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

IV. Stoichiometry of thermal decomposition, thermal stability and stereochemistry of complexes

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Abstract

The stoichiometry of thermal decomposition and the relationship between the thermal parameters (quasi-equilibrium decomposition temperatures T_D and decomposition entalpies ΔH_D) of $NiL_4(NCS)_2$ complexes (L= imidazole derivatives) were studied. It was found that changes in the experimental conditions strongly influence the decomposition stoichiometry. The T_D and ΔH_D can be ordered in the following sequence (according to L): imidazole<2-Me imidazole<2-Et imidazole<1-Me imidazole.

Keywords: Ni(II) imidazole complexes, quasi-equilibrium conditions, thermal decomposition, thermal stability, stereochemistry of complexes

Introduction

Relatively few papers have appeared in the literature about thermal investigations of imidazole complexes of transition metals [1–4], although the bond between imidazole ligands and metal ions is of great biological importance. Many metalloproteins contain metal ions coordinated by the imidazole side-chain of histidine.

This study can be considered as an extension of earlier works [5, 6] on the system Ni–heterocyclic N-donor ligands. Nickel(II) thiocyanate compounds were selected because they can be prepared in the pure form in high yields and occur as well-defined species [7]. In this paper we have studied the thermal

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properties (stoichiometry and heat of thermal decomposition) and stereochemistry of compounds $NiL_4(NCS)_2$, L= imidazole (Iz), 1-methyl (N-methyl)imidazole (1-MeIz), 2-methylimidazole (2-MeIz) and 2-ethylimidazole (2-EtIz).

Experimental

All $NiL_4(NCS)_2$ complexes were prepared as described earlier [7]. The $Ni(1\text{-MeIz})_2(NCS)_2$ complex was prepared by the isothermal heating of the starting complex (n= 4) (finely ground complex packed in a thin layer) at ≈170°C. The thermoanalytical curves were recorded with a Paulik-Paulik-Erdey model MOM derivatograph in air using a standard platinum crucible and a platinum multiplate sample holder.

A Q-derivatograph was used to study the decomposition process under quasi-isobaric and quasi-isothermal conditions. This experimental technique results in stabilization of the decomposition temperature, i.e. the experimental proceeds under quasi-isothermal conditions [8]. Using various sample holder types, it is possible to keep the pressure of the gaseous products almost constant (conical crucible ≈90 kPa).

To study the heats of decomposition reactions a Perkin-Elmer Differential Scanning Calorimeter DSC-7 working on the principle of zero-balance powder compensation was used (sample weight 7–8 mg, pure N_2 gas, scanning rate 10 deg·min^{-1}). Calibration of the temperature axis and enthalpy change was made using pure indium (melting point 156.6°C and enthalpy of fusion ΔH_f= 28.47 J/g).

Results and discussion

Stoichiometry of thermal decomposition

Literature data show [5] that complexes of the type NiL_4X_2 (L= volatile monodentate ligand, X= anionic ligand) can exhibit rather different decomposition stoichiometries. Though the experimental conditions do not differ considerably, the results obtained by the various authors are different. These different results gave us the impulse to carry out a complex study of the stoichiometry of the thermal decomposition of $NiL_4(NCS)_2$ complexes (L= imidazole derivatives) under three sets of experimental conditions (Table 1):

A. Quasi-isobaric and quasi isothermal conditions: a Q-derivatograph with a conical crucible was used (sample weight 200 mg, static atmosphere).

B. Non-equilibrium (dynamic) conditions: a derivatograph with a standard crucible (with an upper diameter of 14 mm) was used (sample weight 100 mg, rate of temperature increase 5 deg·min^{-1}, static atmosphere).

C. Non-equilibrium (dynamic) conditions: a derivatograph with a multiplate sample holder was used (sample weight 100 mg, rate of temperature increase 5 deg·min^{-1}, static atmosphere).

Table 1 Thermal analysis data for thiocyanate Ni(II) complexes with imidazole derivatives

Starting complex	Crucible	Q–TG			TG			DTG	Species formed
		T_D / °C	loss / %		T_{range} / °C	loss / %		T_P /°C	
			obs.	calc.		obs.	calc.		
$Ni(Iz)_4(NCS)_2$	conical	285	59.0	60.88					$Ni(NCS)_2$
(I)	standard				150–390	59.0	60.88	320	$Ni(NCS)_2$
	polyplate				120–230	30.0	30.44	210	$Ni(Iz)_2(NCS)_2$
					230–340	60.0	60.89	250	$Ni(NCS)_2$
$Ni(2\text{-}MeIz)_4(NCS)_2$	conical	290	64.0	65.2					$Ni(NCS)_2$
(II)	standard				190–350	63.0	65.2	250(sh)	$Ni(NCS)_2$
								320	
	polyplate				140–240	32.0	32.6	220	$Ni(2\text{-}MeIz)_2(NCS)_2$
					240–340	65.0	65.2	260	$Ni(NCS)_2$
$Ni(2\text{-}EtIz)_4(NCS)_2$	conical	290	68.0	68.7					$Ni(NCS)_2$
(III)	standard				190–350	67.0	68.8	320	$Ni(NCS)_2$
	polyplate				140–240	34.0	34.4	220	$Ni(2\text{-}EtIz)_2(NCS)_2$
					240–340	68.5	68.8	260	$Ni(NCS)_2$
$Ni(1\text{-}MeIz)_4(NCS)_2$	conical	295	63.0	65.2					$Ni(NCS)_2$
(IV)	standard				170–370	65.0	65.2	230(sh)	$Ni(NCS)_2$
								310	
	polyplate				130–220	30.0	32.6	195	$Ni(1\text{-}MeIz)_2(NCS)_2$
					220–270	47.5	48.9	240	$Ni(1\text{-}MeIz)_1(NCS)_2$
					270–340	65.0	65.2	290	$Ni(NCS)_2$

For the determination of the stoichiometries of the thermal decompositions of the complexes studied in this work we started from the inflection points in the TG and DTG curves. The experimental data indicated (Figs 1 and 2, Table 1) three different instrumental stoichiometries:

$$\mathrm{NiL_4(NCS)_2(s)} \xrightarrow[1]{-4L(g)} \mathrm{Ni(NCS)_2(s)} \tag{1}$$

(Experimental conditions: A and B, L=all derivatives)

$$\mathrm{NiL_4(NCS)_2(s)} \xrightarrow[1]{-2L(g)} \mathrm{NiL_2(NCS)_2(s)} \xrightarrow[2]{-2L} \mathrm{Ni(NCS)_2} \tag{2}$$

(Experimental conditions: C, L=Iz, 2-MeIz, 2-EtIz)

$$\mathrm{NiL_4(NCS)_2(s)} \xrightarrow[1]{-2L(g)} \mathrm{NiL_2(NCS)_2(s)} \xrightarrow[2]{-2L(g)} \mathrm{NiL(NCS)_2} \xrightarrow[3]{-L(g)}$$

$$\xrightarrow[3]{-L(g)} \mathrm{Ni(NCS)_2} \tag{3}$$

(Experimental conditions: C, L= 1-MeIz)

Though the thermal decompositions of solid complexes of the type $\mathrm{NiL_4X_2}$ with monodentate nitrogen ligands are stepwise processes, e.g. for the $\mathrm{Ni(4\text{-}Mepy)_4(NCS)_2}$ complex (–1, –1, –1, –1) [9], it is not always possible to identify all the expected intermediates. It is possible that some of the intermediates are not observed because they are unstable under the given conditions of the thermal process, since the partial pressure of the ligand in the gaseous phase is not suitable. A larger sample and quasi-equilibrium conditions are favourable for a higher partial pressure of the ligand in the gaseous phase and this can result in the formation of certain intermediates [10]. The absence of the intermediates $\mathrm{NiL_n(NCS)_2}$ (n<4) in cases A and B is obviously not caused by thermodynamic factors only. An important part may also be played by the formation kinetics of the intermediates: it may be influenced by the rate of decomposition and the temperature at which the initial complex decomposes. Under dynamic conditions of thermal decomposition only a small amount of the intermediate can arise (the reaction products start to decompose before their formation is complete [2]), so that it is not clearly shown up in the TG curve. It may be identified, however, by reducing the diffusion hindrances (using a multiplate sample holder and experimental conditions C, Table 1).

Thermal (thermodynamic) stability

The Q-TG curves (Fig. 3), which were traced under quasi-isothermal and quasi-isobaric conditions provide comprehensive information about the reaction

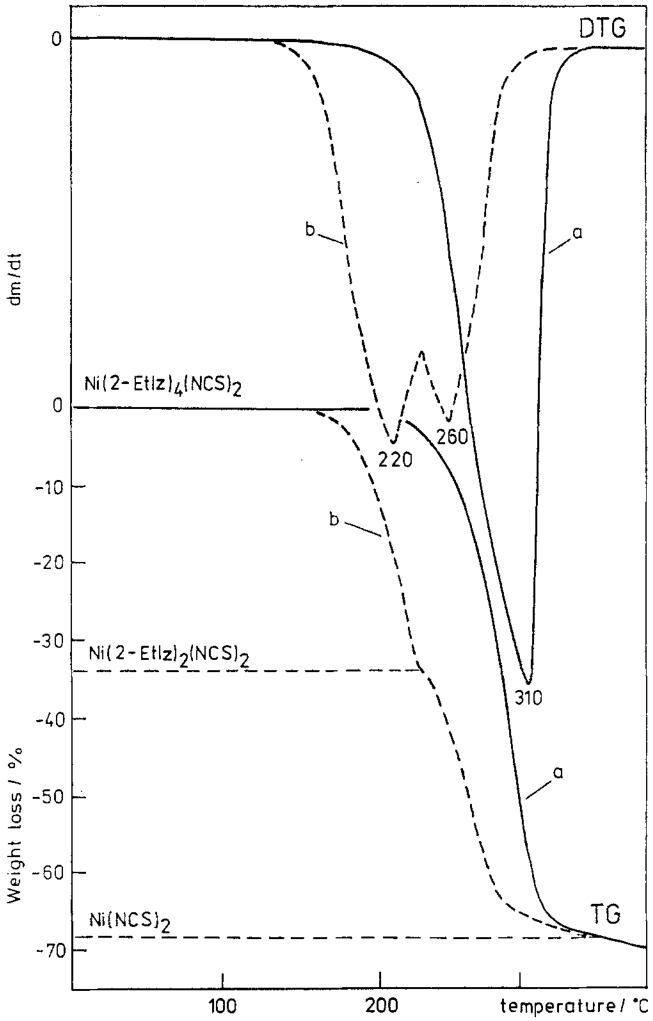

Fig. 1 TG and DTG curves of $Ni(2\text{-}EtIz)_4(NCS)_2$: a – standard crucible, b – multiplate sample holder

stoichiometry as well as the decomposition temperatures [8]. The data listed in Table 1 show that under the conditions used the complexes studied decompose according to Eq. 1. The decomposition temperatures derived from the quasi–isothermal measurements can be used to set up a qualitative sequence of the thermodynamic stabilities of the compounds in identical thermal decomposition reactions [11]. According to the quasi-equilibrium decomposition temperatures T_D (Table 1), the thermodynamic stability of $NiL_4(NCS)_2$ complexes increases in the following order (according to L):

$$\text{Iz} < \text{2–MeIz} \approx \text{2–EtIz} < \text{1–MeIz} \quad (4)$$

To investigate the bond strengths, it would be correct to consider the dissociation heats in the gaseous state

$$ML_nX_2(g) \xrightarrow{\Delta T} MX_2(g) + nL(g) \tag{5}$$

$$\Delta H(5) = \Delta H(1) - \Delta H\,\text{subl.}\,\{ML_nX_2\} + \Delta H\,\text{subl.}\,\{MX_2\} \tag{6}$$

As the sublimation heats of the studied complexes are not known, Beech *et al.* [12] supposed, for simplification, that the differences between the sublima-

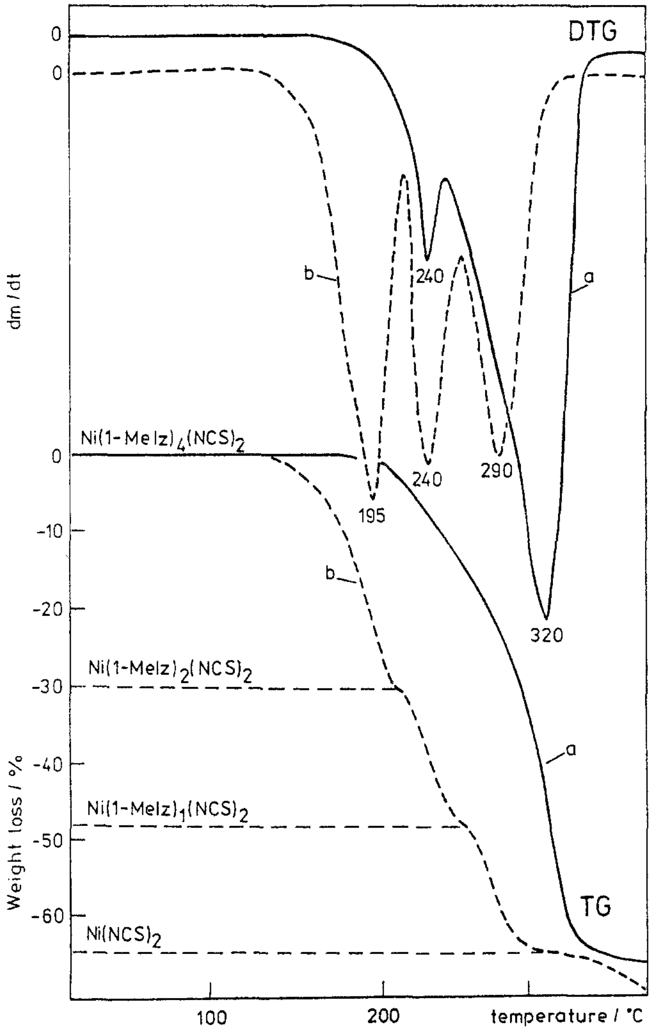

Fig. 2 TG and DTG curves of Ni(1-MeIz)$_4$(NCS)$_2$: a – standard crucible, b – multiplate sample holder

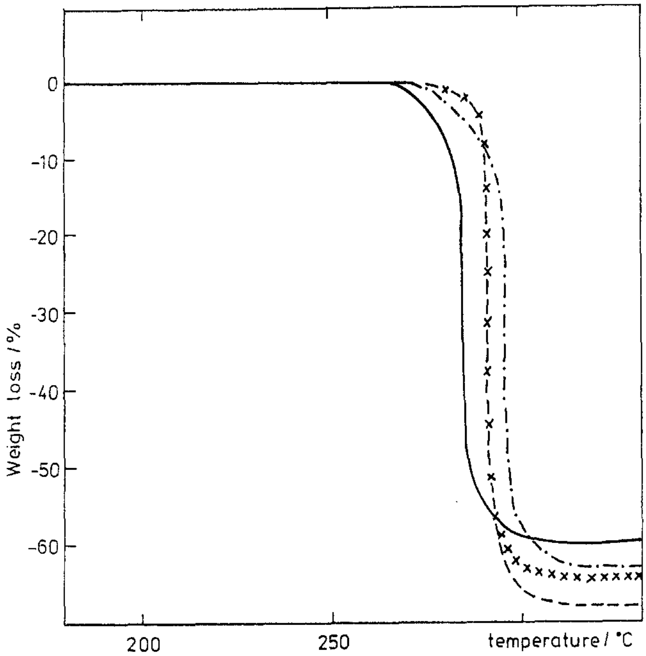

Fig. 3 Q-TG curves of $NiL_4(NCS)_2$ complexes: L= Iz —, 2-MeIz xxx, 2-EtIz - - - , 1-MeIz – · –

Table 2 The DSC data of $NiL_4(NCS)_2$ complexes

Parameter	L			
	Iz	2-MeIz	2-EtIz	1-MeIz
Temperature interval/ °C	211.3–238.8	231.0–257.7	224.1–257.3	183.5–245.1
T_{max} / °C	233.8	255.0	254.1	214.3, 228.8, 236.7
ΔH_D/ kJ·mol^{-1}	54±1	62±1	83±2	91±2

tion heats of MX_2 and ML_nX_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 values of $\Delta H(1)$ as characteristic of the M–L bond strength [12]. Variations in the values of $\Delta H(1)$ for the studied complexes with different L may, however, be attributed not only to changes in the M–L bond strength, but also to hydrogen bonds in this systems [4], recrystallization pro-cesses and further effects in the solid state. According to the overall decom-

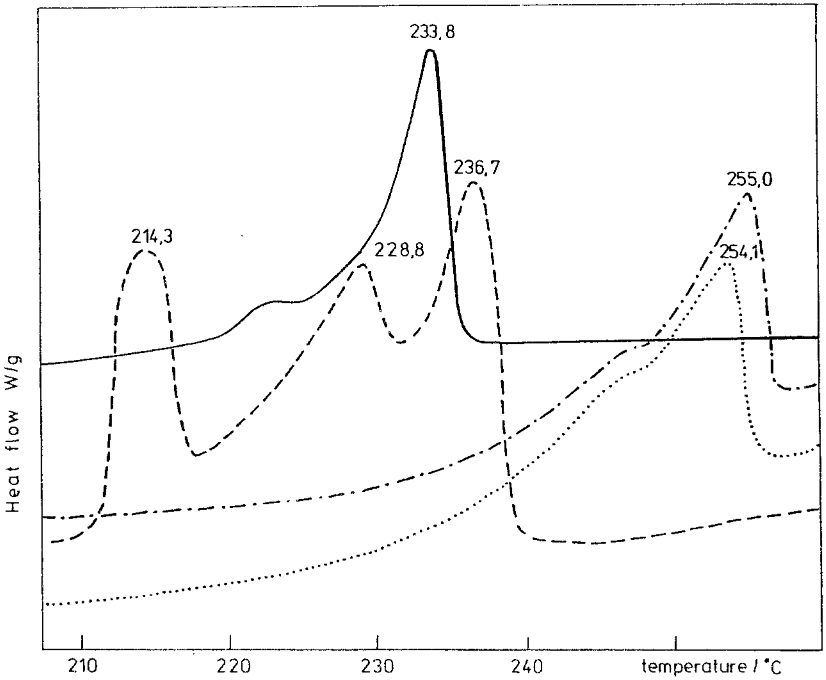

Fig. 4 DSC curves of $NiL_4(NCS)_2$ complexes: — L= Iz, - - - L= 1-MeIz, – · – · – , L= 2-MeIz, · · · · L=2-EtIz

position enthalpies $\Delta H(1)$ (–4L) (Table 2 and Fig. 4), the thermodynamic stabilities of $NiL_4(NCS)_2$ complexes can be ordered in the following sequence:

$$\text{Iz} < \text{2–MeIz} < \text{2–EtIz} < \text{1–MeIz} \qquad (7)$$

This is in agreement with the sequence of the thermodynamic stabilities on the basis of the quasi-equilibrium decomposition temperatures. The highest value of $\Delta H(1)$ for L=1-MeIz compared with other ligands is probably due to the absence of hydrogen bridges. The hydrogen – bonding decreases the decomposition enthalpy for imidazole compounds [4].

Stereochemistry of the studied complexes

The values of the magnetic moments μ_{eff} (B.M.) and the positions of the maxima of the absorption bands in the electronic and IR spectra (ν(CN) and ν(CS)) of the studied complexes are given in Table 3.

All the complexes have an effective magnetic moment in the interval given for hexacoordinated octahedral complexes [13]. The electronic spectra of these complexes in the region 8 000 to 30 000 cm^{-1} contain three broad bands. The

Table 3 Magnetic and spectral properties of $NiL_n(NCS)_2$ complexes

Compound	μ_{eff}	Electronic spectra			Infrared spectra/ cm^{-1}	
	B.M.	$\nu \times 10^{-3}/cm^{-1}$			ν(CN)	ν(CS)
I	3.25	10.5	17.3	27.4	2100s	775m
		8.3(sh)	13.2(sh)		2107s	
II	3.18	10.1	16.8	27.0	2110s	774m
		8.3(sh)	13.2(sh)			
III	3.26	10.3	16.9	30.0	2100vs	790m
		8.3(sh)	13.2(sh)		2133s	
IV	3.15	10.4	17.3	28.4	2092vs	750m
		8.3(sh)	13.4(sh)			757m
V	3.22	9.7	15.7	28.0	2110s	770m
		8.2(sh)			2143s	

first and second bands exhibit pronounced splitting which is more expressed for $NiL_4(NCS)_2$ complexes. The number of bands, their widths and the positions of the absorption maxima on these bands indicate pseudooctahedral configuration of the ligands around Ni(II). The two complex absorption bands can be assigned to the transition $^3B_{1g} \rightarrow {}^3B_{2g}$ and $^3B_{1g} \rightarrow {}^3E_g^a(F)$, or $^3B_{1g} \rightarrow {}^3E_g^b(F)$ and $^3B_{1g} \rightarrow {}^3A_{2g}(F)$ in a weak tetragonal field of D_{4h} symmetry. This is in agreement with the results of the X-ray structure analysis of the $Ni(Iz)_4(NCS)_2$ complex [14]. The equatorial plane of this complex is formed by four N atoms from the imidazole molecules and the axial positions are occupied by two N atoms from the NCS groups. This seems to be in contradiction with the two bands ν(CN) in the IR spectra of complexes I and III. This case has been observed more frequently and can be caused [15] by a deviation of end – bonded NCS groups from linearity or by lattice interactions in the solid state. In the case of complex V, however, the bands at about 2 143 and 2 110 cm^{-1} very probably correspond to the tridentate and monodentate NCS groups (Table 3). Similar splitting of the ν(CN) bands in the IR spectra is observed in the spectrum of the pseudooctahedral complex Ni (quinoline)$_2$(NCS)$_2$ [16].

Conclusions

The present study has shown that changes in experimental conditions strongly influence the stoichiometry of the thermal decompositions of $NiL_n(NCS)_2$ complexes (L= imidazole derivatives). It is not possible to prepare defined intermediates by heating the starting solid complexes with the exception of 1-MeIz complexes. All the studied complexes show pseudooctahedral configurations of the ligands around the Ni(II). The quasi-equilibrium decomposition temperature and the decomposition enthalpy of the 1-MeIz compound are higher than those observed for other complexes under study, probably due to the absence of hydrogen bridges.

References

1 P. S. Gomm, E. A. Underhill and W. A. Oliver, J. Inorg. Nucl. Chem., 34 (1972) 1879.
2 J. C. Van Dam, G. Hakvoort, J. C. Jansen and J. Reedijk, J. C. Jansen and J. Reedijk, J. Inorg. Nucl. Chem., 37 (1975) 713.
3 C. Dash and P. Pujari, J. Inorg. Nucl. Chem., 40 (1978) 1173.
4 J. C. Van Dam, G. Hakvoort and J. Reedijk, J. Thermal, Anal., 20 (1981) 3.
5 E. Jóna, T. Šramko and J. Gazo, J. Thermal Anal., 16 (1979) 213.
6 E. Jóna, J. Thermal Anal., 34 (1988) 1053.
7 A. Mašlejová and J. Kováčik, Z. Anorg. Allg. Chem., 604 (1991) 151.
8 F. Paulik and J. Paulik, Thermochim. Acta, 100 (1986) 23.
9 E. Jóna, I. Horváth and M. Kubranová, Thermochim. Acta, 221 (1993) 41.
10 E. Jóna, I. Horváth, M. Kubranová and M. Koman, Thermochim. Acta, 180 (1991) 307.
11 V. A. Logvinenko, Thermal Analysis of Coordination Compounds and Clathrates (in Russian), Nauka, Novosibirsk, 1982.
12 G. Beech, C. T. Mortimer and E. G. Tyler, J. Chem. Soc. (A) 1967, 925; 1969, 512.
13 E. Jóna and M. Koman, J. Thermal Anal., 34 (1988) 657.
14 M. Koman, E. Jóna and A. Mašlejová, Acta Cryst., C47 (1991) 1206.
15 R. A. Bailey, S. L. Kozak, T. W. Michelsen and W. N. Mils, Coord. Chem. Rev., 6 (1971) 407.
16 E. Jóna, T. Šramko, J. Kohout, A. Sirota and J. Gazo, Chem. Zvesti, 25 (1971) 241.