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HETEROGENEOUS REACTIONS OF SOLID NICKEL(II) COMPLEXES, IV

THERMAL DECOMPOSITION OF COMPOUNDS OF THE TYPE $Ni(NCS)_2L_2$
PART B: THERMOCHEMICAL PROPERTIES

E. JÓNA, T. ŠRAMKO, P. AMBROVIČ* and J. GAŽO

*Department of Inorganic Chemistry, Slovak Technical University and *Institute of Polymers, Slovak Academy of Sciences, Bratislava, Czechoslovakia*

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The decomposition heats (ΔH) for complexes of the type $Ni(NCS)_2L_2$ were studied by means of a differential scanning calorimeter. From the decreasing values of ΔH the following order has been established: *a)* for pseudooctahedral complexes: py $>$ β-pic $>$ $>$ Q; and *b)* for square-planar complexes: 2,6-lut $>$ Q $>$ α-pic. The results obtained are compared with the data from the TG, DTG, and DTA curves.

The thermochemical properties of coordination compounds are investigated not only in solution, but also in the solid state, and the results found for both states are correlated.

In studying this relationship for complexes of the type MX_2py_2[X = Cl, Br, NCS, and M = Mn(II), Co(II), Ni(II)], Bowman and Rogers [1] have found that on heating the release of the two pyridine ligands depends on the increasing stability of the complexes (at increasing temperature) in accordance with the stability order given by Irving and Williams [2]. Analogous results have been found by Liptay and co-workers [3] for the complexes $M(NCS)_2py_4$. They have come to these conclusions by comparing the temperatures corresponding to the minima on the DTA curves [1] and to the maximum decomposition rates (on the DTG curves), respectively [3]. Flóra [4] studied the heat effects on the decomposition of the complexes $[Ni(NH_3)_6]X_2$ (X = Cl, Br, or I) by evaluation of the areas on the DTA curves obtained by the Derivatograph.

Conventional thermal analysis, where sample and inert reference are heated at a constant rate, may only provide qualitative thermochemical information [5]. From this point of view it appears more useful, especially for multistep processes, to apply data of decomposition heats, obtained by means of a differential calorimeter [5–10]. We too, proceeded in this way in studying the thermochemical properties of the isomers of $Ni(NCS)_2Q_2$ (Q = quinoline). In order to come to some partial conclusions for complexes of the same type and structure an analogous study was also carried out on other complexes of the type $Ni(NCS)_2L_2$, as in our earlier work [11].

Experimental

Chemicals, analytical methods, preparation, and analytical results for the complexes under investigation are given in [11, 12]. The grain size for all the complexes was smaller than 0.060 mm.

The Perkin-Elmer Differential Scanning Calorimeter DSC-1B was used to measure the heats of thermal decomposition, automatically recording the rate of liberation and absorption, respectively, of the heat ($\mathrm{d}\Delta H \cdot \mathrm{d}t^{-1}$) as a function of time and temperature. Aluminium sample pans were used, with pressed-on lids having a hole of 1 mm diameter. The weight of the samples was 5±0.02 mg. The heating rate was 8°/min, the sensitivity 4 mcal/s. For the used recorder chart speed

Table 1

The thermodynamic data of the reactions: $Ni(NCS)_2L_{2(s)} \rightarrow Ni(NCS)_{2(s)} + 2L_{(g)}$

Compound	T_i, °K	T_p, °K	T_f, °K	$\Delta H_{(1)}$ kcal · mole^{-1}
$Ni(NCS)_2py_2$	475	557	568	31.60
$Ni(NCS)_2(\alpha\text{-pic})_2$	392	453	468	24.40
$Ni(NCS)_2(\beta\text{-pic})_2$	458	515, 554	566	29.30
$Ni(NCS)_2(2,6\text{-lut})_2$	428	494	507	30.15
$Ni(NCS)_2Q_2$ (I)	437	475, 510	520	28.50
$Ni(NCS)_2Q_2$ (II)	413	471	499	27.80

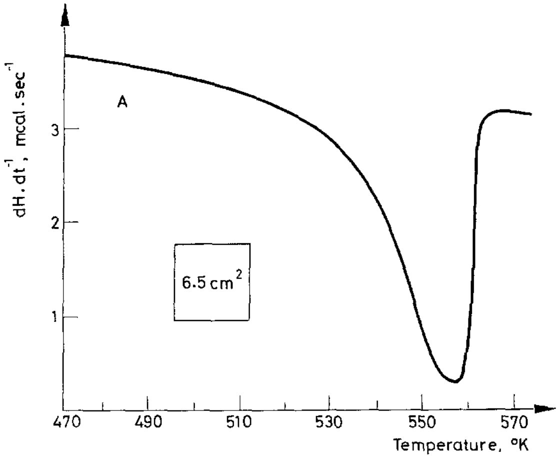
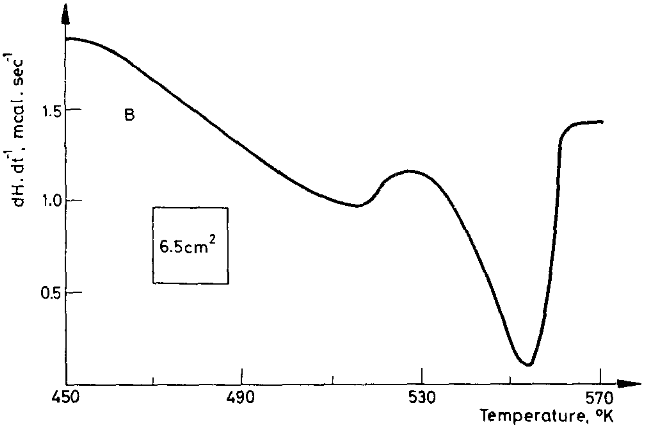
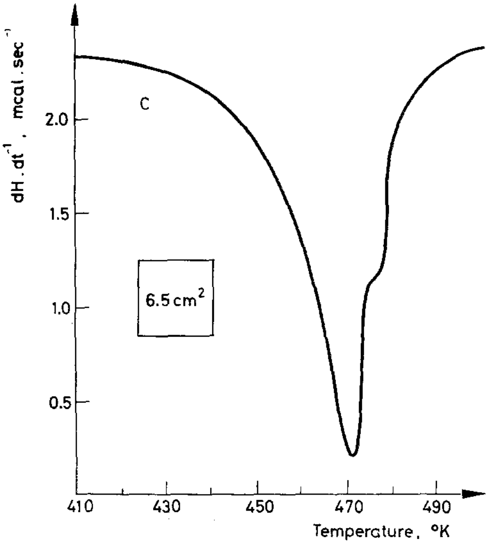
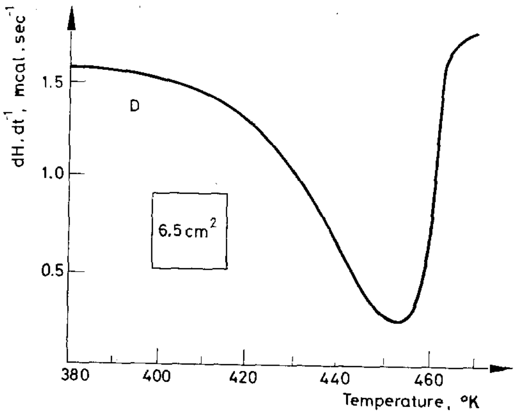
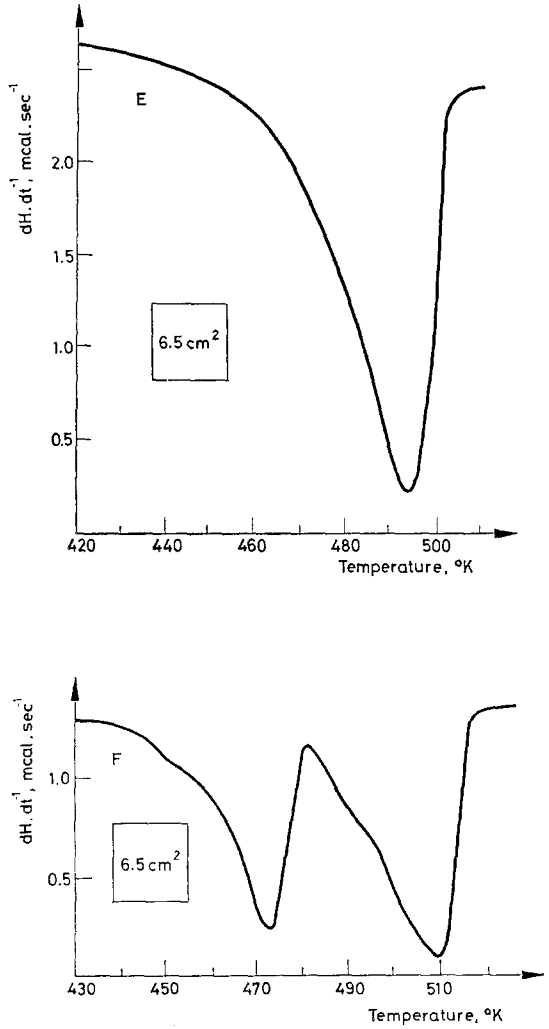


Fig. 1. Dependences of the rate of heat absorption on temperature. A: $Ni(NCS)_2py_2$, B: $Ni(NCS)_2(\beta\text{-pic})_2$, C: $Ni(NCS)_2Q_2$ (II). D: $Ni(NCS)_2(\alpha\text{-pic})_2$. E: $Ni(NCS)_2(2,6\text{-lut})_2$, F: $Ni(NCS)_2Q_2$ (I)


dH.dt^{-1}, mcal.sec^{-1}
1.5
1.0
0.5
B
6.5cm^2
450
490
530
570
Temperature, °K


dH.dt^{-1}, mcal.sec^{-1}
2.0
1.5
1.0
0.5
C
6.5cm^2
410
430
450
470
490
Temperature, °K


dH.dt^{-1}, mcal.sec^{-1}
1.5
1.0
0.5
D
6.5cm^2
380
400
420
440
460
Temperature, °K



of 75 cm/hour, the value of 48 mcal was equivalent to an area of 6.5 cm^2 (only for Ni(NCS)$_2$py$_2$ did an area of 6.5 cm^2 correspond to 96 mcal). Dry nitrogen flowed through the system during the measurements at a rate of 20 ml/min. Calibration of the temperature axis was made by means of pure indium with its melting point of 157°. The decomposition heats were determined by cutting out and measuring the respective areas. The results obtained are to be seen in Fig. 1 (A, B, C, D, E, F), and in Table 1, where T_i is the temperature at the first deflection of the curve from the base line, T_p shows the maximum change of the enthalpy, and at T_f the curve has returned to the base line.

Discussion

Recently published analogous works [5–10] provided the basis for the evaluation of the decomposition heats. Beech and co-workers measured the decomposition heats $\Delta H_{(1)}$ of the reactions

$$MX_2L_{2(s)} \rightarrow MX_{2(s)} + 2L_{(g)} \tag{1}$$

though for investigating the bond strength it would be more correct to consider the dissociation heats in the gaseous state

$$MX_2L_{2(g)} \rightarrow MX_{2(g)} + 2L_{(g)} \tag{2}$$

The relation between the reaction heats in the gaseous state $\Delta H_{(2)}$ and $\Delta H_{(1)}$ is [5]:

$$\Delta H_{(2)} = \Delta H_{(1)} - \Delta H_{\text{subl.}}\{MX_2L_2\} + \Delta H_{\text{subl.}}\{MX_2\} \tag{3}$$

As these sublimation heats are not known, Beech and co-workers suppose for simplification that the differences between the sublimation heats of MX_2 and MX_2L_2, respectively, are approximately constant. Should this assumption prove correct, then the differences between the measured decomposition heats of solid complexes would be similar to those of gaseous complexes and one might then use the value of $\Delta H_{(1)}$ as a criterion for the M–L bond strength [9]. Variations in the values of $\Delta H_{(1)}$ with different L and X may be attributed [5] to changes in "1. $\Delta H_{\text{subl.}}$ MX_2L_2 values, 2. $\Delta H_{\text{subl.}}$ MX_2 values, 3. the strength of the M–L σ-bonds, 4. the strength of the M–X σ-bonds, 5. the magnitude of the M–L π-bonding, and 6. the perturbing effect σ". Steric factors too have to be considered, then the polarisation effects, and especially also the crystal lattice energy, which may markedly vary even for the same complex type. This may account for the fact that the data of the IR spectra (π_{M-L}) [20, 21] do not always correlate with the values of $\Delta H_{(1)}$ [5].

The bond strength between the same central atom and the volatile ligand in different types of coordination polyhedra (octahedral, square-planar, tetrahedral) must be different, as the bonding possibilities of the central atom for different coordination polyhedra vary. Therefore, only complexes of the same stoichiometric type and of identical geometrical configuration may be compared with each other. The decomposition heats arranged on this basis together with the data of the TG, DTG, and DTA curves [11] are listed in Table 2.

T_i is the temperature at which the loss of weight of the sample begins (read off on the TG curve), T_p is the temperature of the peaks on the DTG and DTA curves, respectively.

The results following from Table 2 are:

a) Of the pair of isomers of $Ni(NCS)_2O_2$ in the solid state, the square-planar isomer (I) is thermodynamically more stable; this result is in accordance with the thermochemical results obtained in solution [13].

Table 2

Thermochemical data of the thermal decomposition of complexes of the type $Ni(NCS)_2L_2$

$Ni(NCS)_2L_2$	Geometrical configuration	TG T_i, °K	DTG T_p, °K	DTA T_p, °K	$\Delta H_{(1)}$ kcal · mole^{-1}
$Ni(NCS)_2py_2$	Pseudo-	450	532	534	31.60*
$Ni(NCS)_2(\beta\text{-pic})_2$	octahedral	412	478, 515	480, 518	29.30
$Ni(NCS)_2Q_2$ (II)		390	460	462	27.80
$Ni(NCS)_2(\alpha\text{-pic})_2$	Square-	360	438	438	24.40
$Ni(NCS)_2Q_2$ (I)	planar	405	462, 497	458, 496	28.50
$Ni(NCS)_2(2,6\text{-lut})_2$		412	472	473	30.15

* Kauffman and Beech [10] have found a higher value of $\Delta H_{(1)}$ for $Ni(NCS)_2py_2$.

b) On the basis of the obtained values the following order of stability may be established:

i) for pseudooctahedral complexes:

$Ni(NCS)_2py_2 > Ni(NCS)_2(\beta\text{-pic})_2 > Ni(NCS)_2Q_2$ (II), and

ii) for square-planar complexes:

$Ni(NCS)_2(\alpha\text{-pic})_2 < Ni(NCS)_2Q_2$ (I) $< Ni(NCS)_2(2,6\text{-lut})_2$.

Several authors have studied the thermal stabilities of nickel(II) complexes by means of the decomposition temperatures, i.e. the temperatures at the beginning of loss of weight of the sample [14], though it is known that the decomposition temperatures do not represent established physical parameters for a given compound [15]. Others apply the temperatures of the maximum deviations on the DTG [3] or DTA [1] curves. Another difficulty arises, however, in that the processes to be compared may be of one-step or multi-step character. For example $Ni(NCS)_2L_2$ (where L = β-pic or Q) (isomer I) decomposes in two steps, and it is not clear which temperature should be taken into consideration: that of the liberation of the first or that of the second molecule of L. The most correct temperature appears to be that corresponding to the release of one half of the first molecule. These problems are eliminated if the values of $\Delta H_{(1)}$ used cover the release of 2L, irrespective of the number of steps in the process.

The comparison of the values of $\Delta H_{(1)}$ with those of T_i (from the TG curve) for pseudooctahedral complexes shows that with decreasing value of $\Delta H_{(1)}$ the decomposition temperature also decreases. Equally for square-planar complex some mutual correlation of these values may be observed. The value of T_p from the DTG and DTA curves cannot be correlated with those of $\Delta H_{(1)}$ just because of the multi-step character of the process.

The temperature changes of $\Delta H_{(1)}$ on the release of 2L from complexes of the type $Ni(NCS)_2L_2$ are – except for L = α-picoline – apparently constant in the range 28 – 32 kcal · mole^{-1} (Table 2), in spite of different structure changes. This is in agreement with the respective complexes of $NiCl_2L_2$ [7], but in contrast with the chloride complexes of cobalt(II) with the same volatile ligands [5].

The low value of $\Delta H_{(1)}$ for L = α-picoline compared with the other ligands is probably due to the steric influence of the methyl group in α-picoline. Very low values of decomposition heats have also been found for the complexes $M(II)Cl_2 \cdot (\alpha\text{-pic})_2$, with M = Co or Ni, and were interpreted in the same way [5, 7].

The strengths of the M–L σ-bonds influencing the values of $\Delta H_{(1)}$ are related to the values of pK_a in the nitrogen bases: pyridine 5.22; β-picoline 5.63; quinoline 4.85 [5, 16]. These values appear to indicate that β-picoline forms a stronger bond and quinoline a weaker one than pyridine. The decomposition heat found for $Ni(NCS)_2(\beta\text{-pic})_2$, however, shows the contrary to be true. This is explained [17–19, 22] by the different charge density and charge distribution in the pyridine ring. For these ligands the dative π-bond Ni → L was also taken into account, mainly for the 2, 4, and 6 positions. These are the positions of excess charge in β-picoline (due to the directing influence of the methyl group). The dative π-bond will be impeded in complexes with this ligand compared with pyridine, i.e. the overlapping of the $d_\pi - p_\pi$ orbitals will be lower and the decrease of $\Delta H_{(1)}$ probably follows from this. This explanation, however, cannot be taken as definite, since $\Delta H_{(2)}$ in the gaseous state is not an unambiguous criterion of the M–L bond strength, as in the course of the decomposition of the complex reorganization of its configuration also takes place. Thus $\Delta H_{(2)}$ is the total reaction heat of both the simultaneous partial reactions. $\Delta H_{(1)}$ is therefore only a rough approximation characterizing the bond strength, but provides valuable information on the controlling process and the step-wise nature of the processes, together with the values of the activation energies. Study of the kinetics of thermal decomposition of complexes of the type $Ni(NCS)_2L_2$ will be the subject of further investigation.

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Résumé — Détermination par analyse enthalpique différentielle des chaleurs de décomposition (ΔH) des complexes de formule générale $Ni(SCN)_2L_2$. Le classement des valeurs de ΔH par ordre décroissant montre que pour les complexes pseudo-octaédriques py > β-pic > Q et que pour les complexes plans carrés lut-2,6 > Q > α-pic. Comparaison de ces résultats avec les données des courbes TG, TGD et ATD.

Zusammenfassung — Es erfolgte die Bestimmung der Zersetzungswärmen (ΔH) der Komplexe vom Typ $Ni(NCS)_2L_2$ durch die Differential Scanning Calorimetrie. Mit abnehmenden ΔH Werten ergab sich die Reihenfolge: *a)* Pseudooktaedrische Komplexe: Py > β-Pic > Q; *b)* Quadratische Komplexe: 2,6-Lut. > Q > α-Pic. Ergebnisse mit aus den DTA, TG und DTG-Kurven gewonnenen Resultaten wurden verglichen.

Резюме. — С помощью сканнирующего калориметра изучена теплота распада (ΔH) для комплексов типа $Ni(NCS)_2L_2$. В ряду уменьшающих величин ΔH найден следующий порядок: а) для псевдооктаэдрических комплексов py > β-pic > Q; и б) для планарных комплексов 2,6 lut > Q > α-pic. Полученные результаты сравнены с данными, полученными исходя из кривых ТГ, ДТГ и ДТА.