Supramolecular complexes of podand ligands with xenon

Research Article

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Abstract: Formation of stable complexes between xenon and podand polyoxyethylene ligands was ascertained. The complexation process was studied by ^{129}Xe NMR titration, NMR diffusiometry and heteronuclear NOE measurements. The ligands studied form a 1:1 complexes with Xe(0). Their stability constants depend on the ligand structure, *i.e.*, polyoxyethylene chain length, number of complexating polyether units and the topology of the anchoring centre.

Keywords: Podand • Xenon • ^{129}Xe NMR • Complexation • Supramolecular Chemistry
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1. Introduction

Complexation of gases is one of the fastest developing and most interesting areas of supramolecular chemistry. Bonding of gas molecules is an important process which is employed in gas sensing, gases separation or their purification. Among others, formation of xenon complexes is one of the most fascinating and most widely studied phenomena. The interaction with xenon atoms is an excellent probe for studying porous inorganic, metalorganic and organic materials [1-14], membranes and fullerenes [15,16]. Since the ^{129}Xe isotope is a NMR active nucleus and can be easily observed in NMR experiments, ^{129}Xe NMR spectroscopy is widely used for studying its interactions [17,18]. Moreover, the xenon containing complexes are useful labels used for investigation of proteins, nucleic acids and other biomolecules by NMR spectroscopy [19-23]. ^{129}Xe NMR spectroscopy is an interesting tool in fullerene chemistry of endohedral fullerenes, because of a high sensitivity of the xenon nucleus to a modification of carbon cage [24].

The most important host molecules, used for xenon binding, are the cryptophanes [19-23,25-28]. The other supramolecular ligands, such as cyclodextrins, calixarenes, hemicarcerands or cucurbiturils have been much less intensively studied [25,29-32]. We have been able to find only two reports concerning the interactions of xenon atoms with crown ethers [33,34]. No information on complexation of xenon with acyclic supramolecular ligands (podands) has been published.

Podands, the acyclic supramolecular ligands make an important class of host molecules. Their non-rigid structure permits the complexation of various guests (ions or neutral molecules), but results in a decreasing selectivity of this process and a decrease in the stability constants of the complexes formed [35]. The NMR studies of the interactions between podands and various metal ions and neutral molecules have been published in a large number of papers [36-40]. This paper describes the first results on the interactions between podands and xenon. The high sensitivity of xenon chemical shifts to the interactions with host molecules is an excellent tool for studying a Xe(0) binding by supramolecular ligands. The results obtained have been supported by heteronuclear Overhauser effect measurements and ^{129}Xe NMR diffusiometric studies.

2. Experimental procedure

The compounds studied were prepared according to the procedures described elsewhere [41-49]. All

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spectra were measured at 298 ± 0.1 K. The [129]Xe NMR spectra were recorded on a Bruker Avance DRX 600 spectrometer operating at 166.945 MHz, equipped with a 5 mm triple-resonance inverse probe head {[1]H/^{31}P/BB} with a self-shielded *z*-gradient coil (90° [129]Xe pulse width 11.0 µs). The measurements were made using a simple one-pulse sequence with 30° observing pulse (*zg30*) without proton decoupling. The spectral width was 40 kHz, acquisition time – 5 seconds and relaxation delay – 50 seconds. To obtain a satisfactory signal-to-noise ratio (at least 1:500), between 100 and 500 scans were accumulated. The line broadening with *lb* factor of 1 Hz was applied in all spectra. A 1 mM solution of XeF_2 in acetonitrile was used as a reference (-3227.1 ppm *vs.* Xe gas extrapolated to zero pressure) [18]. The ^{1}H NMR spectra were measured on the same spectrometer using standard acquisition parameters (resonance frequency 600.303 MHz).

To minimize the interactions with solvent, [^{2}H]-chloroform was used for the measurements. The solvents were carefully dehydrated and deoxygenated before use. The samples were prepared by passing pure xenon gas through a solution of a given ligand at 253 K. The samples (0.5 mL) were transferred to NMR tubes which were than sealed at 1013 hPa and left for equilibration at 298 K for 24 hours before spectra were recorded. Inside the NMR tube, a 1 mm capillary containing 0.1 mL of 1 mM solution of XeF_2 in acetonitrile was coaxially mounted. The final concentration of xenon in the sample was calculated from the areas under the Xe(0) and XeF_2 signals. The obtained concentration values were compared with that calculated from the mass of xenon adsorbed, determined by weighting of the sample before and after Xe gas passing. The differences were less than 5%. The errors in established host/guest ratios were smaller than 0.01.

The heteronuclear Overhauser effects (heteroNOE) were measured by selective irradiation of the sample with the resonance frequencies of defined proton signals with simultaneous recording of the [129]Xe spectrum. The xenon signal intensity was compared with that obtained if the ^{1}H frequency was set at *ca.* 8000 Hz downfield from the TMS signal, *i.e.*, outside the region of ^{1}H signals. All spectra were recorded with the same acquisition parameters. 512 scans were accumulated for each spectrum. The relaxation delay of 50 seconds was applied.

The [129]Xe NMR diffusion measurements were performed with 2D LED pulse program (*ledgp2s* sequence from Bruker library). PFGs were calibrated with 1% of H_2O in D_2O ($D = 1.90×10^{-9}$ m² s⁻¹ at 298 K). The gradient strength was changed from 2 to 95% in 30 steps. Each spectrum was acquired with 128 scans

and acquisition time of 10 seconds and the relaxation delay of 50 seconds was used. For ^{1}H NMR diffusiometry measurements 64 repetitions were accumulated for each point. The acquisition time was 3 seconds, while the relaxation delay was 5 seconds for these experiments. The spectra were recorded for 0.05 M solution of the ligand. The ligand to guest ratio ([L]/[Xe]) for [129]Xe NMR diffusion measurements was 10, while the diffusiometric ^{1}H NMR experiments were carried out for ligand solution before and after xenon addition ([L]/[Xe] = 0.1). A solution viscosity was determined at 298 ± 0.1 K with an Ubbelohde viscosimeter, calibrated with distilled water. At least five readings were taken with a repeatability within ± 0.05 s.

3. Results and discussion

The studied ligands belong to two groups. The first one consists of di- and trialkoxysilanes, derivatives of dimethyl and methylsilane. The alkoxy unit is a polyethylene glycol chain, terminated with a methoxy, decyloxy or phenoxy group (Fig. 1). The second class of ligands is derived from cyclic and acyclic oligosiloxanes. The poly(oxyethylene) arms are connected to the silicon atom via 1,3-propylene linker. Three different types of polyethers were used for the synthesis: polyethylene, poly(1,2-propylene) and poly(1-phenylethylene) glycols. Two different types of terminal groups (methoxy and decyloxy) were used (Fig. 2). The compounds studied differ in the number of complexating arms, their length, hydrophobicity and geometry of the anchoring centre.

3.1. [129]Xe NMR chemical shift titration

The relaxation of [129]Xe nuclei of dissolved Xe(0) is slow. For isotropic solvents, T_1 values of 50-200 seconds have been reported [50,51]. The systems studied in this work shows faster relaxation. The T_1 values are less than 10-20 seconds, depending on the ligand used and the host to guest ratio. This permits optimisation of the relaxation delays used during acquisition (50 seconds). A representative example of the [129]Xe NMR spectra is shown in Fig. 3.

As the [129]Xe NMR chemical shift of dissolved xenon is very sensitive to the solvent character, the reference measurements for a solution of Xe gas in chloroform, containing various amounts of non-complexating ethers were made. Tetrahydrofurane and 1,2-dimethoxyethane were used as the ethers not forming supramolecular complexes with xenon. In each sample, the xenon concentration was 0.010 ± 0.001 M. The results are presented in Fig. 4.
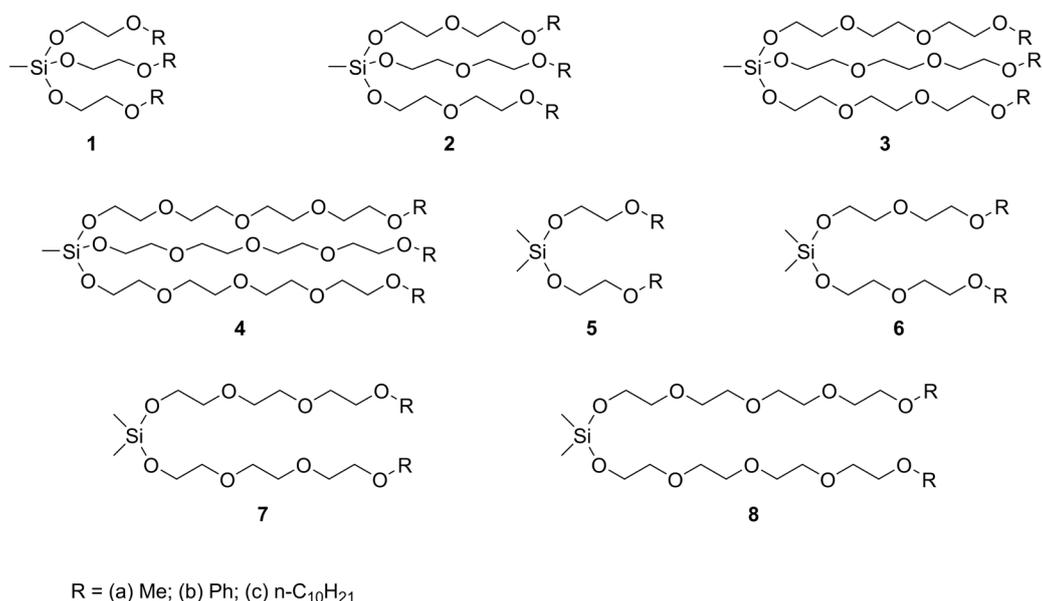
R = (a) Me; (b) Ph; (c) n-C$_{10}$H$_{21}$

Figure 1. Structures of the studied ligands, alkoxysilane derivatives.

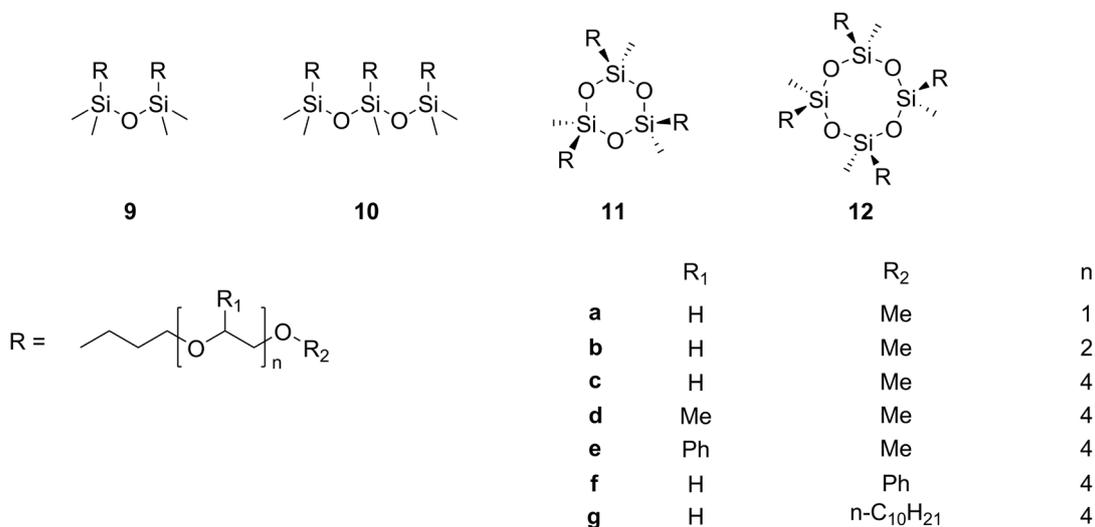|	R$_1$	R$_2$	n
a	H	Me	1
b	H	Me	2
c	H	Me	4
d	Me	Me	4
e	Ph	Me	4
f	H	Ph	4
g	H	n-C$_{10}$H$_{21}$	4

Figure 2. Structures of the studied ligands, oligosiloxane derivatives.

The observed monotonic changes are similar to those reported previously [33,34], *i.e.*, a linear dependence of the chemical shift on the molar ratio of ether was obtained (Eq. 1):

$$\delta_{obs} = \delta_E x_E + \delta_S (1 - x_E) \tag{1}$$

where δ_E and δ_S are the chemical shifts of xenon dissolved in ether and chloroform, respectively; x_E – the molar ratio of ether.

The ^{129}Xe NMR titration of a given xenon solution with podand ligands gave curves of shapes different from that discussed above. An increase in the ligand/xenon ratio causes a strong deshielding of the ^{129}Xe NMR signal. For all studied ligands, only one signal was observed in the xenon spectra, which indicated a fast exchange between the complexed and free xenon atoms. The xenon concentration in the samples was *ca*. 0.01 M and its exact value was determined in each solution to calculate the xenon/ligand ratio, which varied in the range 0.1-10. For each system studied, at least 15 samples of compositions from within this range were prepared and their ^{129}Xe NMR spectra were measured. An example of titration curves of ^{129}Xe NMR are presented in Fig. 5.

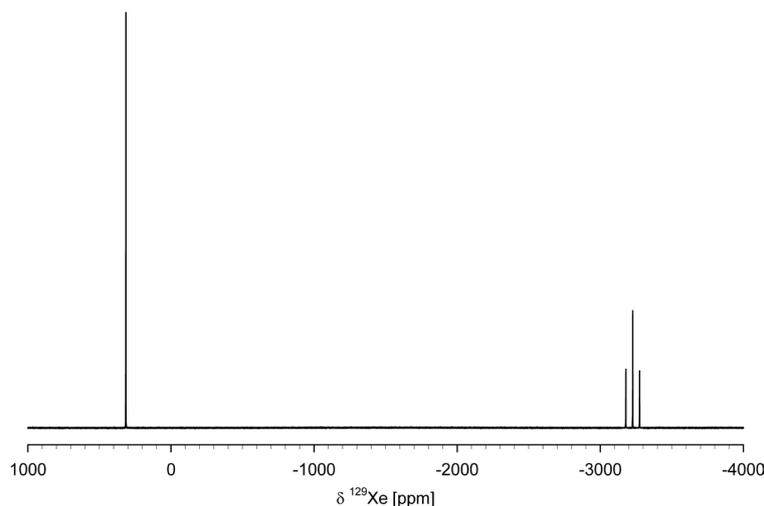**Figure 3.** Example of ^{129}Xe NMR spectrum: 319 ppm – averaged signal of Xe(0) (ligand **3a**, [L]/[Xe] = 9.95, in CDCl$_3$); -3227 ppm XeF$_2$ in CD$_3$CN ($^1J_{XeF}$ = 5640 Hz).

The observed chemical shifts are described by the three site model (Eq. 2) [33].

$$\delta_{obs} = \delta_{out} x_{out} + \delta_B x_B + \delta_{in} x_{in} \quad (2)$$

where δ_B is the chemical shift of xenon solvated by chloroform, δ_{out} – the shift of xenon in close environment of ether ligand, δ_{in} – the chemical shift of encapsulated xenon; the symbol x_i stands for molar ratios of the corresponding xenon forms.

According to the three site model proposed for describing crown ether-xenon interaction, xenon forms a 1:1 complex with a host molecule, while the non-complexed fraction is statistically distributed (solvated) between ether and chloroform molecules. We did not detect formation of complexes of higher host/xenon stoichiometric ratio. For further calculations the chemical shift of xenon in bulk phase (δ_B) was assumed to be equal to the value in pure chloroform (δ_S). If we assume that the ratio of the chloroform (x_B) and ligand (x_{out}) solvated xenon atoms are proportional to the composition of the solution (x_E) (Eq. 3) and express by the equilibrium constant (K) (Eq. 4):

$$x_{out} x_B^{-1} = x_E \left(1 - x_E\right)^{-1} \quad (3)$$

$$K = \frac{[Xe]_{in}}{[Xe]_{free} [L]_{free}} \quad (4)$$

the observed chemical shift may be expressed as (Eq. 5):

$$\delta_{obs} = Z\delta_{in} + \left(1-Z\right)\left[\left(1-x_E\right)\delta_S + x_E\delta_{out}\right] \quad (5)$$

where Z is:

$$Z = \frac{\left(K^{-1} + [Xe]_0 + [L]_0\right) - \sqrt{\left(K^{-1} + [Xe]_0 + [L]_0\right)^2 - 4[Xe]_0[L]_0}}{2[Xe]_0} \quad (6)$$

The obtained titration results were fitted to Eq. 5. The parameters obtained from the fitting (K, δ_{out}, δ_{in}) are presented in Tables 1 and 2. For the calculations, the formation of 1:1 complexes was assumed. The extension of the model used (Eq. 2) by considering formation of complexes of higher stoichiometry does not improve the fitting results.

Xenon atoms are not bonded by ligands with small cavities (*e.g.* **1**, **5**). For these molecules the stability constants are very low ($K < 2$ M^{-1}) and their values are smaller than the estimated error of K determination. Therefore it could be concluded that for these podands the inclusion complexes do not form. The other ligands form stable complexes with xenon. Within the series of alkoxysilyl ligands (**1**-**8**), the stability of the complexes formed increases with the number of the complexing arms and their length. The values obtained for tripodands are about 5-times higher than those for the corresponding dipodands (*e.g.* 51 M^{-1} *vs.* 12 M^{-1} for **3a** and **7a**, respectively). The number of polyoxyethylene units (n) also influences the stability constants. As found, the ligands built of shorter chains ($n = 1$) did not bind xenon atoms. Their homologues, containing two oxyethylene repeat units ($n = 2$) in the complexing arms can encapsulate Xe atoms but the stability constants are rather low (*e.g.* $K = 22$ for **2a**). With increasing n value, more stable complexes with xenon are formed, although the difference between the stabilities of the derivatives with $n = 3$ and $n = 4$ is not very significant

Table 1. Results of the ^{129}Xe NMR titration experiments for alkoxysilane ligands and solvents used.

Ligand	K [M^{-1}]	Chemical shift [ppm]	
		δ_{in}	δ_{out}
CDCl3	-	-	216.4 ± 0.1
THF	-	-	161.9 ± 0.1
1,2-Dimethoxyethane	-	-	185.0 ± 0.1
1a	n.r.	-	194 ± 1
2a	22 ± 2	337 ± 5	192 ± 4
3a	51 ± 3	345 ± 4	192 ± 3
3b	55 ± 2	342 ± 3	188 ± 4
3c	59 ± 1	347 ± 5	190 ± 3
4a	55 ± 2	353 ± 4	191 ± 3
5a	n.r.	-	189 ± 1
6a	9 ± 3	268 ± 8	186 ± 4
7a	12 ± 3	264 ± 5	188 ± 4
8a	22 ± 1	265 ± 3	186 ± 3

n.r. - formation of inclusion complex has not been detected (K < 2 M^{-1})

Table 2. Results of the ^{129}Xe NMR titration experiments for siloxane ligands.

Ligand	K [M^{-1}]	Chemical shift [ppm]	
		δ_{in}	δ_{out}
9a	8 ± 3	232 ± 4	180 ± 5
9b	23 ± 3	230 ± 7	184 ± 3
9c	26 ± 2	235 ± 4	188 ± 3
10a	13 ± 2	237 ± 2	193 ± 1
10b	28 ± 2	240 ± 3	194 ± 3
10c	30 ± 3	240 ± 2	195 ± 2
11a	80 ± 4	355 ± 5	190 ± 2
11b	89 ± 3	360 ± 4	192 ± 3
11c	87 ± 4	361 ± 4	195 ± 3
11d	33 ± 2	270 ± 10	174 ± 7
11e	27 ± 2	220 ± 6	170 ± 5
11f	95 ± 3	366 ± 2	193 ± 3
11g	93 ± 5	365 ± 4	191 ± 4
12a	98 ± 7	403 ± 7	199 ± 3
12b	105 ± 4	411 ± 3	201 ± 3
12c	110 ± 3	406 ± 5	200 ± 2

(K = 51 and 55 M^{-1} for **3a** and **4a**, respectively). This indicates that the channel built of three triethylenoxy units is large enough for effective bonding of the Xe atom. The dipodand molecules could not form a channel and their podand chains did not surround the complexed species effectively. In consequence, the complex formed could readily dissociate. The PM7 calculated structures of the Xe complexes with these ligands reaffirm the NMR titration results (for figures see Supplemental Information), *i.e.*, the xenon atom may be effectively bonded inside the channel by ligands **2** & **3**, but not by **1**. The dipodands do not form a cavity and the binding on Xe atom results in folding of the ligand molecule (Xe⊂**7a**).

The character of the end group (R) did not affect the stability constant significantly. The complexes with phenyl (series **c**) or decyl (series **b**) moieties are slightly more stable than methyl derivatives, but the differences are small (*e.g. K* are 59, 55 and 51 M^{-1} for **3c**, **3b** and **3a**, respectively). This is probably a result of stabilization of the channel structure by Van der Waals interactions of the end phenyl or decyl groups.

Similar trends were observed in the second class of ligands, *i.e.*, the oligosiloxane derivatives. The weakest interactions were found for the ligands derived from linear siloxanes (**9** and **10**). Although the podands belonging to series **10** contain three complexing arms, only insignificant increase in the stability constants of their complexes with xenon was observed in comparison with those of analogous disiloxane derivatives. This is a result of high flexibility of the linear trisiloxane core. The ligands derived from 1,1,2,3,3-pentamethyltrisiloxane do not tend to form stable channels suitable for binding guest atoms. In consequence, series **10** of podands bind xenon
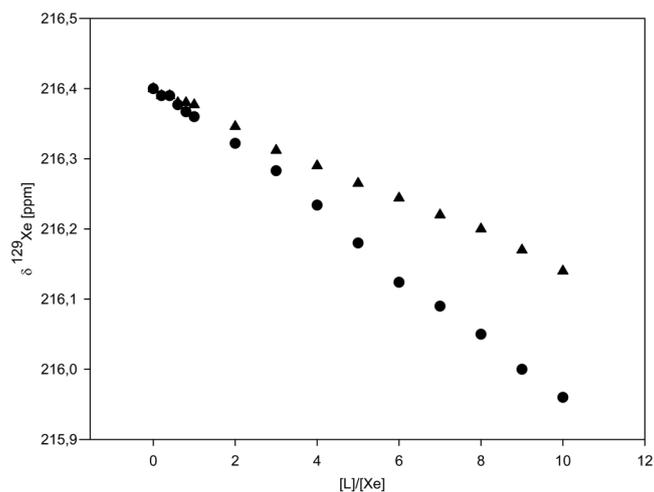
Figure 4. [129]Xe NMR titration curve of Xe(0) chloroform solution by non-complexing ethers: ● – THF; ▲ – 1,2-dimethoxyethane.
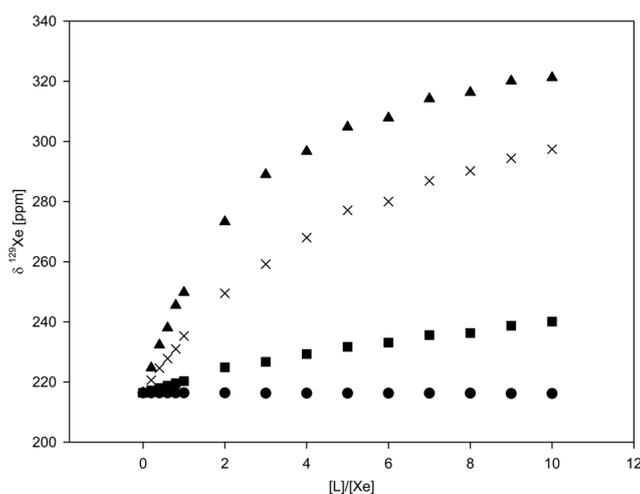

Figure 5. [129]Xe NMR titration curve of Xe(0) chloroform solution by ligands studied: ● – **1a**; ■ – **6a**; × – **2a**; ▲ – **3a**.

atoms in the cavity formed only by two polyoxyethylene chains, similar to that characterizing the ligands from series **9**. A small increase in the *K* values for podands of series **10** *vs*. those for series **9** is a result of a statistical effect. The formation of two-arm surrounded channel is more plausible for molecules containing three polyether units than by those containing two units. In contrast, the ligands derived from cyclic tri- and tetrasiloxane form very stable complexes with xenon guest (*K* values of *ca*. 100 M^{-1}). These ligands contain pre-organized polyoxyethylene chains, forming the bonding cavity of high affinity to guest atoms. The stability constants determined for cyclotetrasiloxane podands (series **12**) higher than those for the analogous cyclotrisiloxane ones (**11 a-c**) indicate that the channel formed by four complexating arms, grafted on eight-membered core, is

more suitable for binding a voluminous xenon atom. The calculated structures of the complexes between selected cyclosiloxane-derived ligands and xenon are presented in Supplemental Information.

The increase in the number of polyoxyethylene units (*n*) increases the stability constants of these complexes. The geometry of the anchoring centre and the presence of a 1,3-propylene linker between the Si atom and polyether units ensure that even the ligand with the smallest number of oxygen atoms (*n* = 1) effectively binds the xenon guest. As for alkoxysilane ligands, the character of the end group (R$_2$) only slightly influences the stability constants of the complexes with a xenon atom. The hydrophobic substituents (Ph, *n*-C$_{10}$H$_{21}$) minutely increase *K* values. The substitution of polyether chains with R$_1$ groups decreases the ability of complex formation

by the ligands studied. These groups disturb the process of channel formation because of steric interactions.

The observed chemical shifts of Xe(0) species solvated by the polyether ligands studied (δ_{out}) are similar for all compounds studied (between 180 and 200 ppm), and are very close to the values determined for xenon non-complexing solvents, THF (162 ppm) and 1,2-dimethoxyethane (185 ppm). The complexation results in deshielding of the xenon nucleus. The chemical shift of the xenon atom encapsulated inside the cavity of the podand molecule varies from 220 ppm (**11e**) to 411 ppm (**12b**). The small values found for poly(phenylethoxy) and poly(1,2-propylenoxy) derivatives result from the interactions of Xe atom with methyl or phenyl moieties, directed into the complexing cavity. Among the poly(oxyethylene) ligands, smaller chemical shifts were found for dipodands (series **5-9**). These ligands could not isolate the Xe(0) guest from the interactions with the medium, *i.e.*, the chloroform molecules. The complexing moieties of tri- and tetrapodands (series **1-4** & **11-12**) surround the xenon atom perfectly. For these ligands the guest interacts only with the inner side of the ligand cavity, resulting in a higher value of the chemical shift.

The line-width of xenon signal for xenon solution in chloroform is 5.5-7.0 Hz. It does not change significantly upon ether (THF or 1,2-dimethylethane) addition. Also the signals detected for the solution containing the podands studied have similar widths, 5.8-9.5 Hz.

As mentioned above, the exchange between bulk and encapsulated xenon atoms is fast in the NMR chemical shift time scale. For the systems containing ligands **3a** or **12c** and xenon ([L]/[Xe] = 1.0) in CDCl$_3$, the ^{129}Xe NMR spectra were recorded in low temperature (223 and 253 K). For these samples also only one signal was observed, as for measurements conducted at 298 K. This indicates that the exchange process is fast also in low temperatures. This behaviour is typical of podand ligands and their complexes with small, spherical guests.

3.2. Heteronuclear NOE measurements

For the ligands studied, forming the complexes with xenon atoms, a strong heteronuclear NOE was detected. The NOE values are defined as:

$$\eta = \frac{I_{ir} - I_{off}}{I_{off}} \times 100\% \tag{7}$$

where I_{ir} and I_{off} are the intensities of the ^{129}Xe NMR signal recorded for the samples during irradiation with proton resonance frequency and during off-resonance irradiation respectively.

Since the gyromagnetic ratio (γ) of the ^{129}Xe nucleus is negative, the observed NOE are negative, *i.e.*, the irradiation with proton resonance frequency results in decreasing intensity of the xenon resonance signal. The results of the NOE measurements are collected in Fig. 6. As shown, the irradiation of hydrogen atoms of the non-complexing ethers (THF, 1,2-dimethoxyethane) causes a small (< 1%), negligible decrease in the ^{129}Xe NMR signal intensity. Similarly, for non-complexing ligands (*e.g.* 1a) the effects are small (< 2%). Moreover, they are site non-specific, *i.e.*, the irradiation of each hydrogen signal in 1H spectrum causes a similar NOE. This is the effect of the intramolecular, non-bonding interactions between dissolved xenon and solute molecules. For xenon-binding podands, the NOE values are much higher. For example, the irradiation of the sample containing **11b**⊃Xe complex with a resonance frequency of CH$_2$O hydrogen atoms causes a decrease in ^{129}Xe signal intensity by 12% in comparison with that in the off-resonance irradiation spectrum. The irradiation of SiCH$_3$ or terminal CH$_3$ signals causes smaller effects, of the values 0.8 and 1.4%, respectively. These values are close to those observed for non-bonding molecules. This indicates a close proximity of xenon atom and hydrogen atoms of the polyether units.

For the ligands from the alkoxysilane series, the ^{1}H-^{129}Xe NOE effects are less pronounced for the methylene groups close to the Si atom (SiOCH$_2$ and SiOCH$_2$CH$_2$ ones) than for those of the next oxyethylene repeat units. This is the effect of the ligand molecule geometry. The space surrounded by the first OCH$_2$CH$_2$ units, the closest to the anchoring centre, is too small to complex effectively a xenon atom. The interaction of Xe with this part of the ligand molecule requires a strong deformation of the binding channel. Therefore, the guest atom is located far from the Si centre, which causes the highest NOEs observed for the second, third and four oxyethylene unit hydrogen atoms.

3.3. ^{129}Xe NMR diffusiometry

To confirm the complexation of xenon atoms by the ligands studied, the ^{129}Xe NMR diffusion studies were made. According to the Stokes-Einstein-Debye equation (Eq. 8), the diffusion coefficient for isotropic diffusion process is expressed as:

$$D = \frac{k_B T}{6\pi\eta a} \tag{8}$$

where k_B is Boltzman constant, T – temperature, η - solution viscosity, a – hydrodynamic radius of the molecule.
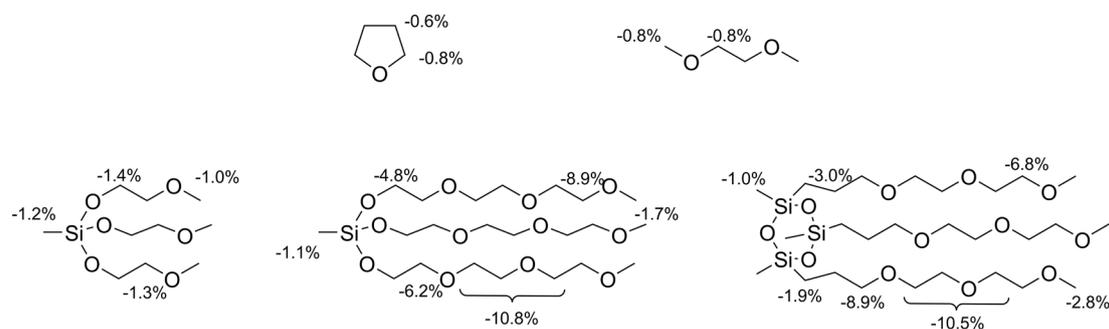
Figure 6. Observed heteronuclear NOE effects for selected ligands and model compounds.

This relation is true for the motion of the solute particles larger than the size of solvent molecules. The Stokes-Einstein-Debye equation may be used for expression of the polyoxyethylene ligands (or their complexes) diffusion. The self-diffusion of free xenon atoms in solution may be described by the Evans equation [52,53] (Eq. 9):

$$D = A\frac{T}{\eta^{\gamma}} \tag{9}$$

where A and γ are the parameters depending mainly on the solute character.

As the xenon atom bonded by the ligand (L⊃Xe complex) has much greater hydrodynamic radius than the free one, the diffusion coefficients of these species must be different. For non-complexing systems, the observed diffusion coefficients of xenon depend only on the solution viscosity and temperature. For the solutions containing xenon-bonding ligands (if the reaction is fast in NMR chemical shifts time-scale), the D_{obs} value depends on the diffusion coefficient of free and bonded xenon and the molar fractions of these two species (Eq. 10).

$$D_{obs} = x_{free}D_{free} + \left(1 - x_{free}\right)D_{bound} \tag{10}$$

The D_{free} was calculated from Eq. 9. The solution viscosities were determined for each sample. The A and γ parameters for the free xenon atom were determined from the NMR diffusiometric measurements performed for xenon solutions in wide range of solvents (see Fig. 7) and are $(1.78\pm0.04)\times10^{-13}$ [N K^{-1}] and 0.57 ± 0.01 at 298 K (lit. 1.86×10^{-13} and 0.56, respectively) [54].

As the complexation of the xenon atom by the ligand molecule is expected not to significantly affect the hydrodynamic radius of the podand molecule, the D_{bound} values of the complexed xenon atom were assumed to be equal to the diffusion coefficients determined

from ^{1}H NMR diffusion measurements. The D_{bound} values calculated from ^{1}H NMR diffusiometry for are the same as for free ligand molecules. The observed differences are less than 0.02×10^{-9} m^2 s^{-1}. The values obtained are summarised in Table 3 and show that the non-complexing ethers and podands do not significantly influence the diffusion coefficient of the xenon atom, *i.e.*, the observed D values are within the experimental error equal to the values calculated from the Stokes-Einstein-Debye equation. The changes observed for the systems containing Xe-binding ligands are higher. The observed diffusion coefficient for xenon atoms is much smaller than that expected for free xenon atom in solution. This confirms the complexation of xenon inside the channel formed by the ligand molecule. The values of the association constants calculated from diffusion measurements are in good agreement with those obtained from ^{129}Xe NMR chemical shift titration. The differences between the K values obtained from these two approaches probably follow from overestimation of the D_{bound} value.

4. Conclusions

The results presented permit us to conclude that xenon may be effectively complexed by podand ligands containing polyether units and therefore these ligands make a new class of the xenon-binding molecules. Unfortunately, the exchange between the bounded and free xenon atoms in studied systems is fast in the NMR time-scale. The stability constants of the complexes formed strongly depend on the structure of the ligand, especially on the number of the complexing moieties and their length as well as the geometry of the anchoring centre of the podand molecule.

The stability constants of the complexes formed reach a value of 200 M^{-1}. This indicates that they are more stable than Xe(0)-α-cyclodextrin complex (K ≈
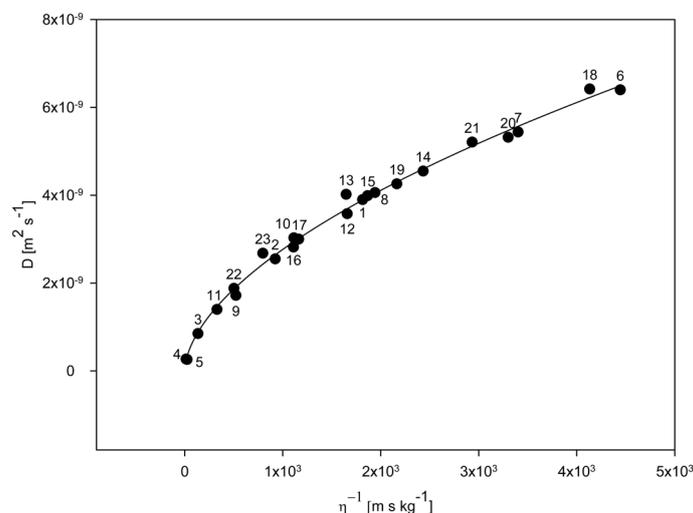
Figure 7. Diffusion coefficient (*D*) of Xe(0) in various solvents; ● – experimental points (1 – methanol, 2 – ethanol, 3 – *n*-octanol, 4 – cyclohexanol, 5 – 2,4-dimethylphenol, 6 – *n*-pentane, 7 – *n*-hexane, 8 – *n*-octane, 9 – *n*-tetradecane, 10 – cyclohexane, 11 – *cis*-decalin, 12 – benzene, 13 – *p*-xylene, 14 – dichloromethane, 15 – chloroform, 16 – tetrachloromethane, 17 – hexafluorobenzene, 18 – diethyl ether, 19 – tetrahydrofuran, 20 – acetone, 21 – acetonitrile, 22 – dimethyl sulfoxide, 23 – dimethylformamide), (—) – power regression graph (*D* = $AT\eta^{-\gamma}$; *T* = 298 K, *A* = 1.78×10^{-13} N K^{-1}, *γ* = 0.57).

Table 3. Results of ^{129}Xe NMR diffusiometric measurements of complexation process.

Ligand	$\eta \times 10^4$ [kg s^{-1} m^{-1}]	$D_{obs} \times 10^9$ [m^2 s^{-1}]	$D_{free} \times 10^9$ [m^2 s^{-1}]	$D_{bound} \times 10^9$ [m^2 s^{-1}]	K [M^{-1}]
-	5.36	3.99 ± 0.05	-	-	-
1a	6.84	3.37 ± 0.05	3.4 ± 0.3	1.14 ± 0.02	n.r.
3a	11.60	1.31 ± 0.05	2.5 ± 0.3	0.76 ± 0.02	47 ± 5
9a	6.02	3.10 ± 0.05	3.6 ± 0.3	0.95 ± 0.02	5 ± 5
11a	8.97	1.25 ± 0.05	2.9 ± 0.3	0.77 ± 0.02	75 ± 10
11c	14.71	0.89 ± 0.05	2.2 ± 0.2	0.56 ± 0.02	85 ± 10
12a	10.40	1.06 ± 0.05	2.7 ± 0.3	0.68 ± 0.02	92 ± 7
12c	19.83	0.71 ± 0.05	1.8 ± 0.2	0.47 ± 0.02	105 ± 12

n.r. - formation of inclusion complex was not detected (K < 2 M^{-1})

23 M^{-1} in H$_2$O) [29] or crown ethers (*K* ≈ 0.08 M^{-1} for 12-crown-4 and 15-crown-5 in CDCl$_3$) [33] but much less stable than Xe(0) adducts with many cryptophanes (*K* values between 10 and 30 000 M^{-1}) [25,27,55]. The values of *K* close to those observed for Xe(0)-podands systems have been reported for cucurbit[n]urils and hemicarcerands [25,31,56].

Acknowledgements

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