

SOLID, PRIMARY ALIPHATIC AMINE COMPLEXES OF TRANSITION-METAL HALIDES

I. Thermal studies on RNH₂ complexes of nickel(II) chloride with $R = \text{H, CH}_3, \text{CH}_3\text{CH}_2, \text{CH}_3(\text{CH}_2)_2, (\text{CH}_3)_2\text{CH, CH}_3(\text{CH}_2)_3, (\text{CH}_3)_2\text{CHCH}_2$

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The thermal decomposition characteristics of the ternary mixed, solid, primary aliphatic amine complexes formed with nickel(II) chloride was investigated by a simultaneous TG-DTG-DTA method.

The course of the thermal decomposition is described in detail, results thus obtained are compared with the literature data and contradictions are pointed out.

In addition to the complexes described in previous papers some new compounds and thermal intermediates have been prepared by solid-gas phase chemisorption and by freezing-out technique. Thermal intermediates containing two-third mole of the ligands, characteristic of the decomposition of pyridine type complexes of transition-metal halides, were identified during the degradation process.

Keywords: amine complexes, transition-metals, thermal analysis

Introduction

Extensive work has been undertaken on ammonia and pyridine type complexes in the last few decades [1–2]. While the preparation methods and thermal properties of these compounds are well known, only a few papers report on the solid, primary aliphatic amine complexes of transition-metals [3–4, 6]. Investigation within the row of these complexes are of interest in order to follow the

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change in thermal properties from ammonia complexes to compounds containing ring systems.

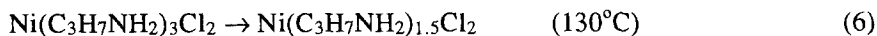
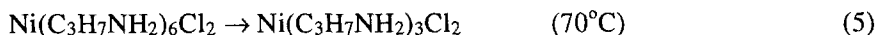
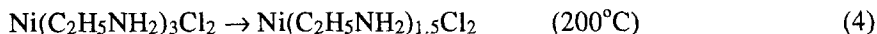
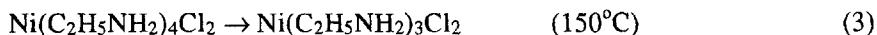
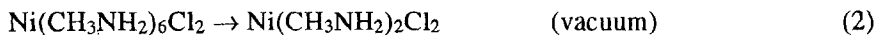
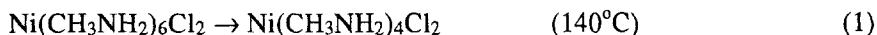
Ephraim and Linn [3] reported on a very complicated apparatus developed for the preparation of primary aliphatic amine complexes formed with different divalent transition-metal halides (e.g. Zn, Cd, Co, Fe, Cu, Mn). In addition to these compounds, they have published the temperatures and heats of dissociation and some other physical-chemical constants for some nickel(II) chloride complexes (Table 1).

Table 1 Temperatures and heats of dissociation for nickel(II) chloride primary aliphatic amine complexes by Ephraim and Linn [3]

Compound	Colour	<i>T</i> / K	<i>Q</i> / cal*
NiCl ₂ ·CH ₃ NH ₂	light blue	413	14.87
NiCl ₂ ·CH ₃ CH ₂ NH ₂	light blue	387	13.85

*Unites used are given by the authors [3].

Fifty-three years later, Uhlig and Staiger [4] reported on the thermal properties of hexakis-methyl, and propylamine and tetrakis-ethylamine complexes of nickel(II) chloride. The thermal degradation has been studied by heating these compounds in a vessel in argon stream containing the amine. The decomposition scheme they have observed was as follows¹:

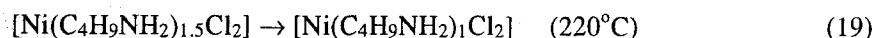
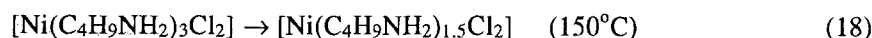
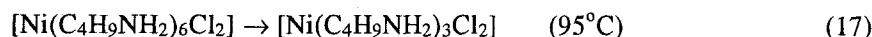
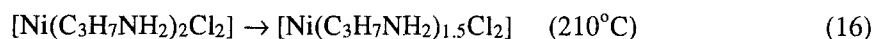
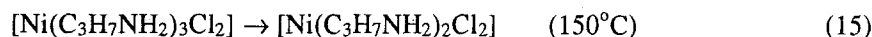
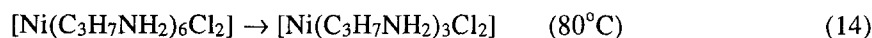
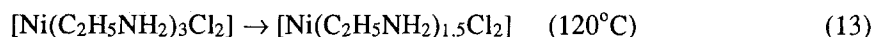
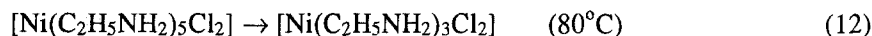
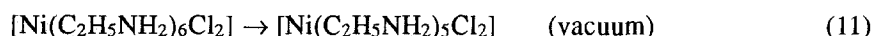
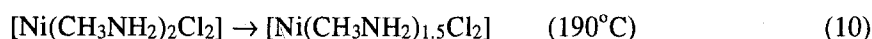
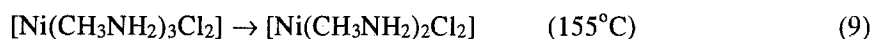
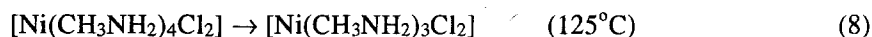
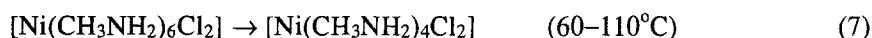


The thermal intermediates were prepared and the magnetic and spectroscopic properties studied. The probable structure of the tris-complex and of the thermal

1 Mark of the chemical reactions was taken from Ref. [4].

intermediate containing one and a half moles of the ligand is discussed on the basis of the work published by Brown *et al.* [5].

Ludwig [6] reported for the very first time on the thermal behaviour of hexakis-methyl-, -ethyl-, -propyl and -butylamine complexes of nickel(II) chloride, which was studied by a conventional thermobalance and a separate DTA apparatus. Although hexakis-ethyl- and -butylamine complexes were not described earlier, there is no reference to the preparation method. The following decomposition scheme was given in the article [6]²:



A careful literature study shows certain contradictions in stoichiometries, decomposition schemes and temperature for these complexes. We decided to apply the earlier described [7] solid-gas phase preparation method to obtain solid primary aliphatic amine complexes. The stable nickel(II) chloride was selected in order to avoid oxidation interferences.

2 Mark of the chemical reactions was taken from Ref. [6].

Table 2 Thermal data of primary aliphatic amine complexes formed with nickel(II) chloride

Compound	TG / °C	$\Delta m / \%$		Ligand lost	Colour
		calculated	found		
$[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$	155	29.39	28.50	4	violet
$[\text{Ni}(\text{NH}_3)_2]\text{Cl}_2$	270	7.35	7.42	1	yellow
$[\text{Ni}(\text{NH}_3)_1]\text{Cl}_2$	315	7.35	7.38	1	orange
$[\text{Ni}(\text{CH}_3\text{NH}_2)_6]\text{Cl}_2$	105	39.32	40.20	4	violet
$[\text{Ni}(\text{CH}_3\text{NH}_2)_2]\text{Cl}_2$	245	19.66	19.51	2	yellow
$[\text{Ni}(\text{C}_2\text{H}_5\text{NH}_2)_4]\text{Cl}_2$	85	29.09	28.95	2	light blue
$[\text{Ni}(\text{C}_2\text{H}_5\text{NH}_2)_2]\text{Cl}_2$	135	14.55	14.52	1	green
$[\text{Ni}(\text{C}_2\text{H}_5\text{NH}_2)_1]\text{Cl}_2$	225	4.85	4.81	1/3	yellow
$[\text{Ni}(\text{C}_2\text{H}_5\text{NH}_2)_{2/3}]\text{Cl}_2$	235	9.70	9.66	2/3	orange
$[\text{Ni}(\text{C}_3\text{H}_7\text{NH}_2)_4]\text{Cl}_2$	80	32.30	32.11	2	light blue
$[\text{Ni}(\text{C}_3\text{H}_7\text{NH}_2)_2]\text{Cl}_2$	130	16.15	16.20	1	green
$[\text{Ni}(\text{C}_3\text{H}_7\text{NH}_2)_1]\text{Cl}_2$	200	5.38	5.39	1/3	yellow
$[\text{Ni}(\text{C}_3\text{H}_7\text{NH}_2)_{2/3}]\text{Cl}_2$	245	10.76	10.71	2/3	orange

Table 2 (cont.) Thermal data of primary aliphatic amine complexes formed with nickel(II) chloride

Compound	TG / °C	$\Delta m / \%$		Ligand lost	Colour
		calculated	found		
$[\text{Ni}((\text{CH}_3)_2\text{CHNH}_2)_4\text{Cl}_2]$	65	32.30	32.20	2	light blue
$[\text{Ni}((\text{CH}_3)_2\text{CHNH}_2)_2\text{Cl}_2]$	125	16.15	16.20	1	green
$[\text{Ni}((\text{CH}_3)_2\text{CHNH}_2)_1\text{Cl}_2]$	225	16.15	16.14	1	yellow
$[\text{Ni}(\text{C}_4\text{H}_9\text{NH}_2)_4\text{Cl}_2]$	55	17.32	17.33	1	light blue
$[\text{Ni}(\text{C}_4\text{H}_9\text{NH}_2)_3\text{Cl}_2]$	90	17.32	17.30	1	light blue
$[\text{Ni}(\text{C}_4\text{H}_9\text{NH}_2)_2\text{Cl}_2]$	130	17.32	17.35	1	green
$[\text{Ni}(\text{C}_4\text{H}_9\text{NH}_2)_1\text{Cl}_2]$	195	5.77	5.81	1/3	yellow
$[\text{Ni}(\text{C}_4\text{H}_9\text{NH}_2)_{2/3}\text{Cl}_2]$	250	11.55	11.50	2/3	orange
$[\text{Ni}((\text{CH}_3)_2\text{CHCH}_2\text{NH}_2)_4\text{Cl}_2]$	115	34.65	34.61	2	light blue
$[\text{Ni}((\text{CH}_3)_2\text{CHCH}_2\text{NH}_2)_2\text{Cl}_2]$	165	17.32	17.30	1	green
$[\text{Ni}((\text{CH}_3)_2\text{CHCH}_2\text{NH}_2)_1\text{Cl}_2]$	265	17.32	17.32	1	yellow
$[\text{Ni}(\text{py})_4\text{Cl}_2]$	130	35.47	35.51	2	light blue
$[\text{Ni}(\text{py})_2\text{Cl}_2]$	175	17.73	17.69	1	green
$[\text{Ni}(\text{py})_1\text{Cl}_2]$	270	5.91	5.87	1/3	yellow
$[\text{Ni}(\text{py})_{2/3}\text{Cl}_2]$	320	11.82	11.86	2/3	orange

Experimental

For the preparation, nickel(II) chloride hexahydrate (Reanal p.a.) was dehydrated at 350°C in a drying oven. After a careful mortaring the pure nickel(II) chloride was placed in a desiccator into vapours of methyl-, ethyl- (Jansen Chimica 40 and 70% water solutions respectively), *n*-propyl-, *i*-propyl-, *n*-butyl- and *i*-butylamine (Jansen Chimica 98–99%). The chemisorption was effected in a few days term with repeated mortaring. The progress of the reaction was fol-

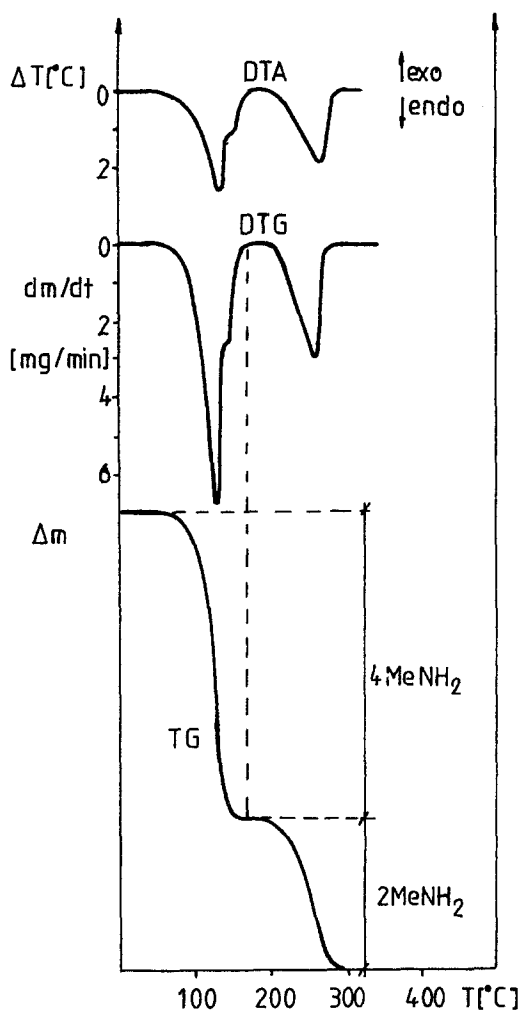


Fig. 1 Thermoanalytical curves for dichloro hexakis-(methylamine)-nickel(II)

lowed by a change in colour from yellow to blue or violet depending on the number of the ligands bonded from the vapour phase.

The nickel(II) content of the complexes was determined by complexometric titration [8].

The thermoanalytical curves were recorded on a MOM-OD2 Derivatograph at a heating rate of $5 \text{ deg}\cdot\text{min}^{-1}$ and with a sample weight of 100 mg. Air and nitrogen atmosphere and platinum crucibles were applied. 100 mg of α -aluminium oxide was used as reference material.

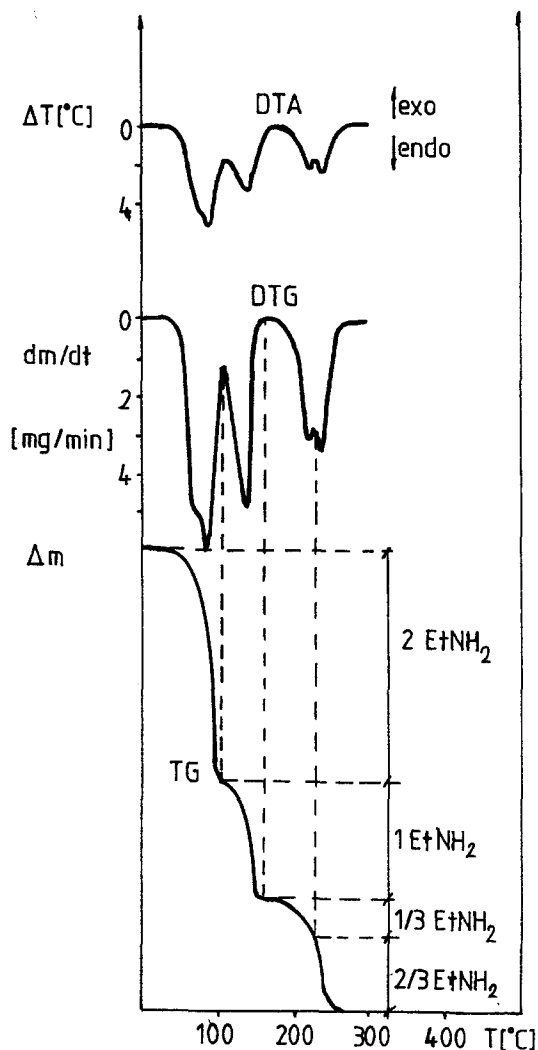


Fig. 2 Thermoanalytical curves for dichloro tetrakis-(ethylamine)-nickel(II)

Results

In Table 2 we summarized the results of the thermal investigations. In addition to the title compounds the ammonia and pyridine derivatives, prepared in the same way, are also presented.

The decomposition of the hexakis-methylamine complex starts with the release of four ligands similarly to the hexakis-ammonia analogue (Fig. 1). The remaining two moles of methylamine decompose in a single step:

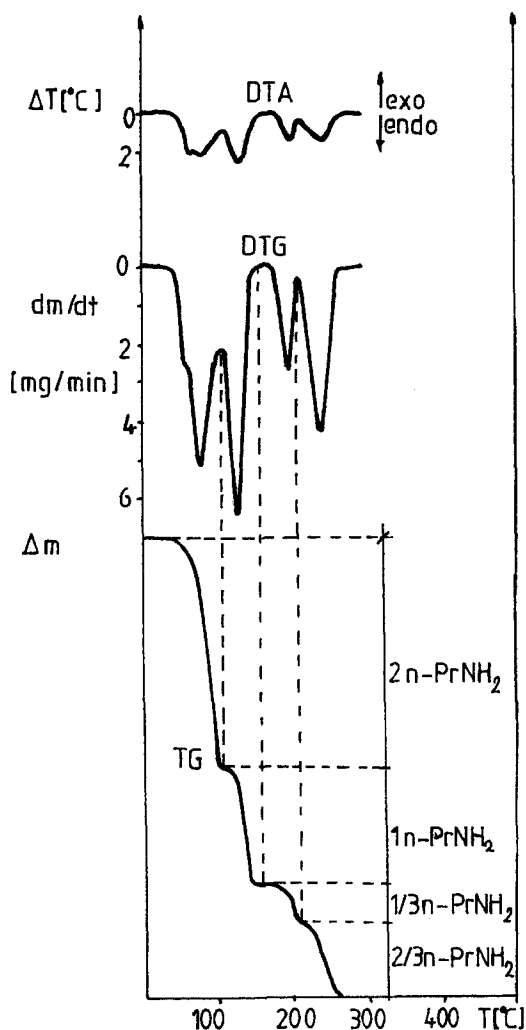
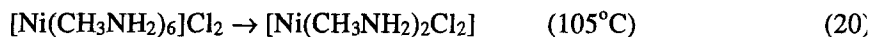


Fig. 3 Thermoanalytical curves for dichloro tetrakis-(*n*-propylamine)-nickel(II)



Ethylamine forms only tetrakis-complex with nickel(II) chloride, and the compound loses first two, and then one mole of ligand during the thermal treatment (Fig. 2). The monoethylamine complex formed in the course of the degrada-

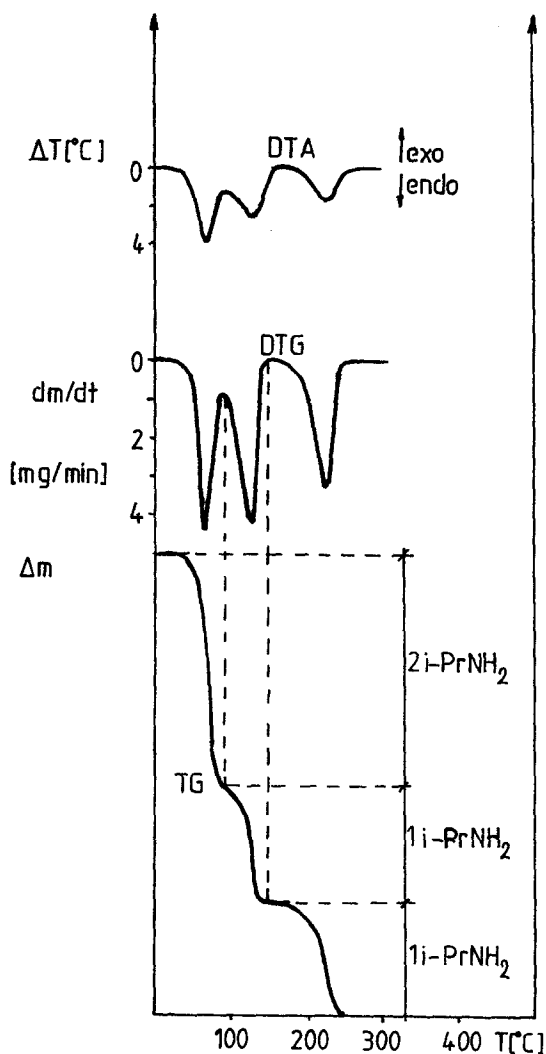


Fig. 4 Thermoanalytical curves for dichloro tetrakis-(*i*-propylamine)-nickel(II)

tion process decomposes in two steps, an intermediate containing two-third mole of the ligand was also identified:

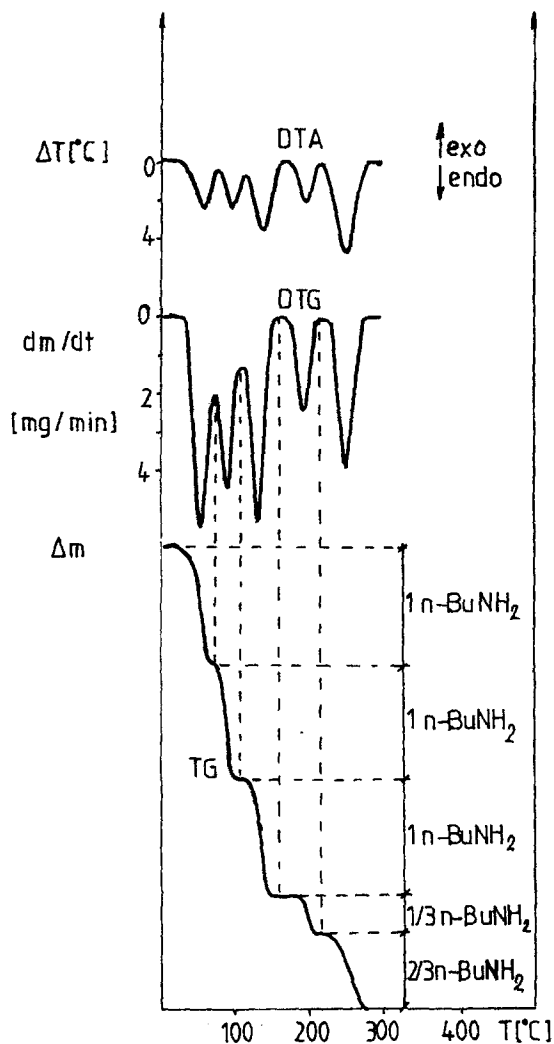
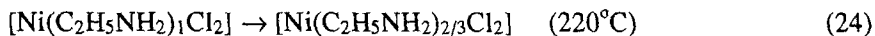
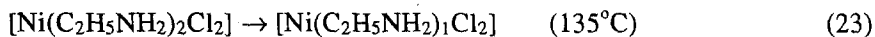
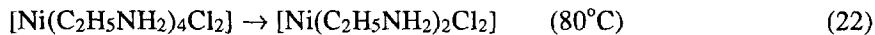


Fig. 5 Thermoanalytical curves for dichloro tetrakis-(*n*-butylamine)-nickel(II)



The stepwise decomposition pattern of the tetrakis-*n*-propylamine complex is similar to that of the ethylamine compound (Fig. 3):

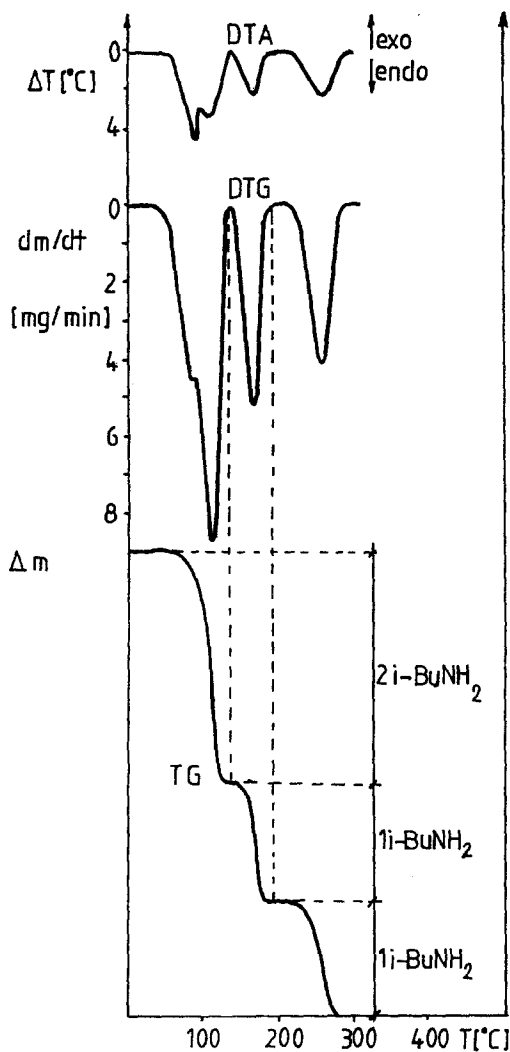
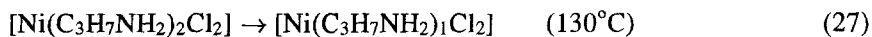
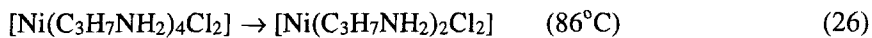
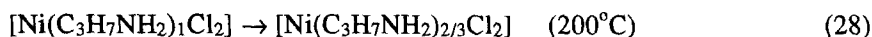
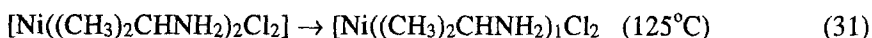
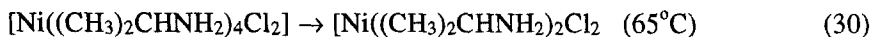


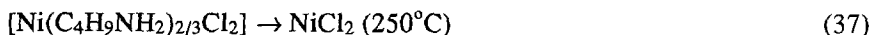
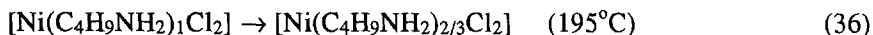
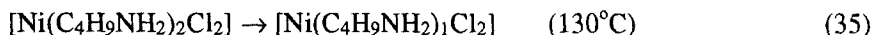
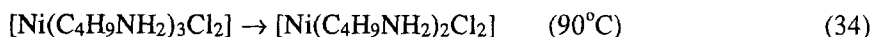
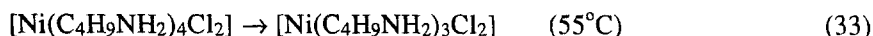
Fig. 6 Thermoanalytical curves for dichloro tetrakis-(*i*-butylamine)-nickel(II)



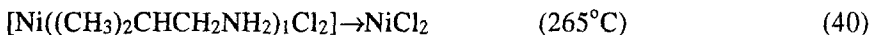
The first two degradation steps of the tetrakis-*i*-propylamine complex are identical with those of the earlier described ethyl- and *n*-propylamine analogues, but the last mole of the ligand decomposes in a single step (Fig. 4):



The degradation of the *n*-butylamine complex is similar to that of the normal primary aliphatic amine derivatives with the exception of the first decomposition step, which is separated into two individual steps on the TG curve (Fig. 5):



The decomposition scheme of the tetrakis-*i*-butylamine complex is identical with the *i*-propylamine analogue (Fig. 6):



The thermal degradation of the complexes was studied in air and nitrogen atmosphere. The decomposition pattern was found to be independent of the atmosphere, the temperatures of the DTG peaks were the same within the accuracy of the measurement.

Discussion

The decomposition of the compounds, studied in this work, start with the fission of the bond between the central metal atom and the nitrogen of the amine. In this case the thermal stability will depend on the strength of the coordination bond, i.e. the stability of the complex. The formation and the thermal stability of the nickel(II) chloride primary aliphatic amine complexes thus could be interpreted by the investigation of the charge densities on the nitrogen and the steric demand of the ligands.

In the case of relatively small bases, e.g. ammonia and methylamine, six ligands could be arranged around the central nickel(II) ion. The chloride pushed into the outer coordination sphere, thus a parent hexakis-complex was formed. When the number of the carbon atoms in the aliphatic chain is equal to or higher than two, the amines form only tetrakis-complexes, however hexakis-compounds are known in solution [9] and were described by Uhlig and Staiger [4] and Ludwig [6].

With ethylamine we obtained tetrakis-complex, which is in good agreement with the fundamental work of Ephraim and Linn [3] as well as with [4], but is different from [6]. The contradiction is complete with [4] and [6] in the case of *n*-propyl- and *n*-butylamine complexes, where they prepared hexakis-compounds.

One possible explanation for these contradictions is that these authors applied cooling during the preparation procedure in order to avoid an increase in temperature due to the reaction heat. Because of the low thermal stability of the hexakis-compounds [6] we suppose that the formation of tetrakis-derivatives is due to the relatively high temperature caused by the exothermic heat of the reaction. The tetrakis-complex thus obtained and the compounds formed with *i*-propyl- and *i*-butylamine are described for the first time according to our knowledge.

The decomposition schemes of the hexakis-ammonia and hexakis-methylamine complexes are similar except for the degradation of the bis-intermediate, which is separated into two steps in the case of the bis-ammonia complex, however this separation was disputed in the literature earlier [10–12]. These results are in a more or less good agreement with [4], but differ from [6], where more steps have been described for the hexakis-methylamine complex. The charge density is lower on the nitrogen atom in the case of methylamine than in ammonia due to the more rigid C–N bond than C–H. This leads to a lower thermal stability (50°C) of the Ni-N bond in the hexakis-methylamine complex of nickel(II) chloride.

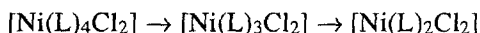
Ternary mixed tetrakis-complexes of primary aliphatic amines formed with nickel(II) chloride could be divided into two classes according to the thermal properties. Compounds with normal aliphatic amines, having straight carbon chain, lose their last mole of ligand in two steps, thus an intermediate containing

two-third mole of the ligand is formed. This type of degradation is similar to that of dichloro-tetrakis-pyridine-nickel(II) [13]. The decomposition pattern given in the literature [4, 6] is quite different from our observations, which we could not explain so far. Aliphatic iso-amines, having branched carbon chains, form complexes of nickel(II) chloride, which lose their last mole of ligand in a single step, similarly to the pyridine complex of nickel(II) bromide [13]. These similarities confirm the assumption that the decomposition pathway could be influenced by the steric demand of large ligands. The larger ionic radius of bromide compared to chloride prevents the formation of the intermediate containing two-third ligand in the case of pyridine complexes. In the case of the aliphatic amine compounds the more bulky iso-amine ligands compared to the normal analogues require more space around the central nickel(II) atom. During the stepwise release of the amines, the nickel(II) ion is possibly octahedrally coordinated, a structure realised by halide bridges, thus a highly polymeric structure is formed. Because of the larger space requirement of the iso-amines in this polymeric structure compared to the normal derivatives, the formation of the intermediates containing two-third ligand is hindered in the case of iso-aliphatic amine complexes.

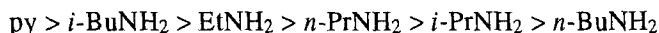
The thermal stability for the tetrakis-derivatives decreases in the following order:



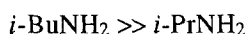
The tetrakis-*n*-butylamine complex is outside this row, because of the splitting of the first decomposition step. There are shoulders on the DTG peaks, representing the first degradation step, in the case of the other amine complexes, thus we suppose the following general decomposition scheme:



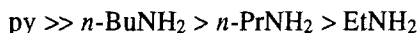
The following decreasing order of thermal stability was observed for the bis-complexes:



The thermal stability can be compared only among the normal- and iso-amine complexes in the case of mono-compounds and intermediates containing two-third mole ligand, because of the similar decomposition scheme. For mono-derivatives we found the following series:



The decreasing order of the decomposition temperatures for the intermediates with two-third ligand is reversed compared to the mono-complexes:



The pK_a values representing the electron densities on the nitrogen atom of the primary aliphatic amines are close to each other, however, a slight decrease can be observed with increasing number of carbon atoms in the aliphatic chain [14–15]. The longer the aliphatic chain gets the greater is the steric demand. These two factors together lead to a decreasing thermal stability from methylamine to butylamine in the case of tetrakis-, bis- and mono-complexes, with the exception of *i*-butylamine, which has an extremely high thermal stability.

Table 3 The $\Sigma\sigma^*$ values for primary aliphatic amines by Taft [16–17]

Aliphatic amines	$\Sigma\sigma^*$
ammonia	1.47
methylamine	0.98
ethylamine	0.88
<i>n</i> -propylamine	0.865
<i>i</i> -propylamine	0.79
<i>n</i> -butylamine	0.85
<i>i</i> -butylamine	0.885

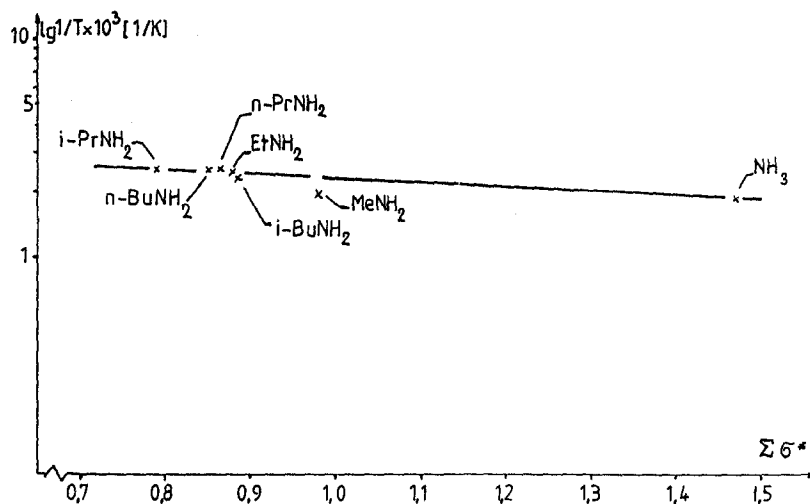


Fig. 7 Logarithm of the reciprocal decomposition temperatures vs. $\Sigma\sigma^*$ values for dichloro bis-(primary aliphatic amine)-nickel(II) complexes

The high thermal stability of the pyridine analogues compared to the primary aliphatic amine derivatives confirm the earlier suggestion that in pyridine type complexes the back donation of electrons from the *d*-orbital of the metal to the non-bonding *p*-orbitals of the nitrogen increases the thermal stability.

Taft [16–17] has shown that the quantity of $\Sigma\sigma^*$, a Hammett type function for aliphatic amines, is a measure of the inductive releasing effect relative to methyl group. The $\Sigma\sigma^*$ values are listed in Table 3 for aliphatic amines.

In Fig. 7 we plotted the decomposition temperatures $\lg(1/T)$ of nickel(II) chloride bis-primary aliphatic amine complexes against the $\Sigma\sigma^*$ values. The points fall on a straight line indicating the influence of the inductive effect on the thermal stability in the case of bis-compounds. This observation is in good agreement with some earlier works of Sacconi and Lombardo [18]. They have shown that there are no steric effects for these primary aliphatic amine complexes formed with diacetyl bis-(benzoylhydrazone)-nickel(II), while for sec- and tert-butylamine and secondary and tertiary amines steric effects have been observed. These facts indicate that the polarity is the main factor, which determines the metal-ligand bond strength, thus the thermal stability in the investigated bis-compounds.

References

- 1 W. W. Wendlandt and J. P. Smith, Thermal properties of transition-metal complexes, Elsevier Publishing Co., Amsterdam 1967.
- 2 S. J. Ashcroft and C. T. Mortimer, Thermochemistry of transition-metal complexes, Academic Press, London and New York 1970.
- 3 F. Ephraim and R. Linn, Ber. Dtsch. Chem. Ges., 46 (1913) 3754.
- 4 E. Uhlig and K. Staiger, Z. Anorg. Alg. Chem., 336 (1965) 42.
- 5 D. H. Brown and R. H. Nuttall, J. Inorg. Nucl. Chem., 25 (1963) 1067.
- 6 W. Ludwig, 3rd. Anal. Conf., Akadémiai Kiadó, Budapest 1970, p. 271.
- 7 G. Liptay, G. Kenessey, L. Bihátsi and J. Mink, J. Thermal Anal., 38 (1992) 899.
- 8 I. Sajó, Komplexometria, Műszaki Könyvkiadó, Budapest 1975.
- 9 L. Sacconi and G. P. Speroni, Inorg. Chem., 7 (1968) 295.
- 10 W. Blitz and E. Birk, Z. Anorg. Allg. Chem., 127 (1923) 34.
- 11 K. Kido and T. Watanabe, J. Phys. Soc. Japan, 14 (1959) 1217.
- 12 T. D. George and W. W. Wendlandt, J. Inorg. Nucl. Chem., 25 (1963) 395.
- 13 G. Liptay, T. Wadsten and A. Borbély-Kuszmán, J. Thermal Anal., 31 (1986) 845; 35 (1989) 1815.
- 14 L. Sacconi and I. Bertini, J. Am. Chem. Soc., 88 (1966) 5180.
- 15 D. D. Perrin, Dissociation constants of organic bases in aqueous solution, Academic Press, London 1965.
- 16 R. W. Taft, Jr., J. Am. Chem. Soc., 74 (1952) 3120.
- 17 R. W. Taft, Jr., *ibid.*, 75 (1953) 4231.
- 18 L. Sacconi and G. Lombardo, *ibid.*, 82 (1960) 6266.

Zusammenfassung — Mittels simultaner TG-DTG-DTA wurden die Merkmale der thermischen Zersetzung von Nickel(II)-komplexen mit gemischten ternären, festen und primären aliphatischen Aminen untersucht.

Der Reaktionsweg der thermischen Zersetzung wird eingehend beschrieben, die so erhaltenen Ergebnisse wurden mit Literaturangaben verglichen und auf Widersprüche hingewiesen.

Zusätzlich zu den in vorangehenden Arbeiten beschriebenen Komplexen wurden mittels Feststoff-Gasphasen Chemisorption und Ausfrierungstechnik einige neue Verbindungen und Thermo-
intermediäre hergestellt. Während des Abbauprozesses wurden Thermo-
intermediäre mit zwei Drittel Mol Liganden beobachtet, die charakteristisch für die Zersetzung der Pyridinkomplexe von Übergangsmetallhalogeniden sind.