis*-1,3,5-trimethylcyclohexane-1,3,5-tricarboxylic acid (Kemp's triacid) (300 mg, 1,16 mmol) and 1,8-diazabicyclo[5.5.0]-undec-7-ene (DBU) (796 mg; 5,23 mmol) and 10 ml toluene was heated at 80 °C for 15 h. After cooling the precipitate DBU-hydrobromide (DBU·HBr) was filtered and washed with toluene. The filtrate was evaporated under reduced pressure at room temperature. The residue was purified by chromatography on silica gel (Fluka type 60). The column was eluted with dichloromethane:acetone (7:1) solvent mixture. The combined fractions were evaporated under reduced pressure. The yield of yellow oily product was 48%.



Scheme 3. The fragmentation routes proposed on the basis of the EI-MS data.

Table 2
The main peaks in the ESI mass spectra of the complexes of KTEG1 with cations at various cone voltages (10–90 V)

Mixture	Cone voltage (V)	Main peaks *m/z*
KTEG1–Li^+	10	440 (**A**)
	30	440 (**A**)
	50	440 (**A**)
	70	440 (**A**), 305 (**B**), 169 (**C**), 150 (**D**), 121 (**E**)
	90	440 (**A**), 305 (**B**), 169 (**C**), 150 (**D**), 121 (**E**)
KTEG1–Na^+	10	455 (**A**)
	30	455 (**A**)
	50	455 (**A**)
	70	455 (**A**), 321 (**B**), 169 (**C**), 150 (**D**), 121 (**E**)
	90	455 (**A**), 321 (**B**), 169 (**C**), 150 (**D**), 121 (**E**)
KTEG1–K^+	10	472 (**A**)
	30	472 (**A**)
	50	472 (**A**), 337 (**B**), 169 (**C**), 150 (**D**), 121 (**E**)
	70	472 (**A**), 337 (**B**), 169 (**C**), 150 (**D**), 121 (**E**)
	90	337 (**B**), 169 (**C**), 150 (**D**), 121 (**E**)

Elemental analysis: $C_{21}H_{36}O_9$ (KTEG1) calculated: C = 58.26%, H = 8.32%; found: C = 58.24%, H = 8.33%.

2.2. ESI-MS and EI-MS measurements

The ESI (Electrospray Ionisation) mass spectra were recorded on a waters/micromass (Manchester, UK) ZQ mass spectrometer equipped with a Harvard apparatus syringe pump. All samples were prepared in acetonitrile. The measurements were performed for the two types of samples being the solutions of Kemp's triacid ester (5×10^{-5} mol dm^{-3}) with: (a) each of the cations Li^+, Na^+ and K^+ (2.5×10^{-4} mol dm^{-3}) taken separately and (b) the cations Li^+, Na^+ and K^+ (5×10^{-5}/3 mol dm^{-3}) taken together. The samples were infused into the ESI source using a Harvard pump at a flow-rate of 20 μl min^{-1}. The ESI source potentials were: capillary 3 kV, lens 0.5 kV, extractor 4 V. The standard ESI mass spectra were recorded at 30 V. The source temperature was 120 °C and the dessolvation temperature was 300 °C. Nitrogen was used as the nebulizing and drying gas at flow-rates of 100 and 300 dm^3 h^{-1}, respectively. Mass spectra were acquired in the positive ion detection mode with unit mass resolution at a step of 1 *m/z* unit and at cone voltages cv = 10, 30, 50, 70, 90 V. The mass range for ESI experiments was from *m/z* = 100 to *m/z* = 1000. Low- and high-resolution EI-mass spectra were recorded using on a AMD-Intectra GmbH (Harpstedt) D-27243 model 402 double-focusing sector mass spectrometer (ionizing voltage 70 eV; accelerating voltage 8 kV; resolution 10,000; 10% valley definition). Kemp's triacid ester sample was introduced using direct insertion probe at a source temperature of ~150 °C. The elemental compositions of the ions were determined using the same instrument by peak matching relative to perfluorokerosene. The mass range for EI experiments was from *m/z* = 50 to *m/z* = 700. The error of mass determination in the EI and ESI experiments was ± 1.

2.3. FT-IR measurements

The FT-IR spectra of Kemp's tracid ester and its 1:1 complexes (0.05 mol dm^{-3}) with $LiClO_4$, $NaClO_4$, and KClO4 were recorded in the mid infrared region in acetonitrile solutions.

A cell with Si windows and wedge-shaped layers was used to avoid interferences (mean layer thickness 170 μm). The spectra were taken with an IFS 113 V FT-IR spectrophotometer (Bruker, Karlsruhe) equipped with a DTGS detector; resolution 2 cm^{-1}, NSS = 125. The Happ–Genzel apodization function was used.

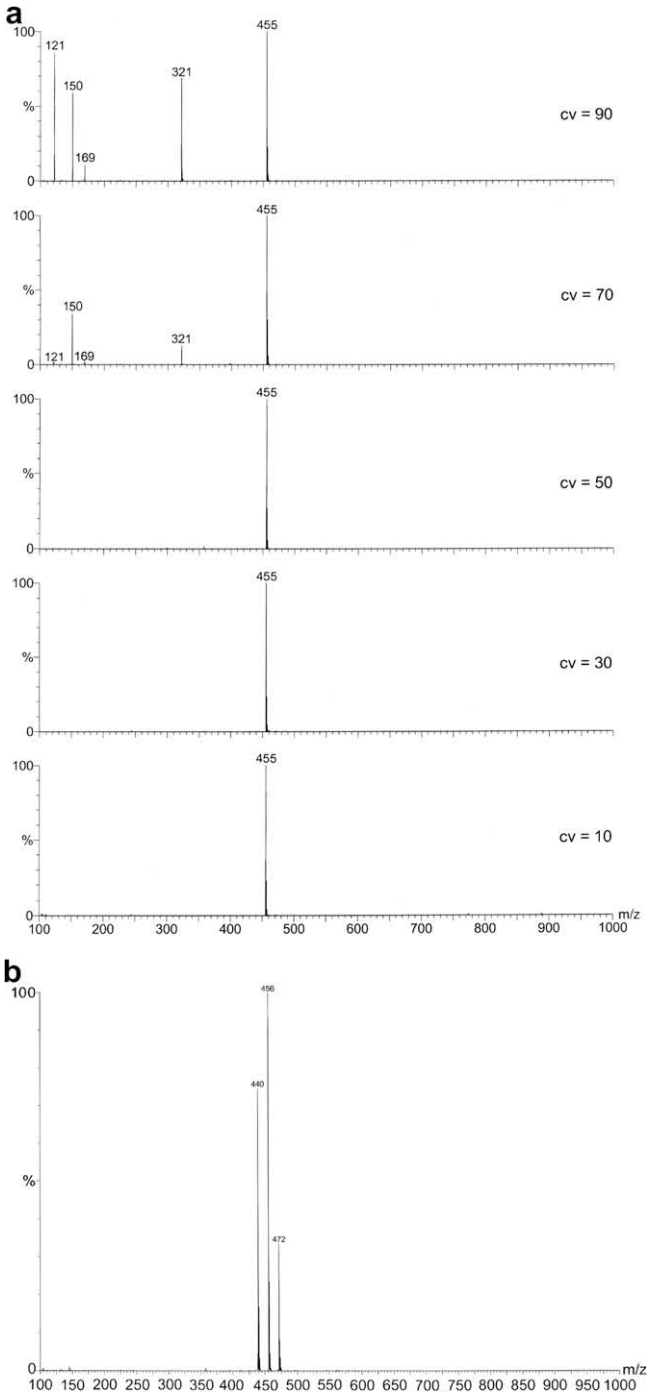


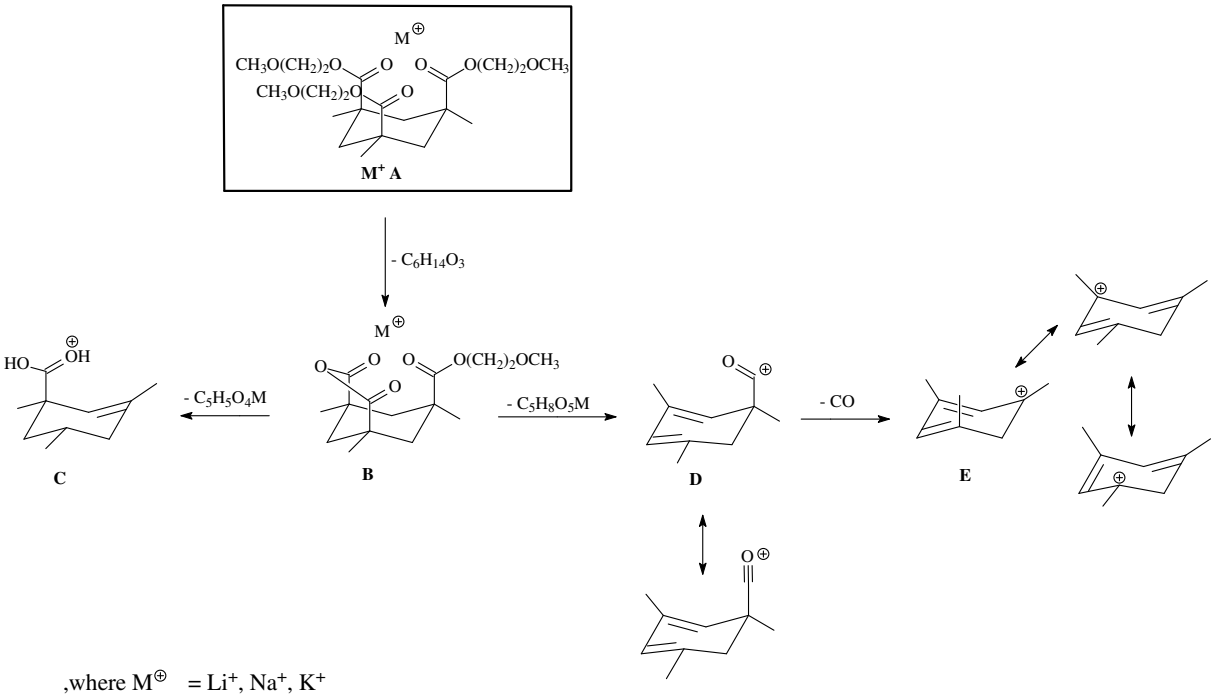
Fig. 1. ESI MS spectra of (a) 1:1 mixture of KTEG1 with $NaClO_4$ at various cone voltages (cv) and (b) 1:1:1:3 mixture of cation perchlorates ($LiClO_4$, $NaClO_4$ and $KClO_4$) with KTEG1 (cv = 30).

All manipulations with the substances were performed in a carefully dried and CO_2-free glove box.

2.4. NMR measurements

The NMR spectra of KTEG1 and its 1:1 complexes (0.05 mol l^{-1}) with monovalent metal cations salts were recorded in CD_3CN solutions using a Varian Gemini 300 MHz spectrometer. All spectra were locked to deuterium resonance of CD_3CN.

The ^{1}H NMR measurements in CD_3CN were carried out at the operating frequency 300.075 MHz; flip angle, pw = 45°; spectral



Scheme 4. The fragmentation pathways proposed on the basis of ESI-MS spectra at various cone voltages.

width, sw = 4500 Hz; acquisition time, at = 2.0 s; relaxation delay, d_1 = 1.0 s; T = 293.0 K and using TMS as the internal standard. No window function or zero filling was used. Digital resolution was 0.2 Hz per point. The error of chemical shift value was 0.01 ppm.

^{13}C NMR spectra were recorded at the operating frequency 75.454 MHz; pw = 60°; sw = 19,000 Hz; at = 1.8 s; d_1 = 1.0 s; T = 293.0 K and TMS as the internal standard. The line broadening parameters were 0.5 or 1 Hz. The error of the chemical shift value was ± 0.1 ppm.

The ^{1}H and ^{13}C NMR signals were assigned for each species using one or two-dimensional (COSY, HETCOR, HMBC) spectra.

2.5. PM5 calculations

Calculations were performed using the WinMopac 2007 program [31,32]. In all cases full geometry optimisation of Kemp's triacid ester as well as its complexes with monovalent cations was carried out without any symmetry constraints using PM5 semiempirical method.

2.6. Elemental analysis

The elemental analysis of Kemp's triacid ester was carried out on Vario ELIII (Elementar, Germany).

3. Results and discussions

3.1. EI-MS and ESI-MS studies

The new triester of KTA (KTEG1, Scheme 2) was characterized by spectroscopic methods and EI-mass spectrometry. The spectroscopic properties of KTEG1 are compared below with those of its complexes with metal cations. For KTEG1 the EI-mass spectrometry studies were performed to determine its fragmentations pathways. The low-resolution EI-MS data of KTEG1 spectrum are collected in Table 1. On the basis of these signals as well as the exact mass measurements and also the B/E and B^2/E linked scan spectra, the principal mass spectral fragmentation pathways of KTEG1 were determined and shown in Scheme 3. The low abundance signal of the molecular ion of KTEG1 arises at m/z = 432. The molecular ion **a** can decompose in three ways with the formation of **b**, **c** and **o** ions. Ion **c** can be form alternatively from ion **b** by the abstraction of one hydroxyl radical. Further decompositions are concerned only with ion **c** and have a complex character. During these mass decompositions always only small neutral molecules are released.

The ESI-MS spectra of KTEG1 with Li^+, Na^+ and K^+ cations at cv = 10 V show m/z signals at 440, 455 and 472, respectively, proving the formation of the respective 1:1 $(KTEG1 + M)^+$ complexes (Table 2, ion **A** type). The exemplary spectra of KTEG1

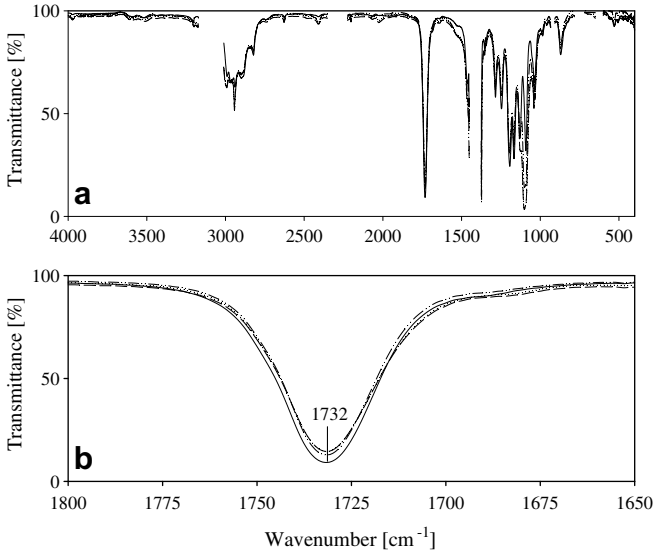


Fig. 2. FT-IR spectra of: (—) KTEG1, (– –) KTEG1–Li^+, (···) KTEG1–Na^+, and (–···–) KTEG1–K^+ in the ranges of (a) 4000–400 cm^{-1}; (b) ν(C=O) stretching vibrations.

Table 3
^{13}C NMR chemical shift (ppm) of KTEG1 and its complexes in CD_3CN

No. atom	Chemical shift (ppm)				Differences (Δ) between chemical shift (ppm)		
	KTEG1	KTEG1:Li^+	KTEG1:Na^+	KTEG1:K^+	Δ1	Δ2	Δ3
1, 1′, 1″	41.93	42.02	42.01	41.99	0.09	0.08	0.06
2, 2′, 2″	43.18	43.02	43.20	43.26	−0.16	0.02	0.08
3, 3′, 3″	31.06	30.97	31.11	31.11	−0.09	0.05	0.05
4, 4′, 4″	176.78	177.28	177.50	177.12	0.50	0.72	0.34
5, 5′, 5″	64.05	64.24	64.41	64.17	0.19	0.36	0.12
6, 6′, 6″	71.00	70.89	70.85	70.94	−0.12	−0.15	−0.06
7, 7′, 7″	58.80	58.92	58.98	58.89	0.12	0.18	0.09

Δ1, $\delta_{KTEG1+LiClO4}-\delta_{KTEG1}$; Δ2, $\delta_{KTEG1+NaClO4}-\delta_{KTEG1}$; Δ3, $\delta_{KTEG1+KClO4}-\delta_{KTEG1}$.

Table 4
^{1}H NMR chemical shift (ppm) of KTEG1 and its complexes in CD_3CN

No. atom	^{1}H NMR chemical shift (ppm) and coupling constants (Hz)			
	KTEG1	KTEG1:Li^+	KTEG1:Na^+	KTEG1:K^+
2_{eq}, $2_{eq}'$, $2_{eq}''$	d 2.62	d 2.62	d 2.62	d 2.62
	^{2}J = 14.8	^{2}J = 14.9	^{2}J = 14.7	^{2}J = 14.7
2_{ax}, $2_{ax}'$, $2_{ax}''$	d 1.09	d 1.09	d 1.09	d 1.09
	^{2}J = 14.8	^{2}J = 14.9	^{2}J = 14.7	^{2}J = 14.7
3, 3′, 3″	s 1.19	s 1.19	s 1.19	s 1.19
5, 5′, 5″	m 4.06	m 4.10	m 4.11	m 4.08
6, 6′, 6″	m 3.54	m 3.55	m 3.58	m 3.56
7, 7′, 7″	s 3.31	s 3.36	s 3.39	s 3.35

Eq, equatorial; ax, axial.

Table 5
Heat of formation HOF (kcal/mol) of KTEG1 and its 1:1 complexes with monovalent metal cations calculated by PM5 method at semiempirical level (WinMopac 2007)

Complex	HOF (kcal/mol)	ΔHOF (kcal/mol)
KTEG1	−424.13	–
KTEG1+$Li^+_{uncomplexed}$	−298.96	−147.52
KTEG1+$Li^+_{complexed}$	−446.38	
KTEG1+$Na^+_{uncomplexed}$	−279.32	−175.23
KTEG1+$Na^+_{complexed}$	−454.55	
KTEG1+$K^+_{uncomplexed}$	−274.33	−128.34
KTEG1+$K^+_{complexed}$	−402.67	

$\Delta HOF = HOF_{complexed} - HOF_{uncomplexed}$.

complex with Na^+ at various cone voltages are shown in Fig. 1a. In the ESI-MS spectra of complexes with Li^+ and Na^+ cations at cv = 70 V as well as at cv = 50 V in the spectrum of K^+ complex additional signals appear due to a beginning fragmentation of the respective complexes. The signals assigned to the **B** type ions arise at *m/z* = 305, 321 and 337 indicating the formation of other types of complexes after the abstraction of two oxaalkyl moieties, as shown in Scheme 4. At the same cv values besides the signals of ion **B** other signals assigned to ions **C**–**E** are present in all spectra. The *m/z* values of these signals are independent of the kind of the cation used indicating the common fragmentation pathways of ion **B**. The proposed fragmentation pathways of the complexes are shown in Scheme 4.

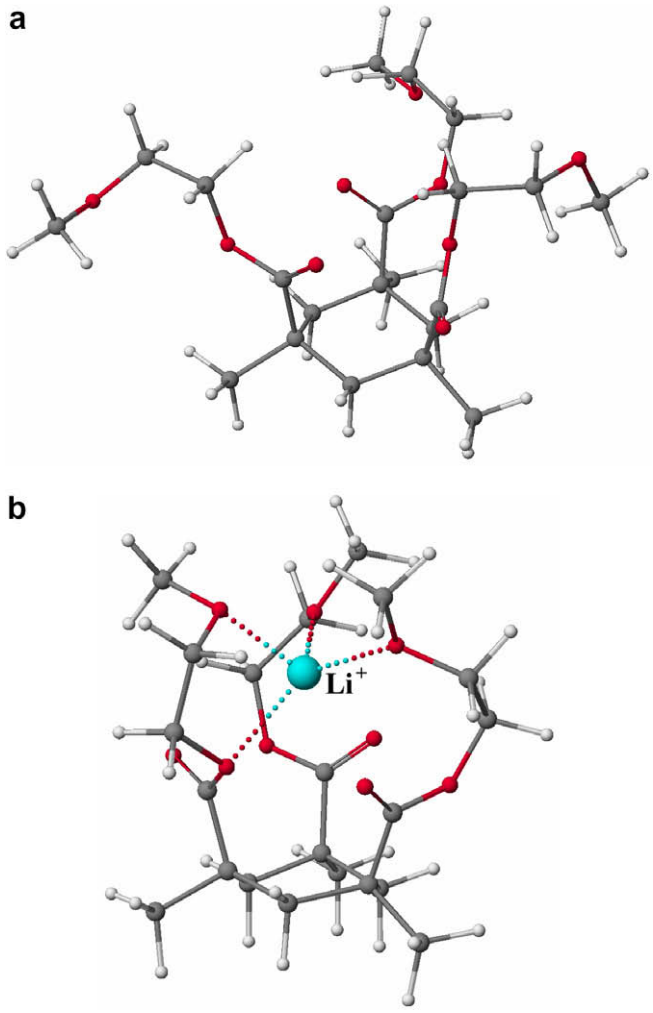
The ESI spectrum of the mixture of Li^+, Na^+ and K^+ cations with 33% of the equivalent concentration of KTEG1 shows three characteristic signals at *m/z* = 440, 455 and 472 assigned to the 1:1 $^+$ species (Fig. 1b). The intensity of the KTEG1–Na^+ complex signal is dominant, clearly indicating that KTEG1 preferentially forms complexes with Na^+ cations. The intensity of the signal of KTEG1–Li^+ complex is slightly lower and that of KTEG1–K^+ complex is significantly lower, demonstrating that KTEG1 shows only low affinity to K^+ cation.

3.2. Spectroscopic studies

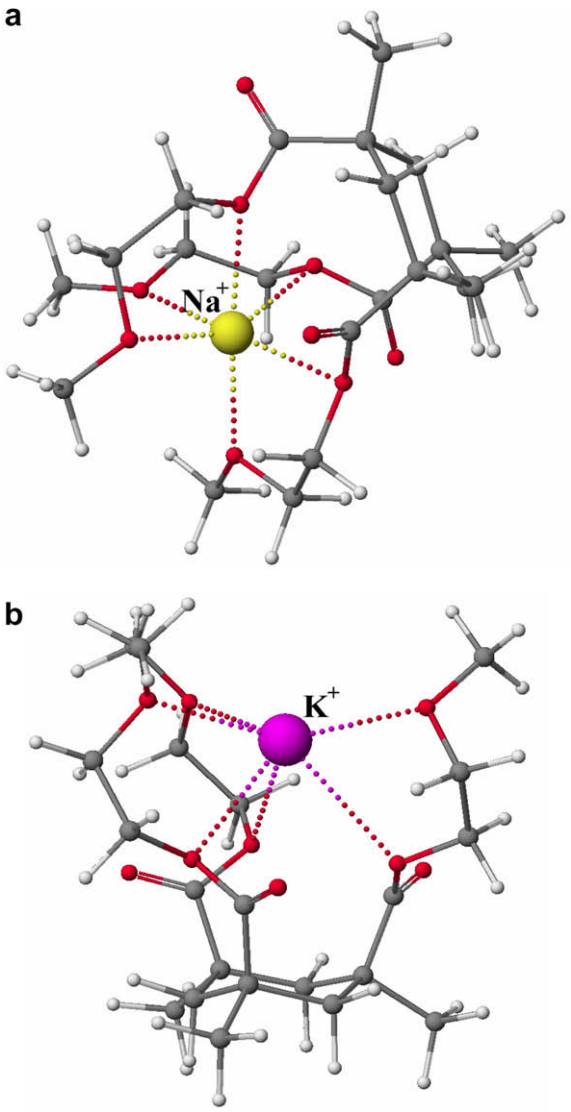
The FT-IR spectra of the KTEG1 triester and its complexes with Li^+, Na^+ and K^+ cations (used as perchlorate salts) in acetonitrile solutions are compared in Fig. 2. These spectra are very similar. The bands assigned to the ν(C=O) stretching vibrations arise in all spectra at 1732 cm^{-1} clearly indicating the lack of participation of the carbonyl groups in the complexation process of metal cations. This result should be taken into account when interpreting the NMR data which are summarized in Tables 3 and 4. The ^{1}H and ^{13}C resonances were assigned on the basis of two-dimensional NMR experiments. The ^{13}C NMR signals of the KTEG1 carbonyl C atoms are shifted towards higher ppm values with the complexation

Table 6
The interatomic distances (Å) and partial charges for O atoms of KTEG1 coordinating metal cations in complexes structures calculated by PM5 method (WinMopac 2007)

Complex with monovalent cation	Monovalent cation partial charge	Coordinating atom	Coordinating atom partial charge	Distance (Å) coordinating atom → cation
KTEG1+Li^+	+0.483	O_{4-5}	−0.401	2.23
		O_{6-7}	−0.384	1.99
		$O_{6'-7'}$	−0.376	2.04
		$O_{6''-7''}$	−0.390	2.06
KTEG1+Na^+	+0.379	O_{4-5}	−0.405	2.27
		$O_{4'-5'}$	−0.419	2.36
		$O_{4''-5''}$	−0.420	2.37
		O_{6-7}	−0.405	2.28
		$O_{6'-7'}$	−0.412	2.31
		$O_{6''-7''}$	−0.402	2.24
KTEG1+K^+	+0.772	O_{4-5}	−0.475	2.98
		$O_{4'-5'}$	−0.428	2.84
		$O_{4''-5''}$	−0.469	2.88
		O_{6-7}	−0.427	2.82
		$O_{6'-7'}$	−0.415	2.72
		$O_{6''-7''}$	−0.421	2.76



Scheme 5. Structures of KTEG1 (a) and KTEG1–Li^+ (b) complex calculated by the PM5 semiempirical method.



Scheme 6. Structures of KTEG1–Na^+ (a) and KTEG1–K^+ (b) complexes calculated by the PM5 semiempirical method.

of metal cations. According to the FT-IR data, these changes in the chemical shift should be explained by the involvement of the O_{4-5} atoms in the coordination process of the metal cation. This result illustrates that the interpretation of the NMR data only would lead to the wrong conclusion that the carbonyl oxygen atoms are involved in the complexation. The greatest chemical shift changes are observed in the spectra of the 1:1 complex of KTEG1 with Na^+ cation and further in the spectrum of KTEG1–Li^+ complex. Relatively low chemical shift changes of the carbonyl carbon atoms are observed in the spectrum of KTEG1–K^+ complex. This result is in very good agreement with the affinity of KTEG1 towards the cations studied, determined by the ESI-MS method. The lowest differences in ^1H and ^{13}C chemical shifts are observed for the cyclohexane moiety of KTEG1. This is understandable because no conformational changes in the cyclohexane ring take place after the complexation of the cations.

3.3. PM5 semiempirical calculations of KTEG1 and its complexes

The heats of formation (HOF) of KTEG1 and its complexes with Li^+, Na^+ and K^+ cations are collected in Table 5. The ΔHOF values of the complexes of KTEG1 with the cations studied, reflecting the energetic profit of the complexation process, demonstrate that the formation of complexes is energetically favorable. These values also correspond very well to the spectrometric and spectroscopic data showing the preferentially complexation of Na^+ cations by the KTEG1. These results are also in agreement with the calculated partial charge values for the metal cations within the complexes (Table 6).

According to the FT-IR measurements the most stable structures of the triester and its complexes involve no interactions between the oxygen atoms of the ester carbonyl groups and the metal cations. Thus, the coordinating oxygen atoms are those of the oxaalkyl chains. The energetically favorable calculated structures are shown in Schemes 5 and 6. In the structure of the triester a tendency to dipole–dipole interactions between the polar carbonyl groups is very limited because they are directed to the outside of the cyclohexane ring. Almost the same situation was detected earlier in the crystal structure of benzyl triester of KTA [25].

The interatomic distances between the oxygen atoms and the cations and partial charges of the cations and O-atoms are given in Table 6. These data show that only four oxygen atoms are always involved in coordination, irrespective of the kind of the cation. The coordinating distances and the number of coordinating oxygen atoms suggest that the Li^+ cation can undergo fast fluctuations within the structure of the complex as it was demonstrated for the complexes of crown-ethers or derivatives of gossypol containing

oxaalkyl chains with the monovalent cations [35]. The interatomic distances between oxygen atoms and Na^+ cation are in close range suggesting the relatively strong localization of this cation within the structure (Scheme 6a). Furthermore, the coordination sphere of the Na^+ cation is the most regular of all calculated ones forming the slightly distorted octahedron. This structure of the complex can be the reason for the hight affinity of KTEG1 towards Na^+ cations.

The calculated structure of KTEG1–K^+ complex is comparable with that of KTEG1–Na^+ complex, however, the interatomic distances between oxygen atoms and K^+ cation are much longer and show greater differences.

Acknowledgement

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