New Crystal Structures of β-[Ni(NCS)₂(4-methylpyridine)₄] Clathrates with Furan, Tetrahydrofuran, Methylene Chloride, Benzene + Ethanol and Methylcellosolve as Guest Molecules

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Abstract. Single crystal X-ray structures of clathrates of β-[Ni(NCS)₂(4-methylpyridine)₄] with furan, tetrahydrofuran, benzene + ethanol, methylene chloride, and methylcellosolve as guests molecules are reported. The location of the guest molecule in the partially decomposed clathrate with methylene chloride was defined by X-ray diffraction and compared with the fully occupied one. The host lattices of all clathrates studied are tetragonal ($I4_1/a$) and do not differ significantly from typical β-phase clathrates of [M(NCS)₂(4-methylpyridine)₄] (M = divalent metal cation). Arrangements of guest molecules represent different types of packing: one type of guest molecule occupies both possible types of positions, two different guest molecules occupy different positions, with only one type of positions occupied by one type of guest molecule. Possible stoichiometries of clathrates with β-type lattices are discussed.

Key words: Werner clathrates, X-ray structure, packing of guest molecules, guest disordering.

1. Introduction

A variety of structures of inclusion compounds, formed by Werner coordination complexes of general formula MX₂A₄ (where M = divalent metal cation, X = anionic ligand and A = neutral substituted pyridine ligand), have been described in the literature [1–3 and references therein]. The clathrate structure of the so-called β-type ($I4_1/a$ symmetry) is common for systems with M = Ni, Fe, Co, Mg, Zn, X =

NCS$^-$ and A = 4-MePy (4-methylpyridine), 4-EtPy (4-ethylpyridine) or 4-ViPy (4-vinylpyridine) [1, 3–8]. A characteristic of these clathrates is a three-dimensional system of zigzag channels that are able to accommodate different types of guest molecules [9]. A typical cross-section of the channel is shown in Figure 1. Two geometrically distinct positions ('sorption centers') with different local symmetry are available for guest molecules in the channels; 'small cavities' with symmetry $\bar{1}$ (marked 'B' in Figure 1: eight cavities of such type per unit cell), and 'large cavities' with symmetry $\bar{4}$ (marked 'A' in Figure 1: four cavities of such type per unit cell). Most of the reported β-clathrate structures contain benzene or pyridine derivatives as guest molecules with a host to guest ratio close to 1 : 1 reported for all of these clathrates [1, 4, 5]. The aromatic part of the guest molecules is located at the inversion center of the B-site of the channel. Where the guest molecules do not possess a centre of symmetry (i.e. m-xylene, 4-MePy), the lattice symmetry is maintained by an orientational disordering of the guest molecule [1]. Crystal structures of clathrates of β-[Ni(NCS)$_2$(4-MePy)$_4$] with methanol [10] and β-[Ni(NCS)$_2$(4-EtPy)$_4$] with carbon disulphide [7] are examples of the arrangement of two guest molecules in the 'small cavity' (which can also be considered as four guest molecules in the 'large cavity'). The accommodation of a guest molecule in the 'large cavity' is illustrated by the crystal structure of the β-[Ni(NCS)$_2$(4-EtPy)$_4$]·0.5 CCl$_4$ clathrate [6]. Such a type of arrangement of guest molecules was postulated for several β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrates based only on the stoichiometry of these clathrates [1]. Three crystal structures of β-[Ni(NCS)$_2$(4-ViPy)$_4$] containing mixtures of two different guest molecules (0.48 tetrahydrofuran + 0.52 1,3-cyclohexadiene, 0.36 tetrahydrofuran + 1.04 1,4-cyclohexadiene, 0.35 tetrahydrofuran + 1.05 benzene) have been reported [2]. It was found that all guest molecules were disordered in these clathrates. Some experiments on the analytical definition of the composition of some β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrates with more than one type of guest molecules were reviewed in [1]. The results obtained were interpreted on the basis of the different types of arrangement of guest molecules in the host lattices and the possible variants of arrangements of guest molecules were theoretically discussed. However, systematic X-ray investigations of different modes of arrangement of guest molecules in β-clathrates are still absent, even for the most studied case of the β-[Ni(NCS)$_2$(4-MePy)$_4$] host. Structural information concerning the types of packing of guest molecules in channels in β-clathrates is necessary for the correct interpretation of physicochemical data studied for these clathrates. In the present work an attempt has been made in order to obtain structural information concerning the arrangement of guest molecules for six clathrates as listed below:
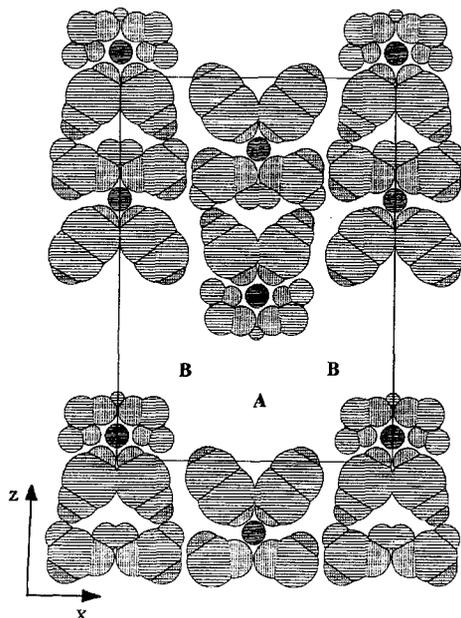
Figure 1. Typical plane section of a β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrate structure parallel to the (010) plane and taken at $y = 0.25$ (guest molecules omitted). B and A = 'absorption centers' with $\bar{1}$ and $\bar{4}$ local symmetry ('small cavity' and 'large cavity', respectively).

β-[Ni(NCS)$_2$(4-MePy)$_4$]·1.5 furan	**1**
β-[Ni(NCS)$_2$(4-MePy)$_4$]·0.5 tetrahydrofuran	**2**
β-[Ni(NCS)$_2$(4-MePy)$_4$]·0.86 benzene · 0.5 ethanol	**3**
β-[Ni(NCS)$_2$(4-MePy)$_4$]·1.2 methylene chloride	**4**
β-[Ni(NCS)$_2$(4-MePy)$_4$]·0.4 methylene chloride	**5**
β-[Ni(NCS)$_2$(4-MePy)$_4$]·0.5 methylcellosolve	**6**

(clathrate **5** was obtained by partial decomposition of clathrate **4**)

2. Experimental

The host powder complex was synthesized as described in [11]. The crystals of clathrates **1**, **2** and **4** were obtained by slow (5–7 day) evaporation of solvent from saturated solutions of the host complex in furan, tetrahydrofuran and methylene chloride, respectively. Due to the low solubility of the [Ni(NCS)$_2$(4-MePy)$_4$] complex in furan, only small crystals of **1** could be obtained by this method. Clathrates **3** and **6** were prepared by slow cooling of saturated hot (50–60 °C) solutions of the host complex in a 1 : 1 (vol.) benzene and ethanol mixture (**3**) and methylcellosolve (**6**). A partially decomposed crystal of **5** was obtained when a large (about $1.0 \times 1.0 \times 1.0$ mm) single-crystal of **4** was removed from the mother solution and quickly frozen at 200 K. Desorption of guest to give the resulting stoichiometry

took place in 1–2 sec and the crystal was partially destroyed. Tetrahydrofuran, benzene, ethanol marked 'pure for analysis' and methylene chloride marked 'pure' were used. Furan 'for syntheses' from Merck was used as supplied. All crystals were dark blue in colour and octahedral in shape. Preliminary data about the composition of the clathrates under investigation were obtained by crystal density measurements (clathrate **4**), studies of sorption isotherms (clathrate **1**, **4**), by weighing crystals before and after guest desorption (clathrates **1–3**, **6**) and during the structure refinement.

Lindemann glass capillary tubes filled with mother solution were used to protect the crystals from guest loss (except for **5** which was frozen and studied in air). Low-temperature data collections were performed on an Enraf-Nonius CAD4 four-circle X-ray diffractometer with graphite monochromated CuK_α ($\lambda = 1.54178$ Å) radiation; the $\omega - 2\theta$ scan mode was applied. Corrections for Lorenz and polarisation effects as well as empirical absorption correction in the case of **4** and **5** were applied.

The structures were solved by the Patterson method (SHELXS-86 [12]), and refined using SHELXL-93 [13]. Non-hydrogen atoms of host molecules were refined with anisotropic thermal displacement parameters; hydrogen atoms were included in the refinement in geometrically calculated positions (d(C–H) = 0.98 Å) and refined as 'riding' atoms on the respective carbon atoms or as elements of rigid methyl groups. The guest molecules were refined with isotropic (clathrates **2**, **4–6**) or anisotropic (clathrates **1**, **3**) thermal displacement parameters as rigid-body models with variable site occupancy factors; the final s.o.f. values were found to be in good agreement with the preliminary defined compositions of clathrates. The rigid-body models of guest molecules were constructed by means of the force-field method (MM2) [14]. Calculations of the host-guest interactions were performed using the EENY program [15]. The details of the data collection structure refinements and determined clathrate stochiometries are summarized in Table I. Fractional atomic coordinates are listed in Tables II–VII.

3. Results and Discussion

The 'windmill' conformation of the pyridine rings of the host molecule, which is typical of β-clathrates [1], is illustrated in Figure 2, values of chosen angles and bond distances are listed in Table VIII. The conformational angles of two symmetrically independent pyridine rings do not differ significantly from those which were reported elsewhere [3, 5, 10]. The conformation of the thiocyanate group varies in different clathrates and the great role of this group in adapting the cavity size to the guest molecules can be assumed. The 4-MePy rings of the host complex for all the clathrates **1–6** are planar within experimental error. The packing pattern of host molecules is shown in Figure 3.

In structure **1** the presence of peaks on difference electron density maps were found close to both the $\overline{4}$ axis and the center of symmetry, which is in agreement with results of the previous definition of the stoichiometry of this clathrate. A

Table I. Data collection and structure analysis parameters for clathrates of β-[Ni(NCS)$_2$(4-methylpyridine)$_4$] with different guests.

Compound Guest 1 (G1) Guest 2 (G2)	(1) Furan	(2) Tetrahydrofuran	(3) Benzene + Ethanol	(4) Methylene chloride	(5) Methylene chloride	(6) Methylcellosolve
Empirical formula NiS$_2$N$_6$C$_{26}$H$_{28}$ +	C$_6$H$_4$O$_{1.5}$	C$_2$H$_4$O$_{0.5}$	C$_{6.2}$H$_{7.7}$O$_{0.5}$	C$_{1.2}$H$_{2.4}$	C$_{0.4}$H$_{0.8}$Cl$_{0.8}$	C$_{1.5}$H$_{3.5}$O
Stoichiometry (host: G1 : G2)	1 : 1.50(3)[1]	1 : 0.51(3)[2]	1 : 0.86 : 0.5[3]	1 : 1.2(3)[1]	1 : 0.4[3]	1 : 0.5(3)[2]
M (g mol^{-1})	649.5	583.4	638.0	663.7	579.2	589.5
$D_{calc.}$ (g cm^{-3})	1.322	1.224	1.296	1.344	1.237	1.244
Crystal size (mm)	0.45 × 0.45 × 0.40	0.50 × 0.45 × 0.45	0.40 × 0.40 × 0.40	0.45 × 0.45 × 0.30	1.00 × 1.00 × 1.00	0.45 × 0.45 × 0.45
Space group	$I4_1/a$	$I4_1/a$	$I4_1/a$	$I4_1/a$	$I4_1/a$	$I4_1/a$
a, (Å)	16.85(6)	16.70(3)	16.82(4)	17.09(4)	16.59(1)	16.738(3)
c, (Å)	22.99(7)	22.71(3)	23.12(7)	22.46(4)	22.61(1)	22.464(4)
V (Å)^3	6527(4)	6334(2)	6541(3)	6560(25)	6221(6)	6293.5(2)
Z	8	8	8	8	8	8
Temperature (K)	173	150	150	150	100	293
Scan range (θ) (°)	3.25–76.44	3.28–76.43	3.25–76.70	3.25–76.32	3.30–75.61	3.29–76.27
hkl range h	0 → 21	0 → 21	0 → 21	−21 → 21	0 → 20	−14 → 14
k	0 → 21	0 → 21	0 → 21	−14 → 21	−20 → 0	−21 → 0
l	−28 → 0	0 → 28	−29 → 0	0 → 28	0 → 28	0 → 28
Absorption coefficient (mm^{-1})	2.340	2.328	2.301	4.500	2.933	2.356
Number of reflections collected	3618	3559	3682	7475	3466	3454
Number of observed unique reflections [$I > 2\sigma(I)$]	1918	2331	2952	1832	2695	2548
Refined parameters	259	179	214	169	163	163
R (based on F)	0.0658	0.1044	0.0610	0.1428	0.0768	0.0638
wR (based on F^2)	0.1462	0.2439	0.1673	0.3516	0.2007	0.1704
Weighting scheme* k_1	0.0834	0.0948	0.0782	0.1961	0.1269	0.1472
k_2	0.7777	40.1486	30.6133	3.1022	20.8718	8.7247
max and min $\Delta\delta$ (eÅ^{-3})	0.56, −0.42	0.48, −0.66	0.37, −0.70	1.40, −2.47	0.91, −1.01	0.83, −0.29
(Δ/σ)max	−0.055	−0.164	−0.052	0.013	0.088	0.032

[1]Data obtained by studies of sorption isotherms.
[2]Data obtained by weighing crystals before and after guest desorption.
[3]Data obtained during structure refinement.
* $w = 1/[\sigma^2(F_0^2) + (k_1P)^2 + k_2P]$ $P = 1/3(F_0^2 + 2F_c^2)$.
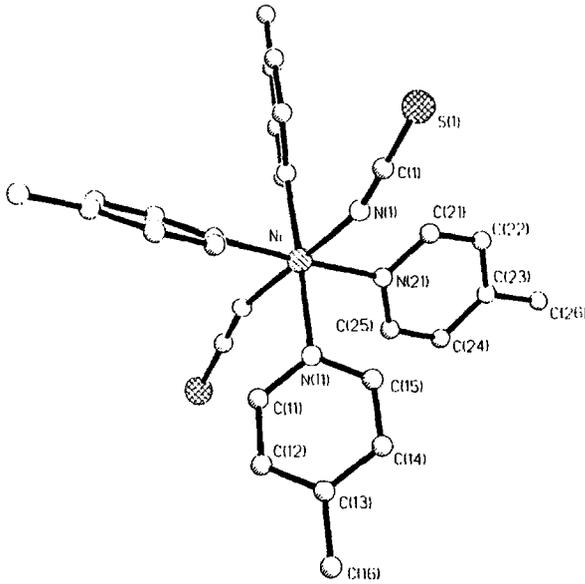
*Figure 2.* Molecule of the host [Ni(NCS)$_2$(4-MePy)$_4$] coordination complex (hydrogen atoms omitted).
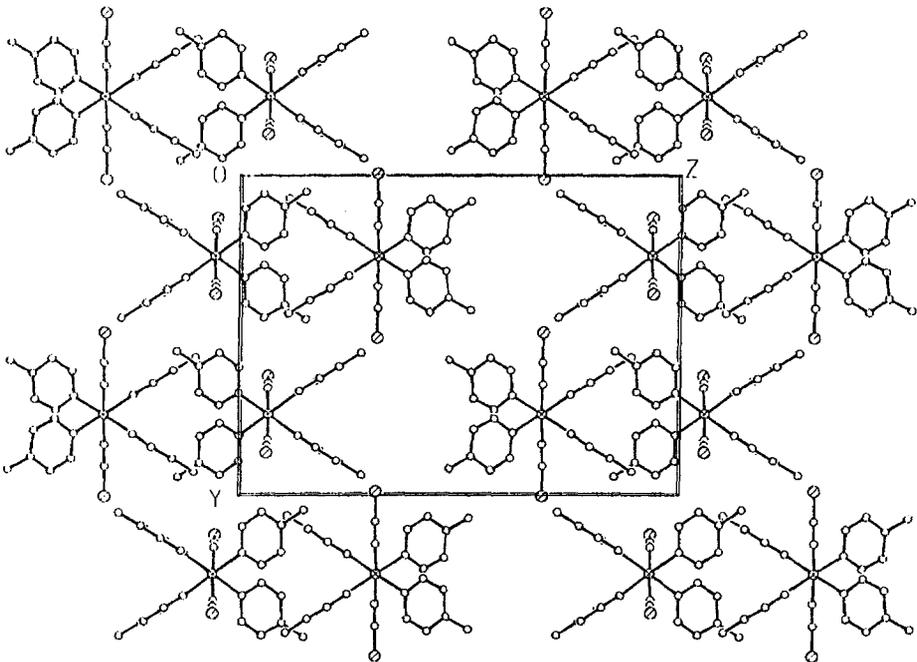
Figure 3. An illustration of the packing of the [Ni(NCS)$_2$(4-MePy)$_4$] molecules in the β-clathrates viewed as the projection of the unit cell content along the x crystal axis.

Table II. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for clathrate **1**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U_{eq}	s.o.f.
Host					
Ni	0	2500	3059(1)	23(1)	
S(1)	1282(1)	−50(1)	3073(1)	41(1)	
C(1)	952(3)	867(3)	3054(2)	27(1)	
N(1)	725(2)	1508(2)	3041(2)	31(1)	
N(11)	702(2)	3062(2)	2403(2)	24(1)	
C(11)	353(3)	3444(3)	1959(2)	27(1)	
C(12)	770(3)	3812(3)	1522(2)	29(1)	
C(13)	1581(3)	3792(3)	1516(2)	29(1)	
C(14)	1953(3)	3413(3)	1977(2)	29(1)	
C(15)	1499(3)	3056(3)	2401(2)	25(1)	
C(16)	2049(4)	3164(4)	1027(3)	43(1)	
N(21)	726(2)	2992(2)	3717(2)	27(1)	
C(21)	1032(3)	2520(3)	4127(3)	40(1)	
C(22)	1503(4)	2793(4)	4583(3)	43(1)	
C(23)	1673(3)	3605(4)	4622(2)	36(1)	
C(24)	1358(3)	4084(3)	4191(3)	35(1)	
C(25)	893(3)	3759(3)	3759(2)	29(1)	
C(26)	2153(4)	3922(5)	5119(3)	56(2)	
Guest					
C(1G)	7071(21)	7900(22)	2575(14)	92(6)	0.5
C(2G)	7670(22)	7792(19)	2943(17)	88(7)	0.5
O(3G)	8104(15)	7206(15)	2661(9)	94(5)	0.5
C(4G)	7745(19)	6985(22)	2136(14)	89(6)	0.5
C(5G)	7153(19)	7400(18)	2122(16)	88(6)	0.5
C(11G)	−57(33)	8171(31)	3702(24)	91(11)	0.25
C(12G)	−129(23)	7569(20)	3274(23)	119(13)	0.25
C(13G)	274(35)	6894(32)	3449(27)	110(15)	0.25
O(14G)	509(24)	7153(25)	3981(21)	111(10)	0.25
C(15G)	291(26)	7907(28)	4114(24)	89(12)	0.25

rigid-body model of a furan molecule was fitted to selected groups of peaks with suitable geometry and energetically favourable orientations of guest molecules were selected by molecular mechanics calculations. Finally it was established that furan molecules occupy both positions ('cavities') of $\bar{1}$ and $\bar{4}$ symmetry and are disordered about four and two equivalent positions, respectively. The packing of guest molecules in this clathrate is represented in Figure 4a.

Table III. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for clathrate **2**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U_{eq}	s.o.f.
Host					
Ni	0	2500	3108(1)	46(1)	
S(1)	1204(2)	−54(1)	3080(1)	90(1)	
N(1)	819(3)	1564(3)	3088(2)	55(1)	
C(1)	983(3)	899(4)	3087(3)	52(1)	
N(11)	664(3)	3111(3)	2445(2)	50(1)	
C(11)	305(4)	3478(4)	2003(3)	55(2)	
C(12)	704(4)	3868(4)	1558(3)	59(2)	
C(13)	1532(4)	3888(4)	1556(3)	57(2)	
C(14)	1904(4)	3503(4)	2012(3)	56(2)	
C(15)	1473(4)	3121(4)	2444(3)	56(2)	
C(16)	1973(6)	4296(6)	1063(4)	91(3)	
N(21)	686(3)	3080(3)	3778(2)	55(1)	
C(21)	1073(4)	2649(5)	4184(3)	68(2)	
C(22)	1478(5)	2989(6)	4649(3)	82(2)	
C(23)	1508(5)	3807(6)	4714(4)	79(2)	
C(24)	1122(5)	4244(5)	4293(4)	82(2)	
C(25)	720(5)	3871(4)	3836(3)	69(2)	
C(26)	1944(7)	4198(7)	5222(4)	113(4)	
Guest					
C(1G)	4428(98)	7135(88)	1557(76)	243(62)	0.25
C(2G)	4540(55)	8020(56)	1338(36)	129(19)	0.25
C(3G)	5133(57)	8174(43)	884(37)	137(21)	0.25
O(4G)	5301(45)	7323(52)	742(29)	222(36)	0.25
C(5G)	5035(73)	6731(43)	1231(39)	134(21)	0.25

Electron density peaks associated with the guest molecule of **2** were found in the 'large cavity' ($\overline{4}$-fold symmetry) but no appropriate model for the tetrahydrofuran molecule could be built. Molecular mechanics calculations of the host-guest interaction energy were performed for a rigid-body tetrahydrofuran molecule located in the 'large cavity'. It was found that for many locations of the tetrahydrofuran molecule the potential energy changes only slightly (within 2–3 kJ/mol) with rotation about any axis. In a final refinement, a rigid-body model of a tetrahydrofuran molecule was located in the energetically most favourable orientation with assumption of $\overline{4}$-fold disorder about the $\overline{4}$ crystallographic axis. It may be concluded that the guest molecule undergoes rapid reorientations and/or oscillations and this may be the explanation for the large thermal displacement parameters observed for the

Table IV. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for clathrate **3**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U_{eq}	s.o.f.
Host					
Ni	0	2500	3057(1)	25(1)	
S(1)	1290(1)	−51(1)	3039(1)	42(1)	
C(1)	961(2)	854(2)	3038(2)	27(1)	
N(1)	728(2)	1512(2)	3038(1)	32(1)	
N(11)	698(2)	3060(2)	2401(1)	26(1)	
C(11)	347(2)	3447(2)	1961(2)	31(1)	
C(12)	759(2)	3810(2)	1521(2)	31(1)	
C(13)	1584(2)	3800(2)	1515(2)	30(1)	
C(14)	1954(2)	3414(2)	1979(2)	31(1)	
C(15)	1503(2)	3056(2)	2404(2)	28(1)	
C(16)	2054(3)	4173(3)	1036(2)	44(1)	
N(21)	723(2)	3000(2)	3712(1)	29(1)	
C(21)	1046(3)	2530(2)	4118(2)	42(1)	
C(22)	1513(3)	2805(3)	4566(2)	45(1)	
C(23)	1677(2)	3610(2)	4608(2)	37(1)	
C(24)	1352(2)	4097(2)	4185(2)	36(1)	
C(25)	879(2)	3775(2)	3754(2)	32(1)	
C(26)	2168(3)	3928(3)	5095(2)	49(1)	
Guest 1					
C(11B)	4625(4)	4298(5)	−113(4)	77(2)	0.86
C(2B)	4423(4)	4721(5)	373(3)	74(2)	0.86
C(3B)	4790(4)	5410(5)	493(4)	77(2)	0.86
Guest 2					
C(1ET)	4914(142)	7059(38)	1277(39)	320(61)	0.5
C(2ET)	5100(36)	6171(37)	1186(32)	253(28)	0.5
O(1ET)	4704(78)	7183(28)	1861(25)	625(113)	0.5

tetrahydrofuran atoms and the rather high magnitude of the final R-factor. The cross-section through the "large cavity" of **2** is shown in Figure 4b.

The crystal structure analysis of **3** revealed the benzene molecule located in the 'small cavity' ($\bar{1}$ symmetry) at early stages of structure refinement; the benzene guest geometry was fixed in subsequent calculations. Electron density maxima found in the 'large cavity' were interpreted as a disordered ethanol molecule, and a similar procedure of guest location as for **2** was applied in the final refinement. The ethanol molecule is disordered about the $\bar{4}$-fold axis and, most probably undergoes rapid reorientations and/or oscillations. Figure 5 depicts the location of guest

Table V. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for clathrate **4**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U_{eq}	s.o.f.
Host					
Ni	0	2500	3076(1)	16(1)	
S(1)	1233(2)	−2(2)	3108(2)	43(1)	
C(1)	941(5)	915(5)	3091(4)	20(2)	
N(1)	743(5)	1551(4)	3060(4)	25(2)	
N(11)	681(4)	3065(4)	2410(3)	17(2)	
C(11)	337(5)	3454(5)	1960(4)	22(2)	
C(12)	754(5)	3833(5)	1520(4)	21(2)	
C(13)	1567(6)	3807(5)	1515(4)	23(2)	
C(14)	1924(5)	3427(5)	1980(5)	24(2)	
C(15)	1461(5)	3055(5)	2412(4)	20(2)	
C(16)	2033(7)	4212(7)	1030(5)	39(3)	
N(21)	706(5)	3034(5)	3736(4)	24(2)	
C(21)	1071(8)	2585(6)	4157(4)	38(3)	
C(22)	1542(7)	2914(7)	4594(5)	36(3)	
C(23)	1661(6)	3708(6)	4627(4)	30(2)	
C(24)	1310(6)	4152(6)	4188(4)	26(2)	
C(25)	825(5)	3800(5)	3769(4)	20(2)	
C(26)	2148(3)	4045(3)	5118(2)	42(3)	
Guest					
Cl(1G)	1778(3)	−1760(3)	2310(2)	44(2)	0.5
Cl(2G)	1578(3)	−2515(3)	3433(2)	80(3)	0.5
C(1G)	1094(3)	−2127(3)	2825(2)	23(4)	0.5

molecules in this case. The presence of ethanol in **3** was also proved by gas chromatography. The dependence of the unit cell parameters on the temperature for **2** and **3** was studied (Table IX). It may be suggested that greater change of the volume of the unit cell with temperature in the case **3** (2.4% for **3** and 1.1% for **2**) is caused by a better filling of the free space by guest molecules in the case of **3**; the assumption being that the contribution of the guest to the overall thermal expansion is significant.

Due to the problems of preparation of good single-crystals and the great absorption of X-rays by the mother solution in Lindemann glass capillary tubes, the X-ray data obtained for **4** were of poor quality. One methylene chloride molecule with s.o.f. = 0.5 was found at the beginning of the structure refinement in the position close to the $\bar{4}$ axis and shifted in the direction of the inversion center. Residual peaks on electron density maps were interpreted as chlorine atoms of a badly disordered methylene chloride molecule and refined in the final refinement to s.o.f. = 0.1.

Table VI. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for clathrate **5**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U_{eq}	s.o.f.
Host					
Ni	0	2500	3111(1)	19(1)	
S(1)	1197(1)	−85(1)	3087(1)	48(1)	
C(1)	978(2)	866(2)	3093(2)	26(1)	
N(1)	816(2)	1557(2)	3095(1)	29(1)	
N(11)	666(2)	3107(2)	2445(1)	22(1)	
C(11)	289(2)	3491(2)	2001(2)	28(1)	
C(12)	696(2)	3879(2)	1553(2)	30(1)	
C(13)	1533(2)	3893(2)	1544(2)	28(1)	
C(14)	1925(2)	3509(2)	2010(2)	29(1)	
C(15)	1480(2)	3124(2)	2443(2)	24(1)	
C(16)	1986(3)	4299(3)	1054(2)	49(1)	
N(21)	681(2)	3082(2)	3781(1)	24(1)	
C(21)	733(2)	3879(2)	3831(2)	34(1)	
C(22)	1134(3)	4267(3)	4287(2)	44(1)	
C(23)	1502(3)	3818(3)	4729(2)	41(1)	
C(24)	1463(3)	2984(3)	4669(2)	44(1)	
C(25)	1049(2)	2644(2)	4201(2)	34(1)	
C(26)	1929(4)	4207(4)	4238(2)	66(2)	
Guest					
Cl(1G)	5209(11)	6554(11)	720(9)	142	0.2
Cl(2G)	4216(15)	7489(14)	1336(12)	168	0.2
C(3G)	4696(44)	7582(54)	925(24)	166	0.2

No attempt was made to locate the disordered methylene chloride molecule. For clathrate **5** a guest molecule was found to be located in the 'large cavity' at the $\bar{4}$ axis and was refined without any restraints on molecular geometry. The stoichiometry of partially decomposed **5** was estimated on the basis of the final s.o.f. for the methylene chloride molecule. Packing diagrams of guest molecules for **4** and **5** are illustrated in Figures 6a and 6b, respectively.

The methylcellosolve guest (CH$_3$—O—CH$_2$—CH$_2$—OH) of **6** was found in the 'large cavity' with the central atom located on the $\bar{4}$ crystallographic axis (Figure 7). The molecule is disordered due to the $\bar{4}$ symmetry but the orientation of the molecule in the cavity was also difficult to establish (the O and C atoms were indistinguishable during refinement). Moreover, the geometry of the guest molecule as obtained from difference electron density maps was unreasonable, so the rigid-body, geometrically 'ideal' model of a methylcellosolve molecule was used and the 'best fit' procedure of SHELXL-93 [13] was applied. The resulting

Table VII. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for clathrate **6**. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor..

	x/a	y/b	z/c	U_{eq}	s.o.f.
Host					
Ni	0	2500	3107(1)	28(1)	
S(1)	1212(1)	−66(1)	3118(1)	55(1)	
C(1)	967(2)	873(2)	3103(1)	34(1)	
N(1)	789(2)	1550(2)	3090(1)	36(1)	
N(11)	677(1)	3092(1)	2436(1)	31(1)	
C(11)	312(2)	3477(2)	1989(1)	35(1)	
C(12)	723(2)	3858(2)	1538(1)	40(1)	
C(13)	1548(2)	3857(2)	1529(1)	38(1)	
C(14)	1928(2)	3469(2)	1998(1)	37(1)	
C(15)	1482(2)	3099(2)	2434(1)	33(1)	
C(16)	2011(2)	4248(3)	1036(2)	55(1)	
N(21)	696(2)	3060(2)	3780(1)	34(1)	
C(21)	1058(2)	2614(2)	4199(1)	43(1)	
C(22)	1497(2)	2944(2)	4657(2)	50(1)	
C(23)	1578(2)	3764(2)	4701(2)	51(1)	
C(24)	1214(3)	4218(2)	4266(2)	56(1)	
C(25)	778(2)	3849(2)	3818(1)	44(1)	
C(26)	2034(3)	4147(3)	5202(2)	69(1)	
Guest					
C(1G)	0	7500	3750	452(32)	0.25
C(2G)	337(57)	6225(20)	3290(22)	452(32)	0.25
O(3G)	542(32)	7057(29)	3337(27)	452(32)	0.25
C(4G)	234(54)	8358(15)	3758(33)	452(32)	0.25
O(5G)	−277(57)	8767(17)	4171(22)	452(32)	0.25

orientation of the guest molecule with a slightly lower R-factor was considered as the final one, but orientational disorder is also very probable..

As already described in [1] specific host-guest interactions do not significantly influence the inclusion of most of the guest molecules by clathrates formed by Werner complexes. The main factor defining the ability of formation of β-phase clathrates as well as the stoichiometry of the clathrate and the localisation of guest molecules in the channels of host lattices is the size and the shape of the guest molecules (this is valid at least for guest molecules of moderate chemical activity and polarity). A second important conclusion is the general non-stoichiometry of β-clathrates. Only steric factors and favorable van der Waals contacts define the final stoichiometry of clathrates. Noninteger values obtained for host : guest molecular ratios in analytical determinations [11] illustrate the above behaviour. The general

Table VIII. Selected bond distances (Å), angles and torsion angles (°) with estimated standard deviations (in parentheses).

Clathrate	1	2	3	4	5	6
Ni—N(1)	2.071(4)	2.078(5)	2.066(3)	2.060(9)	2.069(3)	2.067(3)
Ni—N(11)	2.139(4)	2.130(5)	2.137(3)	2.127(8)	2.122(3)	2.130(2)
Ni—N(21)	2.114(4)	2.136(5)	2.116(3)	2.119(8)	2.123(3)	2.125(2)
N(11)—Ni—N(21)	90.6(2)	90.4(2)	91.0(1)	89.2(3)	90.8(1)	90.4(1)
N(21)—Ni—N(1)	89.4(2)	90.2(2)	89.7(1)	90.0(3)	90.5(1)	91.1(1)
N(11)—Ni—N(1)	90.9(2)	90.1(2)	90.8(1)	90.4(3)	90.3(1)	90.3(1)
S—C(1)—N(1)	179.7(4)	179.1(6)	179.5(3)	177.8(9)	179.7(4)	179.8(3)
C(1)—N(1)—Ni	163.1(4)	152.7(5)	163.0(3)	158.8(7)	152.3(3)	154.9(2)
C(15)—N(11)—Ni—N(1)	−43.5(4)	−40.0(5)	−44.0(3)	−41.6(7)	−40.7(3)	−41.2(2)
C(21)—N(21)—Ni—N(1)	−37.7(4)	−34.5(6)	−36.6(3)	−34.7(9)	−36.2(3)	−35.9(3)
C(1)—N(1)—Ni—N(11)	−144.1(2)	−137.2(1)	−138.7(1)	−147.4(2)	−136.2(6)	−140.5(5)
C(1)—N(1)—Ni—N(21)	125.3(2)	132.4(1)	130.3(1)	123.4(2)	133.1(6)	129.1(5)
S(1)—C(1)—N(1)—Ni	−156.6(1)	30.8(4)	−161.8(1)	111.0(2)	50.6(5)	70.6(7)
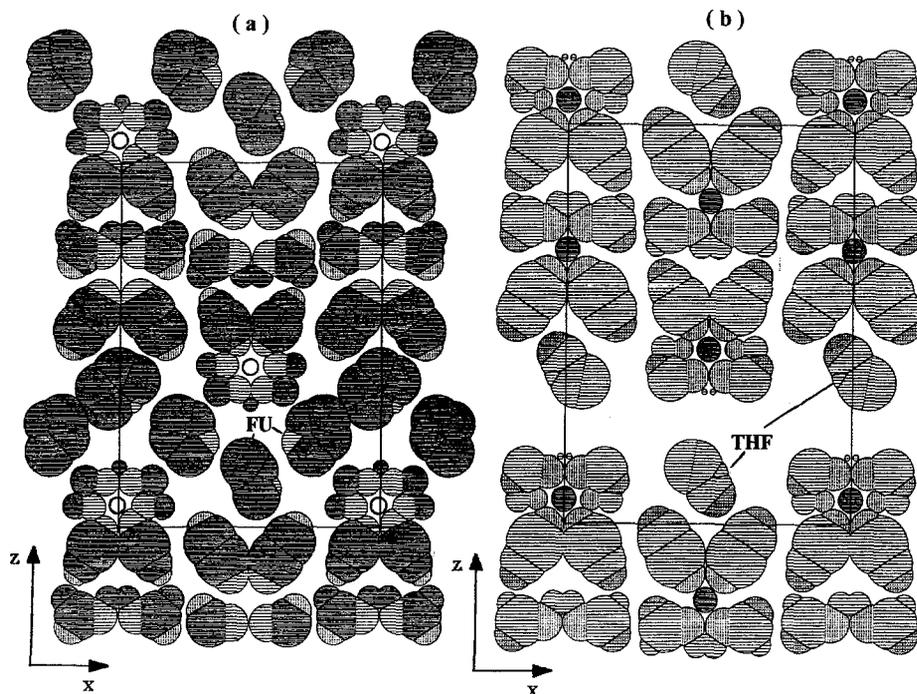
Figure 4. Plane section of the β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrate structures with (a) furan and (b) tetrahydrofuran parallel to the (010) plane and taken at $y = 0.25$. Guest molecules: furan = FU and tetrahydrofuran = THF. Stoichiometries of clathrates 1 : 1.5 and 1 : 0.5 host : guest, respectively.

Table IX. Temperature dependence of the unit cell parameters for clathrates **2** and **3**.

Temperature (K)	a (Å)	c (Å)	Unit cell volume (Å^3)
β-[Ni(NCS)$_2$(4-methylpyridine)$_4$] · 0.5 tetrahydrofuran (**2**)			
300	16.682(5)	22.704(9)	6323
250	16.649(5)	22.699(9)	6293
200	16.605(9)	22.646(13)	6254
β-[Ni(NCS)$_2$(4-methylpyridine)$_4$] · 0.86 benzene · 0.5 ethanol (**3**)			
300	17.027(5)	23.338(6)	6767
250	16.960(10)	23.286(18)	6702
200	16.877(3)	23.188(6)	6605
150	16.812(4)	23.115(6)	6537

information about structures and stoichiometries of β-clathrates available in [1] may be confirmed by the structural data reported here and specified in several
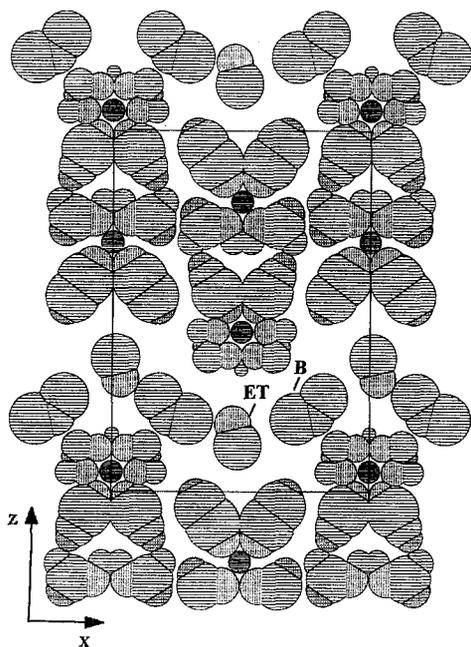
Figure 5. Plane section of the β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrate structure with benzene and ethanol parallel to the (010) plane and taken at $y = 0.25$. Guest molecules: benzene = B and ethanol = ET. Stoichiometry of clathrate 1 : 0.86 : 0.5 host : benzene : ethanol, respectively.

points. Only the stoichiometry of clathrates in equilibrium with the liquid guest (limit stoichiometry) will be discussed.

Planar molecules of suitable size (furan, benzene, *para-* and *meta-*substituted benzene with small side chains, 4-methylpyridine) occupy the 'small cavities'. The location of a flat molecule on the centrosymmetric position ('cavity') in the channel of the β-phase is energetically favourable, as confirmed by high values of the formation enthalpy obtained for clathrates with aromatic guest molecules [1]. The host-to-guest stoichiometry of those clathrates was usually found to be very close to 1 : 1 and corresponds to the stoichiometry expected for occupation of the 'small cavity' by one guest molecule. According to our estimates only approximately 52% of the channel volume is filled by guest molecules in the β-clathrate with benzene and about 70% in the clathrate with p-xylene. The residual space may be filled by an additional guest molecule with a maximum stoichiometry of 1 : 1 : 0.5 for host : aromatic guest (or nonaromatic flat molecule) : additional guest (structure 3). Small-sized, flat guest molecules completely fill both the 'small' and 'large cavities' with one type of guest molecule and a maximum stoichiometry of 1 : 1.5 for host : guest (structure 1). The above results give a good justification of the possibility of partial filling of the 'large cavities' by guest molecules in clathrates with benzene or substituted benzene, and confirms the interpretation of the clathration data obtained for mixtures of aromatic and nonaromatic guests [1]. Most probably, similar locations
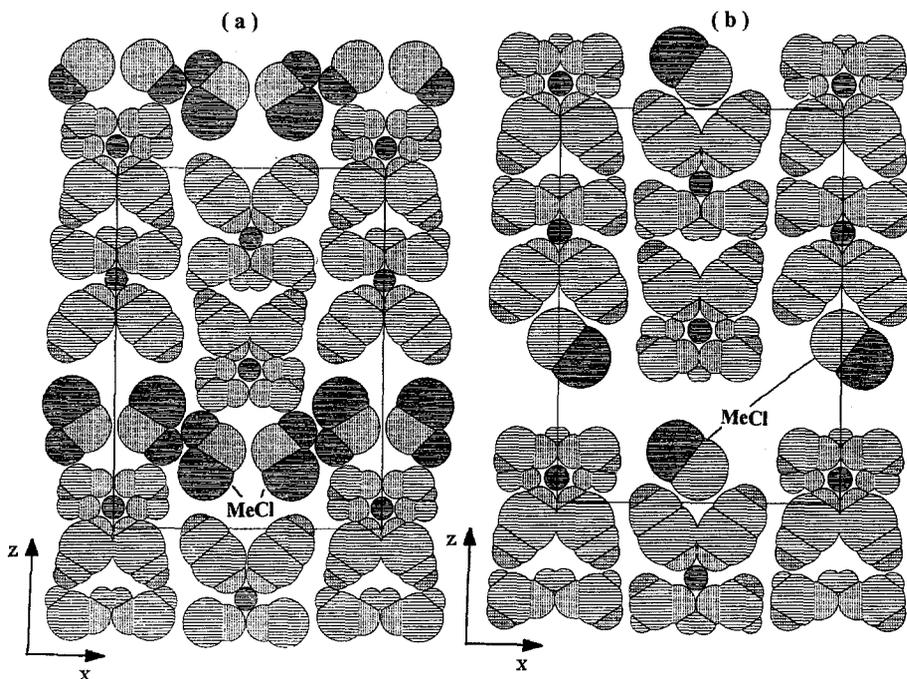
Figure 6. Plane section of the β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrate structure with methylene chloride parallel to the (010) plane and taken at $y = 0.25$. Guest molecules denoted MeCl. Stoichiometries of clathrates close to 1 : 1.2 (a) and 1 : 0.4 (b) host : guest, respectively.

of guest molecules were observed in [2] for clathrates of the β-[Ni(NCS)$_2$(4-ViPy)$_4$] host with 1.04 : 0.36 mixtures of 1,4-cyclohexadiene and tetrahydrofuran and 1.05 : 0.35 benzene and tetrahydrofuran clathrates; the large empty volumes of channels in the β-[Ni(NCS)$_2$(4-ViPy)$_4$] phase allows accommodation of additional guest molecules having a larger size and which cannot be enclathrated by the β-[Ni(NCS)$_2$(4-MePy)$_4$] phase (according to our estimates, the free volume per guest molecule is equal to 215 Å^3 in the clathrate of β-[Ni(NCS)$_2$(4-ViPy)$_4$] with p-xylene and 175 Å^3 in the clathrate of β-[Ni(NCS)$_2$(4-MePy)$_4$] with the same guest molecule). As may be concluded from the results of [1, 3–5], the change of M in the β-[M(NCS)$_2$(4-MePy)$_4$] host does not significantly influence the structure and inclusion capacity of the β-phase. Comparatively little information is available for Schaeffer clathrates with aromatic guest molecules substituted with groups larger than methyl groups. Ethylbenzene is included in β-[Ni(NCS)$_2$(4-MePy)$_4$] in a similar way to other aromatic guest molecules [1]. The isomers of nitrotoluene used to obtain inclusion compounds with [Ni(NCS)$_2$(4-MePy)$_4$] were found to form clathrates with another structure (the so-called γ-phase) [16]. The powder X-ray patterns and analysis of compositions show that significant differences between these clathrates and the β-phase clathrates occur (a hexagonal system instead of tetragonal $I4_1/a$ and, most probably, a cage-type structure). The crystal structure
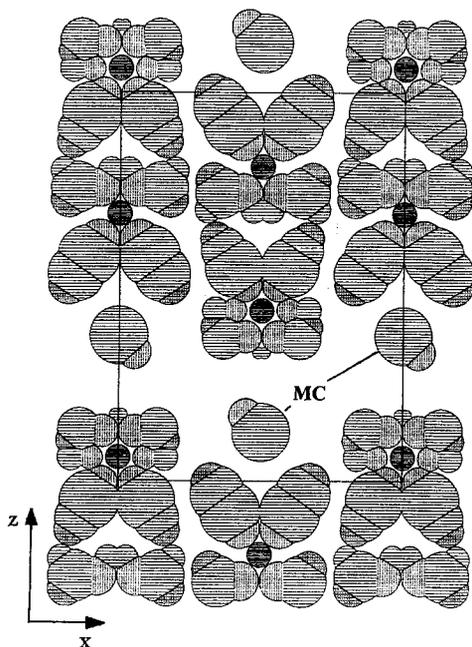
*Figure 7.* Plane section of the β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrate with methylcellosolve parallel to the (010) plane and taken at $y = 0.25$. Guest molecules denoted MC. Stoichiometry of clathrate 1 : 0.5 host : guest.

of the clathrate of [Ni(NCS)$_2$(4-MePy)$_4$] with *p*-cymene (*p*-isopropyltoluene) was reported as a typical β-phase [17] with stoichiometry 1 : 0.66–1 : 0.77 host : guest molecule. The detailed analysis of the channel's shape in this clathrate shows significant distortions compared to the other β-clathrates (Figure 8). The molecular volume of the *para*-substituents in *p*-isopropyltoluene is significantly larger than in *p*-nitrotoluene (58 Å^3 and 23 Å^3, respectively). Taking the above into consideration, two hypotheses can be presumed: the clathrates with nitrotoluene isomers should be reinterpreted as a distorted β-phase or they represent a unique example of the influence of the chemical properties of the guest molecule on the structure of the [Ni(NCS)$_2$(4-MePy)$_4$] clathrate.

Clathration of small (2–4 nonhydrogen atoms) or nonplanar guest molecules may be regarded in terms of accommodating the guest molecule in the 'large cavity'. A gain in energy larger than 3.3 kJ mol^{-1} (the enthalpy of transformation from the nonclathrate α-phase to the 'empty' clathrate β-phase [1]) may be postulated as a requirement for clathrate formation. Experimental proof for this supposition is necessary, but it is not in contradiction with available experimental data. For example, the [Ni(NCS)$_2$(4-MePy)$_4$] complex crystallized from tetrahydrofuran gives the β-clathrate, while the [Ni(NCS)$_2$(4-ViPy)$_4$] complex crystallized under the same conditions gives the nonclathrate α-phase [8]. It can be explained by
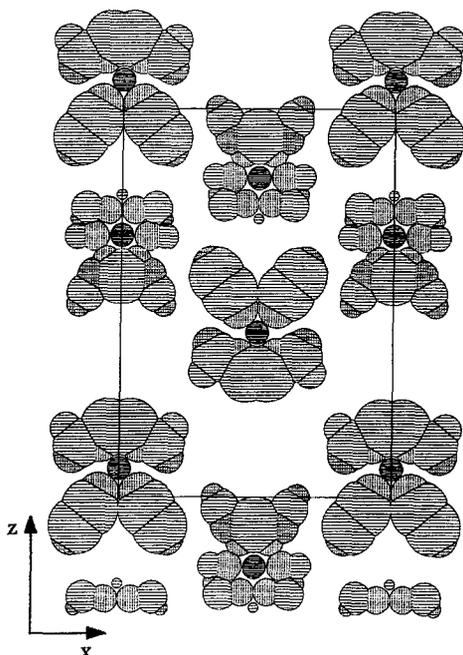
Figure 8. Plane section of the β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrate with p-cymene parallel to the (010) plane and taken at $y = 0.25$ (guest molecules and hydrogen atoms omitted). Shape of channels distorted in comparison with Figure 1.

the less favorable van der Waals interactions between host and guest molecules in the β-[Ni(NCS)$_2$(4-ViPy)$_4$] clathrate caused by the larger size of channels in this structure.

A second example is that crystallisation of [Ni(NCS)$_2$(4-MePy)$_4$] from methylene chloride provides the β-phase clathrate while a similar crystallisation from ethanol results in the non-clathrate α-[Ni(NCS)$_2$(4-MePy)$_4$] phase [11] (the molecules of methylene chloride and ethanol have similar shapes and molecular volumes, but the vapour pressures over these compounds (and hence the chemical potentials) differ significantly). It should be noticed that the absence of clathrate formation at room temperature does not rule out this possibility at low temperatures. The formation of octahedral crystals from ethanol was observed when the [Ni(NCS)$_2$(4-MePy)$_4$] complex was crystallized from ethanol at about $-50\,^{\circ}$C, at room temperature the crystals undergo recrystallization to the non-clathrate α-[Ni(NCS)$_2$(4-MePy)$_4$] form.

The stoichiometry of β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrates with aliphatic (with more than three nonhydrogen atoms) and nonaromatic cyclic guest molecules may be postulated to be equal to a 2 : 1 host : guest molecular ratio with guest molecules occupying the 'large cavities' (structures **2** and **6**). The maximum molecular volume of guest molecule included in the β-[Ni(NCS)$_2$(4-MePy)$_4$] phase in such a man-

ner may be estimated, on the basis of the known structures, as equal to 100–130 Å^3. Examples of the existence of β-[Ni(NCS)$_2$(4-MePy)$_4$] clathrates with non-aromatic guest molecules of greater molecular volume are unknown. Enclathration of methanol leads to a 2 : 1 guest : host stoichiometry [10]: the guest molecules occupy four equivalent positions in the 'large cavity', each one close to the crystallographic center of inversion. Measurements of sorption of different gaseous guest species by the empty β-[Ni(NCS)$_2$(4-MePy)$_4$] phase suggest a similar type of inclusion for other molecules of similar shape (ethane, CH$_3$Cl) and even for linear molecules such as CO$_2$ and CS$_2$ [18]. In the clathrate with methylene chloride (clathrate **4**) the guest molecules occupy the same position as in the clathrate with methanol but only approximately 50% of positions is filled; it may be assumed that the maximum stoichiometry in the case of guest molecules with only two nonhydrogen atoms is equal to a 1 : 2 host : guest ratio. The accommodation of four guest molecules with three nonhydrogen atoms in the 'large cavity' seems to be impossible because of steric barriers. Noninteger numbers for a host-to-guest ratio between 1 : 1 and 1 : 2 and a temperature dependent composition of these clathrates should be expected. Comparison of structures **4** and **5** shows that a shift of guest molecules from the 'large cavity' to the center of inversion (i.e. to the 'small cavity') observed for this type of guest may be caused by guest–guest interactions. Clathrates formed by the [Ni(NCS)$_2$(4-ViPy)$_4$] host with similar patterns of guest allocation have been reported (β-[Ni(NCS)$_2$(4-ViPy)$_4$] with 0.5CCl$_4$ and 2CS$_2$, [6] and [7], respectively). The large channel sizes in the β-[Ni(NCS)$_2$(4-ViPy)$_4$] and β-[Ni(NCS)$_2$(4-EtPy)$_4$] clathrates enable enclathration of guest molecules larger in size or greater in number.

Acknowledgements

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