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THERMAL DECOMPOSITION REACTIONS OF NICKEL(II) COMPLEXES UNDER QUASI-EQUILIBRIUM CONDITIONS

II. Study of the relations between thermal, spectral and diffraction properties of the Werner clathrates $[Ni(4\text{–}Mepy)_4(NCS)_2]\cdot G$, ($G$ = benzene, toluene, *p*-xylene)

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The stoichiometry of thermal decomposition and thermal (thermodynamic) stability was studied for the Werner clathrates $[Ni(4\text{–}Mepy)_4(NCS)_2]\cdot G$, where G = benzene(I), toluene(II) and *p*-xylene(III). The loss of the volatile components occurs in five steps in compounds I and II and in four steps in the complex III.

According to the quasi-equilibrium data the thermodynamic stability of these compounds can be ordered in the following sequence: I<II<III. The increasing host-guest interaction (larger positive band shift in the visible spectra) was accompanied by increasing in the quasi-equilibrium temperature (T_D) for the complexes under study.

Keywords: complexes, Werner clathrate

Introduction

The relation between thermal parameters (quasi-equilibrium decomposition temperature, value of activation energy and frequency factor) and the degree of the tetragonal distortion (R_e/R_a, where R_e and R_a are the mean values of the central atom-ligand distances in the quatorial plane or in the axial directions) of the $NiL_4(NCS)_2$ complexes was studied recently [1].

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In the study presented here attention has been paid to investigate the relation between thermal parameters: decomposition stoichiometry, quasi-equilibrium decomposition temperatures and spectral parameters (especially $^3A_{2g} \rightarrow ^3T_{1g}$ band shift in visible spectra) in Werner clathrates [Ni(4–Mepy)$_4$(NCS)$_2$]·nG (G = benzene, toluene, p-xylene). $^3A_{2g} \rightarrow ^3T_{1g}$ band shift, $\Delta\tilde{\nu} = \tilde{\nu}$(clathrate $-\tilde{\nu}$ (pure complex), was taken as a measure of the host-guest interactions in the clathrates [2]. Additionally, the X-ray diffraction (XRD) study was accomplished to reveal the structural changes of the host complexes during the thermal decomposition.

Experimental

The clathrate compounds were prepared from solution according to the paper [3]. The compound obtained were analyzed for Ni, C, H and N content. The stoichiometry of thermal decomposition of the compounds were studied on a Derivatograph OD 102 instrument. The samples had a mass of 100 mg. The rate of temperature increase was 2.5 deg·min^{-1}. Measurements were made in air atmosphere.

To study the quasi-equilibrium decomposition temperatures the Q-derivatograph was used. This experimental technique results in stabilization of the decomposition temperature, i.e. experiment proceeds under quasi-isothermal conditions [4]. Using special sample holder types it is possible to keep the pressure of the gaseous products to be almost constant (for example conical crucible ≈90 kPa). The electronic absorption spectra were measured on a SPECORD M 40 (Carl Zeiss, Jena).

Powder diffraction patterns were taken on an automatized DRON UM diffractometer. The powder patterns were indexed using the program POUND (E. Wu, 1989). Then the unit cell parameters were computed by the least square methods and corrected for systematic errors employing the program ESTAR 2 (I. F. Ferguson *et al.*).

Results and discussion

Stoichiometry of thermal decomposition and decomposition temperatures

The TG and DTG curves are shown in Figs 1–4 and summarized in Table 1.

The DTG curves indicate clearly the stepwise character of the thermal decomposition of the clathrates. There are the difference in the course of the first stage in the thermal decomposition of the compounds (I), (II) and (III), respectively. The stoichiometry of the thermal decomposition of the individual clathrate can be expressed by the following scheme:

$[NiL_4(NCS)_2]\cdot B$ (I): $-B, -L, -L, -L, -L$
$[NiL_4(NCS)_2]\cdot T$ (II): $-(T+0.3L), -0.7L, -L, -L, -L$
$[NiL_4(NCS)_2]\cdot p\text{-}X$ (III): $-(p\text{-}X+L), -L, -L, -L$

(*L* = 4-Mepy, *B* = benzene, *T* = toluene, *p–X* = *p*-xylene). The volatile components are released in five (I, II) or four steps (III). The percentage weight loss, as reported in Table 1, shows that there is good agreement between experimental and theoretical values.

Table 1 Thermal analyses results (*L* = 4-Mepy, *B* = benzene, *T* = toluene, *p–X* = *p*-xylene)

Thermal decomposition reactions	TG / %		Q-TG	DTG
	Calc.	Found	T_D / °C	°C
(1) $[NiL_4(NCS)_2]\cdot B \rightarrow NiL_4(NCS)_2+B$	12.5	12.0	122	120
(2) $NiL_4(NCS)_2 \rightarrow NiL_3(NCS)_2+L$	14.9	14.0	—	150
(3) $NiL_3(NCS)_2 \rightarrow NiL_2(NCS)_2+L$	14.9	15.0	—	280
(4) $NiL_2(NCS)_2 \rightarrow NiL(NCS)_2+L$	14.9	16.0	—	255
(5) $NiL(NCS)_2 \rightarrow Ni(NCS)_2$	14.9	16.0	—	300
(6) $[NiL_4(NCS)_2]\cdot T \rightarrow NiL_{3.7}(NCS)_2+T+0.3L$	18.8	19.0	130	110
(7) $NiL_{3.7}(NCS)_2 \rightarrow NiL_3(NCS)_2+0.7L$	10.2	11.0	—	150
(3) $NiL_3(NCS)_2 \rightarrow NiL_2(NCS)_2+L$	14.6	15.0	—	180
(4) $NiL_2(NCS)_2 \rightarrow NiL(NCS)_2+L$	14.6	15.0	—	255
(5) $NiL(NCS)_2 \rightarrow Ni(NCS)_2+L$	14.6	15.0	—	300
(8) $[NiL_4(NCS)_2]\cdot p\text{-}X \rightarrow NiL_3(NCS)_2+p\text{-}X+L$	30.4	30.5	165	145
(3) $NiL_3(NCS)_2 \rightarrow NiL_2(NCS)_2+L$	14.2	13.5	—	180
(4) $NiL_2(NCS)_2 \rightarrow NiL(NCS)_2+L$	14.2	15.0	—	255
(5) $NiL(NCS)_2 \rightarrow Ni(NCS)_2+L$	14.2	15.0	—	300

Q-TG curves monitored at quasi-isothermal and/or quasi-isobaric conditions (Fig. 4) provide a comprehensive information about the reaction stoichiometry as well as decomposition temperatures of the first step. It is obvious that there are not differences between the data given in Table 1 and the results presented in Fig. 4 as far as the stoichiometry of the first decomposition stage is concerned.

The decomposition temperatures derived from the quasi-isothermal measurements are suited to set up a qualitative sequence of the thermodynamic stability of the solid compounds [5]. According to quasi-equilibrium decomposition temperatures (Table 1) the thermodynamic stability of $[Ni(4\text{–}Mepy)_4(NCS)_2]\cdot G$ (*G* = benzene, toluene, *p*-xylene) can be ordered in the following sequence:

G: benzene < toluene < *p*-xylene
122°C 130°C 156°C

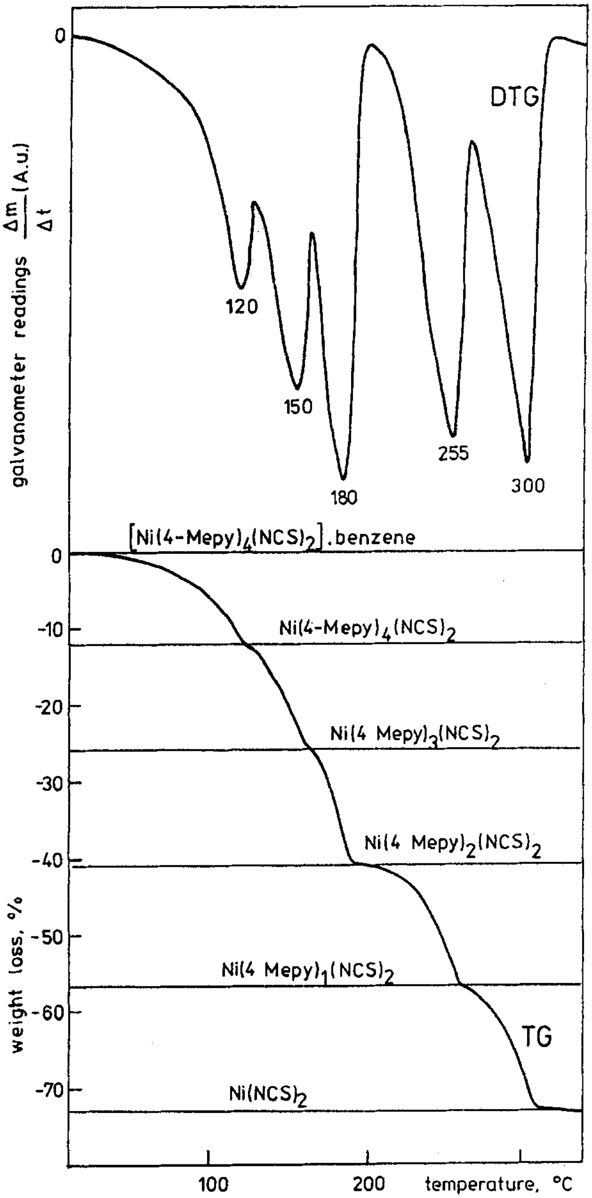


Fig. 1 TG and DTG curves of the [Ni(4-Mepy)$_4$(NCS)$_2$]·benzene

Spectral properties of the clathrates

The absorption spectra of $NiL_4(NCS)_2$ complexes have been already studied [6]. The specific complex employed in this work (*L* = 4-Mepy), as shown by its crystal structure [7], presents a rather small tetragonal distortion.

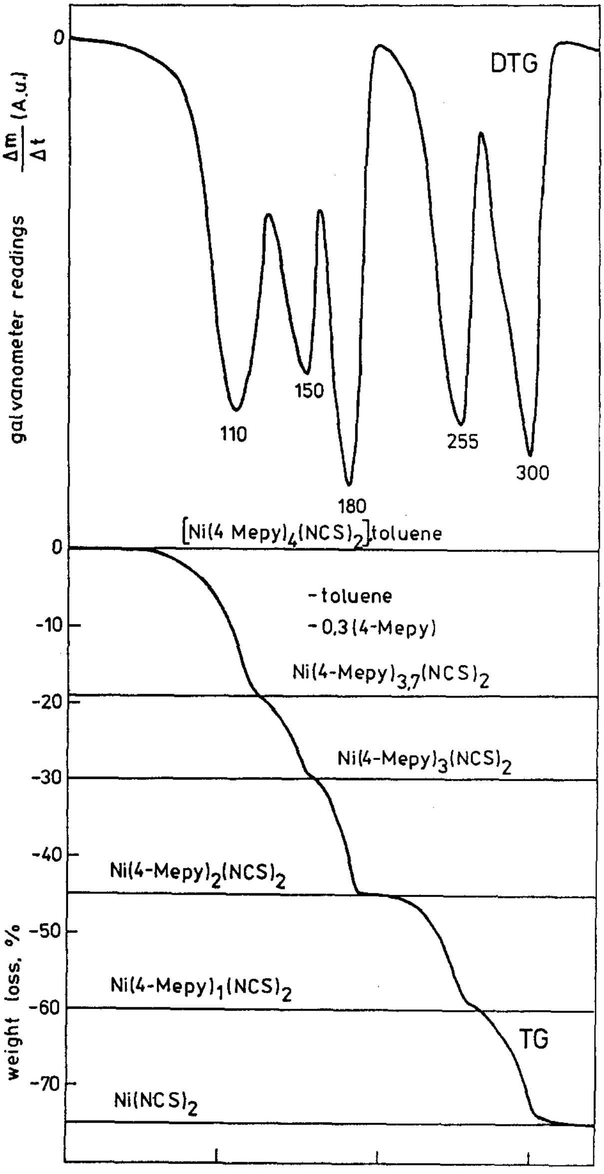


Fig. 2 TG and DTG curves of the $[Ni(4\text{–}Mepy)_4(NCS)_2]\cdot$toluene

No splitting is observed in the spin-allowed $^3A_{2g} \rightarrow {}^3T_{2g}$ transition in the absorption spectra of the clathrates, which practically confirms O_h symmetry [2]. The observed band shifts are reported, for the guest employed in this work, as

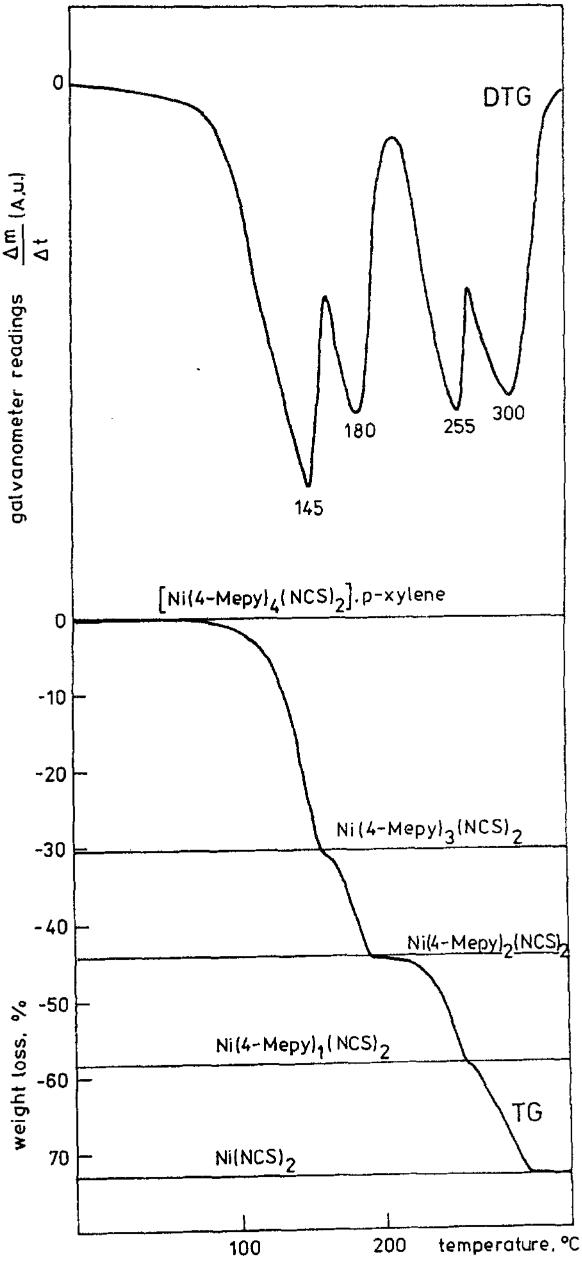


Fig. 3 TG and DTG curves of the [Ni(4–Mepy)$_4$(NCS)$_2$]·p-xylene

$\Delta\tilde{\nu}$, with respect to the pure complex, taking into account only the broad band corresponding to the spin allowed ${}^3A_{2g} \rightarrow {}^3T_{1g}$ transition, in Table 2.

Table 2 Spectral and thermodynamic data clathrates $[Ni(4\text{–}Mepy)_4(NCS)_2]\cdot G$

Compound	$\tilde{\nu}({}^3A_{2g} \rightarrow {}^3T_{1g})$, cm^{-1}	(a) $\Delta\tilde{\nu}$ / cm^{-1}	(b) ΔH_D [8] / kJ·mol^{-1}	T_D / °C
benzene	17 200	–100	60.7	122
toluene	17 250	–50	64.4	130
p-xylene	17 360	60	76.6	165

(a) $\Delta\tilde{\nu} = \tilde{\nu}(\text{clathrate}) - \tilde{\nu}(\text{pure complex})$, (b) $\Delta H_D = \Delta H_{desorb} - \Delta H_{\beta\rightarrow\alpha}$

This band shift was taken as a measure of the host-guest interactions in the clathrates. According to $\Delta\tilde{\nu}$, the complexes under study can be ordered in the following sequence:

$$G\text{: benzene} < \text{toluene} < p\text{-xylene}$$

Diffraction properties of the benzene clathrate and its desorbed decomposition product

The X-ray powder diffraction (XRD) was used to identify the structure of the host complex $[Ni(4\text{–}Mepy)_4(NCS)_2]$ in benzene clathrate and its desorbed decomposition product, i.e. structural changes during the thermal decomposition reaction were studied.

Experimental unit cell parameters calculated from the powder patterns and literature data are listed in Table 3. Benzene clathrate have tetragonal symmetry with space group I $4_1/a$ [8] (β-phase). Observed decrease of unit cell parameters with respect to literature data is probably caused by partial escape of guest benzene molecules.

The clathrate decomposes under quasi-equilibrium conditions (T_D = 122°C) to the host complex which is monoclinic with space group $P2_1/c$ (α-phase) [7].

$$\beta\text{-}[Ni(4\text{–}Mepy)_4(NCS)_2]\cdot B(cr.) \xrightarrow[122^\circ C]{Q-TG} \alpha\text{-}[Ni(4\text{–}Mepy)_4(NCS)_2](cr.) \tag{9}$$

It was proved (Table 3) that the decomposition of the clathrate at room temperature proceeds wholly to the β-phase without essential change of structure

Table 3 Unit cell parameters of $[Ni(4\text{–}Mepy)_4(NCS)_2]\cdot B$ and desorbed decomposition product (*B*-benzene)

Parameter	β–$[Ni(4\text{-}Mepy)_4(NCS)_2]\cdot B$		$[Ni(4\text{–}Mepy)_4(NCS)_2]$			α–phase [7]
	[8]	prepared	a	b	c	
Space group	I $4_1/a$	I $4_1/a$	I $4_1/a$	p $2_1/c$	p $2_1/c$	p $2_1/c$
a (Å)	17.02	16.87 (1)	16.71	19.24 (2)	19.27	19.205
b (Å)	17.02	16.87 (1	16.71	9.79 (2)	9.769	9.768
c (Å)	23.18	22.72 (2)	22.60 (5)	16.80 (2)	16.81	16.765
α (°)	90	90	90	90	90	90
β (°)	90	90	90	113.47 (8)	113.63	13.544
γ (°)	90	90	90	90	90	90

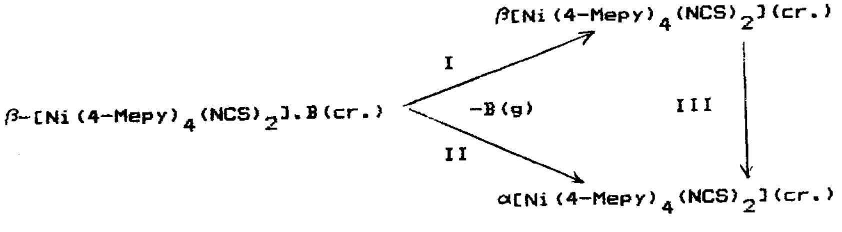
(a — prepared by reaction (10), b — by reaction (9) and c — by reaction (11))

$$\beta - [Ni(4\text{–}Mepy)_4(NCS)_2]\cdot B(cr.) \xrightarrow[25^\circ C]{-B(g)} \beta - [Ni(4\text{–}Mepy)_4(NCS)_2](cr.) \qquad (10)$$

This is in accordance with papers [9, 10] in which analogical clathrate β-$[Ni(4\text{–}Mepy)_4(NCS)_2]\cdot(4\text{–}Mepy)$ was studied. The authors presumed two-stage character of the process and the change in the mechanism from (10) to (9) take place in some stage of the thermal decomposition. Since it was confirmed that β-modification changes to α-modification by isothermal heating (Table 3)

$$\beta\text{–}[Ni(4\text{–}Mepy)_4(NCS)_2](cr.) \xrightarrow{70^\circ C} \alpha\text{–}[Ni(4\text{–}Mepy)_4(NCS)_2](cr.) \qquad (11)$$

the reaction mechanism may by expressed by the following scheme



Based on our experimental results we consider the most probable course of the thermal decomposition to be by reactions I and III.

Thermodynamic properties of the clathrates and conclusions

A total enthalpy (ΔH_D) of the reaction

$$\beta\text{-}[Ni(4\text{-}Mepy)_4(NCS)_2]\cdot G(cr.) \xrightarrow{\Delta T} \alpha\text{-}[Ni(4\text{-}Mepy)_4(NCS)_2](cr.) + G(g) \tag{12}$$

may be subdivided into three components [8]

$$\Delta H_D = -\Delta H_{(\beta\text{->}\alpha)} + \Delta H_{(desorb)} + \Delta H_{(subl,\ evapn)} \tag{13}$$

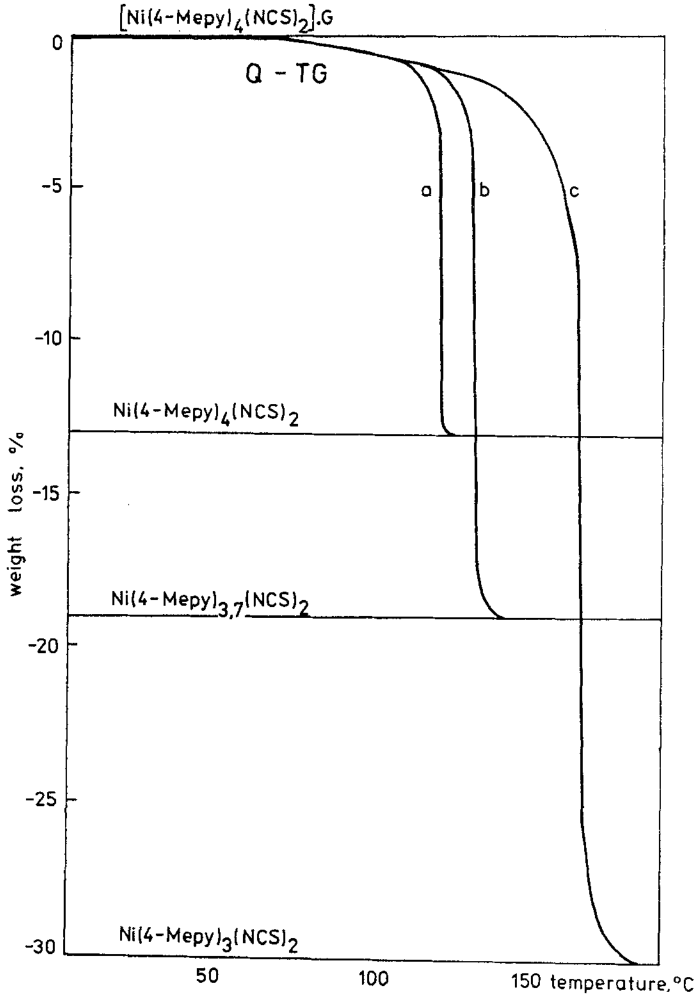


Fig. 4 Q-TG curves of the $[Ni(4\text{-}Mepy)_4(NCS)_2]\cdot G$: G = a – benzene, b –t oluene, c– *p*-xylene (conical crucible, mass of the complex 200 mg)

$\Delta H_{(\beta\text{->}\alpha)}$ represents the enthalpy of $\beta \rightarrow \alpha$ phase transition. $\Delta H_{(\text{desorb})}$ is enthalpy of desorption of guest molecules and $\Delta H_{(\text{subl, evapn})}$ is enthalpy of guest sublimation or evaporation.

Energy of breaking the interaction of a guest to the clathrate lattice ($\Delta H_{(\text{desorb})}$ is determinable if enthalpy of phase transition were known. However, the $\Delta H_{(\beta\text{->}\alpha)}$ is dependent on the type of guest component. Thus values $\Delta H_{(\text{desorb})} - \Delta H_{(\beta\text{->}\alpha)} = \Delta H_D - \Delta H_{(\text{subl, evapn})} = \Delta H'_D$ may be useful for comparative purposes [8]. These values define the energy of clathration of gaseous guest by solid α-phase as listed in Table 2. According to $\Delta H'_D$ the clathrates can be ordered in the sequence (by 6): benzene < toluene < *p*-xylene.

It may be concluded:

i) It was found that the increase if T_D is accompanied by the increase of ${}^3A_{2g} \rightarrow {}^3T_{1g}$ band shift in the visible spectra of the guest molecules of the clathrates under study.

ii) Larger host-guest interactions (larger band shift) mean larger thermodynamic stability (higher values of ΔH_D and T_D) of the clathrates under study.

iii) Quasi-equilibrium decomposition temperatures (T_D) are important thermal parameters and belong to general property of solid metal complexes comprising the volatile components.

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Zusammenfassung — An den Werner-Klathratverbindungen $[Ni(4\text{-}Mepy)_4(NCS)_2]G$ mit G=Benzol (I), Toluol (II) und *p*-Xylol (III) wurde die Stöchiometrie der thermischen Zersetzung und die thermische (thermodynamische) Stabilität untersucht. Der Verlust der flüchtigen Komponenten erfolgt in fünf Schritten bei den Verbindungen I und II und in vier Schritten bei Komplex III.

In Übereinstimmung mit den Quasigleichgewichtsangaben kann die Reihenfolge der thermodynamische Stabilität dieser Verbindungen wie folgt angegeben werden: I II III. Die steigende Wechselwirkung zwischen Wirts- und Gastkomponente (größeres positives Band wird im sichtbaren Bereich verschoben) wird von einem Anwachsen der Quasigleichgewichtstemperatur T_D der untersuchten Komplexe begleitet.