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Thermal decomposition reactions of nickel(II) complexes under quasi-equilibrium conditions.
Part 3. The study of the relations between the thermal, spectral and structural properties of the Werner clathrates $[Ni(4\text{-}Mepy)_4(NCS)_2] \cdot 2G$ (where G represents naphthalene derivatives)

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Abstract

The relationship between the quasi-equilibrium decomposition temperature T_D, the band shift $\Delta\tilde{\nu}(^3A_{2g} \rightarrow {}^3T_{1g})$ in the electronic spectra and the degree of tetragonal distortion (R_e/R_a) of the host complex in the $[Ni(4\text{-}Mepy)_4(NCS)_2] \cdot 2G$ clathrates (where G is 1-methyl-, 2-methyl-, 1-bromo-, and 2-bromonaphthalene) was studied. It was found that with increasing T_d the positive band shift also increases, whereas the degree of tetragonal distortion of the coordination polyhedra decreases. The reasons for these differences are discussed.

INTRODUCTION

There is a wide range of inclusion compounds known as Werner clathrates; they are characterized by the general formula $[ML_4X_2] \cdot nG$, where M is a divalent transition metal, X is an anionic ligand, L is substituted pyridine, and G is a guest organic molecule.

Many problems concerning host–guest interactions may be solved by studying the thermally induced liberation of the G molecules, and by correlating these data with the crystallochemistry and structure of the host complex. Using this approach, Allison and Barrer [1] presented extensive results on the release of numerous organic substances from the β-phases of $[ML_4X_2]$ complexes, where M is Co, Ni, Mn, or Fe^{2+}, L is 4-methylpyridine,

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and X is NCS. Comparing the isosteric heats of sorption, the heats of vaporization and the boiling points of the guest, they emphasized the physical nature of the clathration process and characterized these host complexes as zeolite-like materials.

Lipkowski [2] and Sitarski and Lipkowski [3] proposed that three individual steps take place in the liberation of the guest molecules following the heating of Werner clathrates: the release of the guest molecule from the cavity, diffusion to the crystal surface, and desorption from the crystal surface.

Gavrilova et al. [4] investigated the kinetics of the thermal decomposition of the above-mentioned clathrates. In studying the thermodynamic stability of the clathrates, they used the "quasi-equilibrium temperature" T_D extracted from the thermogravimetric measurements under "quasi-equilibrium" conditions (Q-TG).

We have presented the relations between the thermal, spectral and structural properties of some thiocyanate nickel(II) complexes [5], as well as those of the $[Ni(4\text{-}Mepy)_4(NCS)_2] \cdot G$ clathrates [6] where G is benzene, toluene, and *p*-xylene.

The aim of this work was to study the analogous relations of the above-mentioned complexes when clathrated by more complicated naphthalene derivatives that have differing thermodynamic stabilities and whose structures are already known [7, 8].

EXPERIMENTAL

The clathrate compounds $[Ni(4\text{-}Mepy)_4(NCS)_2] \cdot 2G$, where G is 1-methylnaphthalene (1-MeN), 2-methylnaphthalene (2-MeN), 1-bromonaphthalene (1-BrN), and 2-bromonaphthalene (2-BrN), were prepared from ethanolic solution as described in ref. 9. The compounds obtained were checked for Ni, C, H and N contents.

The thermal decomposition under the dynamic conditions was studied using a Derivatograph OD 102; a sample mass of 100 mg was heated in static air at a heating rate of 2.5°C min^{-1} using an open standard crucible. A Q-Derivatograph was used for the quasi-equilibrium measurements. This experimental technique provides a stabilization in the temperature when the decomposition process commences, i.e. the decomposition proceeds under quasi-isothermal conditions [10]. By using a special sample holder it is possible to keep the pressure of the gaseous products almost constant during the decomposition (when a conical crucible is used this pressure amounts about 90 kPa).

The electronic spectra of the clathrates were recorded on a Specord M 40 (Carl Zeiss Jena).

Infrared absorption spectra were recorded on a UR model 20 spectrophotometer using a nujol suspension.

RESULTS AND DISCUSSION

Thermal properties of the clathrates

According to Hart and Smith [11], the following information is important in the study of clathrate thermochemistry: the temperature at which the guest molecules are released; the temperature at which the breakdown of the host complex begins; and the stoichiometry of these steps.

It is generally known that the decomposition of the initial [Ni(4-Mepy)$_4$(NCS)$_2$] complex (in dynamic conditions) proceeds in four distinct steps in the temperature range 100–310°C, each step corresponding to the release of one mole of 4-Mepy, see Fig. 1. This stepwise is best described in the DTG curves, which exhibit peaks at ≈160, 185, 265 and 305°C.

After clathration, liberation of the guest phase can interfere with the breakdown of the host lattice; this depends on the energy of the host–guest interaction, and on the boiling point and other properties of the guest

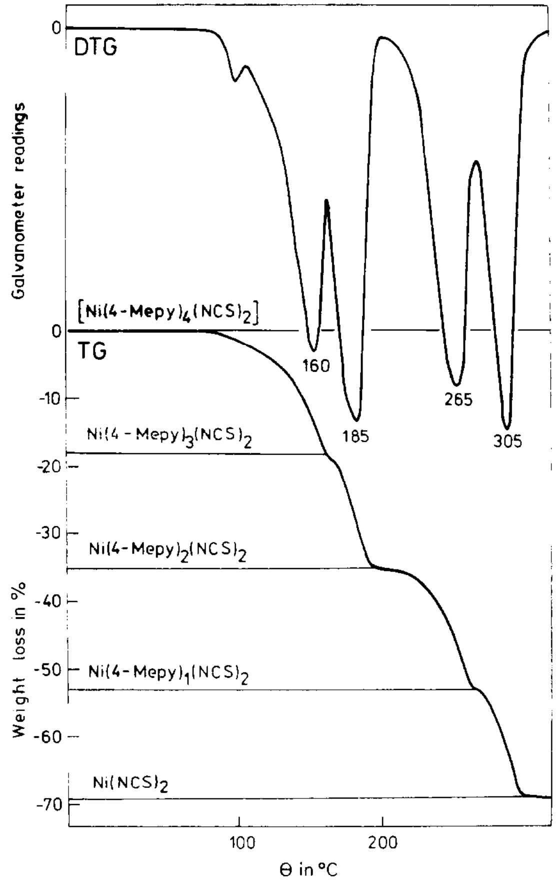


Fig. 1. Thermal decomposition of the host complex [Ni(4-Mepy)$_4$(NCS)$_2$] in dynamic conditions (TG and DTG curves).

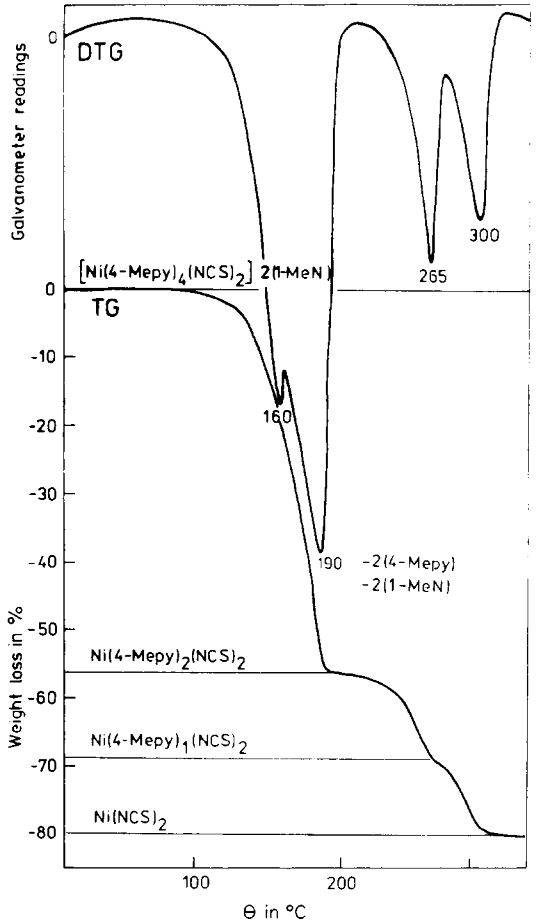


Fig. 2. TG and DTG curves of $[Ni(4\text{-}Mepy)_4(NCS)_2]\cdot 2(1\text{-}MeN)$.

molecule. In studying the thermal properties of the Werner clathrates clathrated by benzene (B), toluene (T) and *p*-xylene (*p*-x), we reported recently [6] the following decomposition stoichiometry when the guest molecules were released (where L is 4-Mepy): -(B); $-(T + 0.3L)$ and $-(p\text{-x} + L)$. Accordingly the liberation of toluene and *p*-xylene from the host lattice is accompanied by a partial breakdown of the host lattice.

Using analogous experimental conditions (dynamic TG analysis), we have determined the stepwise decomposition of the Werner clathrates clathrated by thermally more stable naphthalene derivatives (Figs. 2–5, Table 1). From these results, the stoichiometry of the first decomposition step may be expressed by the overall dissociation reaction

$$[NiL_4(NCS)_2]\cdot 2G(s) \xrightarrow{\Delta T} NiL_2(NCS)_2(s) + 2L(g) + 2G(g) \qquad (1)$$

where L is 4-Mepy and G is 2-MeN, 1-MeN and 1-BrN. However, the peak

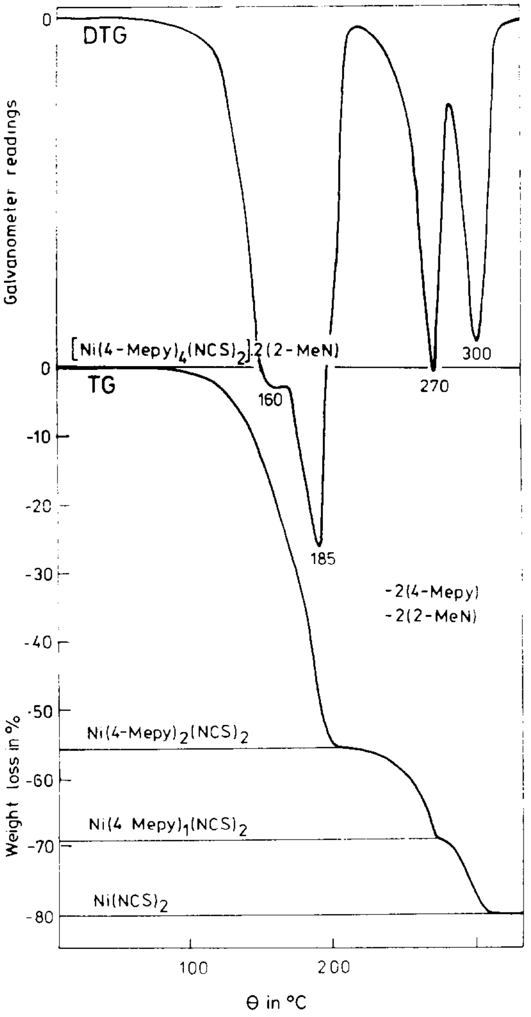


Fig. 3. TG and DTG curves of $[Ni(4\text{-}Mepy)_4(NCS)_2] \cdot 2(2\text{-}MeN)$.

at approx. 160°C on the DTG curves indicates a more complex thermal decomposition. Considering these data, it can be deduced that the breakdown of the host lattice occurs before the guest molecules are released.

Furthermore, it seems that the actual enclathration process proceeds in the second phase at temperatures above 160°C, and that the corresponding DTG peak temperatures follow to some extent the properties of the guest (the release of 1-substituted naphthalene derivatives proceeds at higher temperatures, see Table 1). The further decomposition of the host complex proceeds as for the non-clathrated sample. Nevertheless, some uncertainties in the stoichiometry of the thermal decomposition are evident in

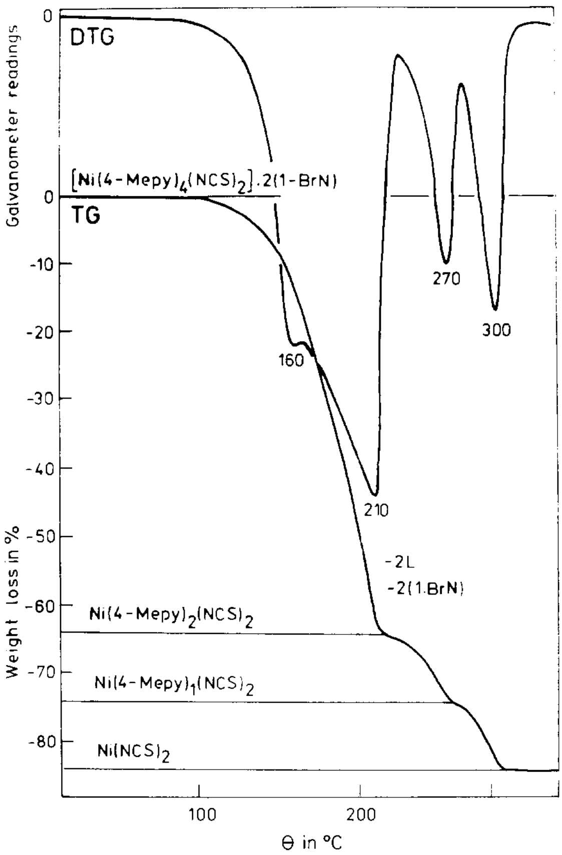


Fig. 4. TG and DTG curves of $[Ni(4\text{-}Mepy)_4(NCS)_2] \cdot 2(1\text{-}BrN)$.

the case of the sample with 2-Br naphtalene (Table 1). Thus, the stoichiometry of the thermal decomposition of the individual clathrates can be described by

$$[NiL_4(NCS)_2] \cdot 2G: -(2L + 2G), -L, -L \qquad (2)$$

where G is 2-MeN, 1-MeN, 1-BrN
and/or

$$[NiL_4(NCS)_2] \cdot 2G': -(2L + 1.4G'), -(L + 0.6G'), -L \qquad (3)$$

where G′ is 2BrN.

The specific thermal behaviour of the clathrate with 2-Br naphthalene may possibly be explained from its spectral and structural properties.

Thermal measurements under quasi-equilibrium conditions

The Q-TG curves recorded under quasi-isothermal heating conditions using a conical crucible [10] provide comprehensive information about the

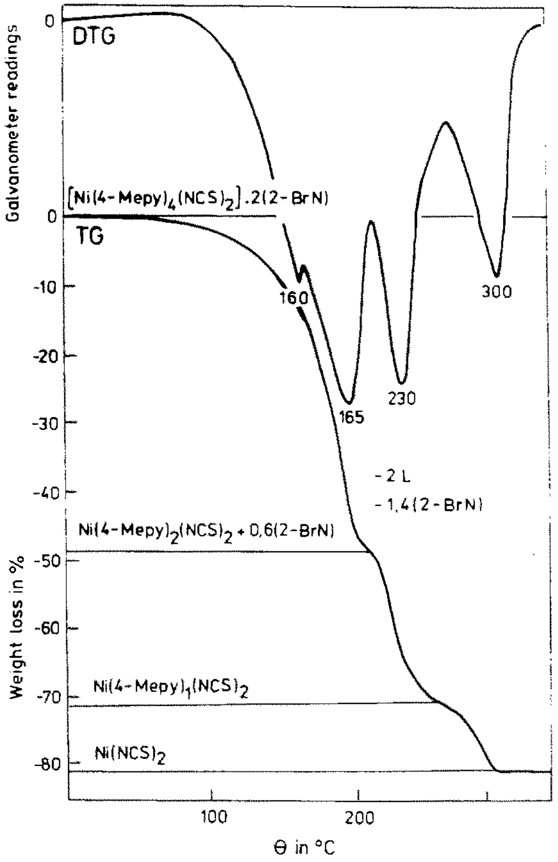


Fig. 5. TG and DTG curves of $[Ni(4\text{-}Mepy)_4(NCS)_2] \cdot 2(2\text{-}BrN)$.

reaction stoichiometry as well as the decomposition temperatures. The curves shown in Fig. 6 and the data listed in Table 1, show that under the conditions used, the first decomposition step of the clathrates follows schemes (2) and (3).

The decomposition temperatures T_D derived from the quasi-isothermal measurements can be used to establish a qualitative sequence for the thermodynamic stabilities of the compounds in identical thermal decomposition reactions [5]. According to the T_D, the clathrates studied can be ordered (by G) in the sequence: 2-Br naphthalene < 2-Me naphthalene < 1-Me naphthalene < 1-Br naphtalene.

The T_D values of the clathrates, and the T_D values and boiling points of the individual guest compounds, are given in Table 2. The results reveal that the release of the guest naphthalene derivatives from the Werner clathrates proceeds at considerably lower temperatures when compared with the tabulated boiling points and decomposition temperatures determined for pure guest molecules using Q-TG measurements. This demon-

TABLE 1

Thermal analysis results for $[NiL_4(NCS)_2] \cdot 2G$ clathrates where L is 4-Mepy and N is naphthalene

Guest (G)	Q-TG θ_D/°C	TG/%		DTG, θ/°C	Resulting intermediate
		Calc.	Found		
2-BrN	185	49.52	49.0	160, 185	$NiL_2(NCS)_2 + 0.6(2BrN)$
		22.60	22.0	230	$NiL(NCS)_2$
	–	9.69	10.0	300	$Ni(NCS)_2$
2-MeN	190	56.59	56.5	160, 185	$NiL_2(NCS)_2$
		11.20	12.0	270	$NiL(NCS)_2$
		11.20	11.5	300	$Ni(NCS)_2$
1-MeN	204	56.69	56.5	160, 190	$NiL_2(NCS)_2$
	–	11.20	12.0	265	$NiL(NCS)_2$
	–	11.20	11.5	300	$Ni(NCS)_2$
1-BrN		62.45	63.5	160, 210	$NiL_2(NCS)_2$
	–	9.69	10.5	270	$NiL(NCS)_2$
	–	9.69	10.0	300	$Ni(NCS)_2$

strates the influence of the host–guest interactions on the enclathration process.

Spectral properties of the clathrates

The electronic absorption spectra of $NiL_4(NCS)_2$ complexes, where L is a pyridine derivative, have already been studied [12]. The specific complex used in this work (4-Mepy) has a rather small tetragonal distortion, as shown by its crystal structure [13]. No splitting was observed in the spin-allowed $^3A_{2g} \rightarrow {}^3T_{2g}$ transition in the absorption spectra of the clathrates, which confirms that they have an approximate O_h symmetry [13]. Table 2 lists the band shifts ($\Delta\tilde{\nu}$) observed for the studied clathrates, expressed relative to the non-treated host complex, when only the broad band corresponding to the $^3A_{2g} \rightarrow {}^3T_{1g}$ transition is taken into account. The band shift can be considered as a measure of the host–guest interaction in the clathrates [14] and can be ordered (by G) in the sequence: 2-Br naphthalene < 2-Me naphthalene < 1-Me naphthalene < 1-Br naphthalene.

Further information on the spectral properties of the studied clathrates was obtained by investigating their infrared spectra, considering the C–N stretching vibrations in the host complex. One single band at 2080 cm^{-1} corresponding to the $\tilde{\nu}$(C–N) vibration occurs in the IR spectra of

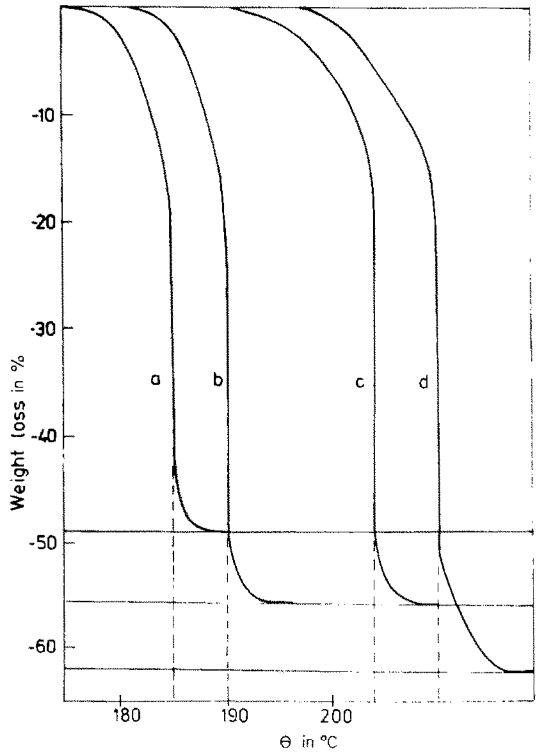


Fig. 6. Q–TG curves of the studied clathrates (first step): curve a, G is 2-BrN; curve b, G is 2-MeN; curve c, G is 1-MeN; curve d, G is 1-BrN.

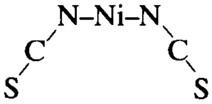
TABLE 2

Thermal, spectral and structural parameters of individual guests and [Ni(4-Mepy)$_4$(NCS)$_2$] · 2G clathrates

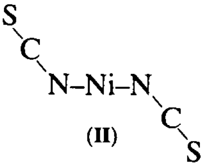
Parameter	2-BrN	2-MeN	1-MeN	1-BrN
Individual guest				
Boiling temperature/°C	281	240	245	281
θ_D/°C	245	218	225	245
Clathrates				
θ_D/°C	185	190	204	210
$\tilde{\nu}(^3A_{2g} \rightarrow {}^3T_{1g})$/cm^{-1}	16900	17000	17500	17450
$\Delta\tilde{\nu}$/cm^{-1} [a]	−400	−300	+200	+150
$\tilde{\nu}$(C–N)/cm^{-1}	2060(sh) 2070 2080(sh)	2060(sh) 2070 2080(sh)	2080	2083
R_e/R_a	1.0651 [7]	1.0567 [7]	1.0299 [8]	–

[a] $\tilde{\nu}(^3A_{2g} \rightarrow {}^3A_{1g})$ of non-treated [Ni(4-Mepy)$_4$(NCS)$_2$] is 17 300 cm^{-1}.

clathrates with 1-substituted naphthalenes. However, a band at 2070 cm^{-1} with two distinct shoulders is present in the spectra of clathrates with 2-substituted naphthalenes. This change can be due to a different arrangement of the isothiocyanate groups as reported by in ref. 12.



(I)



(II)

Arrangement (**I**) represents clathrates with 1-substituted naphthalene derivatives; arrangement (**II**) is for analogous compounds with the substituent in the 2-position.

The relationship between the thermal, spectral and structural properties of the clathrates

The host complex $Ni(4\text{-}Mepy)_4(NCS)_2$ in the clathrates under study occurs in a monomeric octahedral configuration. The equatorial plane is formed by four nitrogen atoms from the four Mepy molecules (the average Ni–N being R_e); the axial positions are occupied by the two nitrogen atoms from the NCS groups (the average Ni–N being R_a). A comparison of the R_e/R_a values (a measure of the relative tetragonal distortion [5]) shows a smaller tetragonal distortion of the host complex with 1-Me and 1-Br naphthalene than with the 2-substituted naphthalene molecules. It is evident from Table 2 that the R_e/R_a values for clathrates with 2-substituted naphthalenes (1.0651 and 1.0567) are considerably different from that of the clathrate with 1-Me naphthalene (1.0229). Thus the properties of the guest molecules and the guest–host interactions play an important role in the tetragonal distortion of the host complex. The degree of tetragonal distortion of this complex for different clathrates increases (by G) in the sequence: 1-Me naphthalene < 2-Me naphthalene < 2-Br naphthalene.

For the clathrates studied, a decrease in the quasi-equilibrium decomposition temperatures T_D with an increasing degree of tetragonal distortion (R_e/R_a) of the host complex is observed (Fig. 7A). However, it was found that T_D increases as the ${}^3A_{2g} \rightarrow {}^3T_{1g}$ band shift ($\Delta\tilde{\nu}$) increases (Fig. 7B). Thus, higher quasi-equilibrium decomposition temperatures indicate a larger positive band shift but a smaller tetragonality parameter.

CONCLUSIONS

From the quasi-equilibrium measurements, the 1-Me naphthalene and 1-Br naphthalene clathrates are thermodynamically more stable than the 2-substituted clathrates. It seems that the reason for the above difference in

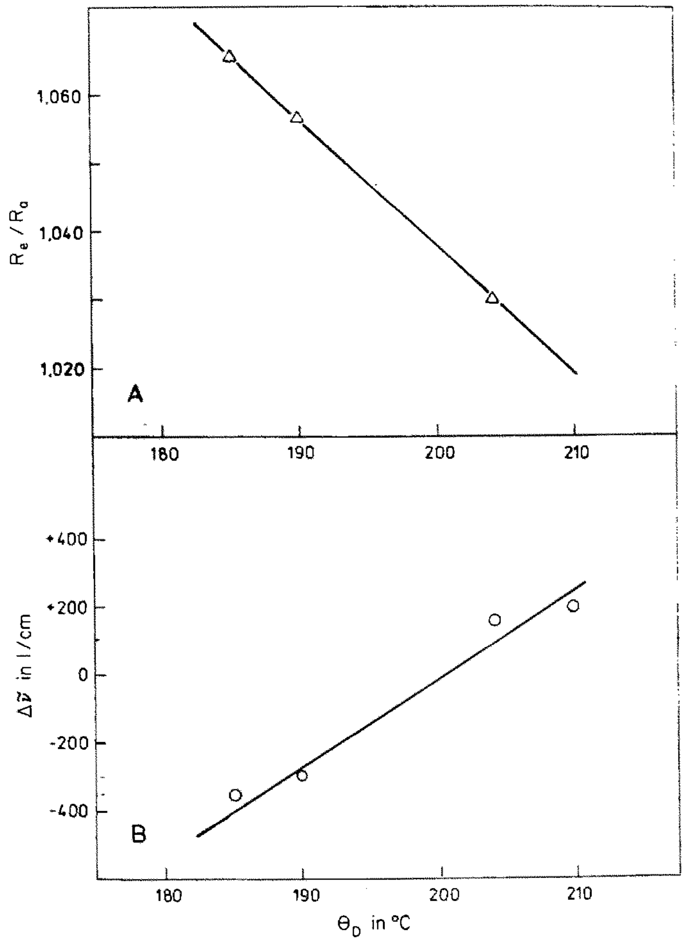


Fig. 7. A. Dependence of R_e/R_a vs. T_D. B. Dependence of $\Delta\tilde{\nu}(^3A_{2g} \rightarrow {}^3T_{1g})$ vs. T_D for the studied clathrates.

thermodynamic stability (and the reason for clathration selectivity in this system) could be the difference in the intramolecular guest–host interaction for the clathrates studied. The guest-to-host interactions influence the ligand–ligand (equatorial–axial [15]) interactions in the host complex and then the total energy content of these systems.

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