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Anti-sieve effect in guest inclusion by thiacalix[4]arene giving a surge in thermal stability of its clathrates prepared by solid-phase guest exchange

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An unusual bell-like relationship between guest size parameter and properties of thiacalix[4]arene (**1**) clathrates was observed, which is a source of their very high thermal stability. For this, calixarene **1** clathrates were prepared in binary ‘solid host – guest vapor’ system and by solid-phase exchange with guests of various molecular structure. The clathrates were studied by thermal analysis and X-ray powder diffractometry. Calixarene **1** was found to have a specific anti-sieve effect excluding smaller guest compounds, while having a preference for the larger ones. This effect may be avoided using solid-phase guest exchange in clathrate preparation, but it contributes much to the thermal stability of exchange products.

Introduction

In search of materials for storage of gases and volatile compounds, the problem is to find a guideline, which helps to understand, in which direction one should modify sorbent (receptor or host) structure to reach a maximal clathrate stability. A wide range of structures is offered for this purpose, from metal organic frameworks[1] to clathrate forming hosts, which have more or less flexible structure giving more or less high inclusion capacity and stability of saturation products[2,3]. The highest stability, as estimated by increase in onset temperature of guest release, T_{on}, compared with guest boiling point, T_{bp} was found for calixarene clathrates, which have this value up to 370°C[2].

The source of this clathrate stability is cooperativity of clathrate crystals, which can be seen from the shape of guest sorption isotherms determined for the hosts being homogeneous enough[4,5]. Once crystal formation is cooperative, so is its decomposition with a strong hysteresis related to this property[6]. Hence, despite the Gibbs energy of guest inclusion (standard state pure liquid guest) is not large, being normally less than 10 kJ per 1 mol of guest[4], clathrates may be very stable because simultaneous movement of a large number of host and guest molecules should occur giving crystal destruction with phase transition.

The problem is how are clathrate cooperativity and related stability linked with the host and guest molecular structure and crystal packing and with the used preparation method? In our previous work, the latter was shown to be relevant for clathrates of *tert*-butylthiacalix[4]arene[3]. Modification of clathrate preparation method using solid-phase exchange of included guest for another one, Procedure II, Fig. 1, may give clathrates with a higher thermal stability than those prepared in binary host-guest systems, Procedure I, Fig. 1. Success of this approach may depend on the size ratio of the initially bound and substitute guests[3].

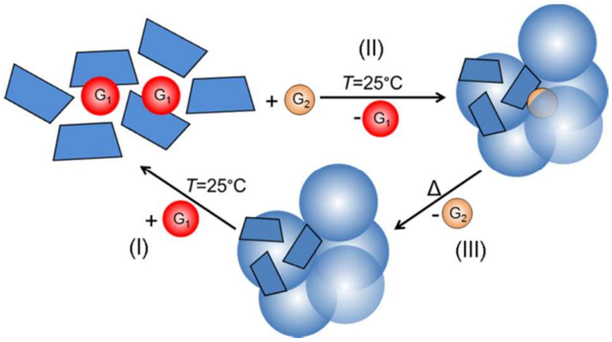
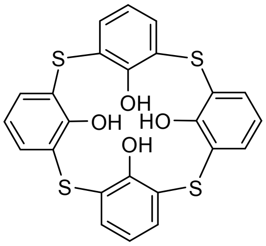


Fig.1 Scheme of the studied clathrate preparation procedures with calixarene **1**.

In the present work, unusual structure-property relationships were studied for clathrates of thiacalix[4]arene (**1**), being relevant for their thermal stability. Calixarene **1** has a close molecular structure and packing of its clathrate[7] to that of calix[4]arene having very stable inclusion compounds with gases and volatile guests[2]. Still, host **1** has a little larger macrocycle than calix[4]arene, which may be favorable for clathrate stability, and more suitable clathrate may be found as an initial one for preparation of other clathrates by guest exchange. In the present work, the clathrates of **1** with guests of various molecular size and composition were studied as prepared by vapor saturation of solid **1** or its clathrate according to Procedures I and II, Fig. 1.



Thiacalix[4]arene (**1**)

For the structure-property relationships to be adequately revealed, the studied clathrates should be prepared under standard conditions, which is possible at saturation of solid host with guest vapors without liquid/solid phase contact[4]. This preparation method helps to avoid possible and rather unpredictable concentrating of guest impurities in crystals formed at the clathrate crystallization from solution in liquid guest, not to say about crystallization from binary solvents. For example, liquid-liquid diffusion of hexane into a chloroform solution of **1** gives crystals of its clathrate with water[7]. Besides, preparation of clathrates in ‘solid host + guest vapor’ systems excludes nonequilibrium temperature effects, which are possible at crystallization from initially hot host solutions[8]. A deficiency of vapor saturation method is preparation of clathrates in only a crystal powder form. The formation of single crystals is excluded when clathrate forms with phase transition.

In the present work, this standard method of clathrate preparation by saturation with the guest vapor having a fixed relative vapor pressure, or thermodynamic activity, is used to reveal an unusual relationship between parameters of host **1** clathrates and guest size. This relationship is a cause of very high thermal stability of its inclusion compounds prepared by guest exchange.

Experimental

Materials. Thiacalix[4]arene (**1**) was synthesized according to a previously described procedure[7] and purified from nonvolatile impurities by multiple recrystallization from the mixture of $CHCl_3$/*n*-hexane. The volatile impurities were removed by heating of host **1** for 5 h at 230°C in a vacuum (100 Pa). Calixarene **1** did not change its initial white color in this drying process, which served as an additional evidence of its purity. Besides, no mass loss and phase transitions were observed for dried calixarene up to 300°C in thermoanalysis described in Electronic Supplementary Information (ESI). Organic guests were purified and dried as described elsewhere[9]. The purity of guests checked by GC analysis was at least 99.5%.

Sample preparation. The samples of clathrates were prepared as described elsewhere[10], by saturation of dried **1** or its pyridine clathrate, 7-15 mg, with vapors of organic guests in aluminum crucibles inside of hermetically closed 15 ml vials for 72 h at 25 °C. Equilibration of pyridine clathrate with water vapors was for 120 h. In these experiments, the samples of liquid organic guest or water were taken in the amount of 100 μl giving nearly saturated vapor pressure of $P/P_0=1$ at the equilibrium. Sample of the intermediate clathrate of **1** with pyridine was prepared by heating of corresponding saturated clathrate from room temperature to 110°C on the air inside oven for 8 min. The sample was removed from the oven immediately after its temperature reached the target value.

Simultaneous TG/DSC/MS experiments. Simultaneous thermogravimetry (TG), differential scanning calorimetry (DSC) with mass-spectrometric detection of evolved vapors (MS) of calixarene **1** and its clathrates were performed using a thermoanalyzer STA 449 C Jupiter (Netzsch) coupled with quadrupole mass-spectrometer QMS 403 C Aeolos as described elsewhere[10]. This experiment was made in argon flow of 75 ml/min. Two different modes of heating were used in thermonalysis: (1) normal mode with a constant heating rate of 10 K/min in the preset temperature range, and (2) dynamic heating at the rate of 10 K/min up to 280°C combined with further isothermal mode for 30 min at this temperature. Composition of exchange products evolving pyridine and substitute guest in the same temperature range were determined using calibration of mass-spectrometer with direct sampling of corresponding liquids to its injection chamber. The error of guest contents determination is below 0.02 mol guest per 1 mol host for stable clathrates.

X-ray powder diffraction (XRPD) experiments. The X-ray studies were performed by Bruker AXS *D*8 Advance diffractometer equipped with Vario attachment and Vantec linear PSD, using $CuK_{\alpha 1}$ radiation (40 kV, 40 mA) via the curved Johansson monochromator (λ = 1.5406 Å). Room-temperature data were collected in the reflection mode with a flat-plate sample. The host and clathrate powder samples were slightly pressed in a standard sample holder or on the quartz plate before experiment. Patterns were recorded in the 2Θ range between 5 and 50°, in 0.0081° steps, with exposure times of 0.3-1.0 s in each point without sample rotation. Three powder patterns were collected and summed for each sample. Indexing and pattern decomposition were performed as described in ESI.

Results and discussion

Composition and thermal stability of calixarene 1 clathrates formed in binary host-guest systems. To test the ability of **1** to form stable clathrates in binary systems, the inclusion by solid guest-free **1** was studied for vapors of guests with various structures: water, aliphatic alcohols, acetonitrile, acetone, chloroalkanes, trichloroethylene, aromatic hydrocarbons, pyridine and cyclohexane. Formed clathrates were studied using simultaneous TG/DSC/MS analysis. Thermograms determined are shown in Fig. 2 and ESI. Clathrate parameters, including mass loss Δm, %, guest contents S, mol guest/mol host, onset temperature T_{on} and enthalpy ΔH_e of guest release, are given in Table 1.

Calixarene **1** was found to include benzene, toluene, cyclohexane, chloroform, tetrachloromethane, trichloroethylene and pyridine with formation of the clathrates, which are stable on the air. Thermograms of these clathrates have a clear step of mass loss in a narrow temperature range corresponding to an ion peak of guest release, Fig. 2 and ESI. On the contrary, host **1** does not bind water, methanol, ethanol acetonitrile, acetone, dichloromethane and 1,2-dichloroethane above the trace level (0.2% by weight). Thermograms of the initial guest-free **1** and products of its saturation with water and methanol are given in ESI. Guest-free **1** loses less than 0.19% of its mass in the temperature range of 30-300°C. It melts at 310°C with enthalpy of $\Delta H_m = 34\pm1$ kJ/mol.

All clathrates of **1** prepared in binary systems lose guest below 280°C in one step, Fig. 2a-e, except for pyridine clathrate, which has two steps of guest release, Fig. 2f. Further heating of studied clathrate samples does not give significant loss of their mass caused by guest elimination. This was checked by thermal analysis in combined mode including an isothermal stage at 280°C. The corresponding thermogram of pyridine clathrate is given in ESI.

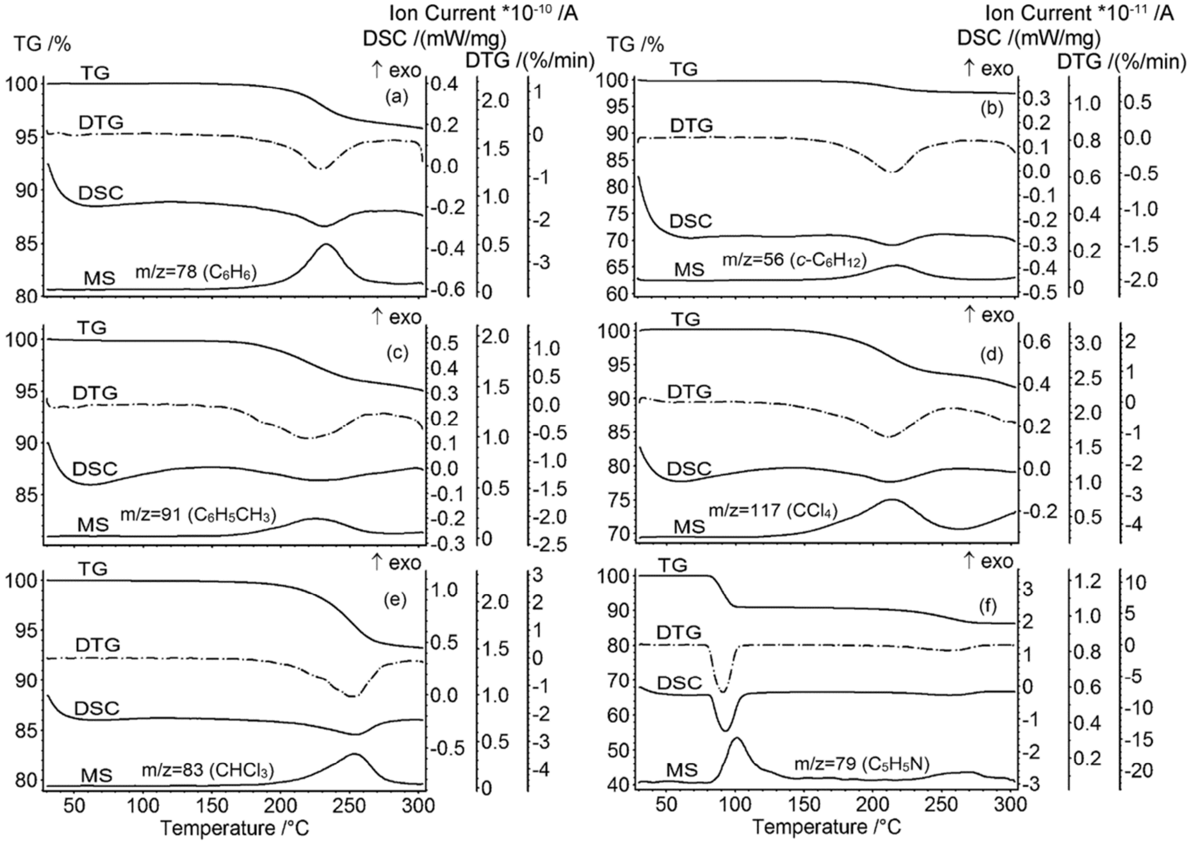


Fig. 2 Thermograms of host **1** clathrates prepared in binary systems by equilibration of solid host **1** with saturated guest vapors, P/P_0=1, 25°C: (a) **1**·$0.25C_6H_6$; (b) **1**·0.14*c*-C_6H_{12}; (c) **1**·$0.25C_6H_5CH_3$; (d) **1**·$0.22CCl_4$; (e) **1**·$0.30CHCl_3$; (f) **1**·$1.00C_5H_5N$.

Table 1 Data of thermal analysis for stable clathrates of host **1**.

Guest	Δm, %	S	T_{on}, °C	ΔH_e, kJ/mol
$CHCl_3$	6.69	0.30	221	31±6
C_2HCl_3[a]	6.58	0.27	233	40±10
CCl_4	6.46	0.22	176	35±8
C_6H_6	3.77	0.25	204	31±8
$C_6H_5CH_3$	4.36	0.25	185	40±6
c-C_6H_{12}	2.28	0.14	186	32±2
C_5H_5N	13.7 (9.28[b])	1.00 (0.32[c])	84; 225	72±2; 38±5

[a] thermogram is given in ESI; [b] mass loss in the first step of guest release; [c] guest contents in clathrate formed after the first decomposition step.

Guest contents in **1** clathrates are in the range of S=0.22÷0.30 for all guests except pyridine and cyclohexane, Table 1. Cyclohexane clathrate contains minimal guest amount of S=0.14. Content of pyridine in its saturated clathrate is S = 1.00. This is the least stable clathrate among those studied as estimated by the first step of decomposition with T_{on} = 84°C. At this stage, it loses two-thirds of the included guest with the formation of **1**·$0.32C_5H_5N$ clathrate, which has a close composition and onset temperature of guest release, T_{on} = 225°C, to those values of the other studied clathrates. The other clathrates have this point in the range of T_{on} = 176 ÷ 233°C, Table 1.

The studied clathrates of **1** have only endo-effects of guest elimination in their DSC curves in the range of 30-300°C, Fig. 2, Table 1. Almost all these effects, except the first step of pyridine release, have the enthalpy values of ΔH_e = 31÷40 kJ/mol being close to the vaporization enthalpies ΔH_V = 31÷40 kJ/mol of corresponding guests[11]. This means a complete collapse of host phase into a dense form when the guest is removed. Enthalpy of pyridine elimination at 84°C is ΔH_e = 72 kJ/mol, which is much higher than the value ΔH_V = 40 kJ/mol of pyridine[11]. This difference may be caused by a looser packing of formed intermediate clathrate **1**·$0.32C_5H_5N$ or by disruption of possible H-bond between pyridine and **1**. For comparison, formation enthalpy of H-bond between pyridine and phenol is –29 kJ/mol[12]. But the latter option is less probable, as *tert*-butylcalix[4]arene does not form H-bond with pyridine[13], and only stronger H-acceptor like *n*-butylamine is capable of breaking intramolecular H-bond of this host[8].

X-ray powder diffractogram of the initial guest-free **1** given in ESI is close to that calculated from single crystal X-ray data for **1**·⅔H_2O clathrate[7], where water is included inside trigonal bipyramids formed by spherical **1** trimers as shown in Fig. 1. The observed small shifts of guest-free **1** reflections correspond to a change of cell parameters from a=14.908(2), c=18.268(2), $P6_3/m$, of **1**·⅔H_2O[7] to a=14.5725(2), c=18.6537(5), $P6_3$, of the most probable cell of dried **1**. Direction and value of this change coincide with those observed for calix[4]arene clathrates[2] having nearly the same cell parameters as pure **1**.

XRPD diffractogram of **1**·C_5H_5N clathrate, ESI, is essentially different from that of guest-free **1**. The most probable cell of

1·C_5H_5N is of orthorhombic space group *Pmn2₁* with dimensions *a*=13.8605(5), *b*=10.1418(2), *c*=9.3916(2), *V*=1320.18(6) Å^3. This cell is much smaller than that of the initial dried **1** having volume *V*=3430.5(1) Å^3. The possible cause of this change is destruction of hexagonal packing with spherical trimeric host aggregates in the initial **1**. For comparison, a similar rather unstable 1:1 clathrate of calix[4]arene with acetone has an orthorhombic cell (*V*=2565.69 Å^3, space group *Pnma*) without such spherical self-included host aggregates[14]. But these aggregates are present in 1:3 acetone/calix[4]arene clathrate, which has a hexagonal $P6_3$/m cell[14]. Such change of packing from orthorhombic to hexagonal one may be a cause of the observed high enthalpy of guest release from **1**·C_5H_5N clathrate ΔH_e = 72 kJ/mol at the first decomposition step. XRPD diffractogram of the intermediate **1**·0.32C_5H_5N clathrate, ESI, indicates its hexagonal packing with space group $P6_3$ and dimensions *a*=15.0159(1), *c*=18.0309(2) of the most probable cell. Thermogram of this sample is given in ESI.

The data obtained on compositions of **1** clathrates, Table 1, show that this host has just the opposite selectivity to the guest molecular size as compared to that of *tert*-butylthiacalix[4]arene[3,4]. Host **1** includes such relatively large guests as benzene, toluene, cyclohexane, trichloroethylene and pyridine, which cannot be bound by *tert*-butylthiacalix[4]arene having larger molecular cavity[3,4]. But no inclusion by **1** is observed for smaller guests as methanol, acetonitrile, acetone, dichloromethane and 1,2-dichloroethane, which form 1:1 or 2:1 clathrates with *tert*-butylthiacalix[4]arene under the same conditions[3,4]. For two guests chloroform and tetrachloromethane, which can be bound both by **1** and *tert*-butylthiacalix[4]arene, clathrates of **1** are more thermally stable by 80 and 47°C, respectively, than those of its *tert*-butyl derivative. The cause of these differences as well as a lower inclusion capacity of **1**, which is close to that of calix[4]arene[2,14], may be its specific self-included packing in clathrate[7] and in pure state as described above, Fig. 1.

Clathrates of calixarene 1 prepared by solid-phase guest exchange. Pyridine clathrate **1**·C_5H_5N was used for guest exchange experiments as the least stable one among those studied, Table 1. For this clathrate, an exchange of included pyridine G_1 was performed according to the Procedure II, Fig. 1, in systems with initial clathrate **1**·C_5H_5N and saturated vapor of a second guest G_2. The exchange was studied with water, methanol, ethanol, acetonitrile, acetone, dichloromethane, chloroform, trichloroethylene, 1,2-dichloroethane, benzene, toluene and cyclohexane. The exchange products were studied using combined TG/MS analysis including isothermal mode at 280°C for 30 min because, in most cases, they do not lose bound guests completely below melting point in normal heating mode with a rate of 10 K/min, ESI. Thermograms obtained are shown in Fig. 3, 4 and ESI. Parameters of exchange products are given in Table 2.

According to the data obtained, Fig. 3 and 4, Table 2, the exchange of pyridine by Procedure II, Fig. 1, is observed for most studied guests, which can be included by **1** in binary system, Table 1. The exception is toluene, which does not enter the solid phase of **1** leaving one third of pyridine in a resulting clathrate. An exchange occurs also for methanol, ethanol, acetonitrile, acetone, dichloromethane and 1,2-dichloroethane, which cannot be bound by **1** in binary system by Procedure I, Fig. 1. In the last case, the exception is water, which is absent in the equilibrated clathrate sample but expels 11% of initially included pyridine. Partial exchange is observed for benzene and cyclohexane, which leave 0.14 and 0.13 mol of pyridine in clathrate, respectively, Fig. 4, Table 2. The other studied guests replace pyridine completely.

Most clathrates prepared by guest exchange, Procedure II, Fig. 1, have a higher thermal stability than those obtained in binary system using Procedure I. The corresponding increase in onset temperature of guest release T_{on} in TG curve varies from 24°C to 46°C, Tables 1 and 2. The exception is cyclohexane, which shows the same clathrate thermostablity irrespectively of the used preparation procedure. Cyclohexane is the largest studied guest that can be included by both methods, if the size of guest is estimated by its molar refraction MR_D, Table 2. So, together with the observed inability of the other large guest toluene to replace pyridine, this may be regarded as a size exclusion effect performed by **1**·C_5H_5N clathrate above some optimal guest size.

Table 2 Thermal analysis data of guest exchange products of host **1** formed by equilibration of **1**·C_5H_5N clathrate with saturated vapors of the second guest, P/P_0=1, at *T*=25°C.

Guest 2	MR_D, cm^3/mol	Δ*m*, %	S_G	S_{Pyr}	T_{on} °C
H_2O	3.72	12.39 (7.79^a)	-	0.89 (0.33^b)	82; 219
CH_3OH	8.2	4.03	0.65	-	157
C_2H_5OH	13.0	2.00	0.22	-	260
CH_3CN	11.1	2.36	0.29	-	231
$(CH_3)_2CO$	16.2	3.61	0.32	-	277
CH_2Cl_2	16.4	2.63 (0.31^a)	0.16 (0.14^b)	-	73; 256
1,2-$C_2H_4Cl_2$^{c}	20.9	1.99	0.1	-	257
$CHCl_3$	21.3	7.18	0.32	-	256
C_2HCl_3	25.3	5.68	0.23	-	257
CCl_4	26.4	7.72	0.27	-	222
C_6H_6	26.3	5.04	0.20^d	0.14^d	241
$C_6H_5CH_3$	31.1	5.39	0.01	0.34	242
c-C_6H_{12}	27.7	5.12	0.19^d	0.13^d	189

[a] mass loss in the first decomposition step of clathrate;
[b] stoichiometry of clathrate formed after the first decomposition step;
[c] thermogram is given in ESI;
[d] error of determination is 0.03 mol of guest per 1 mol of host.

The smaller guests with molar refraction $MR_D \leq 20.9$ cm^3/mol, except water, which are not included by **1** in binary systems, also form very stable clathrates by exchange of pyridine in **1**·C_5H_5N sample. Among these guests, the least stable exchange product with T_{on}=157°C is formed by the smallest compound methanol having MR_D = 8.2 cm^3/mol. The larger guests in this size range form very stable clathrates with T_{on} in the range of 231-277°C, Table 2. The most stable clathrate is formed by exchange for acetone, T_{on}= 277°C. This clathrate has the largest difference between guest release and boiling points $T_{on}–T_{bp}$ = 221°C. The exception is the clathrate of dichloromethane, which evolves a small part of bound guest, 0.02 mol, at relatively low temperature, T_{on}=73°C. Remaining 0.14 mol of CH_2Cl_2 per 1 mol of host is released at much higher point, T_{on}=256°C. In the series of guests methanol, acetonitrile, ethanol and acetone, thermal stability of clathrates increases together with the guest molar refraction, MR_D, Table 2.

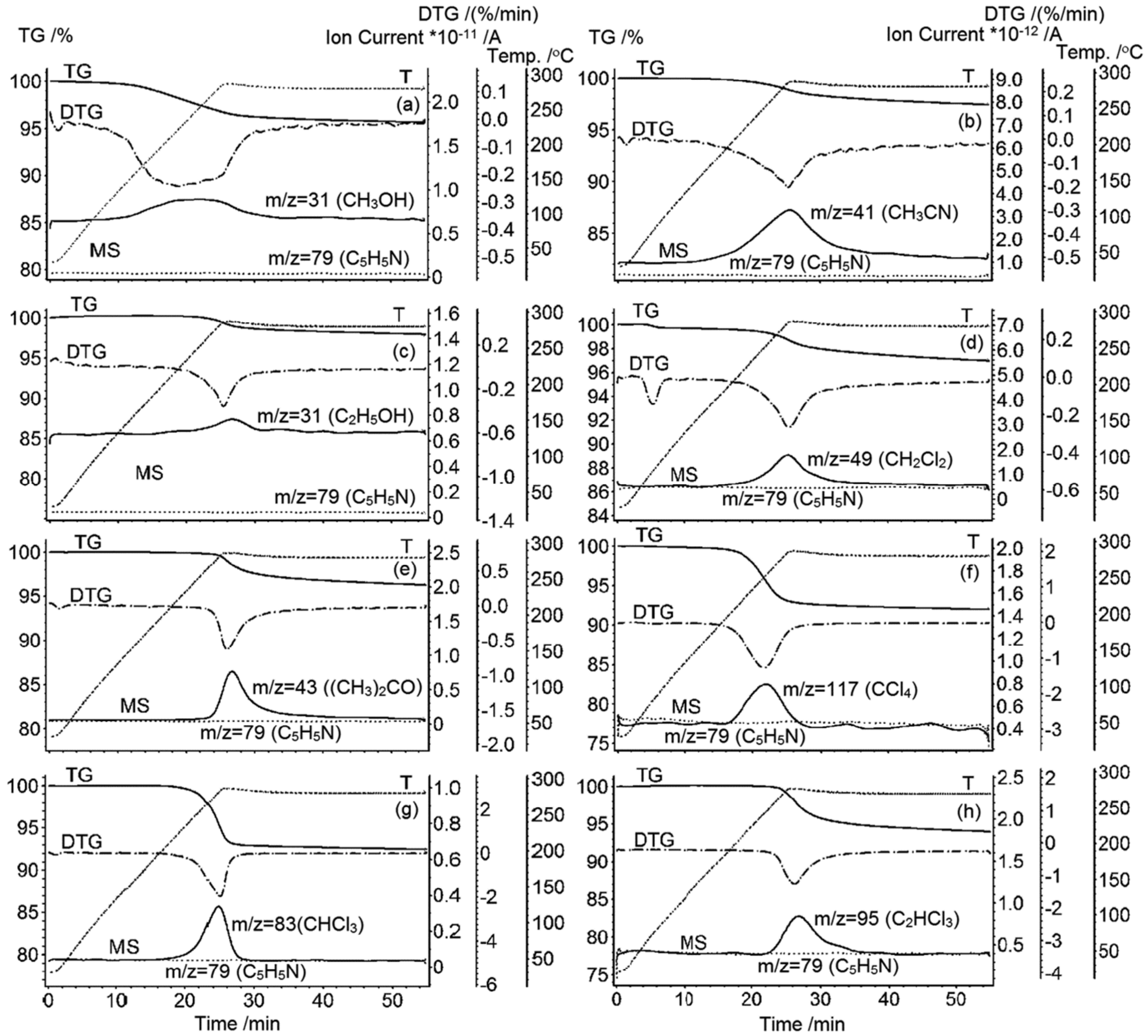


Fig. 3 Data of TG/MS analysis of guest exchange products formed by equilibration of $\mathbf{1}\cdot C_5H_5N$ clathrate with vapors of liquid guests with $P/P_0=1$ at $T=25°C$: (a) $\mathbf{1}\cdot 0.65MeOH$; (b) $\mathbf{1}\cdot 0.29MeCN$; (c) $\mathbf{1}\cdot 0.22EtOH$; (d) $\mathbf{1}\cdot 0.16CH_2Cl_2$; (e) $\mathbf{1}\cdot 0.32Me_2CO$; (f) $\mathbf{1}\cdot 0.27CCl_4$; (g) $\mathbf{1}\cdot 0.32CHCl_3$; (h) $\mathbf{1}\cdot 0.23C_2HCl_3$.

For every guest studied, calixarene **1** forms much more stable clathrates in guest exchange than its substituted analogue *tert*-butylthiacalix[4]arene[3]. The difference in T_{on} values for clathrates of the same guests with these two hosts is in the range of 47-158°C, with the largest value observed for benzene and the smallest increase found for cyclohexane. Besides, clathrate $\mathbf{1}\cdot 0.27CCl_4$ has a higher thermal stability on 22°C than a similar clathrate of tetrachloromethane with calix[4]arene[2]. Clathrates with the same guests formed by calixarenes with a larger macrocycle or larger substituents in upper or lower rim have a lower thermal stability[5,10,15-17]. Thermal stabilty of calixarene **1** clathrates prepared by guest exchange, Procedure II, Fig. 1, is probably restricted from above by the increased host mobility near its melting point of T_m=310°C, ESI.

Guest contents *S* in exchange products does not show any simple relationship with the guest size parameter MR_D, Table 2. All these clathrates, except methanol, have *S* value below one third, Table 2. Methanol clathrate has this value twice as much, S=0.65. The smallest contents, S=0.1, is observed for clathrate of 1,2-dichloroethane, which is the largest guest being not able to enter host **1** phase in binary system, Procedure I, Fig. 1. For those guests, which clathrates can be prepared both in binary system and by guest exchange, the difference in *S* values does not exceed a sum of experimental errors, Tables 1,2.

Despite a large guest content, clathrate $\mathbf{1}\cdot 0.65MeOH$ prepared by guest exchange from $\mathbf{1}\cdot C_5H_5N$ still has a hexagonal packing close to that of dried guest-free host **1** as characterized by XRPD diffractogram, ESI. Its most probable cell has parameters a=14.5437(1), c=18.8812(3), space group $P6_3$, and volume of V=3458.69(8) Å^3. So, formation even of this clathrate with high inclusion capacity gives transition from relatively low-stable orthorhombic crystals of $\mathbf{1}\cdot C_5H_5N$ to the stable hexagonal packing with guest molecules included inside trigonal bipyramids formed by spherical self-included trimers of host, Fig. 1.

This specific packing is the same as for very stable clathrates of calix[4]arene[2], and may be just the cause of the observed record clathrate stability. Spherical self-included trimer aggregates of guest-free **1**, when formed in the outer layers of its clathrate crystals at heating, become impenetrable for small guest molecules inside the crystals. This anti-sieve effect is an additional one to an ordinary hysteresis of clathrate decomposition[6], caused by a threshold in guest thermodynamic activity for inclusion in the guest-free host layers[4], which should occur for the guest going from inside a clathrate crystal. So, a trap for a guest included has a double kinetic barrier, and much higher temperature is necessary for its release from a clathrate.

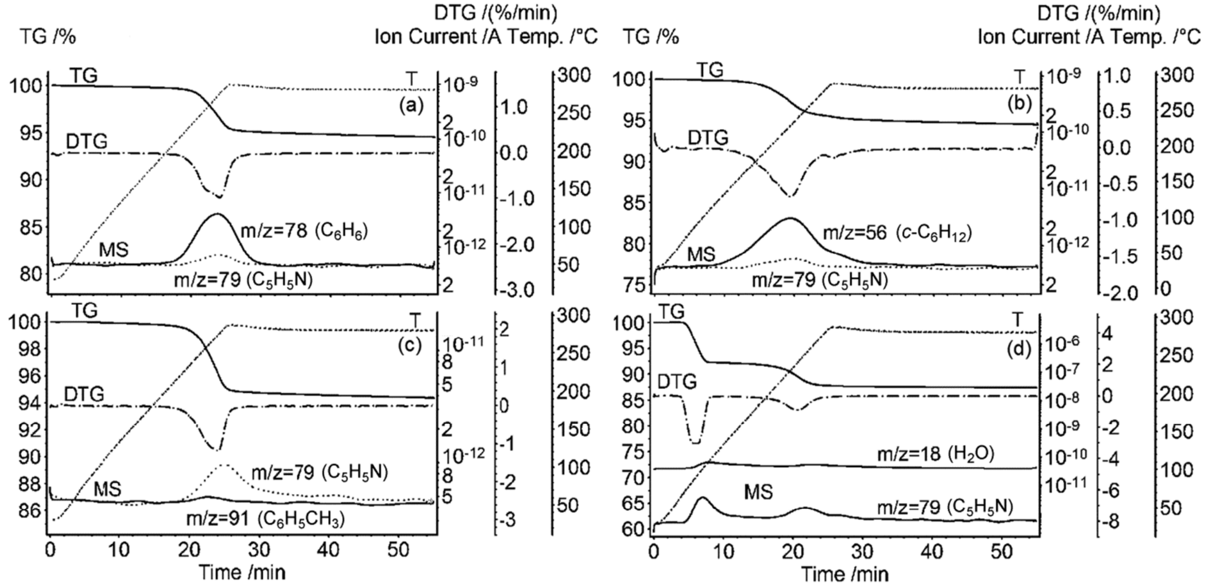


Fig. 4 Data of TG/MS analysis of guest exchange products formed by equilibration of **1**·C_5H_5N clathrate with saturated vapors of the second guest having relative vapor pressure P/P_0=1 at T=25°C: (a) **1**·0.20C_6H_6·0.14C_5H_5N; (b) **1**·0.19c-C_6H_{12}·0.13C_5H_5N; (c) **1**·0.01$C_6H_5CH_3$·0.34C_5H_5N; (d) **1**·0.89C_5H_5N.

Conclusions

Thiacalix[4]arene with its specific hexagonal packing both in clathrates and especially in guest-free state, where its molecules form self-included spherical trimers, has an unusual anti-sieve effect excluding smaller guest molecules. This effect is a source of extremely high clathrate stability when avoided by guest-exchange procedure in clathrate preparation. While any clathrate is relatively stable being formed with significant rearrangement of the initial host packing at the phase transition of guest inclusion, anti-sieve effect contributes much to a hysteresis of guest release from clathrates prepared using tricky methods. This gives a good structural guideline for a design of molecular receptors capable of forming very stable clathrates with volatile compounds for various practical purposes.

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Notes and references

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† Electronic Supplementary Information (ESI) available: data of simultaneous TG/DSC/MS analysis for thiacalix[4]arene and its clathrates, experimental and calculated X-ray powder diffractograms as fitted by indexing and refinement of unit-cell data. See DOI: 10.1039/b000000x/

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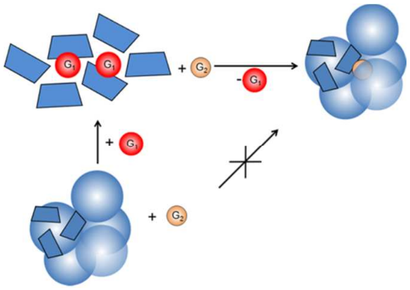

Unusual effect of exclusion of smaller guests by thiacalix[4]arene may be avoided by solid-phase exchange in preparation of clathrates, which thus become extremely thermally stable