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A thermochemical investigation of guest–host interactions in labile Werner clathrates of the $[Ni(4\text{-}EtPy)_4(NCS)_2]\cdot G$ type (G = Methyl derivatives of benzene)

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Abstract

The stoichiometry of thermal decomposition has been studied for (**I**): $[Ni(4\text{-}EtPy)_4(NCS)_2]$ as a host complex as well as for its clathrates $[Ni(4\text{-}EtPy)_4(NCS)_2]\cdot G$ where guest molecule G – toluene, (**II**): T, (**III**): *o*-xylene (*o*-X) and (**IV**): *p*-xylene (*p*-X). The loss of volatile components proceeds in three steps ($-2L$, $-1L$, $-1L$) for **I** and in four steps ($-G$, $-2L$, $-1L$, $-1L$) for **II**, **III** and **IV**. DSC and X-ray powder measurements indicated a phase transition in all compounds under study. However, this process is overlapped by the escape of G in **II** and **III**. The differences in enthalpy changes are associated with different guest–host interactions in the particular clathrates. © 1997 Elsevier Science B.V.

Keywords: Clathrates; DSC; DTG; TG; X-ray diffraction

1. Introduction

Some thirty years ago Schaeffer and co-workers reported a new method [1] for the separation of various aromatic compounds from petroleum fractions. Their paper enhanced the interest in the study of numerous clathrates of the most versatile type $NiL_4X_2\cdot nG$ (L – pyridine derivative, X – anionic ligand and G – guest component) by X-ray structure analysis and other methods [1–8]. A study of the thermally induced release of the guest molecules employing thermal methods and a correlation of the obtained data with those gained by crystal analysis for the host complex, may help to solve some problems concerning guest–host influences in the complexes under investigation as well as the possibilities of regaining the host complex.

We have already presented a relationship between the thermal, spectral and X-ray analyses data for clathrates of the $[Ni(4\text{-}MePy)_4(NCS)_2]\cdot G$ type [9,10]. Since the clathrating ability of a host complex with a composition of ML_4X_2 depends on its molecular structure and, in particular, on the nature of the nitrogen ligand L, in this work the thermal properties of clathrates of $[Ni(4\text{-}EtPy)_4(NCS)_2]\cdot G$ type (G – benzene derivatives) were studied, that is of the clathrates with a more bulky ethyl (Et) substituent on the pyridine ring of the host component. Thermal (TG, DTG, DSC) and powder diffraction analyses were

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used to study the stoichiometry of their thermal decomposition, the thermochemistry of the studied processes, as well as the structural changes during thermally induced release of the guest molecules.

2. Experimental

The host complex $[Ni(4\text{-}EtPy)_4(NCS)_2]$ (**I**) and the clathrates **II**, **III** and **IV** of the $[Ni(4\text{-}EtPy)_4(NCS)_2]\cdot G$ type where G – toluene (T), *o*-xylene (*o*-X) and *p*-xylene (*p*-X), respectively, were prepared as described previously [3,9]. The compounds were analyzed for Ni content using the complexometric titration and for C, H and N contents applying common methods of organic analysis (Table 1).

The host complex can occur in two structural modifications [3] marked as (1) and (2), respectively. The complex **I** described in this work corresponds to the modification (1) as it was confirmed by means of experimentally obtained unit cell parameters (Table 2) and powder diffraction patterns (Fig. 6).

The TG and DTG curves were recorded with a derivatograph OD-102 (MOM, Budapest). In all thermal decompositions a sample mass of 100 mg and a rate of temperature increase of 5°C min^{-1}, was used. The measurements were carried out in an atmosphere of air, with freshly prepared crystals.

The heats of decomposition reactions were measured with a Perkin–Elmer differential scanning calorimeter DSC-7 (sample mass of 3.8–4.1 mg, pure nitrogen N_2 and scanning rate of 10°C min^{-1}). Pure indium (melting point 156.6°C) and enthalpy of fusion ${}_{fus}H^0 = 28.47\ J\ g^{-1}$, were used for calibration of the temperature and change of enthalpy, respectively.

Powder diffraction patterns were recorded with an automated BRAC-BRENTANO DRON UM-1 diffractometer with CuK_α radiation. Only the host complex (**I**) was measured on a transmission powder diffractometer STOE equipped with a germanium monochromator, Cu X-ray tube (40 W and 25 mA) and linear PSD. Simulated powder pattern of the host complex was calculated by the program XQPA 94-DiFK v. 01/PC [11].

The unit cell parameters were computed by the least square method and corrected for systematic errors employing the program FSTAR 2 [12].

3. Results and discussion

3.1. The stoichiometry of thermal decomposition

We reported recently [9] that $[Ni(4\text{-}MePy)_4(NCS)_2]\cdot G$ clathrates release the volatile components in five (G – benzene B, toluene T) or four steps (G – *p*-xylene (*p*-X)). Moreover, the latter clathrates are thermally decomposed differently. It concerns, in particular, the course of the first and second stages as demonstrated by the following scheme (L=4-MePy):

$$[NiL_4(NCS)_2]\cdot B \rightarrow -B, -L, -L, -L, -L \tag{1}$$

$$[NiL_4(NCS)_2]\cdot T \rightarrow -(T + 0.3L), -0.7L, -L, -L, -L \tag{2}$$

$$[NiL_4(NCS)_2]\cdot (p\_X) \rightarrow -(p\_X + L), -L, -L, -L \tag{3}$$

It was challenging, therefore, to make comparative measurement with clathrates with a more bulky 4-EtPy as a ligand L. TG and DTG curves of the host complex **I** and those of studied clathrates **II**, **III**, and **IV** are shown in Fig. 1–4. The thermal decomposition of the host complex (Fig. 1) proceeds in three distinct steps in the 70–300°C range. When one mole of the starting complex **I** is considered, the first step corre-

Table 1
Analytical data for $[Ni(4\text{-}Etpy)_4(NCS)_2]\cdot G$ clathrates (T – toluene; *o*-X – *o*-xylene; *p*-X – *p*-xylene)

Compound	Ni%		C%		H%		N%	
	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
I $[Ni(4\text{-}EtPy)4(NCS)_2$	9.73	9.78	59.71	59.80	6.02	6.16	13.93	14.02
II $[Ni(4\text{-}EtPy)_4(NCS)_2\cdot T$	8.44	8.54	63.88	63.70	6.38	6.25	12.08	12.19
III $[Ni(4\text{-}EtPy)_4(NCS)_2\cdot (o\text{-}X)$	8.27	8.35	64.31	64.22	6.53	6.44	11.84	11.92
IV $[Ni(4\text{-}EtPy)_4(NCS)_2\cdot (p\text{-}X)$	8.27	8.30	64.31	64.26	6.53	6.49	11.84	11.90

Table 2
Unit cell parameters of the host complex [Ni(4-Etpy)$_4$(NCS)$_2$]

The host complex **I** [a]		The host complex, modification (1) [b] [5]	
$a = 10.429$ Å	$\alpha = 85.66°$	$a = 10.359$ Å	$\alpha = 85.62°$
$b = 16.857$ Å	$\beta = 84.06°$	$b = 16.912$ Å	$\beta = 83.83°$
$c = 19.294$ Å	$\gamma = 73.47°$	$c = 19.398$ Å	$\gamma = 73.83°$

[a] Prepared from ethanolic solution.
[b] Prepared from tetrahydrofuran.

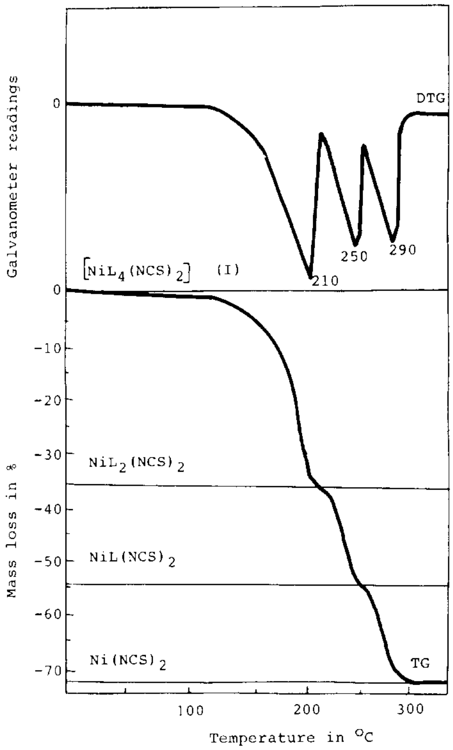

Fig. 1. TG and DTG curves of [NiL_4(NCS)$_2$] (**I**) (L – 4-EtPy).

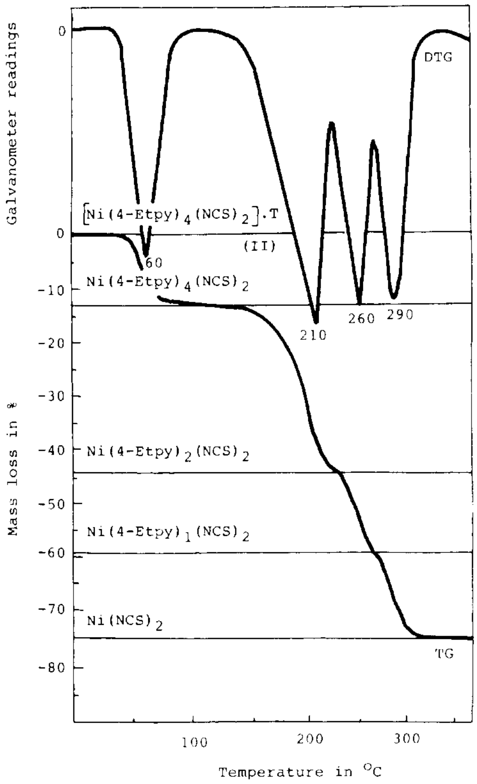

Fig. 2. TG and DTG curves of [Ni(4-EtPy)$_4$(NCS)$_2$]·T (**II**).

sponds to the release of two moles of 4-EtPy, the other two are associated each with the release of one mole of 4-EtPy.

Using analogous experimental conditions (dynamic TG and DTG analyses), we have determined the stepwise decomposition of the [Ni(4-EtPy)$_4$(NCS)$_2$]·G clathrates. The exact results are summarized in Table 3. The TG and DTG curves indicate the same stoichiometry (stepwise character) of the thermal decomposition of all clathrates under study which can be expressed by the following scheme (L – 4-EtPy):

$$\left[\mathrm{Ni}L_4(\mathrm{NCS})_2\right]\cdot G \xrightarrow{T} -G, -2L, -L, -L$$

All studied clathrates release the volatile components in four steps. After the release of the guest molecules the further course of the thermal decomposition of the host complex is similar for all clathrates under study, as verified by the DTG peak temperatures (Table 2). The rate maxima of the guest-molecules escape (the temperature of the 1st peak in the DTG

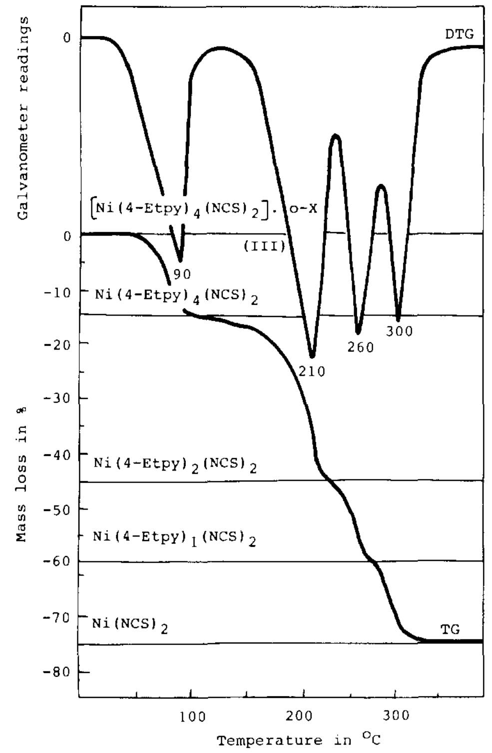

Fig. 3. TG and DTG curves of $[Ni(4\text{-}EtPy)_4(NCS)_2]\cdot(o\text{-}X)$ (**III**).

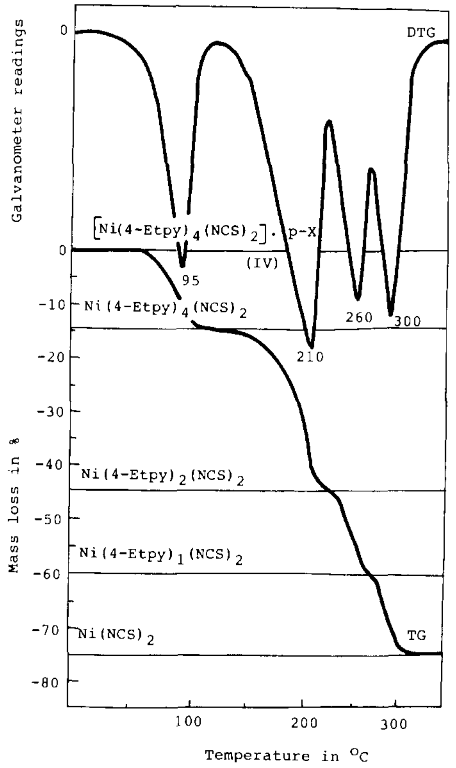

Fig. 4. TG and DTG curves of $[Ni(4\text{-}EtPy)_4(NCS)_2]\cdot(p\text{-}X)$ (**IV**).

Table 3

TG and DTG data on thermal decomposition of host complex $NiL_4(NCS)_2$ and $[NiL_4(NCS)_2]\cdot G$ clathrates (*L* – 4-EtPy, T – toluene, *o*-X - *o*-xylene, *p*-X – *p*-xylene)

Decomposition reaction	Mass loss in %		Temperature range in °C	DTG T_p [a] in °C
	Calculated	Found		
$[NiL_4(NCS)_2]$(**I**)$\rightarrow NiL_2(NCS)_2+2L$	35.5	36.0	70–200	210
$NiL_2(NCS)_2\rightarrow NiL(NCS)_2+L$	53.3	54.0	200–260	250
$NiL(NCS)_2\rightarrow Ni(NCS)_2+L$	71.0	72.0	260–300	290
$[NiL_4(NCS)_2]\cdot T$(**II**)$\rightarrow NiL_4(NCS)_2+T$	13.3	13.0	50–120	60
$NiL_4(NCS)_2\rightarrow NiL_2(NCS)_2+2L$	44.1	44.0	120–220	210
$NiL_2(NCS)_2\rightarrow NiL(NCS)_2+L$	59.5	59.0	220–270	260
$NiL(NCS)_2\rightarrow Ni(NCS)_2+L$	74.9	74.0	270–350	290
$[NiL_4(NCS)_2\cdot(o\text{-}X)$(**III**)$\rightarrow NiL_4(NCS)_2+(o\text{-}X)$	15.0	15.0	60–120	90
$NiL_4(NCS)_2\rightarrow NiL_2(NCS)_2+2L$	45.2	45.0	120–240	210
$NiL_2(NCS)_2\rightarrow NiL(NCS)_2+L$	60.3	60.0	240–280	260
$NiL(NCS)_2\rightarrow Ni(NCS)_2+L$	75.4	75.0	280–350	300
$[NiL_4(NCS)_2]\cdot(p\text{-}X)$(**IV**)$\rightarrow NiL_4(NCS)_2+(p\text{-}X)$	15.0	15.0	60–130	95
$NiL_4(NCS)_2\rightarrow NiL_2(NCS)_2+2L$	45.2	45.2	130–240	210
$NiL_2(NCS)_2\rightarrow NiL(NCS)_2+L$	60.3	60.0	240–280	260
$NiL(NCS)_2\rightarrow Ni(NCS)_2+L$	75.4	75.0	280–350	300

[a] Peak temperature.

curves) increase in the following sequence: T < (o_X) < (p_X).

The release of the guest phase may cause a damage of the host crystal lattice but this depends on the host–guest interactions and the other properties of the guest molecule such as its size and geometry.

3.2. *Thermochemistry and structural changes*

The DSC curves of the host complex (**I**) and the studied clathrates (**II–IV**) are shown in Fig. 5. The DSC curve of $[NiL_4(NCS)_2]$ (**I**) exhibits four maxima. The maxima at ≈ 205, 246 and 276°C correspond to the release of (2+1+1) moles of L per mole of (**I**), respectively. Since no mass loss occurs in the temperature region of ≈ 50°C (Fig. 1) the first peak evidently corresponds to the phase transition (probably $\alpha \rightarrow \beta_0$). The phase transition is a reversible process (Fig. 6) with a very small enthalpy change ($\Delta_{trs}H_1(\alpha \rightarrow \beta_0) = 3.2 \pm 0.3$ kJ mol^{-1}; $\Delta_{trs}H_1'$ $(\alpha \leftarrow \beta_0) = 2.8$ kJ mol^{-1}; and $\Delta_{trs}H_1''(\alpha \rightarrow \beta_0) = 3.3$ kJ mol^{-1}). The above values of ${}_{trs}H_1$, ${}_{trs}H_1'$ and ${}_{trs}H_1''$ are very close to the value of 3.3 kJ mol^{-1} which has been assigned to enthalpy of transformation from the non-clathrate α-phase to the 'empty' clathrate β_0-phase of the host complex [1,13].

The particular curves obtained for **II–IV** exhibit a further peak in the 50–140°C range which is either overlapped (compounds **II** and **III**) with a phase transition $\beta' \rightarrow \alpha$ (β' – various clathrate phase [5]) or distinctly separated (compound **IV**). This effect is connected with the escape of guest component G. The clathrates **II**, **III** and **IV** when heated in the 100–120°C range, give compounds whose X-ray powder patterns resemble those patterns recorded for compound **I**. These results are illustrated by the p-X clathrate (Fig. 7). The small differences may occur due to different methods used for the preparation of the host complex (e.g. from different solutions or after release of the guest compound) and may affect a different extent of defects in the crystal lattice.

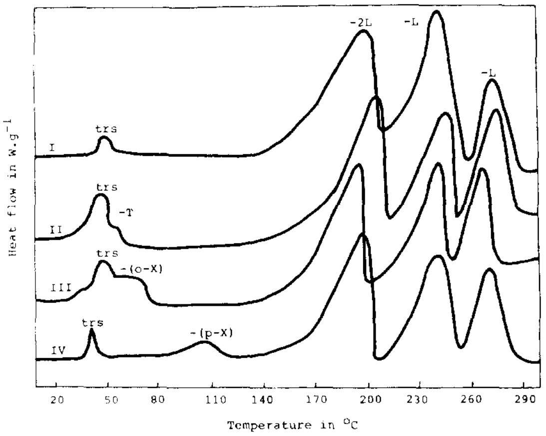

Fig. 5. DSC curves of the host complex **I** and clathrates **II**, **III** and **IV**.

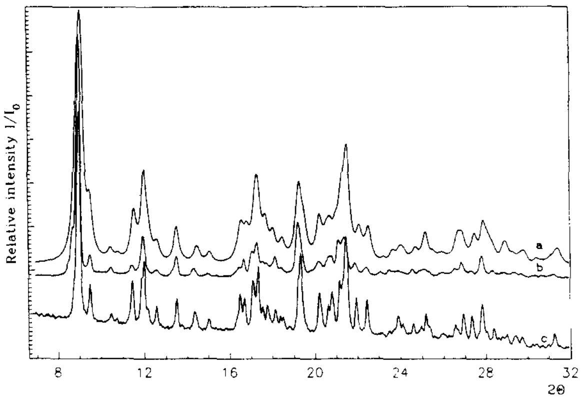

Fig. 6. Powder diffraction patterns of the host complex $[Ni(4\text{-}EtPy)_4(NCS)_2]$: (a) – simulated from crystal data [5]; (b) – complex **I** heated in the 60–70°C range and then cooled to room temperature; and (c) – initial complex **I**.

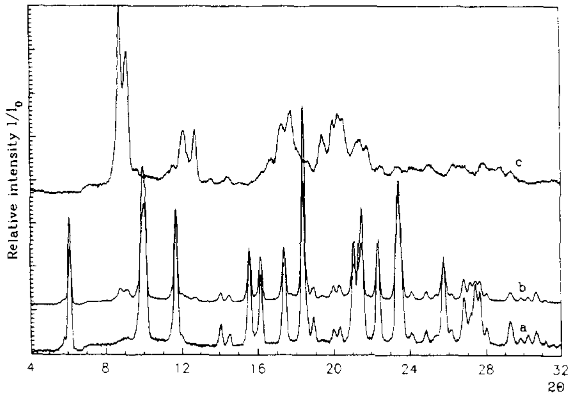

Fig. 7. Powder diffraction patterns of the $[Ni(4\text{-}EtPy)_4(NCS)_2]\cdot(p\text{-}X)$ clathrate (**IV**): (a) – original clathrate **IV**; (b) – clathrate **IV** heated in the 50–60°C range and then cooled to room temperature; (c) – clathrate **IV** heated in the 110–120°C range and then cooled to room temperature.

Table 4
DSC data of host complex $[NiL_4(NCS)_2]$ and $[NiL_4(NCS)_2]\cdot G$ clathrates (L – 4-EtPy, T – toluene, o-X – o-xylene and p-X – p-xylene) at a temperature increase of 10°C min^{-1}

Compound	Process	Peak temperature in °C	ΔH_i in kJ mol^{-1}
$[NiL_4(NCS)_2]$ (**I**)	(1) PT[a]	50	3.2 ± 0.3
	(3) $-2L$	205	75 ± 8
	(4) $-1L$	246	60 ± 6
$m = 4.1$ mg	(5) $-1L$	276	46 ± 5
$[NiL_4(NCS)_2]\cdot$T (**II**)	(1) PT (2) − T	48	18.6 ± 2
	(3) $-2L$	202	79 ± 8
	(4) $-1L$	245	54 ± 5
$m = 3.9$ mg	(5) $-1L$	274	46 ± 5
$[NiL_4(NCS)_2]\cdot$(o-X) (**III**)	(1) PT (2) − (o_X)	49	29 ± 3
	(3) $-2L$	200	79 ± 8
	(4) $-1L$	241	57 ± 6
$m = 4.0$ mg	(5) $-1L$	267	40 ± 4
$[NiL_4(NCS)_2]\cdot$(p-X) (**IV**)	(1) PT	42	3.4 ± 0.3
	(2) −(p_X)	106	7.7 ± 0.8
	(3) $-2L$	201	82 ± 8
	(4) $-1L$	243	67 ± 7
$m = 3.8$ mg	(5) $-1L$	272	47 ± 5

[a] Phase transition.

The enthalpy changes (ΔH_i) corresponding to the individual processes are given in Table 4. Numbers 1–5 are assigned to the following effects:

1. **(1, 2)** *The phase transition and the escape of G.* The values of $({}_{\mathrm{trs}}H_1 + H_2)$ for these effects are different, increasing relative to G, in the following sequence: p_X < T < o_X.
2. **(3, 4, 5)** *The escape of L.* The release of the particular G may cause a different destruction of the host structure [14]. This is illustrated by the ΔH_3, ΔH_4 and ΔH_5 values for the thermal decomposition of the respective clathrates at higher temperatures (Table 4).

4. Conclusions

In comparing the obtained data (Tables 2,3 and 4) with those found for the clathrates $[Ni(4\text{-}MePy)_4(NCS)_2]\cdot G$ (G – benzene derivatives [9]) and $[Ni(4\text{-}EtPy)_4(NCS)_2]\cdot 2G$ (G – naphthalene derivatives [15]) the following conclusions can be drawn:

1. *The substituent on the pyridine ring has been changed (G – benzene derivatives).* With regard to the increase of steric interactions of the ethyl group, all clathrates under study possessing this substituent exhibit a decrease of thermodynamic stability and during the thermally induced release of the guest molecules fine structural changes of the above host complex occurred.
2. *The guest component G has been changes (L – 4-EtPy).* Contrary to naphthalene the benzene derivatives are held more weakly in the host structure as demonstrated by small values of ΔH corresponding to the liberation of G (Table 4).

It may also be concluded that the differences in thermodynamic stability of particular groups of clathrates are assumed to relate to different guest–host interactions. These interactions affect peak temperatures and enthalpy changes accompanying the phase transition, and the escape of different guests from the given host complex.

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