

Structural Investigation of Guest-to-Host and Ligand-Ligand Interactions in Werner Clathrates of $[\text{Ni}(4\text{-Etpy})_4(\text{NCS})_2] \cdot n\text{G}$ Type (G = Naphthalene Derivatives). The Crystal Structure of $[\text{Ni}(4\text{-Etpy})_4(\text{NCS})_2] \cdot 1\text{-Methylnaphthalene}$

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Abstract. The stoichiometry and spectral properties of $[\text{Ni}(4\text{-Etpy})_4(\text{NCS})_2] \cdot n\text{G}$ clathrates have been studied where $n = 2$ for G = 1-BrN (N = naphthalene), $n = 1$ or 2 for G = 1-MeN, and $n = 0.5$ for 2-MeN and 2-BrN. The complexes under study show electronic absorption spectra typical of an octahedral environment of the Ni(II) central atom. The differences found in IR spectra for the ν ($\text{C}\equiv\text{N}$) and ν ($\text{Ni}-\text{N}_{\text{NCS}}$) vibrations are discussed. The crystal structure of $[\text{Ni}(4\text{-Etpy})_4(\text{NCS})_2] \cdot 1\text{-MeN}$ was determined by X-ray diffraction and refined to $R = 0.0586$. Discrete non-centrosymmetric $[\text{Ni}(4\text{-Etpy})_4(\text{NCS})_2]$ molecules form layers of a host structure and the space between the layers is occupied by 1-MeN. The relationship between interatomic distances in the host complex of similar clathrates are discussed.

Key words: Spectral data, X-ray data, Werner clathrates.

Supplementary Data relevant to this publication have been deposited with the British Library as Supplementary Publication No. SUP 82233 (8 pages).

1. Introduction

Schaeffer *et al.* [1] were the first to study thiocyanate coordination compounds with pyridine derivatives as clathrating agents and showed that they could be used for the separation of various aromatic hydrocarbons from petroleum fractions. Among the thiocyanate compounds, $[\text{Ni}(4\text{-Mepy})_4(\text{NCS})_2]$ was studied most thoroughly since it formed clathrates $[\text{Ni}(4\text{-Mepy})_4(\text{NCS})_2] \cdot n\text{G}$ with a variety of aromatic compounds G as guest molecules [2]. In some of our previous papers [3–5] attention was also paid to the above compound, focusing particularly on structural and thermochemical changes dependent on the varied guest molecules G. We have elucidated the relationship between the quasi-equilibrium decomposition temperatures, band shifts in electronic spectra and degree of tetragonal distortion of the host complex.

Table I. Analysis results for $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2] \cdot n\text{G}$ clathrates.

Compound		%Ni	%C	%H	%N
I $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2]$	calcd:	9.73	59.71	6.02	13.93
	found:	9.78	60.31	6.16	14.20
II $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2] \cdot 0.5$ (2-BrN)	calcd:	8.30	59.47	5.63	11.89
	found:	8.21	59.34	5.78	11.66
III $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2] \cdot 0.5$ (2-MeN)	calcd:	8.70	63.22	6.12	12.46
	found:	8.81	62.48	6.15	13.05
IV $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2] \cdot 1$ (1-MeN)	calcd:	7.88	66.06	6.22	11.27
	found:	7.79	66.18	6.30	11.35
V $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2] \cdot 2$ (1-MeN)	calcd:	6.61	70.30	6.36	9.47
	found:	6.66	69.70	6.46	9.71
VI $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2] \cdot 2$ (1-BrN)	calcd:	5.77	59.01	4.95	8.26
	found:	5.71	58.69	5.12	8.35

In this paper our investigation is extended to clathrates with a similar composition; however, a more bulky ethyl substituent (Et) on the pyridine ring has been chosen and some bromo- and methyl derivatives of naphthalene have been used in the role of guest molecule G. The crystal structure of $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2] \cdot 1\text{-MeN}$ is also reported and the results are compared with those found for crystal structures of similar clathrates with xylenes, CS_2 , and CCl_4 [6].

2. Experimental

The host complex $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2]$ (**I**) as well as the clathrates $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2] \cdot n\text{G}$, where $n\text{G} = 0.5(2\text{-BrN})$ (**II**), $0.5(2\text{-MeN})$ (**III**), and $2(1\text{-BrN})$ (**VI**), were prepared from ethanolic solutions according to procedures similar to those given in our previous papers [5,7]. However, when 1-methylnaphthalene (1-MeN) was used as a guest, two different clathrates could be prepared. In dissolving the powdered host complex **I** and 1-MeN in ethanol in the molar ratio 1 : 2, crystals of $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2] \cdot 1(1\text{-MeN})$ (**IV**) were obtained when ether was added to the solution in a volume ratio 1 : 1, while $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2] \cdot 2(1\text{-MeN})$ (**V**) was crystallized by slow evaporation of the solution.

All compounds were analyzed for Ni, C, H, and N content. Nickel was determined by EDTA titration; carbon, hydrogen, and nitrogen by microanalysis (Carlo Erba CHNS-O, model 11-08).

Electronic absorption spectra were measured with a Specord M 40 (Carl Zeiss, Jena). Infrared absorption spectra were measured in Nujol mulls with a Philips analytical PU 9800 FTIR Spectrometer in the range $4000\text{--}200\text{ cm}^{-1}$.

The crystal and molecular structure of $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2] \cdot 1\text{-MeN}$ was determined by single crystal X-ray diffraction. All data were collected with a Syntex P 21 diffractometer at room temperature. Accurate cell parameters were determined

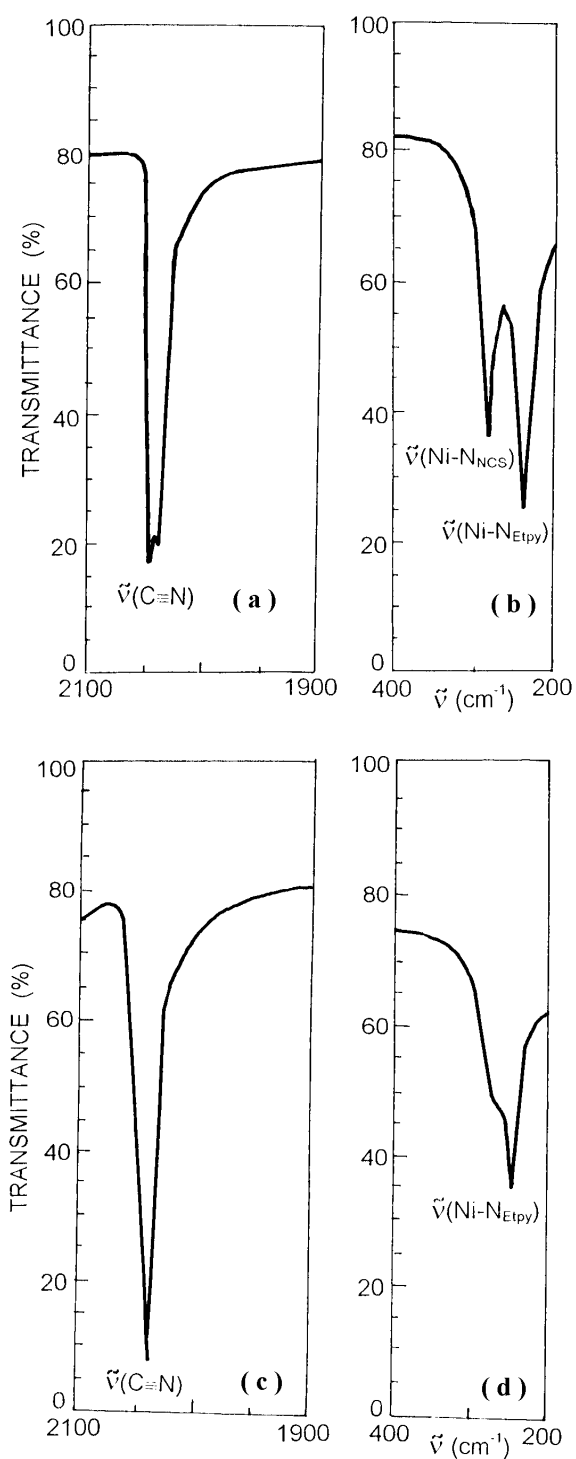


Figure 1. Infrared spectra of the clathrates $\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2 \cdot n\text{G}$; a, b : 2-BrN clathrate, c, d : 1-BrN clathrate.

Table II. Stoichiometry and some IR spectral data of $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2] \cdot n\text{G}$ clathrates.

Compound	Guest G	Host to Guest ratio	Infrared spectra		
			Maxima of bands (cm^{-1})		
			$\nu(\text{C}\equiv\text{N})$	$\nu(\text{Ni}-\text{N}_{\text{NCS}})$	$\nu(\text{Ni}-\text{N}_{4-\text{Etpy}})$
I	–	–	2076	286	237
II	2-BrN	2 : 1	2080	284	235
III	2-BrN	2 : 1	2072 2078	286	235
IV	1-MeN	1 : 1	2074	≈ 270 (sh)	238
V	1-MeN	1 : 2	2072	≈ 275 (sh)	239
VI	1-BrN	1 : 2	2083	≈ 270 (sh)	243

Table III. Some structural data of $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2] \cdot n\text{G}$ clathrates.

Compound ^a	Guest G	n	Space group	Interatomic distances		Ref.
				R_e (Å)	R_a (Å)	
(1)	–	0	$P1$	2.128	2.062	6
(2) ^b	–	0	$P1$	2.130	2.077	6
(3)	CCl_4	1/2	$I4_1/a$	2.135	2.080	6
(4)	<i>p</i> -xylene	1	$P1$	2.134	2.058	6
(5)	<i>m</i> -xylene	1	$P1$	2.147	2.073	6
(6)	<i>o</i> -xylene	1	$P1$	2.126	2.099	6
(7)	CS_2	2	$P1$	2.129	2.099	6
(8)	CCl_4	2	$P2_1/c$	2.154	2.065	6
IV	1-MeN	1	$I4_1/a$	2.109	2.056	This paper

^a Compounds are numbered as given in the respective reference.

^b A modification of compound **(1)**.

by the least squares method from 25 reflections with θ between 8.5 and 17.5° . The intensities of diffractions were corrected for Lorenz and polarization factors, absorption and extinction were ignored.

The structure was solved by locating the nickel and sulphur atoms from a Patterson map while Fourier maps, least squares refinement and the SHELXL 93 program [8] were applied for location of the remaining non-hydrogen atoms. The positions of all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions. The atomic scattering factors were taken from the *International Tables for X-ray Crystallography* [9].

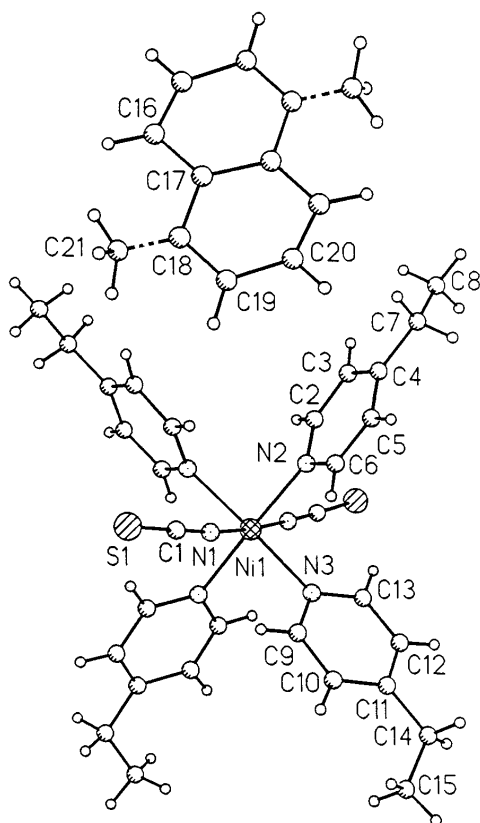


Figure 2. The molecular structure of the $[\text{Ni}(4\text{-Etpy})_4(\text{NCS})_2] \cdot 1\text{-MeN}$ clathrate.

3. Results and Discussion

3.1. THE STOICHOOMETRY AND SPECTRAL PROPERTIES

The compounds under study contain a maximum of two molecules of the guest (1- or 2-substituted naphthalenes) per molecule of the host complex $[\text{Ni}(4\text{-Etpy})_4(\text{NCS})_2]$ (Table I). For the clathrate with 1-bromonaphthalene the host : guest ratio of 1 : 2 was found, while two values of the above ratio are possible in the clathrates with 1-methylnaphthalene, namely 1 : 1 and 1 : 2. However, only a ratio of 1 : 0.5 was observed for 2-bromo- and 2-methylnaphthalene, respectively.

Three spin-allowed absorption bands and no splittings were observed in electronic absorption spectra of the clathrates under investigation. These confirm an approximate octahedral O_h symmetry of the host complex [6].

Further information on the spectral properties of the studied clathrates was obtained by investigating their infrared spectra. In the search for some evidence that would prove the influence of the guest molecules on the host complex, our attention was focused in particular on the $\text{C}\equiv\text{N}$, $\text{Ni}-\text{N}_{\text{NCS}}$ and $\text{Ni}-\text{N}_{4\text{-Etpy}}$ stretching

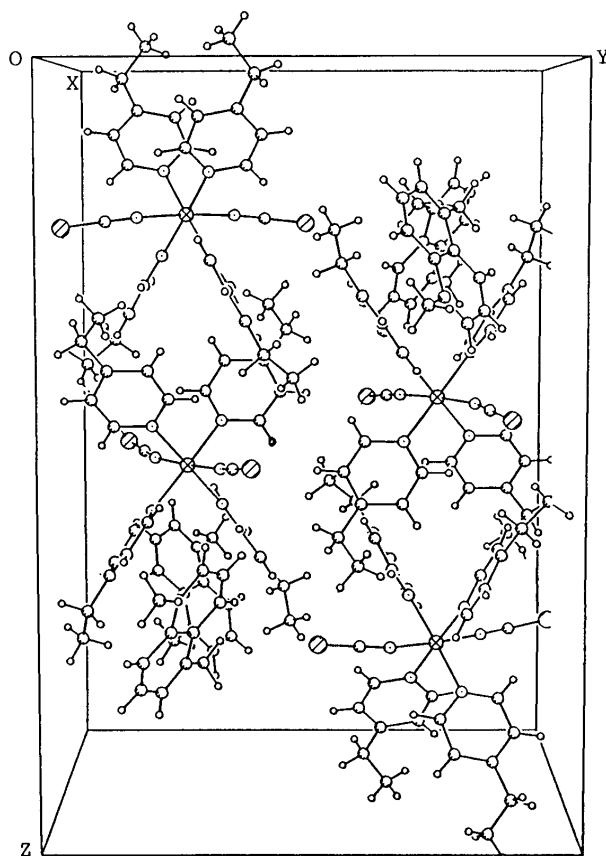


Figure 3. The packing of $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2]$ and 1-MeN molecules in the unit cell.

vibrations (Table II). While one single band at $2072\text{--}2083\text{ cm}^{-1}$, corresponding to the $\nu(\text{C}\equiv\text{N})$ vibration, occurs in the IR spectra of clathrates with 1-substituted naphthalenes, a split band is observed for clathrates with 2-substituted naphthalenes (Figure 1). This difference can obviously occur due to a different arrangement of the isothiocyanate groups, as reported in [2,5]. Differences in far-infrared spectra have also been observed. Two bands assigned to $\nu(\text{Ni}\text{---}\text{N}_{\text{NCS}})$ and $\nu(\text{Ni}\text{---}\text{N}_{4\text{-Etpy}})$, respectively, are predicted [10] to occur in the infrared spectra of monomeric octahedral complexes of the $\text{Ni}(\text{Rpy})_4(\text{NCS})_2$ type (Rpy – alkylpyridines). This assumption is in agreement with the results obtained for clathrates with 2-substituted naphthalenes. In the IR spectra of 1-substituted naphthalene clathrates, however, only one band with a shoulder is observed (Table II, and Figure 1). The appearance of the shoulder may be caused by a shift of the maximum of the $\nu(\text{Ni}\text{---}\text{N}_{\text{NCS}})$ band with a decreased intensity to lower values of wavenumbers. The latter can be referred to changes in binding properties of NCS groups.

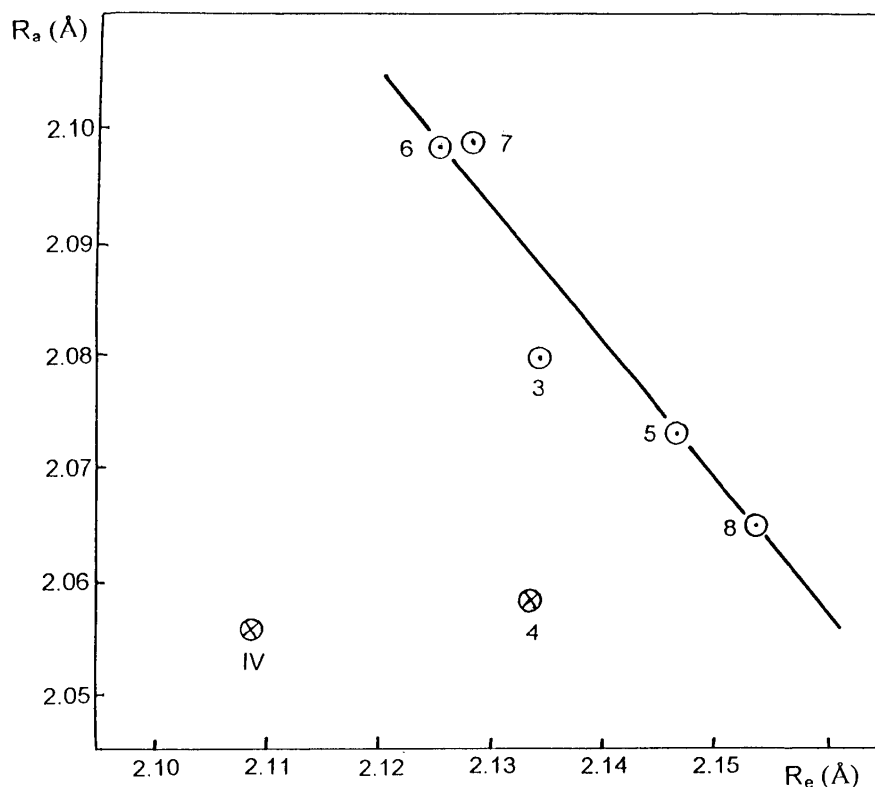


Figure 4. R_a vs. R_e diagram for the title compounds. (See Table III for identification of the compounds.)

3.2. RELATIONSHIPS BETWEEN STRUCTURAL PARAMETERS

Only clathrates $[\text{Ni}(4\text{-Etpy})_4(\text{NCS})_2] \cdot n\text{G}$ with smaller guest molecules, such as CS_2 and CCl_4 or molecules containing one benzene ring (xylenes), have been studied crystallographically to date (Table III) [3]. It was challenging, therefore, to solve the crystal structure of $[\text{Ni}(4\text{-Etpy})_4(\text{NCS})_2] \cdot 1\text{-MeN}$ in which a larger molecule (1-methylnaphthalene) is introduced in the clathrate as a guest. Complete experimental and refinement data are summarized in Table IV. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (\AA^2) are listed in Table V, while important interatomic distances and bond angles are given in Tables VI and VII, respectively. Anisotropic thermal parameters for non-hydrogen atoms, positions of hydrogen atoms and list of structure factors are included in the supplementary material (Tables VIII, IX, X). In the crystal structure of $[\text{Ni}(4\text{-Etpy})_4(\text{NCS})_2] \cdot 1\text{-MeN}$ the nickel atom is in an irregular octahedral environment, being coordinated to four nitrogen atoms of 4-ethylpyridine and two nitrogen atoms of thiocyanate groups in a trans position (Figure 2). The $\text{Ni}-\text{N}_{\text{Etpy}}$ distances are nearly equal and their mean value is 2.109 \AA , whereas that of $\text{Ni}-\text{N}_{\text{NCS}}$ is 2.056

Table IV. Crystal data and structure refinement for $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2] \cdot \text{1-MeN}$.

Empirical formula	$\text{C}_{41}\text{H}_{46}\text{N}_6\text{NiS}_2$
Formula weight	745.67
Temperature	293(2) K
Wavelength $\text{CuK}\alpha$	1.54180 Å
Crystal system	tetragonal
Space group	$I4_1/a$
Unit cell dimensions	$a = 17.474(2)$ Å $c = 25.400(5)$ Å
Volume	$7756(2)$ Å ³
Z	8
Density (calculated)	1.277 Mg m^{-3}
Density (measured)	1.283 Mg m^{-3}
Absorption coefficient	2.007 mm^{-1}
$F(000)$	3152
Crystal size	$0.25 \times 0.29 \times 0.40 \text{ mm}$
θ range for data collection	4.99 to 76.22°
Index ranges	$0 \leq h \leq 18.0$, $k \leq 21.0$, $l \leq 32$
Reflections collected	2832
Independent reflections	2633 ($R_{\text{int}} = 0.0719$)
Absorption correction	No
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2620/0/231
Goodness-of-fit on F^2	1.013
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0586$, $wR2 = 0.1512$
R indices (all data)	$R1 = 0.2141$, $wR2 = 0.2331$
Largest diff. peak and hole	0.572 and $-0.432 \text{ e \AA}^{-3}$

Å. The carbon atom C(21) lies in the plane of the aromatic ring and when regarding its statistical position (site occupation factor of 0.5) the guest molecule 1-MeN can be considered as centrosymmetric.

The packing of $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2]$ and 1-MeN molecules in a unit cell in a layer with $x = 0.5$, is shown in Figure 3. Discrete non-centrosymmetric $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2]$ molecules form layers that are perpendicular to a at $x = 0.0$; 0.5 and to b at $y = 0.25$; 0.75 . Isothiocyanate groups penetrate the space between the layers and are perpendicular to the a axis. The space between layers is occupied by 1-MeN guest molecules.

Metal–ligand distances in the host complex are of the greatest interest and, those marked as R_e (mean interatomic Ni—N_{Etpy} distances between the central and donor atoms in the equatorial plane) and R_a (Ni—N_{NCS} distances in axial positions) for $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2] \cdot n\text{G}$ clathrates, are given in Table III. Some conclusions taken from the results are as follows:

Table V. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2] \cdot \text{1-MeN}$. $U(\text{eq})$ is defined as one third of the trace of orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
Ni(1)	0	2500	2972(1)	39(1)
S(1)	1342(2)	4878(1)	2821(1)	98(1)
N(1)	701(4)	3444(4)	2946(2)	67(2)
N(2)	677(4)	1971(4)	2390(2)	62(2)
N(3)	693(4)	2018(4)	3566(2)	67(2)
C(1)	962(5)	4046(5)	2897(3)	57(2)
C(2)	337(5)	1623(5)	1994(4)	70(2)
C(3)	719(6)	1294(5)	1590(3)	76(3)
C(4)	1521(6)	1284(5)	1590(4)	79(3)
C(5)	1857(5)	1635(5)	2004(4)	79(3)
C(6)	1443(5)	1967(5)	2395(3)	69(2)
C(7)	1974(7)	921(9)	1169(5)	127(4)
C(8)	1597(12)	370(8)	838(6)	188(8)
C(9)	1070(7)	2466(5)	3891(3)	88(3)
C(10)	1461(6)	2206(6)	4308(3)	88(3)
C(11)	1502(5)	1432(6)	4405(3)	69(2)
C(12)	1132(5)	980(5)	4067(4)	80(3)
C(13)	731(5)	1280(5)	3654(3)	66(2)
C(14)	1916(6)	1094(7)	4849(4)	96(3)
C(15)	2053(9)	1566(8)	5281(6)	166(6)
C(16)	4282(10)	5626(10)	-324(10)	142(6)
C(17)	4802(7)	5334(7)	42(6)	112(4)
C(18)	4967(14)	5729(11)	517(9)	155(7)
C(19)	5425(13)	5422(16)	874(6)	149(7)
C(20)	5792(12)	4782(16)	739(10)	157(8)
C(21)	4644(15)	6329(27)	594(18)	418(28)

- (i) In clathrates of the type $[\text{Ni}(\text{4-Etpy})_4(\text{NCS})_2] \cdot n\text{G}$, axially distorted coordination polyhedra, namely slightly compressed tetragonal bipyramids are preferred in the coordination polyhedra of the host complex.
- (ii) The properties of the guest molecules affect the mentioned distortion. A comparison of the mean values of R_e and R_a shows that the interatomic distances in the clathrates with 1-MeN are evidently smaller than those found for similar clathrates with other guest molecules. This is probably due to a greater volume of 1-MeN.
- (iii) Using statistical methods a nearly linear R_a vs. R_e inverse correlation has been confirmed for some known structures of $[\text{Ni}(\text{4-Mepy})_4(\text{NCS})_2] \cdot n\text{G}$ clathrates [3]. When applying a similar procedure to compounds with 4-Etpy it has been

Table VI. Bond lengths [Å] for [Ni(4-Etpy)₄(NCS)₂]·1-MeN.

Metal–ligand bonds:		NCS group:	
Ni(1)—N(1)	2.056(7)	N(1)—C(1)	1.153(9)
Ni(1)—N(2)	2.108(6)	C(1)—S(1)	1.610(10)
Ni(1)—N(3)	2.110(7)		
4-Ethylpyridines:			
N(2)—C(2)	1.318(10)	N(3)—C(13)	1.310(9)
C(2)—C(3)	1.350(11)	C(13)—C(12)	1.365(12)
C(3)—C(4)	1.401(12)	C(12)—C(11)	1.334(12)
C(4)—C(5)	1.352(12)	C(11)—C(10)	1.376(12)
C(5)—C(6)	1.357(11)	C(10)—C(9)	1.338(12)
C(6)—N(2)	1.337(9)	C(9)—N(3)	1.315(10)
C(4)—(7)	1.474(14)	C(11)—C(14)	1.466(13)
C(7)—(8)	1.44(2)	C(14)—C(15)	1.39(2)
1-Methylnaphthalene:			
C(16)—C(17)	1.40(2)	C(19)—C(20)	1.33(2)
C(17)—C(18)	1.42(2)	C(20)—C(16)**	1.28(2)
C(18)—C(19)	1.32(2)	C(17)—C(17)**	1.37(2)
C(18)—C(21)	1.21(4)		

Symmetry transformations used to generate equivalent atoms:

* $-x + 1 - 1, -y + 1/2, z + 1 - 1$.

** $-x + 1, -y + 1, -z$.

shown, however, that this conclusion cannot unambiguously be extended to all compounds under study (Figure 4). Two exceptions to this correlation (especially compound **IV**) demonstrate a greater mutual steric influence between the host complex with more bulky ethyl groups (comparing with methyl groups), and guest molecules.

The bonding angles are also affected when 1-MeN enters the crystal structure of the host complex **I**. Namely the value of the angle C(1)—N(1)—Ni(1) is lowered (Table VII) and consequently, the Ni—N_{NCS} vibrations in the far-infrared spectra (Table V) may be influenced as well.

It may be concluded that the differences in interatomic distances could be caused by different intermolecular guest-to-host interactions that may influence the ligand–ligand interactions as well, and consequently, the bond lengths in the host complex.

Table VII. Bond angles [°] for [Ni(4-Etpy)₄(NCS)₂]:1-MeN.

Angles between the central and donor atoms:			
N(1)—Ni(1)—N(2)	89.7(3)	N(3)—Ni(1)—N(2)	90.2(2)
N(1)—Ni(1)—N(3)	90.1(3)	N(3)—Ni(1)—N(3)*	88.7(4)
N(1)—Ni(1)—N(2)*	87.7(3)	N(1)—Ni(1)—N(1)*	176.3(4)
N(1)—Ni(1)—N(3)*	92.6(3)	N(3)—Ni(1)—N(2)*	177.5(3)
N(2)—Ni(1)—N(2)*	90.8(3)		
Angles in NCS group:			
C(1)—N(1)—Ni(1)	166.2(7)		
N(1)—C(1)—S(1)	178.8(8)		
Angles in 4-Etpy groups:			
C(2)—N(2)—Ni(1)	119.0(6)	C(10)—C(11)—C(14)	124.0(10)
C(13)—N(3)—Ni(1)	122.9(6)	C(12)—C(11)—C(14)	119.8(10)
C(6)—N(2)—Ni(1)	123.9(6)	C(11)—C(14)—C(15)	117.0(10)
C(9)—N(3)—Ni(1)	119.9(6)	—	
N(3)—C(9)—C(10)	123.4(8)	N(2)—C(2)—C(3)	123.5(8)
C(9)—C(10)—C(11)	120.1(9)	C(2)—C(3)—C(4)	120.0(8)
C(10)—C(11)—C(12)	116.2(8)	C(3)—C(4)—C(5)	115.4(8)
C(11)—C(12)—C(13)	121.1(8)	C(4)—C(5)—C(6)	122.0(8)
C(12)—C(13)—N(3)	122.3(8)	C(5)—C(6)—N(2)	121.9(8)
C(13)—N(3)—C(9)	117.07	C(6)—N(2)—C(2)	117.1(7)
C(3)—C(4)—C(7)	122.9(10)		
C(5)—C(4)—C(7)	121.8(10)		
C(4)—C(7)—C(8)	117.8(12)		
Angles in 1-methylnaphthalene:			
C(20)—C(16)—C(17)	114(2)	C(19)—C(20)—C(16)**	129(2)
C(16)—C(17)—C(18)	121(2)	C(17)—C(18)—C(21)	118(3)
C(17)—C(18)—C(19)	121(2)	C(19)—C(18)—C(21)	122(3)
C(18)—C(19)—C(20)	117(2)		
C(16)—C(17)—C(17)**	122(2)		
C(17)**—C(17)—C(18)	116(2)		

Symmetry transformations used to generate equivalent atoms:

* $-x + 1 - 1, -y + 1/2, z + 1 - 1$.** $-x + 1, -y + 1, -z$.

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