

Thermal stability of nickel complexes formed with phenylazothioalkylcarboximides in various solvents

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Abstract

Thermogravimetric TG/DTG and calorimetric DSC studies of four types of complexes: (A) $\text{Ni}(\text{RL})_2\text{I}_2 \cdot 2\text{S}$, (B) $\text{Ni}(\text{RL})_2\text{I}_2 \cdot \text{S}$, (C) $\text{Ni}(\text{RL})_2\text{I}_2$, and (D) $\text{Ni}(\text{RL})_2(\text{I}_3)_2$ were performed. The decomposition steps of these compounds were observed. The important role of the solvent molecules S in stabilization of the crystal structure of the examined complexes is suggested.

Keywords: Decomposition; DSC; Nickel complexes; Phenylazothioalkylcarboximides; TG; Thiosemicarbazide derivatives

1. Introduction

Thiosemicarbazide (TSC) is known as a chelating ligand able to form coordination compounds with many metallic ions. The stability of TSC complexes in solutions, their preparation methods, and their structural and physical properties have been reported [1].

N(1)-substituted TSCs were earlier proposed for the analytical determination of various metals [2–4]. Although metal complexes with different *N*(1)-, *N*(2)- and *N*(4)-substituted TSCs have been widely studied, the investigation of the thioalkylated TSCs was not undertaken until later [5, 6]. It was then observed that thioalkylation changes the mode of ligand coordination and the properties of the formed complexes. Thus, new unusual coordination compounds resulting from reactions between nickel

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Table 1
Composition of the complexes III and VII

Complex	Formula	Composition in %			
		Ni	C	H	N
Ni(CH ₃ L) ₂ C ₂ H ₄ Cl ₂ (III)	C ₁₈ H ₂₂ I ₂ Cl ₂ N ₆ NiS ₂	7.54 (7.63)	27.91 (28.08)	2.75 (2.88)	10.83 (10.92)
Ni(CH ₃ L) ₂ I ₂ (VII)	C ₁₆ H ₁₈ I ₂ N ₆ NiS ₂	8.68 (8.75)	29.10 (28.64)	2.68 (2.70)	12.44 (12.53)

Figures in parentheses denote calculated values.

Table 2
Characteristics of complexes and TG data of their decomposition

Symbol of the complex	R	S (T _b /K)	Desolvation			Mass loss %	Thermolysis			Mass loss %
			Temperatures/K				Temperature/K			
			T _e	T _p	T _f		T _e	T _p	T _f ^Δ	
I	CH ₃	CHCl ₃ (334.4)	358.5	366.4	374.1	25.9 (26.2)	442.3	444.5	445.4	26.2
II	CH ₃	CCl ₄ (349.9)	380.5	392.5	397.5	31.1 (31.4)	444.6	446.1	448.0	25.7
III	CH ₃	C ₂ H ₄ Cl ₂ (356.8)	380.2	391.6	397.2	12.7 (12.8)	448.8	452.1	453.7	32.4
IV	C ₂ H ₅	CHCl ₃	354.0	362.3	370.1	24.9 (25.5)	434.8	437.9	438.8	26.4
V ^a	CH ₃	I ₂	–	–	–	–	443.3	453.3	458.8	59.5
VI ^a	C ₂ H ₅	I ₂	–	–	–	–	432.4	444.2	450.3	64.0
VII	CH ₃	–	–	–	–	–	439.5	440.2	444.0	42.2

Figures in brackets in the mass loss column are calculated values. Subscripts of *T* denote: b, boiling point; e, extrapolated onset; p, peak; f, final on DTG curves; T_f^Δ is the final temperature of the main, "rapid" effect of thermolysis.

^a Desolvation overlaps with thermolysis, hence all values concern the total effect.

VII), an equimolar amount of dissolved iodine (in the same solvent) is added. The resulting dark brown crystals, after cooling, are filtered, washed with the respective cold solvent, and dried at room temperature. The results of elemental analysis (Ni, C, H, N) obtained for complexes I, II, IV, V and VI are in good agreement with the compositions

reported in Ref. [10]. The analytical data for the newly synthesized complexes III and VII are given in Table 1.

Nickel was determined gravimetrically with dimethylglyoxime, after mineralization of the complexes with H_2O_2 in concentrated H_2SO_4 .

All solvents, ("POCh" S.A. Gliwice) were used without purification.

2.2. Thermal analysis

The thermophysical properties of crystalline, homogenized samples were studied over the temperature range 298 to 623 K using a Du Pont TGA 951 thermogravimetric analyser and a DSC 910 differential scanning calorimeter.

The DSC and TG experiments were performed at a scan rate of 10 K min^{-1} in an atmosphere of dry flowing argon (100 ml min^{-1}). The DSC device was calibrated using the indium samples from the Polish Committee for Standardization, Measures and Quality Control (Warsaw, Poland). The determined temperature of melting was 156.8°C (it should be 156.6°C). The relative error of determination for the heat effect measurements was 1%.

Calibration of the TGA cell was performed using a sample of calcium oxalate monohydrate at various scan rates from 0.5 to 20 K min^{-1} . The accuracy of the weight measurements was better than 1.5%.

The numerical analysis of the experimental data was performed by means of software associated with the Du Pont 2100 Thermal Analyst, including the DSC and TGA Standard Data Analysis Programs, and the TGA Decomposition Kinetics Data Analysis Program.

3. Results

The results of the thermogravimetric analysis of the seven complexes are given in Table 2. The heat effects corresponding to the examined processes are collected in Table 3.

Table 3
Heat effects (kJ mol^{-1}) of the thermal decomposition of the complexes

Complex	Desolvation ΔQ_1	Thermolysis $-\Delta Q_1$	Total heat of decomposition $\Delta Q_t = \Delta Q_1 + \Delta Q_2$
I	90.2 ± 0.3	122 ± 1	-32 ± 1
II	32.6 ± 0.2	43 ± 3	-10 ± 3
III	31.4 ± 0.2	50 ± 3	-19 ± 3
IV	93.3 ± 0.2	126 ± 2	-33 ± 2
V ^a	$75(\pm?)$	$78(\pm?)$	-3.1 ± 0.2
VI ^a	$29(\pm?)$	$18(\pm?)$	$+11.1 \pm 0.2$
VII	–	104 ± 15	-104 ± 15

^a Although the integrals of the endo and exo portions of the DSC curves are well defined, their values do not correspond exactly to the effects of desolvation and thermolysis because of overlapping processes.

Heating of the complexes I–IV in the temperature range 298 to 523 K is accompanied by two distinctly separated stages of mass loss. The first mass loss corresponds to the total release of the solvent from the complex and is associated with an endothermic heat effect. The observed second mass loss and corresponding exothermic heat effect are connected with the thermolysis of the complex remaining after desolvation. The TG, DTG and DSC curves for complex II, as an example of the decomposition observed for complexes I–IV, are shown in Fig. 1.

The shapes of the TG and DTG curves of complexes V and VI are quite different from those observed for complexes I–IV. The heating of samples V and VI is accompanied by a single mass loss at a temperature characteristic for the thermolysis of complexes I–IV (see Table 2). However, this mass loss occurs over a greater temperature range than that for the thermolysis of complexes I–IV. Moreover, the DSC curves for complexes V–VI reveal two different heat effects related to this single peak on the

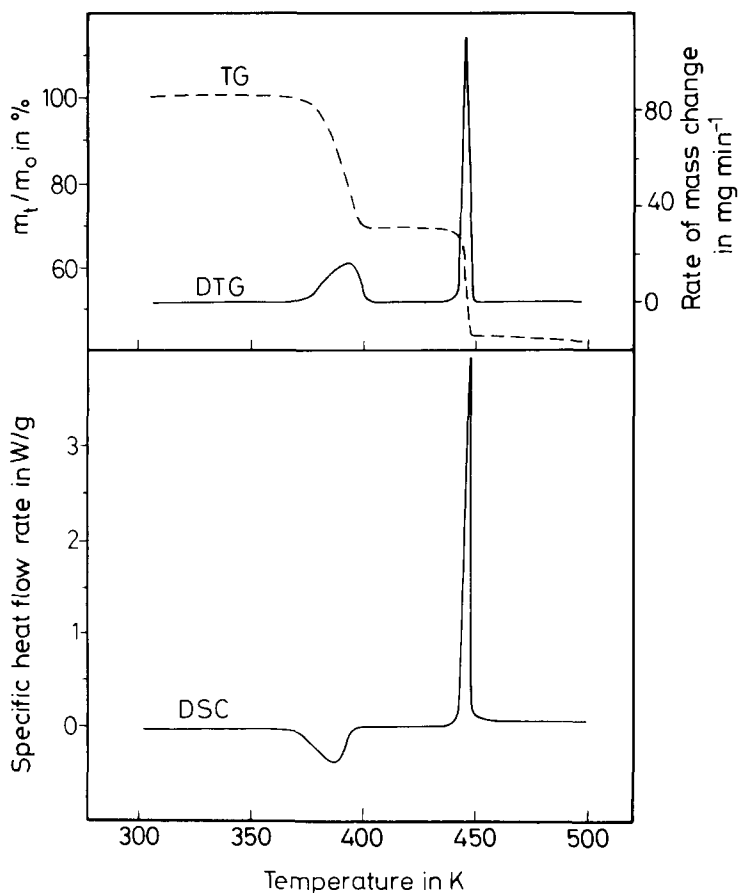


Fig. 1. TG, DTG and DSC curves for the complex $\text{Ni}(\text{CH}_3\text{L})_2\text{I}_2 \cdot 2\text{CCl}_4$ (II), heating rate $\beta = 10 \text{ K min}^{-1}$; m_0 , m_t denote the initial mass of the sample and the mass at time t , respectively.

DTG curve. To illustrate this decomposition pathway, TG, DTG and DSC curves for complex V are given in Fig. 2. The first heat effect, endothermic, may be associated with the release of iodine molecules from the complex. The second, exothermic (with two distinct maxima), corresponds to the thermolysis of the sample. In this case, desolvation and thermolysis overlap considerably. For this reason it was impossible to separate mass losses as well as heat effects for individual processes. The heating of complex VII, which does not contain any solvent molecules, is accompanied by a single mass loss and exothermic heat effect connected only with thermolysis (Fig. 3).

For all the compounds under consideration, the DTG and more clearly the DSC curves have shown that thermolysis of the complexes remaining after desolvation consists of several steps: the first, a relatively rapid one, is followed by secondary processes (tail). Hence, the end of the thermolysis could not be determined very well. This results in the values of the approximative errors for the heat effects shown in Table 3 (columns 3 and 4).

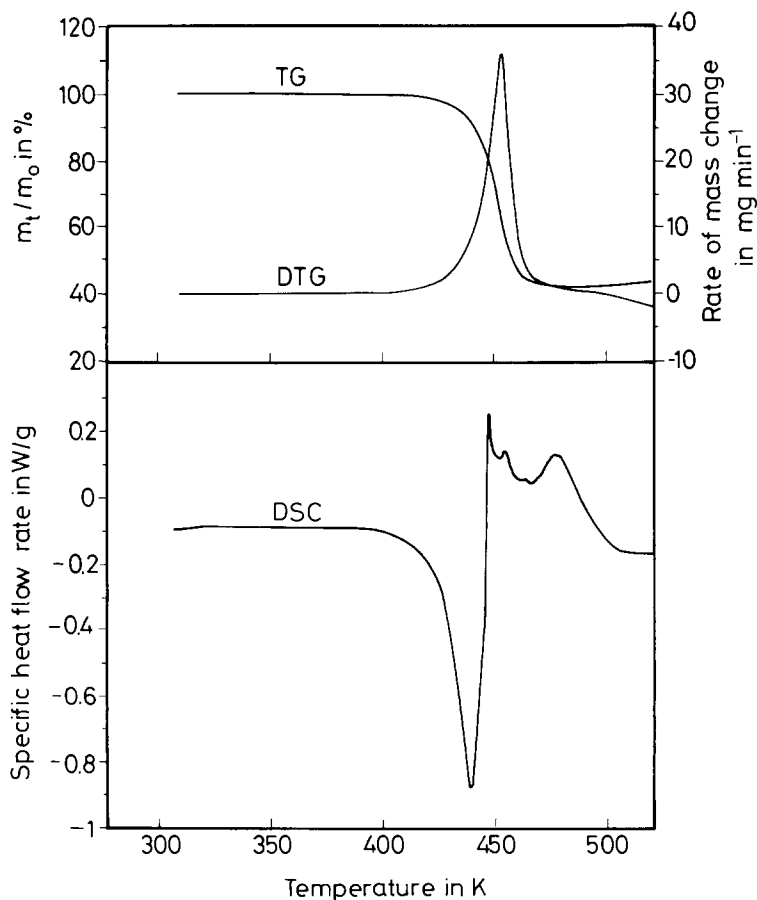


Fig. 2. TG, DTG and DSC curves for complex $\text{Ni}(\text{CH}_3\text{L})_2(\text{I}_3)_2$ (V), $\beta = 10 \text{ K min}^{-1}$, symbols as in Fig. 1.

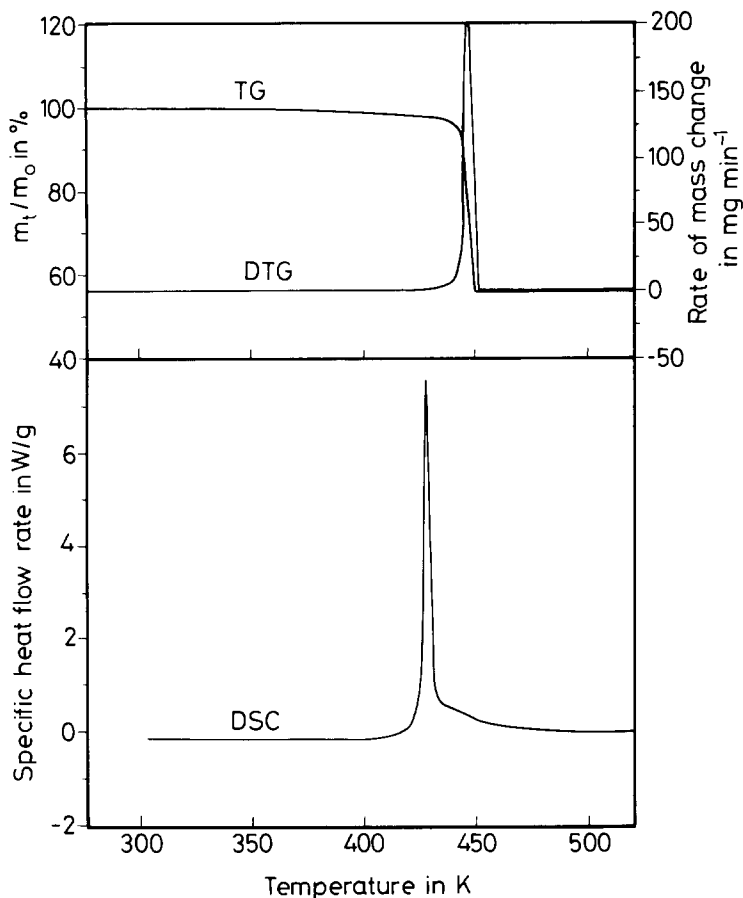


Fig. 3. TG, DTG and DSC curves for complex $\text{Ni}(\text{CH}_3\text{L})_2\text{I}_2$ (VII), $\beta = 10 \text{ K min}^{-1}$, symbols as in Fig. 1.

It is noted here that volatilization of coordinated neutral phenylazothioalkylcarboximides was not observed for all of the studied complexes.

The influence of the heating rate on the shape and characteristic temperatures of the TG and DTG curves recorded in the region of desolvation of complexes I, II and IV was noticed. This influence was examined in more detail for the complex II, applying six heating rates in the range from 0.5 to 20 K min^{-1} . As an illustration, Fig. 4 shows the results for three rates. The two maxima apparent on the DTG curve at low heating rate suggest that the desolvation occurs in two steps. A series of experiments under isothermal conditions was undertaken over the temperature range 348 to 363 K to explore the possibility of separating the two steps of desolvation and isolating the intermediate product, i.e. complex II with one molecule of CCl_4 .

The results of these experiments are presented in Figs. 5 and 6. In Fig. 5, the example of the change of mass with time, $m_t = f(t)$, and its derivative (corresponding to the rate

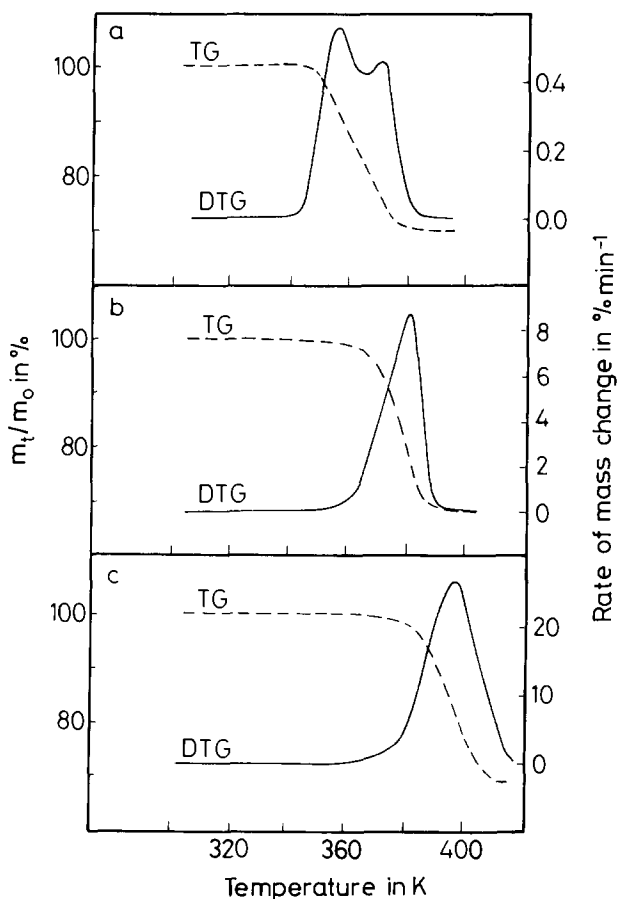


Fig. 4. Variation of DTG curves with heating rate for the complex $\text{Ni}(\text{CH}_3\text{L})_2\text{I}_2 \cdot 2\text{CCl}_4$ (II), 0.5 (a); 5 (b) and 20 K min^{-1} (c), symbols as for Fig. 1.

of desolvation) is shown. The existence of two overlapping effects is noticed, the first very rapid and the second slow and extended in time. The influence of the temperature of the experiment on the evolution of desolvation is presented in Fig. 6.

4. Discussion

The formation of the phenylazothioalkylcarboximide nickel complexes is due to the transfer of two electrons from a delocalized π -system from $\text{Ni}(\text{RL}^*)_2$ to the iodine atoms. The redox potential of the $\text{I}_2/2\text{I}^-$ couple used in non-aqueous solutions is optimal for this electron transfer. When other oxidizing agents, e.g. Cl_2 or Br_2 , are used in the same solvents, a destructive oxidation of the organic part of the parent complex

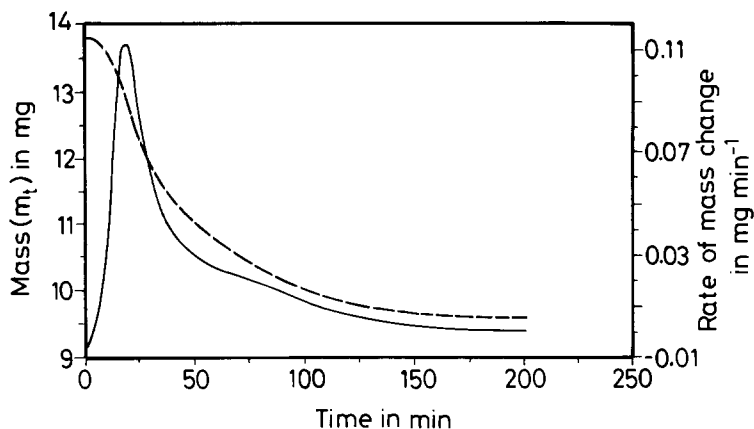


Fig. 5. Isothermal desolvation of complex $\text{Ni}(\text{CH}_3\text{L})_2\text{I}_2 \cdot 2\text{CCl}_4$ (II) at 353 K: mass of sample m_t vs. time (broken line); desolvation rate dm_t/dt vs. time (solid line).

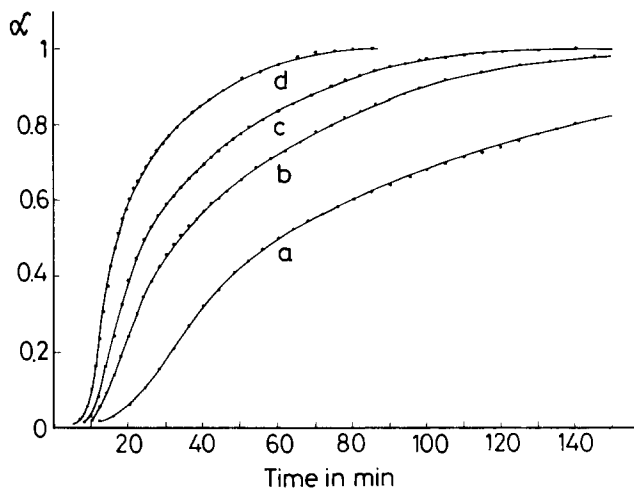
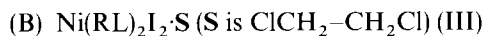


Fig. 6. Fractional extent of desolvation, α ($\alpha = m_0 - m_t / m_0 - m_f$), of complex $\text{Ni}(\text{CH}_3\text{L})_2\text{I}_2 \cdot 2\text{CCl}_4$ at isothermal conditions: curve a, 348 K; curve b, 353 K; curve c, 358 K; curve d, 363 K; m_0 , m_t and m_f denote initial mass, during the process, and final mass, respectively.

takes place. The composition of the complexes depends on the nature of the solvent and on the $\text{Ni}(\text{RL}^*)_2 \cdot \text{I}_2$ stoichiometry. The investigated nickel complexes with RL may be divided into four compositional groups as follows:



(C) $\text{Ni}(\text{RL})_2\text{I}_2$ (VII)

(D) $\text{Ni}(\text{RL})_2(\text{I}_3)_2$ (V, VI)

The A-, B-, and C-type complexes may be obtained when the molar ratio $\text{Ni}(\text{RL}^*)_2:\text{I}_2$ is 1:1 and a suitable solvent is used, e.g. chloroform or tetrachloromethane for A, dichloroethane for B, and benzene for C). The D-type complexes may be prepared in the above solvents if the stoichiometry of $\text{Ni}(\text{RL}^*)_2:\text{I}_2$ is 1:3.

The obtained complexes are stable as solids under a dry atmosphere, and in solutions of the above solvents. In the presence of coordinating reagents (such as water or alcohols), an immediate decomposition of the complexes takes place. The coordinated RL molecules are rapidly substituted by the solvents. This suggests a weak RL coordination capacity. For this reason, the typical solvation effects of the polar solvents (water, alcohols) usually used for dissolving the initial metal salts and organic reagents, prevent the preparation of the coordination compounds with RL by known methods. Thus the oxidation of $\text{Ni}(\text{RL}^*)_2$ by iodine in non-coordinating solvents is seemingly the only possibility for preparation of the metal complexes with RL. The solvation ability of the solvents used in each case is lower than the coordination properties of RL, and there are consequently no complexation interferences in these systems. However, the solvents play an important role in the binding of the complex molecules in the crystal lattice. The number of retained solvent molecules varies. For the C_1 derivatives (CHCl_3 , CCl_4), there are two solvent molecules per complex unit, while in the case of 1,2-dichloroethane, only one molecule is required for crystallization. The number of solvent molecules per complex does not change as the length of R increases [10].

The results of the TG and DSC measurements show that despite obvious differences in composition, the thermal behaviour of complexes A, B and D has the same nature. Decomposition thus takes place in two stages: release of solvents (case A and B) or iodine (D) molecules, followed by thermolysis of the complexes. For the A- and B-type complexes (I–IV), in each case the loss of bonded solvent was detected at a temperature T_p higher than the boiling point (T_b) of this solvent (see Table 2). The difference $T_p - T_b$ is not related to the nature of the solvent but rather to the energy of the binding of S in the crystal lattice. Large intervals between the temperatures of desolvation and thermolysis are characteristic for the A and B type of complexes. For the D type, the release of iodine occurs at a higher temperature than for the desolvation of S in A and B types and this first stage overlaps with the second (thermolysis). The thermal behaviour of the C type of complex (empty) is characterized by only one stage of decomposition, i.e. thermolysis, which takes place in the range of temperature similar to that observed for thermolysis of A, B and D types of complexes.

The above observations may be explained by taking into account the crystal structure of complexes I and V [10]. Both complexes have an octahedral structure. RL molecules are situated in the equatorial plane. The two transpositions of the octahedra are occupied by two I^- ions in complex I and by two I_3^- ions in V. The CHCl_3 molecules occupy cavities in the molecular packing of the complexes. One of the chlorine atoms of chloroform forms a hydrogen bond ($\text{Cl}\cdots\text{H}-\text{N}=3.796 \text{ \AA}$) with a coordinated NH-group. Thus the different binding of the solvent molecules S or I_2 in the crystal explains the observed differences in the thermal stability of these complexes.

It seems that the role played by the *S* or I_2 molecules in the crystal structure is the same for all complexes: to occupy the intermolecular cavities in the crystal lattice, thereby assuring a better packing of the crystals. The prerequisite is that solvent molecules may form some energetic interaction within the crystal cavities in the non-solvated complex. This notion was confirmed by an experiment performed for complex VII (no solvation molecules) in benzene solution. A comparison of the molecular size parameters [11] of the solvent molecules does not indicate steric hindrance for the inclusion of benzene in the intermolecular cavities of the crystal structure. As the benzene molecule cannot form hydrogen bonds, the complexes should crystallize in the form $Ni(CH_3L)_2I_2$.

The number of retained solvent molecules is not random. A complex containing one solvent molecule was isolated from the dichloroethane solution. An attempt was made to obtain a modification of complex II containing only one molecule of CCl_4 . The potential feasibility of this experiment was supported by the presence of two maxima on the DTG curve at low scan rate (Fig. 4). This suggested that desolvation occurs as two consecutive reactions



However, isothermal heating at different temperatures shows that the two reactions cannot be separated. The first reaction is more rapid. The second occurs slowly, but begins before the first reaction is complete (see Figs. 5 and 6). This suggests that the intermediate product $Ni(CH_3L)_2 \cdot I_2 \cdot CCl_4$ is not stable. The existence of complex III with only one *S* may be explained by the peculiarities of 1,2-dichloroethane: each moiety of the molecule plays a role in forming a bridge bonded to two different complexes.

The recrystallization from chloroform or dichloroethane of desolvated complexes I–IV yields the respective solvated complexes. The conversion by the same route from CCl_4 is not possible because of the low solubility of the investigated complexes in this solvent. The TG, DTG, and DSC curves for samples obtained by recrystallization are identical with those recorded for I, III, or IV.

In the solid state, the removal of *S* is irreversible. The desolvated samples maintained in an atmosphere saturated with *S* do not change in mass over 24 h. Thus, the elimination of *S* modifies the structure of the solids. Desolvation of complexes I–III and loss of iodine by V, give products of the same composition as VII; hence one could suppose that in all these cases in the second stage, the same compound decomposes. However, the heat effects of their thermolysis are quite different (Table 3). This may be explained by the different crystal structure of the solids which remain after desolvation. In such a case, it is interesting to compare the total heat effects of the complete thermal decomposition of these complexes (see column 4, Table 3). If one assumes that the total heat effect of decomposition is an approximate measure of the stability of the complex, complexes I–III and V are more stable than complex VII. These data confirm the earlier suggestion that the inclusion of solvent molecules stabilizes the crystal lattice of the examined compounds.

5. Conclusion

During the oxidation of $\text{Ni}(\text{RL}^*)_2$ complexes by iodine in organic solvents (including chloroform, tetrachloromethane, dichloroethane or benzene), four types of complexes have been obtained: (A) $\text{Ni}(\text{RL})_2\text{I}_2 \cdot 2\text{S}$, (B) $\text{Ni}(\text{RL})_2\text{I}_2 \cdot \text{S}$, (C) $\text{Ni}(\text{RL})_2\text{I}_2$ and (D) $\text{Ni}(\text{RL})_2(\text{I}_3)_2$. Despite apparent differences in the composition of complexes (A), (B) and (D), their thermal behaviour reveals a similar nature. Decomposition of these complexes is characterized by two stages. The first stage involves the loss of S or I_2 with the formation of a C-type complex. Differences are observed only in the temperature range in which desolvation takes place. For the type-D complexes, the first (desolvation) stage is close to the second one (thermolysis) and cannot be resolved on the TG curves. The second stage, thermolysis, is common for all the complexes (types A, B, C and D) and occurs almost in the same temperature range.

The inclusion of solvent (or iodine) molecules in the cavities of the crystal structure appears to play an important role in the stabilization of the complexes in the solid state.

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