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THERMAL ANALYSIS OF Ni(II) N-METHYLIMIDAZOLE COMPOUNDS

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In this study the thermal decomposition of compounds with the formula $Ni(NMIz)_nX_2$ ($NMIz$ = *N*-methylimidazole, $n = 6$, 4, 2 or 1 and X = Cl, Br or I) has been investigated with the aid of differential scanning calorimetry (DSC), thermogravimetry (TG), evolved gas analysis (EGA) and X-ray powder diffraction in the temperature region 20—500°. The reaction steps were obtained with TG. The intermediate products of the reactions were also confirmed by high-temperature Guinier-de Wolff X-ray photographs.

The decomposition enthalpies were calculated from differential scanning calorimetry analysis. The enthalpies were compared with the data from a previous study of the imidazole compounds in order to get more information about the hydrogen bonding in the imidazole compounds. The hydrogen-bonding is stronger for smaller anions and decreases the decomposition enthalpy for imidazole compounds. The decomposition enthalpy of *N*-methylimidazole compounds is hardly influenced by the anion size.

In nature the linkage between imidazole ligands and transition-metal ions is of great importance, since many metalloproteins contain metal ions coordinated by the imidazole side-chain of histidine. This type of interaction occurs especially with Zn(II), Fe(II), Fe(III), Cu(I) and Cu(II) [1, 2].

During the last decade a large number of model coordination compounds containing imidazoles and substituted imidazole ligands have been investigated, both spectroscopically and magnetically [3, 4], and also by X-ray analyses [4—9].

However, the number of thermochemical analyses on these compounds has been limited so far. Only recently have studies been reported for Co, Ni [10—13] and Pd [14]. This study can be considered as an extension of earlier work on the system Ni-imidazole [11, 13]. Nickel(II) compounds were selected because they can be prepared pure in high yields and occur as well-defined species. Moreover, Ni(II) is not very sensitive for redox reactions. Related work in our laboratory has shown that in the case of copper compounds redox reactions interfere strongly with ligand dissociation reactions, making study very difficult [15].

We have selected N-methylimidazole for the present study. In natural systems the imidazole ligand not only acts as a base, by using its sigma free-electron pair (to accept protons or metal ions), but can also act as a hydrogen-bond donor to

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other bases. This phenomenon is known to be responsible for the stability of many systems, but also for many catalytic reactions.

By comparing the thermal analytical results for a group of similar imidazole and *N*-methylimidazole compounds, we hope to be able to separate the hydrogen-bond effects from the coordination effects.

Experimental

Compounds with the general formula $NiL_nX_2(H_2O)_x$ (L = *N*-methylimidazole and X = Cl, Br and I) were prepared as described elsewhere [16], except NiL_2Cl_2, which was prepared by heating $NiL_2Cl_2(H_2O)_2$ up to 140°. The compounds were characterized by chemical nickel analysis, UV, VIS, IR and FIR spectroscopy and X-ray analysis.

Differential scanning calorimetry

The 910 Differential Scanning Calorimeter (DSC) of Du Pont Instruments was used. The instrument was calibrated with indium during or after each series of measurements of one compound. The samples, with a weight of about 4 mg, were heated in aluminium sample cups at a heating rate of 5°/min in a high-purity nitrogen stream (20 ml/min) which contained less than 2 ppm oxygen [11].

Heats of reaction were obtained with the relation $Q = K\int \Delta T\,dt = KA$, in which Q = the heat of the reaction in mJ, K = a constant expressed in mJ/inch^2, which depends on the recorder sensitivity, and A = the peak area expressed in inch^2.

Thermogravimetric analysis

A symmetrical thermobalance [11] was used under the same experimental conditions as for the DSC experiments and with the same sample cups. This instrument was used for accurate determination of the weight losses of the reaction steps.

Thermogravimetric analysis/Differential thermal analysis/Evolved gas analysis

A TG/DTA apparatus from Sartorius-Werke GMBH and a Topatron B from Leybold-Heraeus were used for simultaneous analysis of the weight loss, the heat changes and the composition of the evolved gases during the thermal decomposition.

The samples, weighing about 5 mg, were heated in a helium stream (20 ml/min) at a heating rate of 6°/min. At least one scan of the mass spectrum was made every three minutes.

High-temperature Guinier-de Wolff photographs

The diffraction patterns were obtained using a standard high-temperature Guinier-de Wolff camera with Cu-Kα radiation. The samples were heated at a heating rate of 0.5°/min in a nitrogen stream. The line patterns obtained as a function of the temperature were compared with known patterns of pure compounds of NiL_nX_2 and NiX_2.

Results

Figures 1–4 represent, respectively, the TG and DSC decompositions of the following compounds: $NiL_6Cl_2(H_2O)_2$, $NiL_6Br_2(H_2O)_2$, $NiL_2Cl_2(H_2O)_2$ and NiL_2Br_2 (L = NMIz = N-methylimidazole). These Figures show some of the most characteristic decomposition curves. In the DSC decomposition curve of $NiL_6Br_2(H_2O)_2$ (Fig. 2), it is impossible to draw a base-line, because the decomposition reaction starts already at room temperature. During the heating of the samples, the compounds decompose in several steps, which were calculated from TG analyses and were observed via high-temperature X-ray analyses. Table 1 represents these steps. In Table 2 the decomposition steps (column 2), which are (almost) completely separated from each other, are listed. For each of these steps Table 2 gives the temperature region (column 4), the calculated and experimentally determined weight loss percentages (columns 6 and 7) and the decomposition enthalpy per mol ligand L, ΔH_L (last column). Column 3 gives the sample size relating to the temperature region. The number of samples (columns 5 and 8) is the number of experiments for which the experimental weight loss percentage, the decomposition enthalpy and their standard deviations in parentheses are calculated.

The decomposition reactions can be interpreted using the following general reaction equations (s = solid, g = gas):

$$NiL_nX_2(H_2O)_x(s) \rightarrow NiL_nX_2(s) + xH_2O(g) \tag{1}$$

$$NiL_nX_2(H_2O)_x(s) \rightarrow NiL_{n-p}X_2(s) + pL(g) + xH_2O(g) \tag{2}$$

$$NiL_nX_2(s) \rightarrow NiL_{n-p}X_2(s) + pL(g) \tag{3}$$

Table 1

Decomposition scheme of nickel(II) N-methylimidazole halogenides

Complex	Number of ligands L*					
	6 L	4 L	2 L	1 L	2/3 L	0 L
$NiL_6Cl_2(H_2O)_2$		+	+	+	+	+
NiL_4Cl_2			+	+	+	+
$NiL_2Cl_2(H_2O)_2$			+	+	+	+
$NiLCl_2$					+	+
$NiL_6Br_2(H_2O)_2$	+		+	+	+	+
NiL_2Br_2				+	+	+
$NiLBr_2$					+	+
NiL_6I_2			+			+

* + means that this stoichiometry has been determined.

In the first reaction (1), the decomposition enthalpy is calculated per mol H_2O, so $\Delta H_L = \Delta H_{H_2O} = \Delta H/x$.

The enthalpy of reaction (2) is listed in Table 2 as enthalpy per x mol H_2O + p mol L, $\Delta H_L = \Delta H$.

The reaction enthalpy of reaction (3) is calculated per mol L, so $\Delta H_L = \Delta H/p$.

Table 2

The decomposition temperatures, percentages and enthalpies of separated or almost separated decomposition steps in compounds $NiL_nX_2(H_2O)_x$

Compound	Step	Sample size, mg	Temp. region, °C	TG			DSC	
				number of samples	weight loss		number of samples	ΔH_L + kJ/mol L
					calc., %	exp. %		
$NiL_6Cl_2(H_2O)_2$	$6L(H_2O)_2 \rightarrow 4L$	4	70–165	4	30.4	30.2 (1.9)	5	256 (10)*
	$4L \rightarrow 1L$		165–250	5	37.4	37.2 (0.5)	6	89 (2)
	$1L \rightarrow O$		310–380	5	12.5	13.0 (0.8)	6	120 (3)
NiL_4Cl_2	$4L \rightarrow 1L$	4	105–260	3	53.8	53.4 (0.4)	4	91 (2)
	$1L \rightarrow O$		300–380	3	17.3	18.2 (0.1)	4	116 (4)
$NiL_2Cl_2(H_2O)_2$	$2L(H_2O)_2 \rightarrow 2L$	6	40–150	3	10.9	11.1 (0.3)	5	67 (1)**
	$2L \rightarrow 1L$		150–240	3	24.9	24.6 (0.1)	5	71 (1)
	$1L \rightarrow O$		260–385	3	24.9	24.9 (0.1)	5	126 (8)
$NiLCl_2$	$1L \rightarrow O$	6	280–390	3	38.8	38.4 (1.0)	5	117 (2)
$NiL_6Br_2(H_2O)_2$	$6L(H_2O)_2 \rightarrow 2L$	5	35–255	4	48.8	48.9 (0.3)	–	–
	$2L \rightarrow O$		255–360	4	22.0	21.7 (0.7)	–	–
NiL_2Br_2	$2L \rightarrow O$	3	160–380	2	42.9	42.6 (0.7)	5	97 (2)
	$2/3L \rightarrow O$		350–380	1	14.3	14.2	5	106 (4)
$NiLBr_2$	$1L \rightarrow O$	5	230–370	3	27.3	27.1 (0.1)	5	111 (3)
NiL_6I_2	$6L \rightarrow O$	2.5	130–350	3	61.8	63.1 (0.4)	4	100 (5)

* enthalpy per 2 mol H_2O + 2 mol L

** enthalpy per mol H_2O

\+ uncertainties are indicated in parentheses

Table 3

Melting points and melting enthalpies of NiL_nX_2 compounds

Compound	Temperature, °C	Number of samples	ΔH kJ/mol NiL_2X_2
NiL_4Cl_2	175	5	a
NiL_2Cl_2	200	3	21 (1)
NiL_2Br_2	190	5	26 (1)
NiL_2I_2	175	1	a
$NiLBr_2$	270	5	14 (1)

a: not determined

A few compounds show melting points. They are listed in Table 3. For some of these melting reactions the enthalpy has been calculated. Column 3 gives the number of experiments for which the melting enthalpy and its standard deviation are calculated.

The high-temperature X-ray photographs were used to compare the line patterns and relative intesities in order to get information about the starting compounds, intermediate products and residues. The following starting compounds have the same line patterns with the same relative intensities, and can therefore be considered to be X-ray isomorphous:

$NiL_6X_2(H_2O)_2$	X = Cl, Br
$NiL_2X_2(H_2O)_2$	X = Cl, Br
NiL_2X_2	X = Cl, Br, I
$NiLX_2$	X = Cl, Br
$NiL_{2/3}X_2$	X = Cl, Br.

Discussion

The intermediate and final decomposition products represented in Table 1 were deduced from TG analyses and high-temperature Guinier-de Wolff photographs. Owing to the different heating rates and the quite different geometries of the sample holders or cups in the two techniques, the decomposition reactions need not a priori be identical.

For example, when NiL_2Br_2 is heated in a closed cup with a small hole in the lid, $NiLBr_2$ is not found but $NiL_{2/3}Br_2$ is formed (Fig. 4). If NiL_2Br_2 is heated in an open cup at a low heating rate (<0.5°/min) the first decomposition product is $NiLBr_2$, while the next product is $NiBr_2$. These and other analyses clearly show that the temperature region, in which the decomposition reaction proceeds, depends strongly upon the experimental conditions.

From a comparison of the TG and the high-temperature X-ray results of the decomposition of $NiL_6Cl_2(H_2O)_2 \xrightarrow{1} NiL_4Cl_2 \xrightarrow{2} NiL_2Cl_2$ with each other, the following temperature regions were found:

step 1: 70–165° (TG) and 35–70° (X-ray)
step 2: 165–250° (TG) and 70–100° (X-ray).

Besides the geometrical conditions, the temperature region also varies with the sample size. The consequences are that listing of temperature regions is hardly useful if sample size, geometry of the sample cup and other experimental conditions are not presented too.

The high-temperature Guinier-de Wolff X-ray photographs of the decomposition products were compared with the X-ray photographs of the prepared intermediate compounds. They were the same, except for the decomposition products NiL_4Cl_2 and NiL_2Cl_2 obtained from $NiL_6Cl_2(H_2O)_2$. These products gave different line patterns compared with the prepared complexes NiL_6Cl_2 and NiL_2Cl_2. The origin for this is not clear. The high-temperature X-ray photograph of $NiL_6Br_2(H_2O)_2$ indicated that a decomposition product must exist between NiL_6Br_2 and NiL_2Br_2, but TG analysis under X-ray conditions and also DSC analysis gave no evidence for the existence of an intermediate compound, as suggested earlier [13].

The EGA of $NiL_6Cl_2(H_2O)_2$ indicated that this compound first loses part of the water, so that the compound is no longer stable and loses two ligands together with the rest of the water. The same decomposition was expected for $NiL_6Br_2(H_2O)_2$, but in this case EGA showed that this compound loses water in an almost completely separate step from the loss of ligand L. This denotes that NiL_6Cl_2 can not exist without water, whereas NiL_6Br_2 can. This is remarkable, because up to the present NiL_6Br_2 could only be prepared with some lattice water [16]. An EGA of NiL_6I_2 demonstrated that CH_3I was formed during the step $NiL_2I_2 \rightarrow NiI_2$. This product can only be formed by a reaction between L and iodine. It is not clear whether this reaction occurs during the decomposition of the solid, or in the gas phase, so that the influence upon the decomposition enthalpy is unknown. During the decomposition of $NiL_6Cl_2(H_2O)_2$ no halogenated organic products are formed; this was also checked with a sensitive high-resolution mass spectrometer [17].

The experimental weight losses in Table 2 are in good agreement with the calculated amounts, except for NiL_6I_2, because this compound looses iodine. It is seen from Table 2 that the standard deviation for the first step of $NiL_6Cl_2(H_2O)_2$ is higher than the other standard deviations. This is probably due to water losses during the evacuation of the sample compartment (to replace oxygen by nitrogen) and to difficulties in drawing the base-line (see Fig. 1).

When the decomposition enthalpies of the corresponding steps for the chlorides are compared with each other, they seem to be almost the same, except for the last step ($1L \rightarrow 0$) of the decomposition of $NiL_2Cl_2(H_2O)_2$. The value of this enthalpy is probably too high, due to difficulties in drawing the base-line (Fig. 3). Nevertheless, it is clear that the last ligand in the chloride and bromide compounds has a stronger binding energy than the other ligands, while the decomposition enthalpy of the step $NiL_2Cl_2 \rightarrow NiLCl_2$ is rather low compared with the other steps. This low enthalpy is affected by the change in coordination of the nickel ion. The compounds NiL_2X_2 (X = Cl, Br and I) have a tetrahedral nickel coordination [16], while the other complexes have an octahedral coordination. The influence of a change in coordination of the nickel ion on the decomposition enthalpy is also found in the first decomposition step of $NiL_2Cl_2(H_2O)_2$. The dehydration enthalpy per mol H_2O is rather high compared to the enthalpy of the corresponding imidazole compound [11].

During the dehydration the nickel coordination changes from octahedral to tetrahedral, while the octahedral nickel coordination of the corresponding imidazole compound does not change to another geometry [18].

The calculated decomposition enthalpies of the overall reaction $NiL_nX_2(s) \rightarrow$ $\rightarrow NiX_2(s) + nL(g)$ are listed in Table 4. Owing to the small differences in these

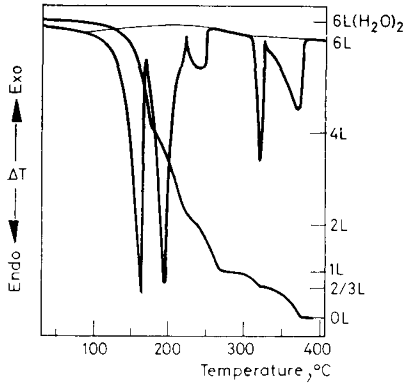

Fig. 1. DSC and TG curves of $[NiL_6Cl_2](H_2O)_2$

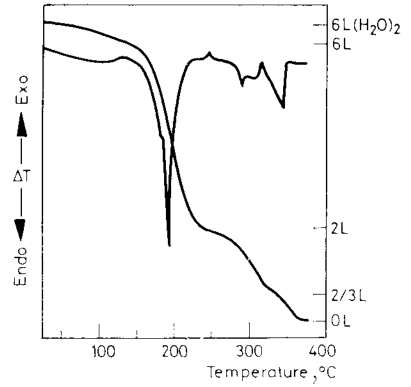

Fig. 2. DSC and TG curves of $[NiL_6Br_2](H_2O)_2$

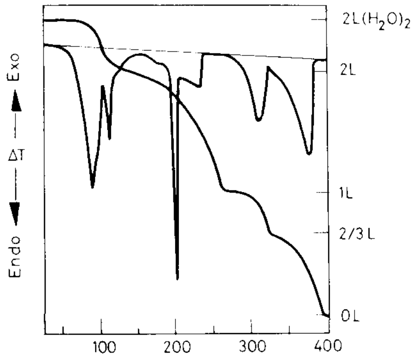

Fig. 3. DSC and TG curves of $NiL_2Cl_2(H_2O)_2$

Table 4

Enthalpies of the reaction $NiL_nX_2(s) \rightarrow NiX_2(s) + L(g)$ (s = solid, g = gas)

Anion	Number of evolved ligands n in kJ/mol L			
	6L	4L	2L	1L
Cl	$<90_+$	97	98	117
Br	—	—	97	111
I	100	—	—	—

$^+$ the H_2O binding is assumed to be 52 kJ/mol H_2O

values, it is clear that the influence of the anions on the binding enthalpies is small. The overall decomposition enthalpy of $NiL_6Cl_2(H_2O)_2$ is calculated and the sublimation enthalpy of two mol H_2O is subtracted to get the enthalpy for the hypothetic reaction $NiL_6Cl_2(s) \rightarrow NiCl_2(s) + 6\ L(g)$. The decomposition enthalpy for this reaction is small compared to the other values. This is most probably due to hydrogen-bonds between H_2O and Cl^-.

Now the results for the NMIz (= *N*-methylimidazole) compounds will be compared with the results for the *Iz* (= imidazole) compounds [11]. Tables 5 and 6 report the results of both investigations. In Table 5 compounds with the same number of ligands and different anions are listed. From this Table it is clear that the decomposition enthalpies of *Iz* compounds with the same number of ligands (= *L*) become smaller with anions with a smaller radius. The influence of the anion

Table 5

Comparison of *MNIz* and *Iz* compounds with the same number of ligands and different anions

Compound	ΔH_{Iz}, kJ/mol L	Nickel* coordination	ΔH_{NMIz}, kJ/mol L	Nickel** coordination
NiL_6Cl_2	103	oct	(90)$^+$	oct
NiL_6Br_2	111	oct	—	
NiL_6I_2	117	oct	100	oct
NiL_4Cl_2	102	oct	97	oct
NiL_4Br_2	118	sq	—	
NiL_4I_2	122	sq	—	
NiL_2Cl_2	104	oct	98	tetra
NiL_2Br_2	109	oct	97	tetra
$NiLCl_2$	109	oct	117	oct
$NiLBr_2$	119	oct	111	oct

* see ref. 18
** see ref. 16
$^+$ see Table 4
oct = octahedral, tetra = tetrahedral and sq = square planar

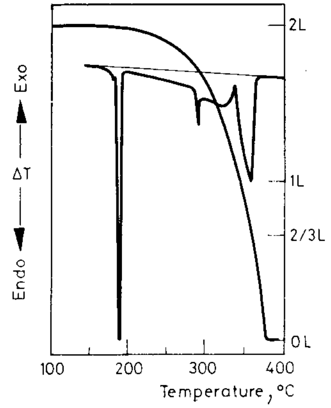

Fig. 4. DSC and TG curves of NiL_2Br_2

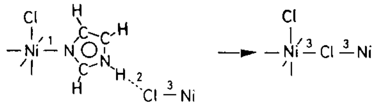

Fig. 5. Bonds in NiL_nX_2 before and after the decomposition to NiX_2

radius is not so clear in *NMIz* compounds, due to the small number of comparable values. Nevertheless, it seems that the anion influence is small. The $Ni(NMIz)X_2$ compounds even have a higher ΔH_L for smaller anions.

In order to get an impression of the influence of the anion size on the ΔH_L values, it is necessary to consider which lattice changes occur during the decomposition reactions. Figure 5 schematically shows the lattice changes during the decomposition of $NiL_nX_2 \rightarrow NiX_2$ ($n = 1, 2, 4$; in the case $n = 6$, no Ni−X bond is present).

Apart from the fact that existing bonds can be strengthened or weakened during thermal decomposition, the following bond changes and corresponding heat effects ΔH are expected to occur:

Ni−N	$+\Delta H_1$
N−H. . .X	$+\Delta H_2$
Ni−X	$-\Delta H_3$.

The overall ΔH_L value is composed of the following contributions:

$$\Delta H_L = \Delta H_1 + \Delta H_2 - \Delta H_3 \tag{4}$$

ΔH_1 is the enthalpy necessary for breaking down the Ni−N bonds between nickel and the imidazole ring, ΔH_2 is the enthalpy necessary for breaking down the hydrogen-bridges between Iz and the chloride ion, N−H−X, and ΔH_3 is the

Table 6

Comparison of *NMIz* and *Iz* compounds with the same anion and a different number of ligands *L*

Compound	ΔH_{Iz}, kJ/mol *L*	Nickel coordination	ΔH_{NMIz}, kJ/mol *L*	Nickel coordination
NiL_6Cl_2	103	oct	(90)$^+$	oct
NiL_4Cl_2	102	oct	97	oct
NiL_2Cl_2	104	oct	98	tetra
$NiLCl_2$	109	oct	117	oct
NiL_6Br_2	111	oct	—	
NiL_4Br_2	118	sq	—	
NiL_2Br_2	109	oct	97	tetra
$NiLBr_2$	119	oct	111	oct
NiL_6I_2	117	oct	100	oct
NiL_4I_2	122	sq	—	

$^+$ see Table 4
oct = octahedral, tetra = tetrahedral and sq = square planar

enthalpy released during the formation of Ni–X bonds and the contribution of a changing Ni–X distance (the values of ΔH_1, ΔH_2 and ΔH_3 are considered to be positive).

From ligand field spectra it is known that the crystal field energy (Dq) hardly varies when the anion size changes [18]. Thus, ΔH_1 is assumed to be almost constant for compounds with the same nickel coordination and different anions. It is also known that hydrogen-bridges are stronger for smaller anions, so that ΔH_2 becomes larger for smaller anions. The difference in sublimation energy between *Iz* and *NMIz* (*Iz*: $\Delta H_{subl} = 75$ kJ/mol and *NMIz*: $\Delta H_{subl} = 56$ kJ/mol) is 19 kJ/mol and gives an indication of the order of ΔH_2. The value of ΔH_3 is also influenced by the anion size, because the energy released in the formation of Ni–X bonds becomes larger for smaller anions. However, it should be realized that different lattices may occur for different anions. Now it is clear that the differences in the ΔH_2- values caused by the anion size are essentially due to variations in ΔH_2 and ΔH_{Iz}.The differences in ΔH_{Iz} for Cl and Br compounds with the same nickel coordination lie between -5 and -10 kJ/mol Iz. Due to the negative sign before ΔH_3 and to the fact that ΔH_{Iz} becomes smaller for smaller anions, it is evident that the influence of ΔH_3 is larger than the influence of the hydrogen-bridges, represented by ΔH_2.

For *NMIz* compounds Eq. (4) can be used too, but now $\Delta H_2 = 0$ owing to the absence of hydrogen-bridges. The differences in ΔH_{NMIz} for Cl and Br compounds with the same nickel coordination lie between $+1$ and $+6$ kJ/mol *NMIz*. These differences are opposite to the differences in the imidazole compounds and can be due to crystal lattice changes and to variations in the ΔH_1 values. One would expect that the presence of hydrogen-bridges would raise the decomposition energy, but the different crystal lattice appears to cause an opposite effect. Therefore, ΔH_L values for compounds with ligands having N–H groups cannot be compared in detail with values for compounds with ligands without N–H groups.

In Table 6 similar data as in Table 5 are listed, but now compounds with the same anions and different numbers of ligands are compared. From this Table it can be seen that the number of ligands does not influence the decomposition enthalpy much, except for the $NiLX_2$ compounds. The $NiLX_2$ compounds have larger decomposition enthalpies. This cannot be due to hydrogen-bridges, because *NMIz* cannot form these. The greatest difference with the other compounds is that the ligand is surrounded by a much larger number of anions.

Table 6 also shows the influence of the nickel coordination. In compounds with 6, 4 or 2 ligands *L*, the influence of a tetrahedral coordination compared to an octahedral coordination on the decomposition enthalpy seems to be small, while a square planar coordination compared to an octahedral coordination gives a higher decomposition enthalpy.

The overall decomposition enthalpy per mol ligand *L* is about the same for tetrahedral $Ni(NMIz)_2Cl_2$ and octahedral $Ni(NMIz)_4Cl_2$, but the decomposition enthalpies of the separated steps ($4L \rightarrow 1L$ and $2L \rightarrow 1L$) shows a significantly lower value for the tetrahedral compound (see Table 2).

During the decomposition step $4L \rightarrow 1L$ the nickel coordination remains octahedral, which means that three Ni–N bonds are replaced by three Ni–Cl bonds, but in the decomposition step $2L \rightarrow 1L$ the nickel coordination changes from tetrahedral to octahedral, so that one Ni–N bond is replaced by three Ni–Cl bonds, through which the value of ΔH for this decomposition step is strongly influenced. This effect is masked, however by the large value of the last decomposition step, $1L \rightarrow 0$, which averages out almost the same overall decomposition enthalpy for the two compounds.

Conclusions

The present study has shown that changes in nickel coordination during the decomposition reaction strongly influence the enthalpies of the separated steps, e.g. $Ni(NMIz)_2Cl_2$ (tetrahedral) → $Ni(NMIz)Cl_2$ (octahedral).

It is not possible to prepared $Ni(NMIz)_6Cl_2$ without lattice water. The water molecules are evidently needed for stabilization by forming hydrogen-bridges with the anions.

The decomposition enthalpies of Iz compounds become smaller with a smaller anion, due to hydrogen-bridges, while the decomposition enthalpies of the *NMIz* compounds are almost the same with changing anion radius.

The Ni–N binding in $Ni(NMIz)X_2$ compounds is stronger than in the corresponding Iz compounds, and probably all $Ni(NMIz)_nX_2$ compounds have stronger Ni–N bonds than the corresponding *Iz* compounds.

The number of ligands (*Iz* and *NMIz*) hardly influences the decomposition enthalpies, except in the case of the $NiLX_2$ compounds.

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RÉSUMÉ — La décomposition thermique des composés de formule Ni(NMIz)nX_2 (*NMIz* = *N*-méthyl-imidazole, *n* = 6, 4, 2 ou 1 et *X* = Cl, Br ou I) a été étudiée par analyse calorimétrique différentielle (DSC), thermogravimétrie (TG), analyse des gaz émis (AGE) et diffraction sur poudre des rayons X dans l'intervalle des températures comprises entre 20 et 500°.

Les étapes réactionnelles ont été suivies par TG. Les phases intermédiaires formées ont été déterminées par rayons X à hautes températures d'après la méthode de Guinier-de Wolff.

Les enthalpies de décomposition ont été calculées à partir des courbes DSC. On a comparé les valeurs ainsi trouvées à celles d'une étude préalable des composés de l'imidazole, afin d'obtenir plus d'informations sur les liaisons d'hydrogène dans les composés de l'imidazole. Les liaisons d'hydrogène sont plus fortes si les anions sont petits et diminuent l'enthalpie de décomposition des composés de l'imidazole. L'enthalpie de décomposition des composés du *N*-méthyl-imidazole n'est presque pas influencée par la taille de l'anion.

ZUZAMMENFASSUNG—In diesen Untersuchungen wird über die thermische Zersetzung von Verbindungen der Formel $Ni(NMIz)_nX_2$ (*NMIz* = *N*-methylimidazol, *n* = 6, 4, 2 oder 1 und *X* = Cl, Br oder I) mit Hilfe der Differential-Scanning-Kalorimetrie (DSC), der Thermogravimetrie (TG), der Analyse der entwickelten Gase (EGA) und der Röntgenpulverdiffraktion im Temperaturbereich von 20 bis 500° berichtet. Die Reaktionsstufen wurden durch TG erhalten. Die Zwischenprodukte der Reaktionen wurden durch Guinier-de Wolff-sche Hochtemperatur-Röntgenaufnahmen bestätigt.

Die Zersetzungsenthalpien wurden aus den Ergebnissen der Differential-Scanning-Kalorimetrie berechnet. Die Enthalpien wurden mit den Angaben aus einer vorangegangenen Untersuchung der Imidazolverbindungen verglichen, um mehr Informationen über die Wasserstoffbindungen in den Imidazolverbindungen zu erhalten. Die Wasserstoffbindung ist für kleinere Anionen stärker und setzt die Zersetzungsenthalpie der Imidazolverbindungen herab. Die Zersetzungsenthalpie der *N*-Methylimidazolverbindungen wird durch die Grösse des Anions kaum beeinflusst.

Резюме — Исследовано термическое разложение солей общей формулы $Ni(NMIz)_nX_2$ (*NMIz* = *N*-метилимидазол, *н* = 6,4,2 или 1, а *X* = Cl, Br или I) с помощью дифференциальной сканирующей калориметрии, термогравиметрии (ТГ), анализа выделенного газа и порошковой рентгенографии в области температур 20—500°. Реакционные стадии были исследованы с помощью ТГ. Образование промежуточных продуктов реакции было подтверждено рентгенограммами, снятыми в высоко-температурной камере Гюнье-деВольф. Энтальпии разложения были вычислены из данных ДСК. Полученные значения энтальпии разложения были сопоставлены с результатами предыдущего изучения имидазольных соединений с целью получения большей информации о водородной связи в имидазольных соединениях. Водородная связь более сильная в случае меньших анионов и уменьшает энтальпию разложения имидазольных соединений. Энтальпия разложения *N*-имидазольных соединений в малой степени затрагивается размером аниона.