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THERMOCHEMICAL INVESTIGATION OF GUEST-HOST INTERACTIONS IN WERNER CLATHRATES OF TYPE [Ni(4-Etpy)$_4$(NCS)$_2$]·nG (G=NAPHTHALENE DERIVATIVES)

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Abstract

The stoichiometry of thermal decomposition and the thermochemistry were studied for [NiL$_4$(NCS)$_2$] (I) as a host complex, and for its clathrates of type [NiL$_4$(NCS)$_2$]·2G, where L=4-ethylpyridine and guest molecule G=1-methylnaphthalene in clathrate (II), 1-chloronaphthalene in (III) or 1-bromonaphthalene in (IV). For I, the loss of volatile components proceeds in three steps (-2L, -L, -L); the first steps for II–IV also involve the release of G (-2G, -2L). DSC and X-ray powder measurements indicated a phase transition in the host lattice, and allowed differentiation of the escape of G and L molecules. The enthalpy changes give the following sequence of thermodynamic stability for the studied chlathrates: I>II>III.

Keywords: complexes, DSC, guest-host interactions, X-ray

Introduction

Interest in Werner clathrates was stimulated by Schaeffer and co-workers [1], who reported a new method for the separation of various aromatic compounds from petroleum fractions. Numerous clathrates of the most versatile type [Ni(4-Mepy)$_4$(NCS)$_2$]·nG have been investigated by X-ray structure analysis and other methods [2].

The clathrating ability of a host complex [MX$_2$L$_4$] depends on its molecular structure and, in particular, on the nitrogen-containing ligand L coordinated to M. The ability to act as a host complex is ascribed to the remarkable freedom of rotation of the pyridine ring around the Ni–N bond [2], the complex being able to adjust its molecular shape according to the size and shape of the substituent on the incoming guest molecule. The present paper reports structural and thermochemical properties of new clathrates with an ethyl substituent on the host component.

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A number of problems relating to guest-host effects may be solved by studying the thermally induced release of the G molecules and by correlating these data with the crystallochemistry and structure of the host complex.

Relations between the thermal, spectral and structural properties of Werner clathrates of the above type were presented previously [3–5]. Thermal analysis results (TG, DTG and DSC) have now been used to study:

i) the stoichiometry of thermal decomposition of clathrates $[Ni(4\text{-}Etpy)_4(NCS)_2]\cdot nG$ (G=naphthalene derivatives),

ii) the temperature at which the guest molecules are released, and the thermochemistry of these reactions.

The study of thermally induced reactions of guest release, and application of the results to other host complexes, may be expected to facilitate the syntheses of new complexes with host lattices exhibiting specific selectivities towards different isomers [6, 7], and subsequent recovery of the isomers.

Experimental

The clathrate complexes $[Ni(4\text{-}Etpy)_4(NCS)_2]\cdot nG$, where G is 1-methylnaphthalene (1-MeN), 1-chloronaphthalene (1-ClN) or 1-bromonaphthalene (1-BrN), were prepared from ethanolic solutions, similarly as described previously [4, 5]. The products were checked for Ni, C, H and N contents (Table 1).

The TG and DTG curves were recorded on a Paulik-Paulik-Erdey derivatograph (type OD 102, MOM, Budapest) in air atmosphere. Standard platinum crucibles, a sample mass of 100 mg and a heating rate of 5°C min^{-1} were used for all measurements.

For calorimetric study of the decomposition reactions, the Perkin-Elmer Differential Scanning Calorimeter DSC-7 was used (the null-balance power compensating principle, a sample mass of 7–8 mg, pure nitrogen, and a scanning rate of 10°C min^{-1}). Calibration of the temperature and change of enthalpy axes was made with pure indium, with melting point 156.6°C and $\Delta_f H=28.47$ J g^{-1}.

Results and discussion

Stoichiometry of thermal decomposition of clathrates

We recently reported [5] that the clathrates $[Ni(4\text{-}Mepy)_4(NCS)_2]\cdot nG$ (G=1-MeN, 1-BrN, 2-MeN and 2-BrN) undergo thermal decomposition in three steps, involving the release of both guest and ligand molecules. When similar experimental conditions were applied to $[Ni(4\text{-}Etpy)_4(NCS)_2]\cdot nG$, (G=1-MeN, 1-ClN and 1-BrN), a stepwise decomposition mechanism was similarly observed.

Table 1 Analytical data

	Compound	Ni(%)		C(%)		H(%)		N(%)	
		calcd.	found	calcd.	found	calcd.	found	calcd.	found
I	$Ni(4\text{-}Etpy)_4(NCS)_2$	9.73	9.78	59.71	60.31	6.02	6.16	13.93	14.20
II	$[Ni(4\text{-}Etpy)_4(NCS)_2]\cdot 2(1\text{-}MeN)$	6.61	6.66	70.30	69.70	6.36	6.46	9.47	9.71
III	$[Ni(4\text{-}Etpy)_4(NCS)_2]\cdot 2(1\text{-}ClN)$	6.32	6.24	64.67	65.12	5.42	5.58	9.05	9.12
IV	$[Ni(4\text{-}Etpy)_4(NCS)_2]\cdot 2(1\text{-}BrN)$	5.77	5.71	59.01	58.69	4.95	5.12	8.26	8.35

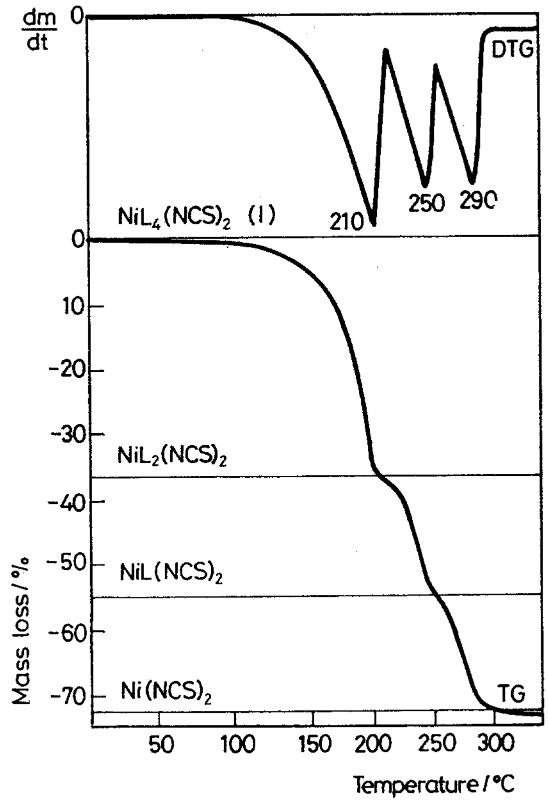

Fig. 1 TG and DTG curves of [Ni(4-Etpy)$_4$(NCS)$_2$] (I)

The TG and DTG curves of the host complex (I) and the studied clathrates (II–IV) are shown in Figs 1–4. Figure 1 reveals that the thermal decomposition of I (under dynamic conditions) proceeds in three distinct steps in the temperature range 70–300°C. The first step corresponds to the release of 2 moles of 4-Etpy per mole of starting complex, while the other two each reflect the release of 1 mole of 4-Etpy. The results are summarized in Table 2. It is worth noting that under similar conditions the ligands L escape from the complex [NiL$_4$(NCS)$_2$] (L=4-Mepy) in a four-step process (-L, -L, -L, -L).

The initial steps and peaks in the TG and DTG curves, respectively, for the clathrates under study (Figs 2–4) indicate a more complex thermal decomposition; the stoichiometry can be expressed by the following scheme:

$$\begin{array}{llll} [\mathrm{NiL_4(NCS)_2}]\cdot 2\mathrm{G(s)} \xrightarrow{\Delta T} & -(2\mathrm{G}+2\mathrm{L})(\mathrm{g}), & -\mathrm{L(g)}, & -\mathrm{L(g)} \\ (\mathrm{L}=4\text{-Etpy}) & \text{1st step} & \text{2nd step} & \text{3rd step} \end{array}$$

Table 2 Data on thermal decomposition of $[NiL_4(NCS)_2 \cdot nG$ compounds (*L* =4-Etpy)

Decomposition reactions	Δm/%		Temperature/	DTG peak/
	calcd.	found	°C	°C
$NiL_4(NCS)_2 \rightarrow NiL_2(NCS)_2 + 2L$	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
$[NiL_4(NCS)_2] \cdot 2(1\text{-}MeN) \rightarrow NiL_2(NCS)_2 + 2(1\text{-}MeN) + 2L$	56.2	58.0	70–200	180, 190
$NiL_2(NCS)_2 \rightarrow NiL(NCS)_2 + L$	68.3	69.0	200–260	250
$NiL(NCS)_2 \rightarrow Ni(NCS)_2 + L$	80.4	81.0	260–300	280
$[NiL_4(NCS)_2] \cdot 2(1\text{-}ClN) \rightarrow NiL_2(NCS)_2 + 2(1\text{-}ClN) + 2L$	58.1	59.0	70–210	≈180, 200
$NiL_2(NCS)_2 \rightarrow NiL(NCS)_2 + L$	69.6	72.0	210–270	250
$NiL(NCS)_2 \rightarrow Ni(NCS)_2 + L$	81.1	83.0	270–310	290
$[NiL_4(NCS)_2] \cdot 2(1\text{-}BrN) \rightarrow NiL_2(NCS)_2 + 2(1\text{-}BrN) + 2L$	61.8	63.0	70–200	180,200
$NiL_2(NCS)_2 \rightarrow NiL(NCS)_2 + L$	72.3	74.0	200–230	230
$NiL(NCS)_2 \rightarrow Ni(NCS)_2 + L$	82.8	85.0	230–300	270

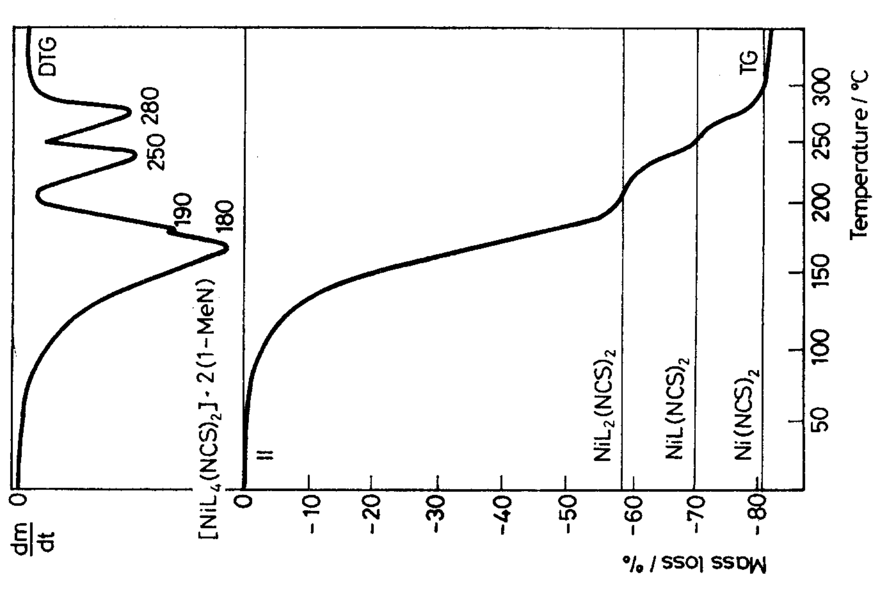

Fig. 2 TG and DTG curves of $[Ni(4\text{-}Etpy)_4(NCS)_2].2(1\text{-}MeN)$ (II)

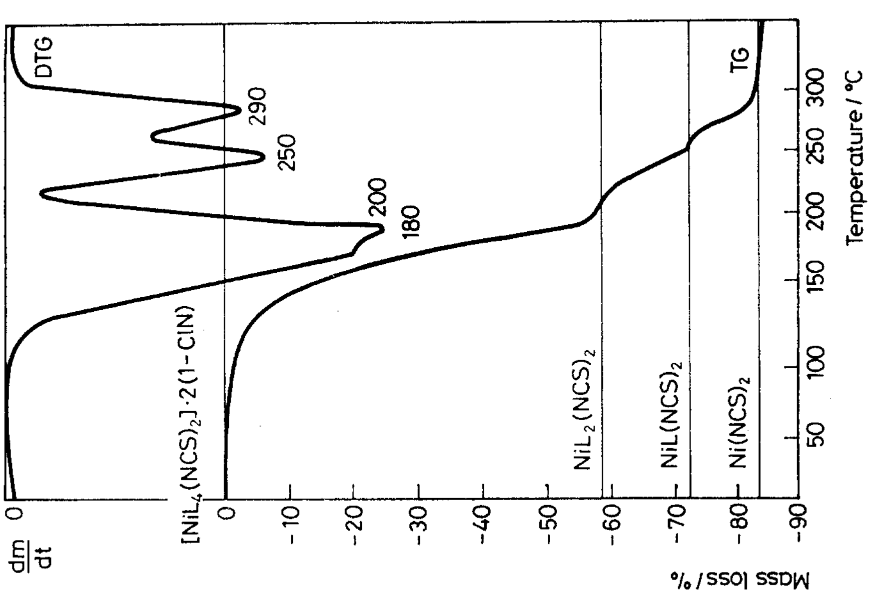

Fig. 3 TG and DTG curves of $[Ni(4\text{-}Etpy)_4(NCS)_2].2(1\text{-}ClN)$ (III)

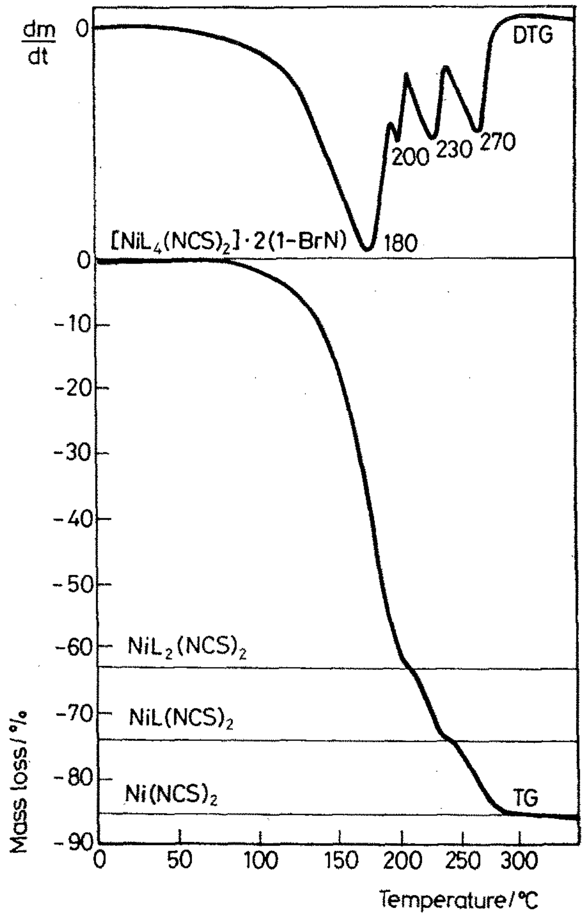

Fig. 4 TG and DTG curves of [Ni(4-Etpy)$_4$(NCS)$_2$]·2(1-BrN) (IV)

The first step involves the release of a proportion of the L molecules besides the G molecules [4, 5]. However, the acquisition of more detailed information on these partial processes requires the application of other methods too.

The decomposition of all the studied clathrates at higher temperatures proceeds similarly to that of I (-L, -L), with DTG peaks at ca 250 and 290°C (except for compound IV, with peaks at 230 and 270°C). For elucidation of the different effects included in particular in the first step, DSC measurements were used.

Thermochemistry of studied processes

DSC data on the studied compounds are listed in Table 3. The DSC curve (Fig. 5) of I exhibits maxima at 207, 246 and 276°C. The maxima correspond to the release of 2+1+1 moles of L, respectively, per mole of I. In contrast, the curves obtained for II–IV indicate a strong effect in the interval 106–137°C, where the mass loss is just starting. This effect is assumed to be connected with the liberation of G molecules and a phase transition of the host complex [4]. The above processes were confirmed by means of powder diffraction patterns.

For example, when heated in the range 115–119°C and then cooled to room temperature, II gives a compound whose diffractogram differs from that recorded for the initial clathrate II, but is much more reminiscent of that recorded for the host complex I. The small differences may be connected with either a phase transition or the existence of a mixture of two isomeric forms of the initial complex $[Ni(4\text{-}Etpy)_4(NCS)_2]$ [7].

Two further effects in the interval 119–202°C correspond to the escape of 2 moles of naphthalene derivatives and 2 moles of L (for IV, these two processes overlap). The last 2 moles of L escape in two steps in the interval 202–284°C (Fig. 5).

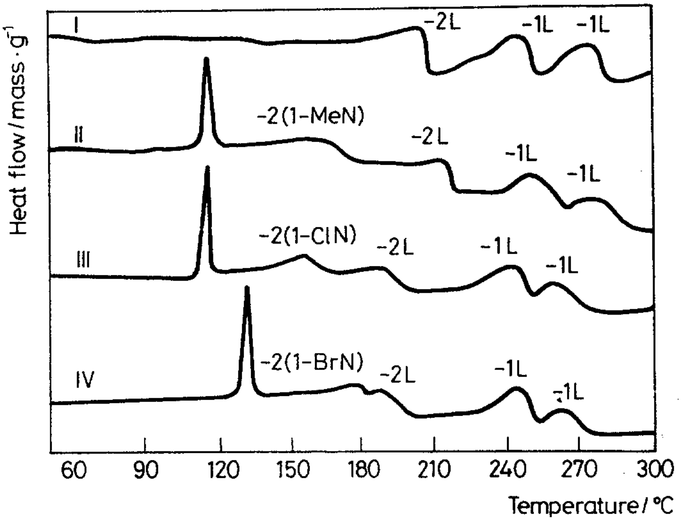

Fig. 5 DSC curves of $[Ni(4\text{-}Etpy)_4(NCS)_2]$ (I) and $[Ni(4\text{-}Etpy)_4(NCS)_2]\cdot nG$ clathrates [G=1-MeN (II), 1-ClN (III), and 1-BrN (IV)]

The enthalpic changes (ΔH) corresponding to the individual processes are given in Table 3. Numbers 1–5 are assigned to the following effects:

(1) The liberation of G from the host lattice and a phase transition. The values of $\Delta H_{(1)}$ for these effects are somewhat different, increasing in the sequence (as concerns G) 1-MeN<1-ClN<1-BrN.

(2) The escape of G. The values of $\Delta H_{(2)}$ decrease with the rise in volume of G: 1-MeN>1-ClN>1-BrN.

Table 3 DSC data of [NiL$_4$(NCS)$_2$]·nG compounds (L=4-Etpy)

Compound	Process		Temperature/ °C	Peak/ °C	ΔH/kJ mol^{-1}	
					total	partial*
[NiL$_4$(NCS)$_2$]	(3)	−2L	177–210	207	50±1.0	–
(I)	(4)	−1L	211–287	246	107±2.1	63±1.2
	(5)	−1L		276		44±0.9
[NiL$_4$(NCS)$_2$]·2(1-MeN)	(1)	phase transition	108–119	115	29±0.6	–
(II)	(2)	−2(1-MeN)	119–213	156	158±3.2	83±1.7
	(3)	−2L		209		75±1.5
	(4)	−1L	213–284	244	106±2.1	65±1.3
	(5)	−1L		272		41±0.8
[NiL$_4$(NCS)$_2$]·2(1-ClN)	(1)	phase transition	106–119	115	30±0.6	–
(III)	(2)	−2(1-ClN)	119–199	154	118±2.4	64±1.3
	(3)	−2L		191		54±1.1
	(4)	−1L	202–279	241	115±2.3	78±1.6
	(5)	−1L		262		37±0.7
[NiL$_4$(NCS)$_2$]·2(1-BrN)	(1)	phase transition	121–137	132	33±1.0	–
(IV)	(2)	−2(1-BrN)	137–202	175	87±1.7	56±1.1
	(3)	−2L		186		31±0.6
	(4)	−1L	205–275	244	111±2.2	76±1.5
	(5)	−1L		263		35±0.7

* partial ΔH were stated by using method of partial areas

(3–5) The escape of L. The release of G causes destruction of the host structure [6] to different extents. This is illustrated by the $\Delta H_{(3)}$, $\Delta H_{(4)}$ and $\Delta H_{(5)}$ values for the thermal decompositions of the respective clathrates at higher temperatures (Table 3). Smaller defects due to a structure rearrangement are presumed for the 1-MeN clathrate, inasmuch as similar values of $\Delta H_{(3)}$, $\Delta H_{(4)}$ and $\Delta H_{(5)}$ were observed for I and II. For III and IV, the values of $\Delta H_{(3)}$ and $\Delta H_{(4)}$ are very close.

Conclusions

The thermal effects accompanying the escape of G molecules indicate that the thermodynamic stability of the studied clathrates $[Ni(4\text{-}Etpy)_4(NCS)_2]\cdot nG$ decreases in the sequence 1-MeN>1-ClN>1-BrN. The differences in thermodynamic stability and clathration selectivity are assumed to have their roots in different intramolecular guest-host interactions in the studied clathrates [5]. These interactions affect the stoichiometry of the thermal decomposition and the enthalpic changes accompanying the escape of different guests from the given host complex, and also the ligand-ligand interactions in the host complex.

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