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Bis{phenyl[di(methoxyethyloxy)phosphoryl]methyl}amine as a new ligand for metal ions and cationic organic molecules

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1. Introduction

ABSTRACT

The bis(phenylphosphorylmethyl)amine containing binding units based on "crown-ether like" ester moiety was tested as a supramolecular host molecule. The complexation properties towards metal ions (Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Mg²⁺, Ca²⁺, Ba²⁺) and hydrochlorides of amino acids (Lys, Arg), diethylenetriamine (2EN3A) and pentaethylenehexaamine (5EN6A) were studied. In order to assess the binding affinities of the receptor to selected guest molecules in various solvents, the ESI-MS and NMR techniques were applied. The results were also supported by theoretical studies. The ESI-MS studies revealed the selective binding of Cs⁺ and 5EN6 by the phosphonate molecule, whereas NMR investigation in solution indicated tighter association of the host-guest system obtained for Mg²⁺ and Arg. The discrepancies between the results originating from both used methods are most likely caused by influence of the solvent on intermolecular interactions.

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Crown ethers and polyglycol podands play an important role in supramolecular chemistry as molecular hosts for metal ions and organic cations. These compounds are also believed to perfectly mimic the behavior of natural ionophores [1]. Moreover, the noteworthy features are attributed to polyoxaalkyl arms which are well recognized binding motifs [2,3]. Their anchoring centers possessing various heteroatoms may serve as a suitable polyvalent system for metal ions chelation [4,5]. Nevertheless, there is still a strong demand for the development of novel specific and selective hosts for many purposes. In this light new organophosphorus compounds appear to be interesting and scarcely developed class of receptors [4].

Recently, we have described the hybrid phosphonate host molecule suitable for metal ions binding [5]. Combining polyoxaalkyl chains and phosphonic acid unit in one molecule allowed to obtain a selective receptor for mono- and divalent metal ions from the first and the second group of periodic table. Although, organic molecules possessing ammonium cation were found to not interact with this molecule.

In this work we report the "second generation" of the host molecule having tetra-2-methoxyethyl aminophosphonate binding unit. The investigations involve synthesis of the receptor, evaluation of its binding properties and theoretical studies by computational methods. Application of ESI-MS spectrometry and NMR spectroscopy enabled to determine binding properties towards selected inorganic and organic cations with detailed description of host-guest interactions.

2. Experimental

2.1. Synthesis of bis{phenyl[di(methoxyethyloxy)phosphoryl]methyl}amine (receptor) **1** (Scheme 1)

The chemical synthesis of the receptor 1 was carried out basing on the literature data [6,7]. The excess of NH₄OH was added to the freshly distilled benzaldehyde (10 ml, 0.095 mole) and the mixture was stirred under reflux for 30 min. Afterwards, the solution was cooled, which resulted in precipitation of white solid. The obtained product was filtered off, washed with water and dried to give intermediate hydrobenzamide in a yield of 85%.

In the next step, 6 g (0.02 mole) of hydrobenzamide was dissolved in toluene and then 3.85 ml (0.02 mole) of the diphenyl phosphite was added. The mixture was refluxed for 5 h and the solvent was evaporated in vaccuo. The resulted yellow oil was



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dissolved in acetone and cooled to 4-6 °C giving a white precipitate (yield 80%). Then, the obtained product was reacted with diphenyl phosphite (0.02 mole) and the sequence of reaction steps was repeated.

One gram of the obtained compound was transesterified with excess of 2-methoxyethanol, which was added together with the catalytic amount of KF and 18-crown-6 ether. The mixture was refluxed for 30 min. and left at room temperature for 8 h. The volatile components were evaporated under reduced pressure and the resulting yellow oil was purified by HPLC. The product was obtained as a mixture of diastereoisomers in the 2:1 molar ratio. They are denoted as iii (major) and ii (minor) stereoisomer assigned from NMR spectra.

¹H NMR (MeOD): δ (ppm): iii 3.26 (s, -CH₃); ii 3.28 (s, -CH₃); ii 3.33 (s, -CH₃); iii 3.35 (s, -CH₃); iii 3.42 (m, -CH₂--); ii 3.46 (m, -CH₂--); iii and ii 3.57 (t, -CH₂--, *J* = 4.5 Hz); iii 3.91 (d, *J*_{H-P} = 21.8 Hz, α-CHP); iii 3.90 (m, -CH₂--); ii 3.97 (m, -CH₂--); iii 4.04 (m, -CH₂--); ii and iii 4.08-4.24 (m, -CH₂--); ii 4.38 (d, *J*_{H-P} = 17.6 Hz, α-CHP); iii and ii 7.40-7.26 (m, Ar).

¹³C NMR (MeOD): δ (ppm) iii 58.72 (dd, α-CHP, $J_{C-P} = 158.3$ Hz, $J_{C-P} = 17.5$ Hz): iii 59.00 (s, $-CH_3$); ii 59.09 (s, $-CH_3$); ii 59.94 (dd, α-CHP, J = 156.8, J = 11.1 Hz); 67.08–67.41 m ($-CH_2-$); 67.51 (bs, $-CH_2-$) 72.43 (bs, $-CH_2-$), 72.6 (bs, $-CH_2-$); 129.31 (s, Ar); 129.58 (d, Ar, J = 13.7 Hz); 129.78 (bs, Ar); 129.97 (d, J = 6.0 Hz); 130.40 (s, Ar), iii 135.15 (s, Ar); ii 130.38 (s, Ar).

³¹**P NMR (MeOD)**: *δ* (ppm): iii 24.04; ii 24.40.

2.2. ESI-MS studies

The ESI (electrospray ionization) mass spectra were recorded on a Waters/Micromass (Manchester, UK) ZQ mass spectrometer equipped with a Harvard Apparatus syringe pump. The measurements were performed in methanol and acetonitrile solutions for the receptor concentration $(1-5) \times 10^{-4}$ mol dm⁻¹ and metal to ligand ratio 1:1 and 1:2. The samples were infused into the ESI source using a Harvard pump at a rate 20 µdm³ min⁻¹. The ESI source potentials were: capillary 3 kV, lens 0.5 kV, extractor 4 kV, and the cone voltage 30 V. The source temperature was 120 °C and the desolvation temperature was 300 °C. Nitrogen was used as a nebulizing and desolvation gas at a flow rate of 100 and 300 dm³ h⁻¹, respectively.

2.3. NMR measurements

NMR measurements were performed on BRUKER 600 MHz Avance II spectrometer equipped with TBO 5 mm probe with *z*-gradient and temperature control unit ($T = 298 \pm 0.1$ K) in D₂O, MeOD CD₃CN. The 1D and 2D (HMQC, COSY, TOCSY, T1-pseudo 2D) NMR techniques were applied using receptor concentration (2–7) × 10⁻³ mol dm⁻¹ and metal to ligand ratio 1:1. Titration experiment were performed in the metal to ligand ratio from 0:1 to 4:1. The diffusion coefficient determination were performed using stimulated echo and LED pulse sequence with two spoil gradients (ledgp2s) [8]. All samples were temperature equilibrated in the spectrometer during 0.5 h. Individual calibration of the diffusion time Δ and gradient pulse δ values for each investigated systems were carried out. Chemical shifts are given in relation to TMS, TSP, 85% phosphoric acid and D₂O containing appropriate metal perchlorate salt as external standards.

2.4. Computational methods

The metal-ligand complexes were studied (Semiempirical PM6 method) [9] by using the MO-G for SCIGRESS program [10]. All initial structures were optimized first by molecular mechanics

method (MM2). In all cases full geometry optimization was carried out without any symmetry constraints.

The ligand–organic guest supramolecule geometries were optimized by using density functional theory (DFT), with B3LYP hybrid functional [11,12]. Quantum chemical calculations were done using 6-31++G^(d,p) basis set considering the polarization and diffuse functions on all atoms. Moreover, the frequency analyses were carried out for all the molecules to confirm that they were in the local minima. All the calculations were performed in Gaussian 03 [13], using CPCM [14] continuum solvent models, with water as a solvent. Atomic charges were received from natural bond orbital analysis (NBO) [15].

Additionally, conformational analysis of the complexes formed between aminobisphosphonate receptor and amino acids was performed using simulated annealing method. The analyzed systems were preheated to 1000 K and cooled down to 300 K. Each of the generated structure was optimized to energy minimum using *Discover* module implemented in molecular modeling environment package *Insight II*.

3. Results and discussion

3.1. ESI-MS, NMR and theoretical calculation studies for the receptor

The ESI-MS studies of the free receptor revealed three signals: a molecular signal at (+) **591**[L + H]⁺ m/z and two other originating from fragmentation of the molecule at (+) 393 [L-PO(R)₂]⁺ and (-) 531 [L-(R)]⁻ m/z. This fragmentation pattern seems to be characteristic for this compound.

The ³¹P NMR investigation of the receptor showed the presence of two diastereoisomers (see experimental section) in 2:1 molar ratio. Theoretical calculation of the metal free receptor revealed that the RR isomer (HOF -2056,29 kJ/mol) is more stable than RS form (HOF -2032.76 kJ/mol).

Intriguingly, the ¹H- and ³¹P NMR titration exhibited acidic character of the amino group ($pK_a > 1$). There can be two explanations for the low pK value of this group: (i) the attached polyglycolic fragment may prompt hydrolysis of apparently bound water molecule; (ii) the presence of 2-metoxyethyl and phenyl groups causes strong electron withdrawing effect from central amine group. To elucidate this issue the "one-arm" analog of studied receptor was synthesized and the NMR titration was performed (Figs. 1 and 2).

The comparison of the titration curves support hypothesis of a strongly withdrawing electron effect of polyglycolic arms from amine group, because in the case of compound **1** the great change in the chemical shift is observed, while for its acylated analog **2** not.

3.2. Complexation properties of bis{phenyl[di(methoxyethyloxy)-phosphoryl]methyl}amine

3.2.1. Towards metal ions

The presence of polyglycol units strongly assures the occurrence of interaction with hard sphere metal ions [3,16,17]. ESI



Fig. 1. The structure of one arm analog 2.



Fig. 2. The ³¹P NMR titrations of compound **1** (\blacksquare and \bullet) and **2** (Δ).

studies revealed the chelation abilities of this receptor towards Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Mg²⁺, Ca²⁺ and Ba²⁺ ions with formation of molecular complexes in 1:1 ratio (metal to ligand) for the first and 1:2 for the second group (Table 1). Monovalent metal ions are complexed as free ions, whereas divalent cations are bound together with their perchlorate counterions and formed in 1:1 metal to ligand ratio. This phenomenon is consisted with the results obtained for the systems published recently [5].

The fragmentation pattern of the formed complexes could reflect the strength of metal binding to the receptor (Table 1). The studied phosphonate host appears to bind most effectively Cs^+ ion in ESI-MS gas-phase conditions. This is the most probably due to best fitting of ion radius of Cs^+ to the binding cavity formed by the ligand. This also seems to support the rule, that the host, which possesses stronger chelating abilities, preserves the molecular complex against defragmentation processes.

To prove this statement additional ¹H and ³¹P NMR measurements in solution were conducted. As an indicative factor of host-guest (metal ions) interaction the complexation induced chemical shift CIS ($\Delta\delta$) was assumed [18]. Initially, D₂O was used as a solvent. Unfortunately, in aqueous solution only very small CISs were observed in ³¹P NMR spectra (up to 0.008 ppm), which did not exceed the half-width of the phosphorus signal. This prompted us to employ CD₃OD. Admittedly, changing solvent to methanol $\Delta\delta$ grew up to 0.07 ppm but during host-guest titration the lack of curve saturation was observed. Therefore, the further studies were performed in CD₃CN. At the beginning, the heteronuclear NMR measurements were performed to affirm the influence of ligand on metal binding (Table 2). All the investigated metal ions revealed the significant changes.

The receptor binding abilities were also reflected in ¹H NMR and ³¹P NMR spectra. The observed changes in CIS values observed for

Table 1

The main peaks (m/z) and their defragmentation pattern in the ESI-MS spectra at 30 V cone voltage upon formation of the molecular complexes with metal ions.

Cation	Main peaks (m/z)
Li ⁺	597 [L + Li] ⁺ , 393 [L-PO(OR) ₂] ⁺
Na ⁺	613 [L + Na] ⁺ , 393 [L-PO(OR) ₂] ⁺
K ⁺	629 [L + K] ⁺ , 393 [L-PO(OR) ₂] ⁺
Rb ⁺	675 [L + Rb] ⁺ , 393 [L-PO(OR) ₂] ⁺
Cs ⁺	723 [L + Cs] ⁺
Mg ²⁺	602 [2L + Mg] ²⁺ , 714 [Mg + L + ClO ₄] ⁺
Ca ²⁺	610 [2L+Ca]²⁺ , 730 [Ca+L+ClO ₄] ⁺ , 393 [L-PO(OR) ₂] ⁺
Ba ²⁺	659 [2L+Ba]²⁺ , 827 [Ba+L+ClO ₄] ⁺ , 393 [L-PO(OR) ₂] ⁺

ester protons may be classified as a characteristic feature for the first and for the second group of elements of periodic table.

In general, CIS values of CH₃ groups are apparently visible for all the investigated metal ions as one type of "binding shoulder" (Scheme 2) for molecule **1** (in order: Na⁺ > Li⁺ > K > Rb⁺ > Cs⁺; Mg²⁺ > Ca²⁺ > Ba²⁺), while for the second type of esters group the CIS alterations are a little for (Li⁺, Na⁺, K⁺, Rb⁺) and much bigger for (Mg²⁺, Ca²⁺, Ba²⁺). The cesium ions force the change of CH₃ group shift similar to the divalent ions. The most probably this phenomenon was observable due to its great ion radius. For divalent metal ions the significant CIS changes are also detected for CH₂ groups in the following order: Mg²⁺ > Ca²⁺ > Ba²⁺ reflecting the size of the metal ions and the "deepness" of interaction with ester groups. While for the first group of elements the effect was seen only for Li⁺ ions.

The chemical shift changes in ${}^{31}P$ NMR spectra reflected the order described for CH₃ and CH₂ groups with only exception observed for Li⁺ ions, where phosphorus signals are much more shifted in comparison to the rest of first group metal ions.

All these findings may suggest that alkali metal ions effectively interact with receptor via two methoxyglycol chains located on different phosphorus atoms, which is accompanied by weak binding by the second chains. Moreover, the lithium ions, as ³¹P NMR spectra have proved, are bound in the closer proxymity to the phosphorus atoms (which might suggests involvement of central nitrogen donor). The alkaline earth metal ions formed metal to ligand complexes of 1:2 ratio and this is reflected by other type of binding pattern. They are bound "deeper" by two chains indicated by arrows in Scheme 2, but in this case the second type of arms also seem to participate in the metal-receptor interactions. It clearly indicates that ions of smaller radius are bound stronger. Additionally, the charge of the metal ion plays important role in the ligandmetal binding and thus divalent metal ions are bound better than monovalent ones. This effect is, most likely, also associated with counter ion.

In order to determine association constant two experimental facts have to be considered. The previously performed investigations showed the lack of significant influence of 1:1 complex concentration (in the range 2–7 mM) on chemical shifts of protons. In addition, ³¹P NMR studies appeared to be only roughly indicative, due to the use of the mixture of diastereoisomers (Table 3). Therefore, during the calculation of the association constants few assumptions were done: (i) the concentration of each diastereoisomer was calculated as a molar fraction taken form phosphorus signal integration of metal free host: (ii) the assumption of formation 1:1 and 1:2 complexes was assumed on basis of the ESI-MS studies, however, the formation of more complexes such as multiple assembled polymeric structures can not be excluded (*vide supra*).

All the observed changes are reflected with the approximate log *K* values (Table 3), which are the highest for alkaline earth metal ions. Moreover the metal-ligand interactions patterns obtained

Table 2
The heteronuclear chemical shifts observed for investigated metal
ions recorded in CD ₃ CN [*] .

Metal ions	$\Delta\delta$ (ppm)
Li*	–0.41
Na*	–0.46
K ⁺	–1.09
Rb ⁺	significant broadening of the signal
Cs ⁺	–0.678

 * Mg², Ca²+, Ba²+ broadening of the line or nucleus not detected.







Scheme 2. The solid type arrows indicate the ester groups, which provide bigger CIS and type dashed indicate fragments of smaller CIS (this is contractual system).

by NMR measurements appear to be in line with the theoretical calculations (Table 4, Fig. 3). The lithium ion is bound deeper in the binding cavity hence having {O, N} donors from both type esters group, while potassium ion is bound shallower by methoxy oxygen's. Calculated structures of 1:1 metal to ligand complexes of second group of elements indicate that magnesium ion might be bound similarly to lithium ion, however less symmetrically. The most probably the formation of the system of higher stoichiometry is preferred for that ion. However, barium ion possessing greater ionic radius and divalent charge is surrounded symmetrically by {O, N} donors. The detailed calculations were performed for all ligand–metal ion complexes and are collected in Table 4.

The results are close to these obtained from NMR studies and the trend in differentiation between first and the second group of elements is well visible. Moreover, the most stable supramolecule is established for the system formed by ligand–magnesium ion; this finding is in accord with the results obtained so far.

Furthermore, NMR self-diffusion studies were performed for each system at 1:1 molar ratio (Table 5). The highest difference in ΔD ($D_{\text{free ligand}} - D_{\text{ligand metal complexes}}$) values was found for the Mg²⁺ ions. It confirms the finding that this metal has the highest affinity to the investigated receptor. The calculated relaxation time T_1 for free ligands revealed the higher values, than obtained for metal-ligand systems. This is in agreement with the assumption that correlation time τ_C increases and tumbling of the molecule is slower due to enlargement of the system. Because, the diffusion coefficient strongly depends on the molecular mass of the complex (constant mass of *L* and changing mass of metals ions) therefore the *D* and T_1 values can not be straightforwardly related to the roughly indicative calculated log *K*.

The observed ΔD and ΔT_1 changes are in general higher for alkaline earth than alkali metal ions (Table 5). This result seems to be confirmed looking at the trend of log *K* and β values and ESI-MS studies, where complexes containing greater mass were found. However, these values revealed apparent discrepancy in relation to ΔD values of formed complexes among the same group of elements. The determined ΔD is extremely high for Mg²⁺ complexes, where formation of polymeric species can not be excluded.

Table 3

	ii-Stereoisomer		iii-Stereoisomer			
	$\log k_{11}$	$\log k_{12}$	$\log \beta_{12}$	$\log k_{11}$	$\log k_{12}$	$\log \beta_{12}$
Li ⁺	3.05 ± 0.09	-	-	2.75 ± 0.17	-	-
Na ⁺	1.76 ± 0.06	_	-	1.6 ± 0.40	_	-
K ⁺	1.45 ± 0.12	_	-	_	_	-
Rb⁺	2.05 ± 0.63	_	-	_	_	-
Mg ²⁺	3.54 ± 0.31	_	-	3.91 ± 0.79	2.5 ± 0.90	6.41
Ca ²⁺	2.80 ± 0.81	_	-	_	_	$5.98 \pm 0.30^{*}$
Ba ²⁺	3.63 ± 0.14	3.43 ± 0.35	7.06	3.16 ± 0.06	_	-

Roughly calculated association constants for investigated guest-host systems basing on NMR studies

Some log K_{12} values were not calculated for that cases where the data do not fit to the assumed model, or overlapping of signal occurred. The log K_{11} value was not calculated for Cs⁺ ions due to small CIS value for both stereoisomers.

^{*} Only the cumulative constants can be calculated.

Table 4

The heat of formation Δ HOF = HOF (complexed) – HOF (uncomplexed) calculated for investigated metal-ligand systems.

Isomer of (1)	Complexed cation	Δ HOF (kJ/mol)
RS	Li ⁺	-334.05
RS	Na ⁺	-343.20
RS	K ⁺	-212.68
RS	Rb ⁺	-212.75
RS	Cs ⁺	-174.98
RS	Mg ²⁺	-1258.37
RS	Ca ²⁺	-1138.39
RS	Ba ²⁺	-1047.13
RR	Li ⁺	-316.57
RR	Na ⁺	-318.61
RR	K*	-194.15
RR	Rb ⁺	-166.42
RR	Cs ⁺	-152.62
RR	Mg ²⁺	-1185.88
RR	Ca ²⁺	-1096.01
RR	Ba ²⁺	-1004.74



Fig. 3. The examples of the calculated structures of the complexes formed between compound 1 and: (a) Li^+ ; (b) K^+ ; (c) Mg^{2+} ; (d) Ba^{2+} .

The undertaken attempts of $\log K_2$ value calculations from the obtained curves by the used algorithm for the firs group of elements did not bring any reasonable results.

Table 5	
$\Delta D (D_{\text{ligand}} - D_{\text{comp}})$ and $\Delta T_1 (T_1 \text{ ligand} - T_1 \text{ co})$	mp) determined by ¹ H NMR method

Metal ion	$\Delta D imes 10^{-9} \ (m^2 \ s^{-1})$	$\Delta T_1 (s^{-1})$
Li ⁺	0.2	0.3
Na ⁺	0.1	0.1
K ⁺	0.3	0.1
Rb ⁺	0.3	0.2
Cs ⁺	0.1	0.1
Mg ²⁺	0.9	0.85
Ca ²⁺	0.3	0.6
Ba ²⁺	0.3	0.6

3.2.2. Towards organic cations

The polyglycol aminophosphonate published already did not disclose any supramolecular properties towards organic cations [5]. The modification of this receptor resulting in more compact structure of polyglycol pincers significantly enhanced its binding features.

The ESI-MS studies revealed formation of molecular complexes formed by studied aminophosphonate with dihydrochlorides of Lys and Arg. Moreover polyamines 2EN3A (diethylenetriamine) and 5EN6A (pentaethylenehexaamine) acidified with formic acids in methanol- d_4 were also tested as a guest molecules (Table 6). All of these compounds exhibited good host–guest association properties in the gas phase. The complex of appropriate polyamine with aminophosphonate in methanol resulted in fragmentation processes in all cases. The exception was the 5EN6A, which was not fragmented, most probably due to the highest affinity to the host molecule in ESI-MS conditions.

In order to confirm the MS results NMR spectroscopy was employed. At first, the titrations in MeOD and/or CD₃CN were performed. In these experimental conditions the highest changes in the chemical shift were observed both for phosphorus and proton signals originating from of aryl and $-CH_2--CH_2--O-CH_3$ groups. However, due to very small change of all parameters (chemical shift, T_1 and ΔD) the obtained results did not shed the light to the binding properties in solution. The relatively small, but not negligible, shift is characteristic for all investigated systems but is not sufficient for determination of association constants. The performed relaxation T_1 ¹H NMR measurements showed very small deviation (0.03 s, which is in the range of experimental error)

Table	e

The main peaks (m/z) of the molecular complexes with organic cations with their defragmentation pattern in the ESI-MS spectra at 30 V cone voltage.

Cation	Main peaks (m/z)
Arg	765 [L+G+H2O] ⁺ ; 591 [L] ⁺ ; 393 [L-PO(OR) ₂] ⁺
Lys	737 [L+G] ⁺ , 591 [L] ⁺ ; 393 [L-PO(OR) ₂] ⁺
2EN3A	694 [L+G] ⁺ , 591 [L] ⁺ ; 392 [L-PO(OR) ₂] ⁺
5EN6A	823 [L+G] ⁺



Fig. 4. The calculated structures of complexes of arginine with involvement of ammonium and guanidinium cation and oxygens originating from (O)—P, R—O—R' entities as calculated by molecular dynamics.

between free receptor and receptor complexed with guest molecule. These values were the most significant for CH₃ groups and T_1 was always longer for free receptor than for two-component system. The small changes were also noticed for the ΔD diffusion coefficient (0.1–0.3 × 10⁻⁹ [m²/s]) values, where the highest value was found for arginine. This contribution to ΔD could be explained on the basis of theoretical calculations, where weak interactions were predicted (Fig. 4). This phenomenon is caused by the poor interactions between host and guest in the investigated systems.

4. Conclusions

The synthesis of aminophosphonate podant containing tetraglycol moiety provided entry into new group of promising host molecules. This ligand exhibits a very low pK of amine group which was assigned to strong electron withdrawing properties of 2methoxyethyl ester units. The designed receptor exhibited different supramolecular properties in the gas phase (ESI-MS studies) and in solution as revealed by NMR investigation. As demonstrated, in the gas phase all metal ions were bound to the receptor, what was revealed by signals originating from the formed complexes and by the pattern of their fragmentations. The only exception was found for Cs⁺, an ion of the biggest radius amongst monovalent cations where defragmentation of the host molecule did not occur. This is the most probably due to close intramolecular binding. In solution, the reversed binding affinities were found. In that case the most suitable metal ions to form supramolecules were the smallest ones in each studied group, namely Li⁺ and Mg²⁺ ions. Similarly to metal ions also ammonium cationic of organic molecules were strongly bound to the host in the gas phase with preferences towards pentaetylenehexamine (5EN6A). Quite surprisingly, only moderate interactions were found in solution.

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