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Structure–Properties Relations in Werner β-[Ni(NCS)$_2$(4-MePy)$_4$] Clathrates. Part 2. Host–Host Interactions as a Function of the Guest Molecular Size and Shape and the Amount of Absorbed Guest Compound

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Abstract. Careful analysis of changes in the geometry of the host lattice structure on inclusion of different guest molecules was performed for 11 β-[Ni(NCS)$_2$(4-methylpyridine)$_4$] clathrates reported in the literature, and specific features were established for the geometry of the host crystal lattice structure, which are characteristic for different modes of location of the guest molecules. A new method is suggested for the analysis of the volume and shape of the empty space in clathrates. Experimental data are reported on the dependence of the a and c parameters of the unit cell of clathrate phases (with furan and dichloromethane as guest components) from the guest uptake. Consideration of these data permit us to construct a model of the changes of host–host interactions in the β-[Ni(NCS)$_2$(4-methylpyridine)$_4$] clathrates with change of guest uptakes. Modeling of the process of diffusion of the guest molecule through the channel of the β-[Ni(NCS)$_2$(4-methylpyridine)$_4$] clathrate allowed the nature of the rate-determining step of diffusion to be established. Part 1 of this series has been published as [3].

Key words: β-[Ni(NCS)$_2$(4-methylpyridine)$_4$] clathrates, geometry of the host lattice, host–host interactions, guest–host interactions, dependence of the unit cell parameters from the guest uptake

Abbreviations used: H, host (β-[Ni(NCS)$_2$(4-MePy)$_4$]), **B**, benzene, **ET**, ethanol, **MC**, methylcellosolve, **MeCl**, methylene chloride, **CY**, *p*-cymene, **FU**, furan, *m*-**XY**, *m*-xylene, *p*-**XY**, *p*-xylene, **METH**, methanol, **THF**, tetrahydrofuran, **4-MePy**, 4-methylpyridine, clathrate **2** = **H·0.86B·0.5ET** = β-[Ni(NCS)$_2$(4-MePy)$_4$]·0.86 (benzene)·0.5 (ethanol), clathrate **3** = **H·0.5MC** = β-[Ni(NCS)$_2$(4-MePy)$_4$]·0.5 (methylcellosolve), clathrate **4** = **H·1.2MeCl** = β-[Ni(NCS)$_2$(4-MePy)$_4$]·1.2 (methylene chloride), clathrate **5** = **H·0.4MeCl** = β-[Ni(NCS)$_2$(4-MePy)$_4$]·0.4 (methylene chloride), clathrate **6** = **H·0.66CY** = β-[Ni(NCS)$_2$(4-MePy)$_4$]·0.66 (*p*-cymene), clathrate **7** = **H·1.5FU** = β-[Ni(NCS)$_2$(4-MePy)$_4$]·1.5 (furan), clathrate **8** = **H·m-XY** = β-[Ni(NCS)$_2$(4-MePy)$_4$]·(*m*-xylene), clathrate **9** = **H·2METH** = β-[Ni(NCS)$_2$(4-MePy)$_4$]·2 (methanol), clathrate **10** = **H·p-XY** = β-[Ni(NCS)$_2$(4-MePy)$_4$]·(*p*-xylene), clathrate **11** = **H·0.51THF** = clathrate β-[Ni(NCS)$_2$(4-MePy)$_4$]·0.51 (tetrahydrofuran).

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1. Introduction

The sorption equilibria and energy of sorption in solid β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrate – gaseous guest systems, the modes of guest molecule allocation which are possible in this group of clathrates, and the decomposition kinetics of the β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrates with aromatic guests have been elaborated in our previous papers [1–3]. The first task of the present work is to analyze distortions of the β-[Ni(NCS)$_2$(4-MePy)$_4$] host lattice geometry caused by the inclusion of guest molecules of different sizes and shapes. The necessary structural informa-tion is supplied by the numerous reported X-ray single-crystal structures of the β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrates [2, 4–7]. The data concerning the dependence on guest uptake of the a and c unit cell parameters of β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrates with furan and methylene chloride guest molecules were obtained by the authors (by the powder diffraction method) and will be presented below. The second task is to find and analyze correlations between the distortions of the host lattice and properties of the β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrates. The number of physicochemical studies reported on clathrates with this host allows analysis of an extensive set of data obtained by the different methods (reviewed in [8]).

The host lattice of the β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrates is built up from in-dependent coordination complex molecules in a 'propeller' conformation (twofold axial symmetry, Figure 1) [8]. The energies of the different conformations of the host complex were calculated in [15] and the 'propeller'-like conformation was found to be the most favorable. The methyl group in the 4 position of the pyridine ring does not allow favorable contacts of the flat sides of pyridine rings (removal of the methyl group or shifting of this group to the 3 position leads to formation of another type of structure with such contacts [16, 17]). In the clathrates with the β-[Ni(NCS)$_2$(4-MePy)$_4$] host lattice the host molecules form 'pairs' (Figure 2a), which pack to form layers with the empty channels of complex shape (Figures 2b, c). The same 'pairs' of the [Ni(NCS)$_2$(4-MePy)$_4$] molecules are in the non-clathrate α-form of this compound, but the packing mode of these 'pairs' (and the resulting structure) is different from the clathrate β-form. The clathrate lattice is built by the ABAB... packing of such layers. The B-layer may be obtained from the A-layer by 180° rotation around the z-axis and shifting 0.25 along the z-axis. The resulting structure (of I $4_1/a$ symmetry) has a three-dimensional sys-tem of channels (Figure 3) their shape giving two geometrically different types of positions for guest accommodation (the so-called 'large cavities' and 'small cavities' see Figure 2c) [8]. Effective support by the neighboring layers of another type prevents collapse of the channels after removal of the guest molecules. Bond lengths, angles and torsion angles which may be used for description of the β-type host lattice geometry are shown in Figure 1. It should be stressed that in addition to the parameters characterizing the geometry of the host molecule we are taking into consideration parameters which characterize the spacial orientation of the host molecule and the a and c parameters of the unit cell.
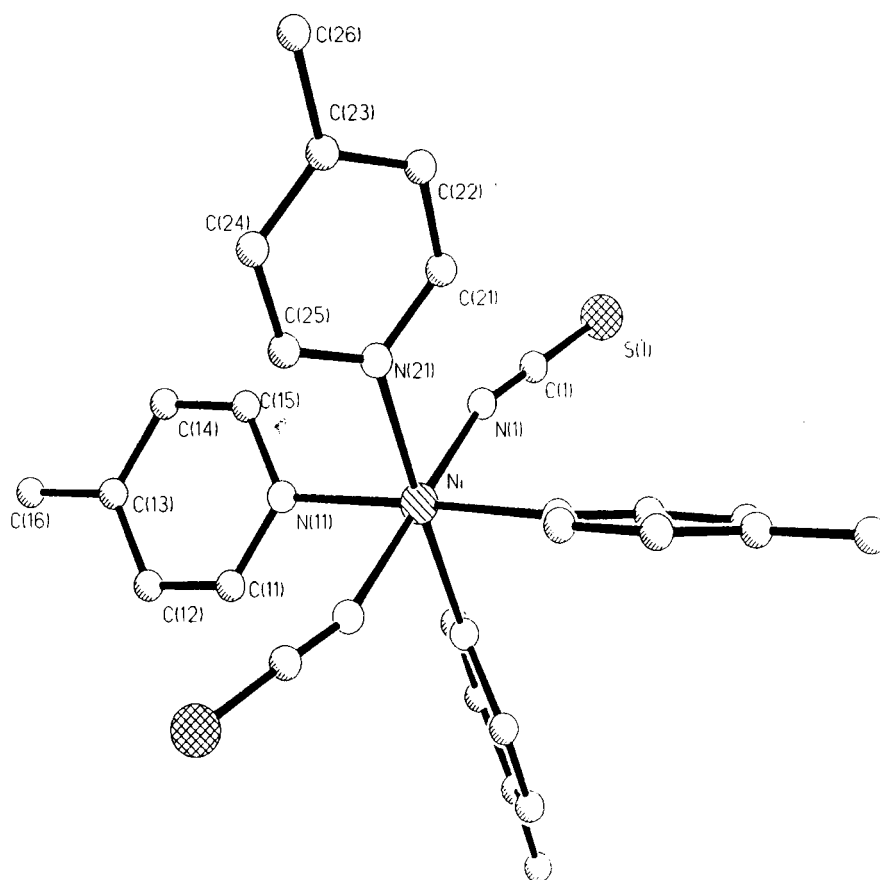
BOND LENGTHS:

Ni - N(1) = d_1

Ni - N(11)= d_2

Ni - N(21)= d_3

BOND ANGLES:

Ni - N(1) - C(1) = α_1

N1 - C(1) - S(1) = α_2

N(11) - Ni - N(21) = γ_1

N(21) - Ni - N(1) = γ_2

N(11) - Ni - N(1) = γ_3

TORSION ANGLES:

C(15) - N(11) - Ni - N(1) = φ_1

C(21) - N(21) - Ni - N(1) = φ_2

C(1) - N(1) - Ni - N(21) = ω_1

ANGLES, CHARACTERISING SPACE ORIENTATION OF THE HOST MOLECULE

N(1) - Ni - positive direction of the y crystallographic axis = ε_1

N(21) - Ni - positive direction of the z crystallographic axis = ε_2

Figure 1. The molecule of the [Ni(NCS)$_2$(4-MePy)$_4$] host coordination complex. In β-type clathrates this molecule has two-fold axial symmetry. Atoms of the independent part of the molecule are marked. The conformation and space orientation of the host molecule in the β-clathrates may be described by the parameters shown.
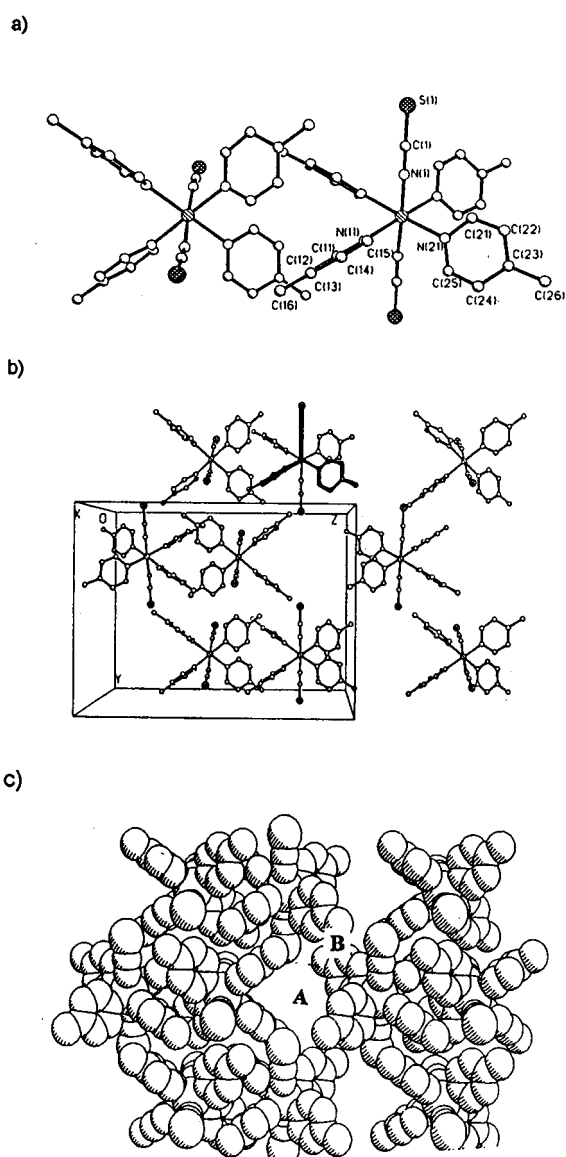
a)

b)

c)

Figure 2. A 'pair' of the host molecules. The independent part of the molecule is enumerated
(a). Packing diagram of one layer of the host lattice. The independent part of the host molecule
is selected by the bold sticks (b). Space-filling packing diagram of one layer of the host
lattice. Different types of sorption positions, which may be occupied by guest molecules are
marked 'B' ('small cavities', $\bar{1}$ local symmetry) and 'A' ('large cavities', $\bar{4}$ local symmetry)
(c). Orientation of the selected part in (b) and marked part in (a) are the same.
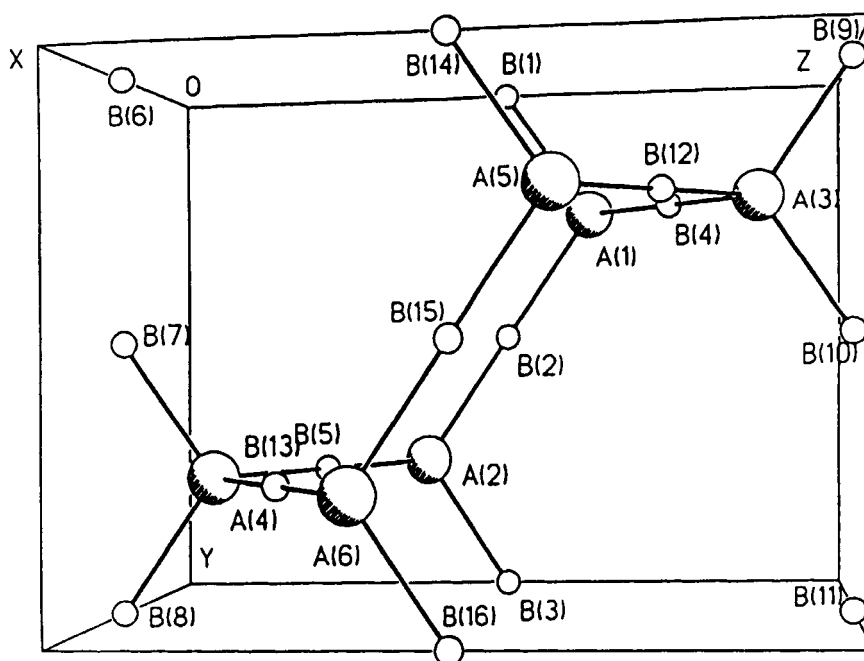
Figure 3. Scheme of the channel system in the β-phase. Large cavities are marked A (large spheres), small cavities are marked B (small spheres).

2. Experimental

X-Ray powder patterns were recorded on a Rigaku–Denki standard diffractometer with CuK_α radiation in the θ–2θ scanning mode by the step-by-step counting technique. Samples of the α-[Ni(NCS)$_2$(4-MePy)$_4$] phase, synthesised according to [9], were spread onto a porous glass plate (sample holder) and placed into an X-Ray diffraction (XRD) camera which allowed recording of the powder patterns in a controlled atmosphere. This was achieved using argon carrier gas saturated by the guest (furan or methylene chloride) vapors by bubbling through the respective liquid guest kept in the thermostat at different temperatures. After that, argon was passed around the sample. The partial pressure of guest vapors in the camera was equal to the pressure of the saturated vapors of the liquid guest in the thermostat. The XRD camera was kept at 21 °C. The design of the camera allowed the recording of the XRD pattern within a range of 18–30 degrees (2θ). The inertness of the argon with respect to the host compound (under the given experimental conditions) was shown by recording the X-ray diffraction patterns before and in the course of passing of pure argon. The pattern was indexed assuming a known structure. Average lattice parameters were calculated by the least squares minimisation of their values with respect to those calculated independently from all reflections. At the beginning of the experiments the samples were kept in an atmosphere which was saturated at 15–18 °C with vapours of the respective guest. In the case of

furan as the guest the samples of the α-[Ni(NCS)$_2$(4-MePy)$_4$] phase were completely transformed into the clathrate β-[Ni(NCS)$_2$(4-MePy)$_4$] phase. However the residual quantities of a non-clathrate phase remained when dichloromethane was used as guest. The composition of the clathrate samples was determined by comparison of a known partial pressure of the guest vapours and sorption isotherms of the respective guest in the β-[Ni(NCS)$_2$(4-MePy)$_4$] host phase, which were determined as described in [3]. To determine lattice parameters of clathrates with a maximum stoichiometry, the samples impregnated with the respective guest (furan or methylene chloride) were used.

Activation energies of the diffusion of the guest molecules through the channels of the β-[Ni(NCS)$_2$(4-MePy)$_4$] host phase were calculated from the dependence of the rate of the respective clathrate decomposition on temperature. The experimental apparatus and procedure were comprehensively described in [1].

Calculations of the intermolecular interactions energy in the β-[Ni(NCS)$_2$(4-MePy)$_4$] lattice were performed using the EENY [10] program; the rigid-body models of guest molecules being constructed by the force-field method (MM2) [11]. The nickel and nitrogen atoms of the host molecule were not taken into account during the calculations of the non-covalent interactions. The CRYSRULER [12] and XP [13] programs were used for calculations of the bond angles, torsion angles, interatomic distances and for the analysis of the molecular structures.

For calculations of the volume and linear sizes of the 'free space' within a clathrate lattice (space available for the guest molecules) an original algorithm was used. The total space of the unit cell was represented as a set of points obtained by a linear combination of three basis vectors of a chosen length with their origin at the centre of coordinates and parallel to the crystallographic axis. A point is believed to be in a 'free space' if at least one 'probing sphere' of a chosen radius includes this point and does not intersect any atom of the host molecules (in the opposite case the point is believed to be in an 'occupied space'). The same algorithm was used for construction of sections of the host lattices, but with two chosen basis vectors determining the plane of the section. All calculations were performed using a dedicated computer program, written by the authors. The system of van der Waals atomic radii, suggested in [14], was used for calculations. Lengths of the basis vectors were chosen as 0.2 Å and the radius of the 'probing sphere' chosen as 1 Å.

3. Results and Discussion

The parameters, characterizing known structures of the β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrates, are summarized in Tables I and II. All parameters characterizing the geometry of the host lattice were calculated from the X-ray single-crystal data reported in [2, 4–6]. Volumes of the 'free' space and the 'occupied' space were calculated using the algorithm described in the Experimental section (for definitions of the 'occupied' and 'free' space see the Experimental section). The structure of the clathrate with benzene as a guest molecule was excluded due to the lack of a com-

plete data set [7]. As already described in [8], specific host–guest interactions do not significantly influence the inclusion of the guest molecules by clathrates formed by Werner complexes, hence only the size and shape of the guest molecules will be taken into account in this work. As a first step of structure analysis the effectiveness of packing of the host molecules in the 'occupied' space and guest molecules in the 'free' space was examined as suggested in [18], and of the total effectiveness of the clathrate packing (packing coefficient [19]). The volumes of the host and guest molecules were calculated according to [19], the positions of the hydrogen atoms were calculated by means of the XP program and the C—H distances were chosen as in the SHELX-93 [20] program. X-ray experiments performed at different temperatures allow comparisons of calculated packing coefficients for only a part of these clathrates. From the data in Table I it can be concluded that in most cases the effectiveness of guest packing in the empty space is determining the total effectiveness of the clathrate packing. The packing coefficient of the host molecules in the occupied space depends dramatically on the type of position, occupied by the included guest molecule.

The very effective configuration of van der Waals contacts in the host subsystem stabilises the β-phase host lattice after even slight filling of the free volume by guest molecules (the thermodynamically metastable 'empty' β-[Ni(NCS)$_2$(4-MePy)$_4$] possess a very high kinetic stability [8]). The values of parameters characterising the empty β-phase, are shown in Tables I and II and the shape of the empty space is illustrated in Figure 4a. All the changes which the host lattice demonstrates after guest inclusion may be regarded as its adaptation to the shape of the included guest molecules leading to the energetically optimal configuration of van der Waals host–host and host–guest interactions and thermodynamic stability of the clathrate phase.

The case of localisation of the included guest molecules in the 'large cavities' of the β-[Ni(NCS)$_2$(4-MePy)$_4$] host lattice (limit ideal host : guest ratio 1 : 0.5 [8]) may be regarded as an example of non-specific inclusion because of the comparative insensitivity of this mode of inclusion to the shape of a guest molecule. The low degree of filling of the empty space by the guest molecule is characteristic of these clathrates (Table I). Inclusion of guest molecules whose size and shape are similar to the size and shape of the empty 'large cavity' (clathrates **3** and **11**, clathrate **5** with a non-limit host : guest ratio demonstrates the same mode of guest allocation) proceeds with only insignificant changes of the host lattice parameters and geometry of the empty space (Table II, Figure 4b). The distance between the Ni atoms in a 'pair' of the host molecules reduces to the value which is characteristic for almost all clathrates and may be considered to be the most favourable energetically. An increase of the angles φ_2 (turning of the pyridine ring) and reduction of the ω_1 angle (turning of the NCS group) slightly increases the internal volume of the 'large cavity'. Comparatively large variations of the ω_1 torsion angle and c-parameter of the unit cell suggest their sensitivity to the details of the geometry of the included guest molecule. The geometry of the host lattice of clathrate **5**,

Table I. Volumes of the unit cell, free space and occupied space ($Å^3$) for different β-[Ni(4-MePy)$_4$(NCS)$_2$] clathrates. Precision of the unit cell parameters is better than 0.5% in all cases.

Clathrate	Without guest [6]	H·0.86B·0.5ET [2]	H·0.5MC [2]	H·1.2MeCl [2]	H·0.4MeCl [2]	H·0.66CY [5]	H·1.5FU [2]	H·*m*-XY [4]	H·2METH [4]	H·*p*-XY [4]	H·0.51THF [2]
a/Å	16.74	16.82	16.74	17.09	16.59	17.11	16.85	17.28	16.99	16.98	16.70
c/Å	22.66	23.12	22.46	22.46	22.61	23.84	22.99	23.87	22.29	23.62	22.71
V of unit cell/Å^3	6350	6541	6294	6560	6221	6974	6527	7127	6434	6810	6333
V (empty space)	863	1204	939	1167	827	1464	1168	1568	1013	1319	895
% of total	13.6	18.4	14.9	17.8	13.3	21.0	17.9	22.0	15.7	19.4	14.1
V (host molec.)	456.0	456.7	455.6	456.8	456.8	456.1	456.8	453.0	454.2	451.8	455.2
V (guest molec.)		0.86·75.2 + 0.5·43.4	0.5·63.7	1.2·63.0	0.4·63.0	0.67·131.9	1.5·56.0	108.9	2·29.2	108.9	0.5·62.8
k_{pack} total	57.4	66.4	62.0	64.9	62.0	62.5	66.3	63.1	63.7	65.9	61.5
k_{pack} of guest in empty space		57.4	27.1	51.8	24.4	48.3	57.6	55.6	46.1	66.1	28.0
k_{pack} of host in occupied space	66.5	68.5	68.1	67.8	67.8	66.2	68.2	65.2	67.0	65.8	67.0
Temperature of X-ray experiment	Room	150 K	Room	150 K	100 K	Room	175 K	Room	Room	Room	150 K

Table II. Selected bond distances (Å), angles and torsion angles (degrees) in different β-[Ni(NCS)$_4$(4-MePy)$_2$] clathrates. Estimated standard deviations are given in parentheses, if available.

| Clathrate	Without guest [6]	H·0.86B·0.5ET [2]	H·0.5MC [2]	H·1.2MeCl [2]	H·0.4MeCl [2]	H·0.66CY [5]	H·1.5FU [2]	H·m-XY [4]	H·2METH [4]	H·p-XY [4]	H·0.51THF [2]
Distance Ni–Ni(a) 'in pair'	8.593	8.355(1)	8.344(1)	8.201(3)	8.417(1)	8.443(3)	8.318(1)	8.445(1)	8.319(3)	8.432(3)	8.440(2)
d_1 (Ni–N1)	2.064	2.066(3)	2.067(3)	2.060(9)	2.069(3)	2.094(7)	2.071(4)	2.068(4)	2.070(10)	2.055(7)	2.078(5)
d_2 (Ni–N11)	2.129	2.137(3)	2.130(2)	2.127(8)	2.122(3)	2.165(7)	2.139(4)	2.145(2)	2.131(9)	2.142(7)	2.130(5)
d_3 (Ni–N21)	2.125	2.116(3)	2.125(2)	2.119(8)	2.123(3)	2.128(7)	2.114(4)	2.145(5)	2.119(9)	2.132(7)	2.136(5)
ϵ_1 (N1–Ni–y)	139.8	143.6(1)	140.3(1)	141.9(3)	139.1(2)	143.5(2)	143.8(1)	143.4(1)	141.3(3)	143.9(2)	138.8(1)
ϵ_2 (N21–Ni–z)	44.8	44.3(1)	44.7(1)	45.6(3)	44.5(1)	44.4(2)	44.3(1)	44.5(6)	44.6(3)	44.0(2)	44.6(2)
γ_1 (N11–Ni–N21)	90.5	91.0(1)	90.4(1)	89.2(3)	90.8(1)	90.9(3)	90.6(2)	90.5(1)	89.9(4)	91.3(3)	90.4(2)
γ_2 (N21–Ni–N1)	88.3	89.7(1)	91.1(1)	90.0(3)	90.5(1)	93.1(3)	89.4(2)	90.0(2)	90.3(4)	89.1(3)	90.2(2)
γ_3 (N11–Ni–N1)	90.1	90.8(1)	90.3(1)	90.0(4)	90.3(1)	88.2(3)	90.9(2)	90.3(2)	90.2(4)	91.1(3)	90.1(2)
α_1 (C1–N1–Ni)	154.3	163.0(3)	154.9(2)	158.8(7)	152.3(3)	163.0(6)	163.1(4)	165.1(3)	158.2(12)	163.0(7)	152.7(5)
α_2 (S1–C1–N1)	179.2	179.5(3)	179.8(3)	177.8(9)	179.7(4)	178.5(7)	179.7(4)	179.4(4)	179.0(14)	176.1(8)	179.1(6)
φ_1 (C15–N11–Ni–N1)	−44.1	−44.0(3)	−41.2(2)	−41.6(7)	−40.7(3)	−44.7(6)	−43.5(4)	−43.2(5)	−39.7(10)	−43.2(7)	−40.0(5)
φ_2 (C21–N21–Ni–N1)	−36.4	−36.6(3)	−35.9(3)	−34.7(9)	−36.2(3)	−37.5(7)	−37.7(4)	−33.5(5)	−34.9(10)	−36.7(7)	−34.5(6)
ω_1 (C1–N1–Ni–N21)	137.8	130.3(1)	129.1(5)	123.4(2)	133.1(6)	133.3(22)	125.3(2)	141.5(16)	125.9(29)	141.2(23)	132.4(1)

a)

b)
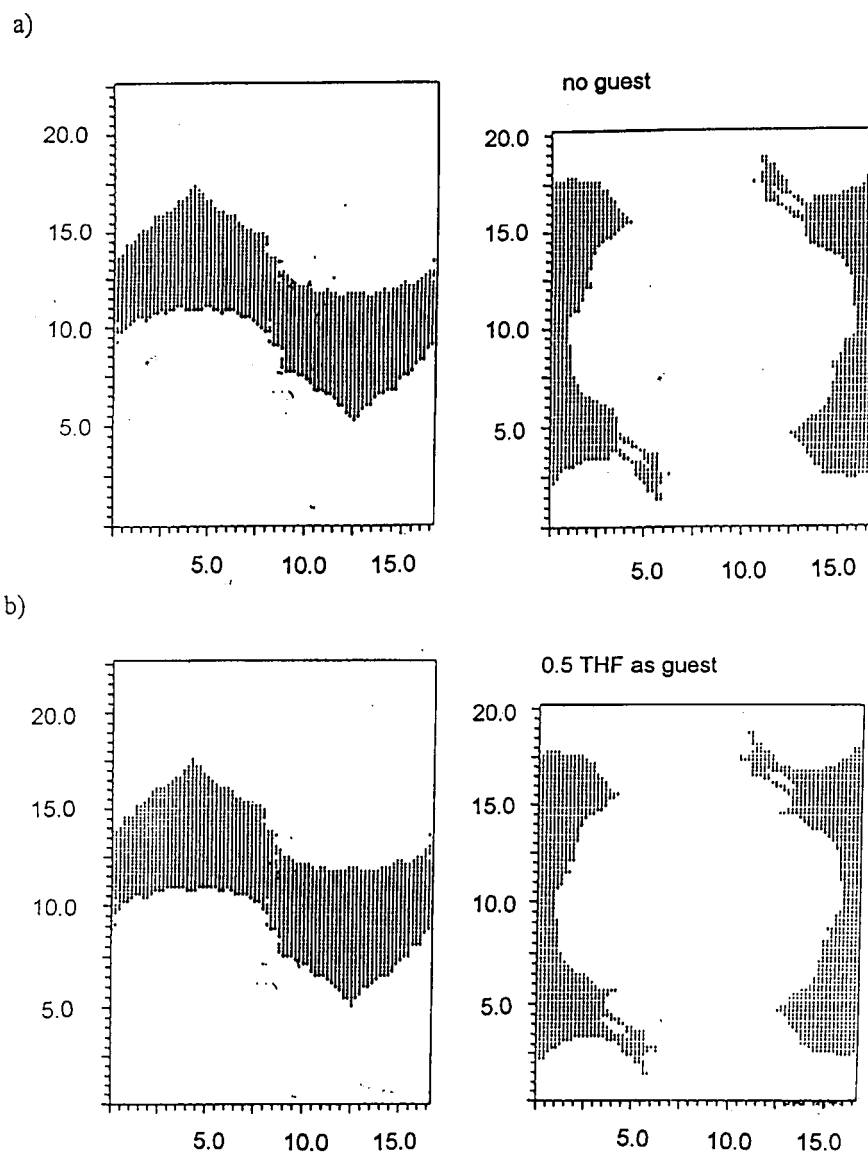
Figure 4. Diagrams showing the size and shape of the empty space in different β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrates with localisation of guest molecules in the 'large cavity' or without the guest molecule. Left diagrams illustrate a section of the clathrate structure parallel to the (100) plane and taken at $x = 0$ (b-axis in the horizontal, c in the vertical directions). Right diagrams illustrate a section of the clathrate structure in the plane passing through the axis of the channel and perpendicular to the (100) plane. Labels on the axis denote size in Å.

which was obtained by the decomposition of clathrate **4** (it has less than a limit host : guest ratio) is intermediate between the geometry of the empty β-phase and the geometry of the clathrates of this group. If the volume of the guest molecule is significantly smaller than the volume of the 'large cavity', inclusion of more than one guest molecule is necessary for stabilisation of the β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrate (the stoichiometries of such clathrates are discussed in [2, 8]). This is the case of a more effective filling of the empty space of the methanol clathrate (Table I). Methanol guest molecules are located in positions shifted from the central part of the 'large cavity' to the centre of inversion, and the most significant guest– guest interactions directed along the a crystallographic axis. An increase of the free volume in this case is mainly provided by an increase of the a-parameter of the unit cell and also by an increase of φ_2 and decrease of ω_1, as discussed earlier. Inclusion of the CH$_2$Cl$_2$ molecule causes similar distortions of the host (with additional decrease of the Ni—Ni distance in the 'pair' of host molecules, Table II). Removal of the excess guest molecules leads here to the formation of the clathrate with typical geometry of the host lattice (clathrate **5**).

Since inclusion of a molecular fragment of a given size and shape into the 'small cavity' (flat 5- or 6-membered ring) occurs for all guests with suitable size of the aliphatic radicals and is accompanied by a great heat effect [8], it allows us to qualify this type of inclusion as an example of molecular recognition. Two parallel 4-MePy rings, whose flat sides constitute the 'walls' of the 'small cavity' give very effective van der Waals contacts with the part of the guest molecule 'inserted' between them and play here the role of receptor. Inclusion of the guest molecule into the 'small cavity' is accompanied by typical changes in the geometry of the host lattice. Increase of the a and c lattice parameters (accompanied by a significant shift of the 'pairs' of the host molecules in respective directions) causes significant widening of the channel in the a and ac directions. Simultaneously, increase of the ϵ_1 and decrease of the φ_2 angles causes additional widening of the channel in the a-direction (Figure 5); angle φ_1 decreases to compensate the relative rotation of the host molecular pairs and decrease of the φ_2 angle. Contact of the C-atom of the NCS group with guest molecules causes an increase of the α_1 angle and changes the shape and widens the channel in the ac direction (Figure 5). Rotation of the NCS group (changes of the ω_1 angle) allows adaptation of the host lattice to the size and shape of the aliphatic part of the guest (or second guest molecule) which occupies the 'large cavity'. If the aliphatic parts of the guest molecule are very large (p-cymene) or situated in *meta*-positions (m-xylene), an additional increase of the free volume may be provided by an increase of the a and c lattice parameters. In the case of p-cymene such an increase is insufficient, and less than the stoichiometric content of p-cymene occurs (in this case, the residual part of the channel space may be filled by the solvent molecules, but such a possibility was not discussed in [5]). Dilation of the c-parameter may be accompanied by the increase of the Ni— Ni distance in the 'pair' to minimize an energetically unfavourable relative shift of 'pairs' in the c-direction.
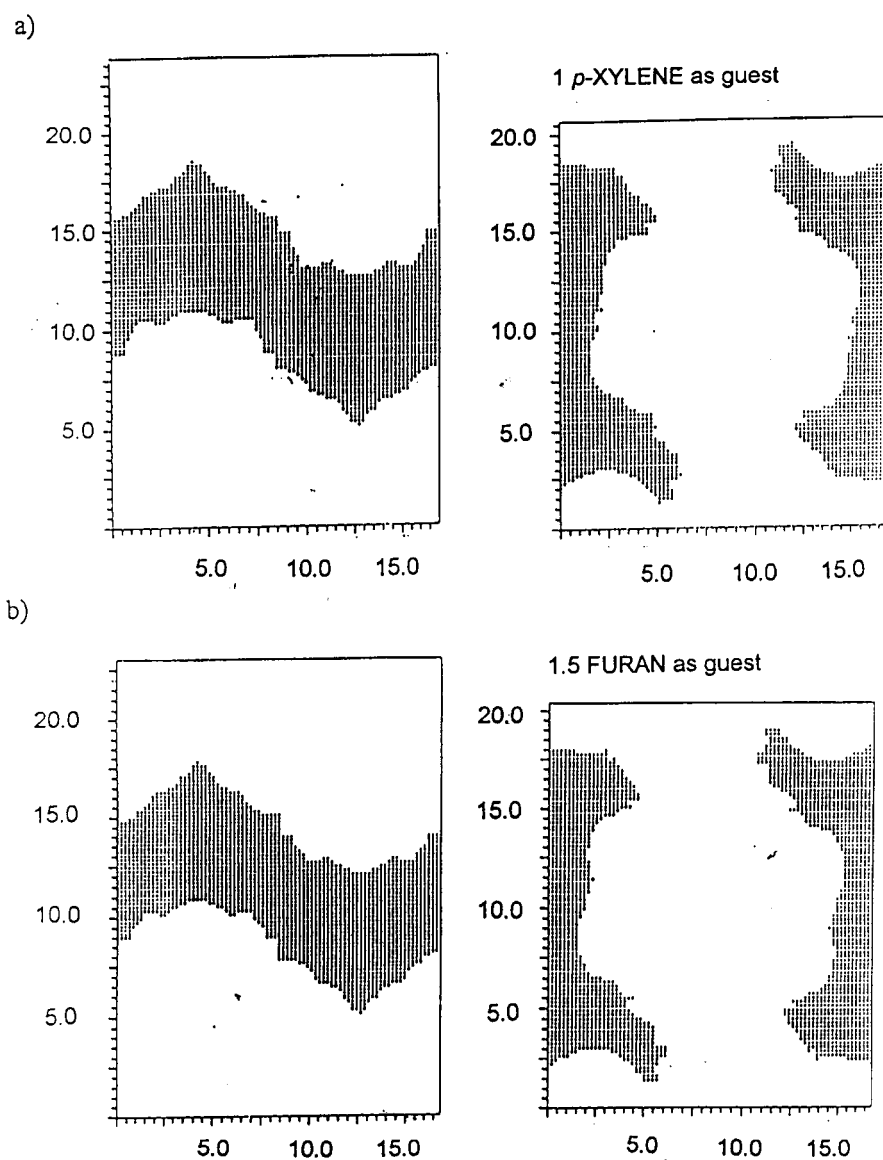
a)

1 *p*-XYLENE as guest

b)

1.5 FURAN as guest

Figure 5. Diagrams, showing the size and shape of the empty space in different β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrates with localisation of guest molecules in the 'small cavity' or in both types of cavities. Left diagrams illustrates a section of the clathrate structure parallel to the (100) plane and taken at $x = 0$ (b-axis in the horizontal, c in the vertical directions). Right diagrams illustrates a section of the clathrate structure in the plane passing through the axis of the channel, and perpendicular to the (100) plane. Labels on the axis denote Å.

As shown earlier, parameters characterizing the geometry of the β-[Ni(NCS)$_2$(4-MePy)$_4$] host lattice vary significantly for clathrates with different guests. This is caused by the adaptation of the host lattice to the included guest molecules of the given type, and may be regarded as an illustration of the guest to host influence in clathrates with a 'soft' host lattice. Unfortunately, we are able to study experimentally only the influence of the guest content on the a and c lattice parameters. According to [21], significant β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrate lattice dilation is linear with 4-MePy guest concentration. We have studied the dependence of the a and c lattice parameters as a function of the composition for clathrates with furan and dichloromethane as guests (Figure 6a,b). The results obtained show two different types of changes of a and c with guest content (similar types of changes may be postulated for other parameters). The parameters are proportional to the guest content for 4-MePy and furan as guests and an abrupt change of a and c occurs for dichloromethane as guest. The most probable interpretation of the almost linear proportionality observed for 4-MePy and furan clathrates, is that the removal of the guest molecule from the sorption position changes the geometry of the neighbouring part of the host lattice from that characteristic for the clathrate lattice to the one characteristic for the empty β-phase. The partially decomposed clathrate crystal may be represented as a sum of differently distorted blocks (each block is formed by host molecules surrounding one sorption position, Figure 7) and the observed parameters (a and c lattice parameters in our case) may be obtained by averaging of the parameters that are characteristic for each block. If interactions between differently distorted blocks of the host lattice are extremely unfavourable, the situation observed for the dichloromethane clathrate may take place; all sorption positions take the conformation, which is characteristic for the occupied position, after filling of only some of the positions. Undoubtedly, the suggested scheme is a simplified one and does not take into account complications caused by different ways in which different parameters change and changes of the host–guest interactions caused by the changes of the host lattice geometry. A similar treatment may be applied to the β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrates with more than one guest species, if all guest molecules occupy the same type of sorption positions (unoccupied positions may be represented as positions occupied by the guest molecule with a very small volume). The difference in the interaction energy between differently distorted blocks and equally distorted blocks may cause deviations from the additivity of the thermodynamic properties of this type of clathrates. The additivity of the heats of clathrate formation has been observed experimentally when a mixture of p-xylene and p-dibromobenzene was used as guest (these guests distort the host lattice in the same way) [22]. The situation when different guest molecules distort the host lattice differently leads to the negative deviation from the additivity of the clathration enthalpies; that was the case for a mixture of m- and p-xylenes as guest [23]. As shown in [3], values of partial molar heats of guest sorption changes with a change of guest uptake, this fact is in accord with the idea presented in this paragraph.
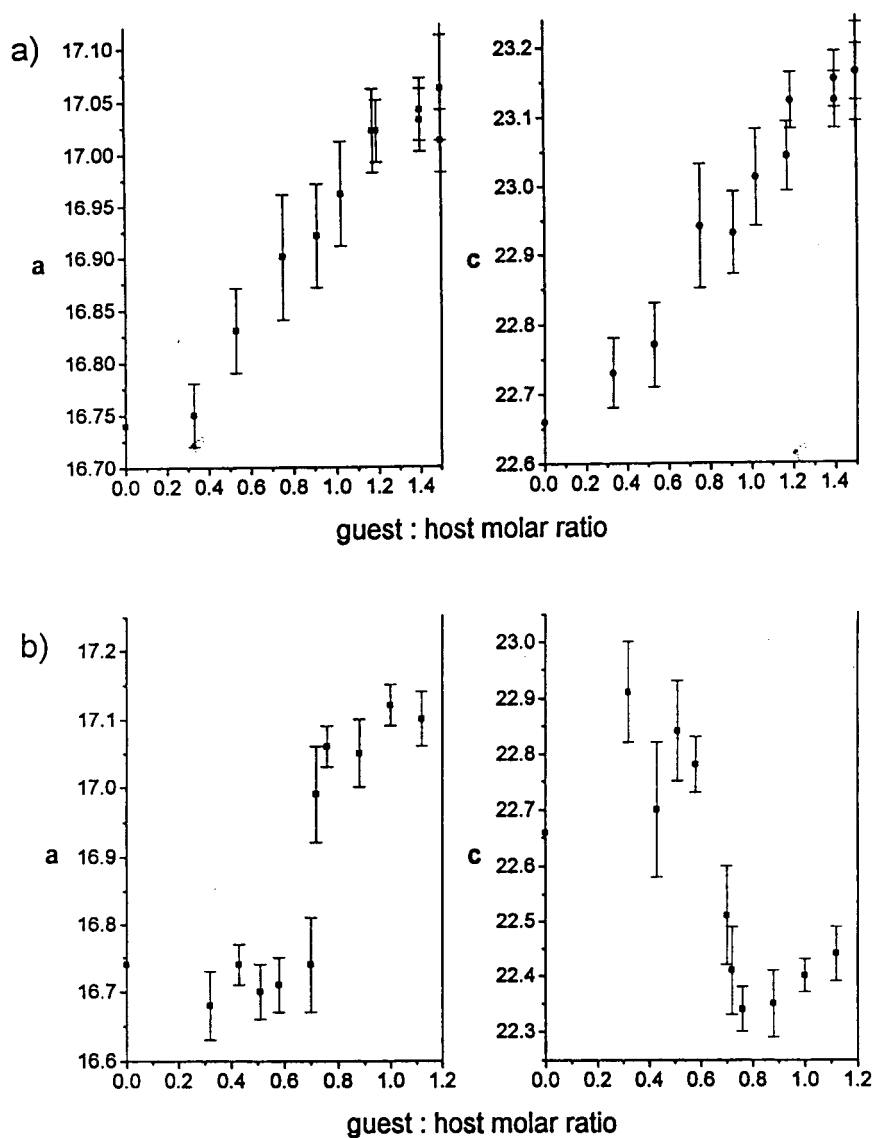
Figure 6. Dependence of the unit cell parameters (in Å) of the clathrates with the β-[Ni(NCS)$_2$(4-MePy)$_4$] host lattice, (a) for furan as guest, (b) for dichloromethane as guest.

The decomposition kinetics of the β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrates has been studied and is reported in [1, 24]. It was found that diffusion of the guest molecule in channels is a rate-determining step for decomposition of the clathrate with benzene as guest; the slowest step of the decomposition of the clathrate with p-xylene guest molecule is preparation of the guest molecule for diffusion. To clarify the nature of the rate-determining stage we modelled diffusion of different guest mo-
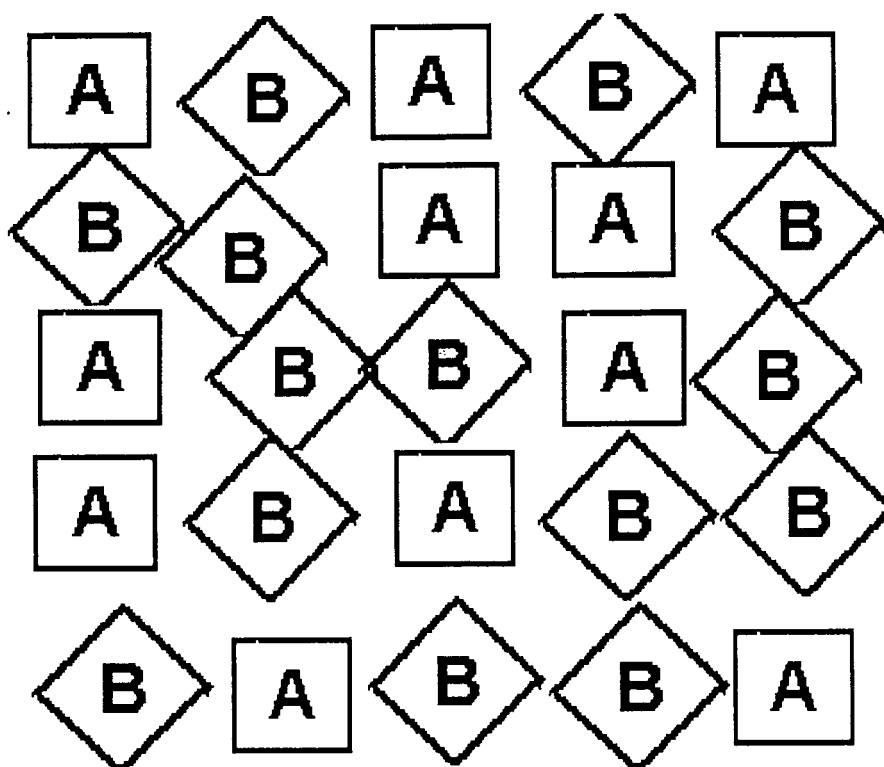
Figure 7. Schematic representation of the β-[Ni(NCS)$_2$(4-MePy)$_4$] host lattice with sorption positions filled by mixed guest. Different types of guest molecules distort neighboring parts of the host lattice differently, as represented schematically by differently oriented squares. For further explanations see text.

lecules through the channels of the β-phase clathrate structure with a given guest. The sum of the host–host and host–guest (for one host and one guest molecule) interaction energies were minimized for different positions of the guest molecule in the channel (the centre of mass of the guest molecules was initially situated at the axis of the channel and its projection on the bc section of the channel was kept the same during the experiment). Ten parameters of minimization were used (φ_1, φ_2, ω_1, α_1, ϵ_1, ϵ_2, three Euler angles of the guest molecule, and the shift of the guest molecule in the a direction). The results of calculations are shown in Figure 8. The calculated positions of the minimum of the potential energy minimum of the guest molecules in a channel roughly agree with those determined in the X-ray experiment [2, 4, 7]. Analysis of the host lattice geometry shows that the maxima of the potential energy which are situated at the centre of the 'small cavity' ('M3') for tetrahydrofuran and dichloromethane guest molecules correspond to unfavour-able geometry of their contacts with the 4-MePy rings. Maxima, shifted to the centre of a 'large cavity' (denoted as 'M1'), were similarly interpreted for all guest
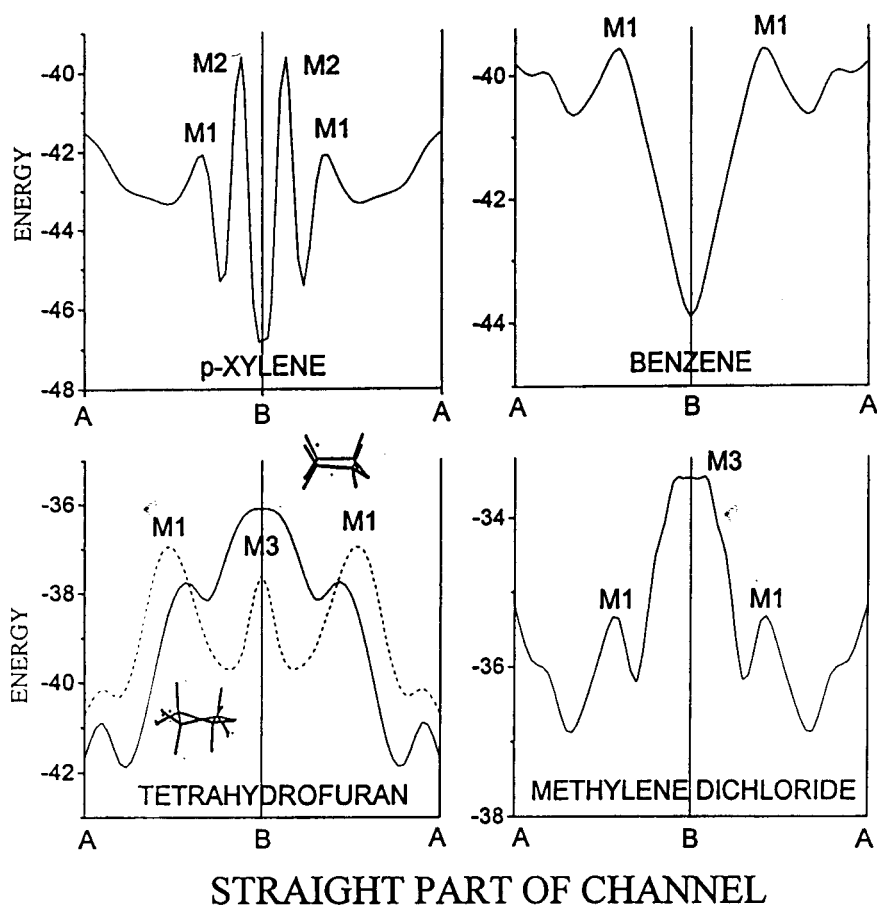
Figure 8. Calculated minimised potential energies of non-covalent interactions for different positions of the guest molecule at the axis of the channel in the β-[Ni(NCS)$_2$(4-MePy)$_4$] host lattice.

molecules; these maxima correspond to the repulsion between the guest molecule and the sulphur atom of the NCS group and to the simultaneous rotation of the pyridine ring (increase of the φ_2 angle) which allows the guest molecule to enter into the space between the pyridine rings. A change of the guest molecule conformation during the diffusion is postulated for the tetrahydrofuran molecule. The space orientation of the guest molecule changes after passing through this potential maximum. The great length of the p-xylene molecule complicates its reorientation in the channel. The reorientation of this guest molecule proceeds in two steps, the first ('M2') corresponds to the highest potential maximum and may be associated with a 'preparation of the guest molecule for diffusion' [24]; the second step may be interpreted in the same way as the 'M1' maxima for other guest molecules.

Table III. Activation energies of diffusion of different guest molecules through the channels of the β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrate.

Guest molecule	Activation energy (kJ/mol)	Guest molecule	Activation energy (kJ/moI)
Furan	35–44	Methanol	31–45
Benzene	38.5 ± 2.5	Dichloromethane	34–47
Toluene	>82.1	Tetrahydrofuran	63–75
p-Xylene	>96.8	Carbon tetrachloride	63–88

To obtain numerical characteristics of the diffusion process, we experimentally determined activation energies for diffusion of different guest molecules (Table III). A tendency to increase an activation energy with an increase of the molecular length for guest molecules which occupy 'small cavities' (furan, benzene, toluene and *p*-xylene) may be explained, by hindrance of the guest reorientation with increasing guest molecule length (see discussion of calculated potential curves). The higher activation energy of diffusion, which was obtained for tetrahydrofuran and carbon tetrachloride in comparison with methanol and dichloromethane guest molecules may be caused by more significant distortions of the host lattice, which are necessary for accommodation of larger guest molecules of non-planar shape in a 'small cavity'. The high kinetic stability of the β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrates with such guests may be postulated based on the high activation energy of guest diffusion and our experimental observations.

Acknowledgement

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