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Thermochemical investigation of nickel(II)–nicotinamide–solvent interactions in solid halogeno and thiocyanato complexes ☆

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Abstract

Stoichiometries of thermal decompositions have been studied for the following Ni(II) nicotinamide (NA) complexes: $Ni(NA)_2Cl_2 \cdot 2H_2O$ (**I**), $Ni(NA)_3Br_2 \cdot 4H_2O$ (**II**), $Ni(NA)_4I_2 \cdot 4H_2O$ (**III**) and $Ni(NA)_4(NCS)_2 \cdot 2C_2H_5OH$ (**IV**). Heating the compounds first results in a release of solvent molecules and desolvated compounds **I′**–**IV′** are formed. NA molecules are released in two steps for complexes **I′**, **II′**, and **III′**, and in one step for complex **IV′**. Magnetic and spectral properties, as well as thermochemical data (quasi-equilibrium decomposition temperatures, DSC data) indicate an octahedral monomeric structure for complexes **III**, **IV**, **III′** and **IV′**, and a polymeric structure for complexes **I**, **II**, **I′** and **II′**, with adsorbed (**I**) and crystal water (**II**, **III**) or ethanol (**IV**).

Keywords: Decomposition; Halogeno complex; Thiocyanato complex

1. Introduction

Nicotinamide (NA) is known as an important component of biological systems. It is not surprising, therefore, that many authors have investigated nicotinamide and also examined it as a ligand in coordination compounds of several central atoms, including nickel(II).

☆ Part VI in the series: Thermal decomposition reactions of nickel(II) complexes under quasi-equilibrium conditions, Part V: J. Therm. Anal., (1995) (in press).

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The nature of the bonds between nickel(II) ions and nicotinamide molecules has been studied in coordination compounds, in particular by spectral and magnetic methods [1–4]. Moreover, several complexes of nicotinamide Ni(II) contain solvent molecules. However, the nature of their interactions with the complex unit is not known. In order to clarify Ni(II)–nicotinamide–solvent (S) interactions, we focused our investigation on the thermochemical properties of solvated halogeno and thiocyanato complexes, $Ni(NA)_xX_2 \cdot n$ S, and their desolvated products $Ni(NA)_xX_2$, in particular on the stoichiometry of their thermal decomposition, heat of thermal decomposition $\Delta_{dec}H$, and quasi-equilibrium decomposition temperatures T_{dec}. Spectral and magnetic data were used to support conclusions on the structures of the compounds.

2. Experimental

Compounds $Ni(NA)_2Cl_2 \cdot 2H_2O$ (**I**), $Ni(NA)_3Br_2 \cdot 4H_2O$ (**II**), $Ni(NA)_4I_2 \cdot 4H_2O$ (**III**) and $Ni(NA)_4(NCS)_2 \cdot 2C_2H_5OH$ (**IV**) were prepared by crystallization from cold aqueous–ethanolic solutions in which molar ratios Ni(II):NA of 1:4 were maintained. Complexes **I′, II′, III′** and **IV′** were obtained by isothermal heating of complexes **I, II, III, IV** at 100, 100, 150, and 120°C, respectively. The compounds obtained were checked for Ni, C, H and N contents. The analysis results are given in Table 1.

Thermal decompositions under dynamic conditions were studied using a Derivatograph OD 102. Samples (100 mg) were heated in static air at a heating rate of 9 °C min^{-1} in open standard crucibles.

A Q-derivatograph was used to study decomposition processes under quasi-equilibrium conditions. This technique provides a stabilization of decomposition tempera-

Table 1
Analysis results for solvated and desolvated complexes

Compound		%Ni	%C	%H	%N
I	Calcd:	14.32	35.16	3.93	13.67
	Found:	14.23	34.81	3.81	13.54
II	Calcd:	8.94	32.88	3.99	12.78
	Found:	8.88	33.61	3.97	12.87
III	Calcd:	6.72	32.99	3.69	12.84
	Found:	6.81	32.07	3.38	12.68
IV	Calcd:	7.77	47.68	4.80	18.54
	Found:	7.86	47.24	4.94	18.32
I′	Calcd:	15.70	38.55	3.23	14.90
	Found:	15.62	38.59	3.27	14.87
II′	Calcd:	10.04	36.96	3.10	14.36
	Found:	10.12	36.97	3.38	14.28
III′	Calcd:	7.33	35.99	3.02	13.99
	Found:	7.38	35.82	2.98	13.90
IV′	Calcd:	8.85	47.03	3.62	21.16
	Found:	8.91	46.58	3.58	21.05

tures and thus secures decompositions under quasi-isothermal conditions [5]. When using a special sample holder it is possible to keep the pressure of gaseous products at an almost constant value during the entire decomposition process. (When a conical crucible is used the value of the pressure is about 90 kPa.)

In order to study the heats of decomposition reactions, a Perkin-Elmer differential scanning calorimeter DSC-7 was used, the method being based on the null-balance power compensating principle (sample weight, 7–8 mg; pure nitrogen; scanning rate, 10°C $\min^{-1}$). Calibrations of the temperature and enthalpy change axes were made with pure indium (melting point, 156.6°C; enthalpy of fusion, $\Delta_{\mathrm{fus}}H$, 28.47 J g^{-1}).

Magnetic susceptibility was measured by the Faraday method using a sensitive Cahn RG-HV electrobalance. Reflectance spectra were recorded with a Beckman UV 5240 spectrophotometer in the region of 350–2000 nm. Infrared spectra were measured in nujol mulls in the range 4000–200 cm^{-1} using a Phillips analytical PU 9800 FTIR spectrophotometer.

3. Results and discussion

3.1. Stoichiometry of thermal decomposition

The analysis results obtained for the compounds show that two molecules of nicotinamide in relation to one Ni(II) atom are contained in complex **I** (chloride), three in complex **II** (bromide), and four in complexes **III** and **IV** (iodide and thiocyanate, respectively). Moreover, all compounds contain solvent molecules, namely crystallization water (**I**–**III**) and ethanol (**IV**).

The data for the TG, DTG and DTA curves of the complexes are given in Table 2. Because all of the complexes are solvated, as expected, the first mass losses can be assigned to solvent evolution. The release of H_2O or C_2H_5OH molecules takes place in well-defined steps that can clearly be observed on the TG and DTG curves (Figs. 1–4). The rate maxima of H_2O evolution (the temperatures of the first peak in DTG curves) decrease in the sequence: $I^- > Br^- > Cl^-$.

The thermal analysis results (Table 2) show that the release of volatile ligands is a four-step (complexes **I**–**III**) or a three-step (complex **IV**) process. The release of the last portion of nicotinamide is mostly accompanied by a total decomposition of the compounds (exothermic effect on the DTA curves).

The stoichiometry of the thermal decompositions of complexes **I**–**IV** can be expressed by the following schemes

$$\mathrm{Ni(NA)_2Cl_2{\cdot}2H_2O}\ (\mathbf{I}) \xrightarrow{(1)} \mathrm{Ni(NA)_2Cl_2}\ (\mathbf{I'}) \xrightarrow{(2)} \mathrm{Ni(NA)_{2/3}Cl_2} \xrightarrow{(3)} \mathrm{NiCl_2}\ (\mathrm{decomp.}) \xrightarrow{(4)} \mathrm{NiO} \tag{1}$$

$$\mathrm{Ni(NA)_3Br_2{\cdot}4H_2O}\ (\mathbf{II}) \xrightarrow{(1)} \mathrm{Ni(NA)_3Br_2}\ (\mathbf{II'}) \xrightarrow{(2)} \mathrm{Ni(NA)_2Br_2} \xrightarrow{(3)} \mathrm{Ni(NA)_{1/2}Br_2} \xrightarrow{(4)} \mathrm{NiO} \tag{2}$$

Table 2
Thermal analysis results for Ni(II) complexes with nicotinamide

Starting complex	Q-TG			TG(%)		DTG T_p/°C	DTA T_p/°C	Resulting intermediate
	T_{dec}/°C	% Loss of solvent		Calcd.	Found			
		Calcd.	Found					
$Ni(NA)_2Cl_2 \cdot 2H_2O$	30–100	8.78	8.0	8.78	9.0	60	60	$Ni(NA)_2Cl_2$
(I)				48.51	47.0	400	400	$Ni(NA)_{2/3}Cl_2$
				68.25	67.0	460	460,480 (exo)	$NiCl_2$
				82.62	82.0	680	680	NiO
$Ni(NA)_3Br_2 \cdot 4H_2O$	84	10.96	12.0	10.96	11.0	100	110	$Ni(NA)_3Br_2$
(II)				29.53	30.0	260	260	$Ni(NA)_2Br_2$
				57.4	58.5	380	380, 470 (exo)	$Ni(NA)_2Br_2$
				88.9	88.0	650	580	NiO
$Ni(NA)_4I_2 \cdot 4H_2O$	110	8.25	8.0	8.25	9.0	150	150	$Ni(NA)_4I_2$
(III)				22.24	24.0	280	215, 260	$Ni(NA)_3I_2$
				36.23	37.0	320	320	$Ni(NA)_2I_2$
				91.44	90.0	460, 600	500, 700 (exo)	NiO
$Ni(NA)_4(NCS)_2 \cdot 2C_2H_5OH$	138	12.17	11.0	12.17	12.0	140	140	$Ni(NA)_4(NCS)_2$
(IV)				76.88	77.0	310	200, 310	$Ni(NCS)_2$
				90.33	90.0	540	540 (exo)	NiO

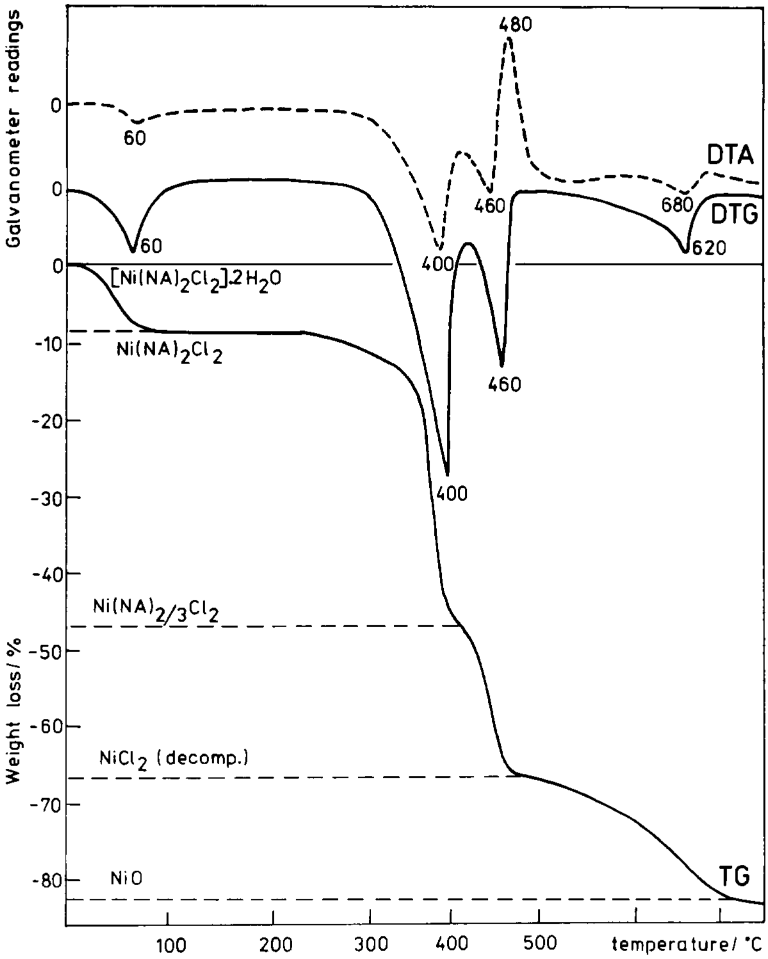

Fig. 1. Thermal curves of $Ni(NA)_2Cl_2 \cdot 2H_2O$.

$$Ni(NA)_4I_2 \cdot 4H_2O\ (\mathbf{III}) \xrightarrow{(1)} Ni(NA)_4I_2\ (\mathbf{III'}) \xrightarrow{(2)} Ni(NA)_3I_2 \xrightarrow{(3)} Ni(NA)_2I_2 \xrightarrow{(4)} NiO \qquad (3)$$

$$Ni(NA)_4(NCS)_2 \cdot 2C_2H_5OH\ (\mathbf{IV}) \xrightarrow{(1)} Ni(NA)_4(NCS)_2\ (\mathbf{IV'}) \xrightarrow{(2)} Ni(NCS)_2 \xrightarrow{(3)} NiO \qquad (4)$$

3.2. *Structural investigation of thermal desolvation processes*

It is to be expected that the release of either water or ethanol molecules from the complexes under study will evoke some changes in their structures. Thus, it was

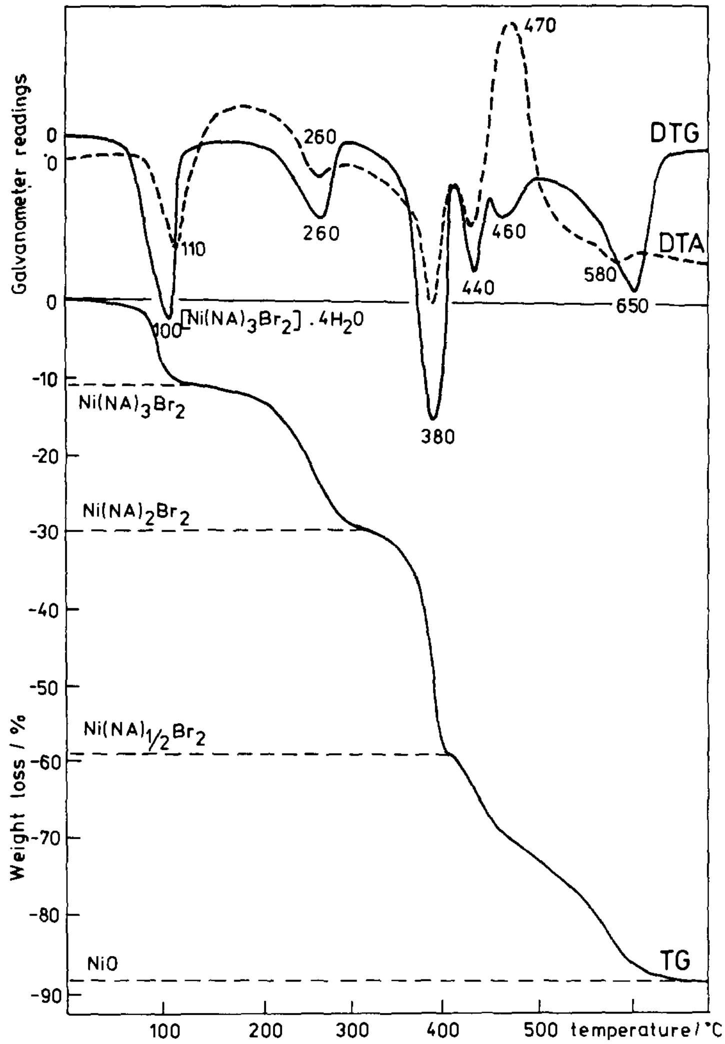

Fig. 2. Thermal curves of $Ni(NA)_3Br_2 \cdot 4H_2O$.

necessary to investigate the magnetic and spectral properties of the starting complexes (**I**–**IV**) as well as their desolvated forms (**I′**–**IV′**).

The values of magnetic moments listed in Table 3 support unambiguously the conclusion that all of the complexes are pseudo-octahedral, because they are paramagnetic, and the values are in the range usually given for octahedral nickel(II) complexes [6]. Electronic absorption spectra of the complexes are characterized by three broad bands corresponding to $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2), and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3) transitions in the O_h symmetry. The shoulders at about 12300 and 22700 cm^{-1},

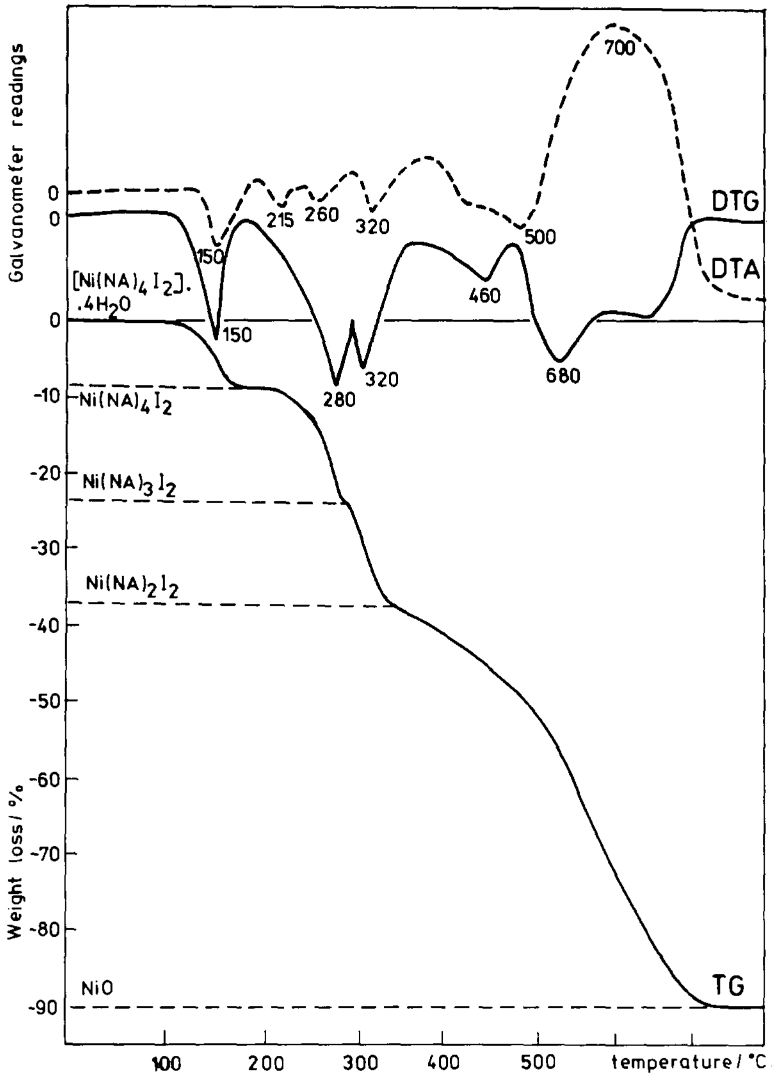

Fig. 3. Thermal curves of $Ni(NA)_4I_2 \cdot 4H_2O$.

observed for chloro complexes (**I**, **I'**), can obviously be assigned to the spin-forbidden transitions ${}^3A_{2g} \rightarrow {}^1E_g$ and ${}^3A_{2g} \rightarrow {}^1T_{2g}$, respectively [7]. The lower frequencies for the maxima of the absorption bands of the chloro complexes, when compared with those observed for the other complexes, are due to a lower ligand field value of the chloride anions. Small differences between the spectra of the solvated and desolvated complexes indicate that the solvent molecules do not enter the primary coordination sphere of the starting complexes **I**–**IV** [3].

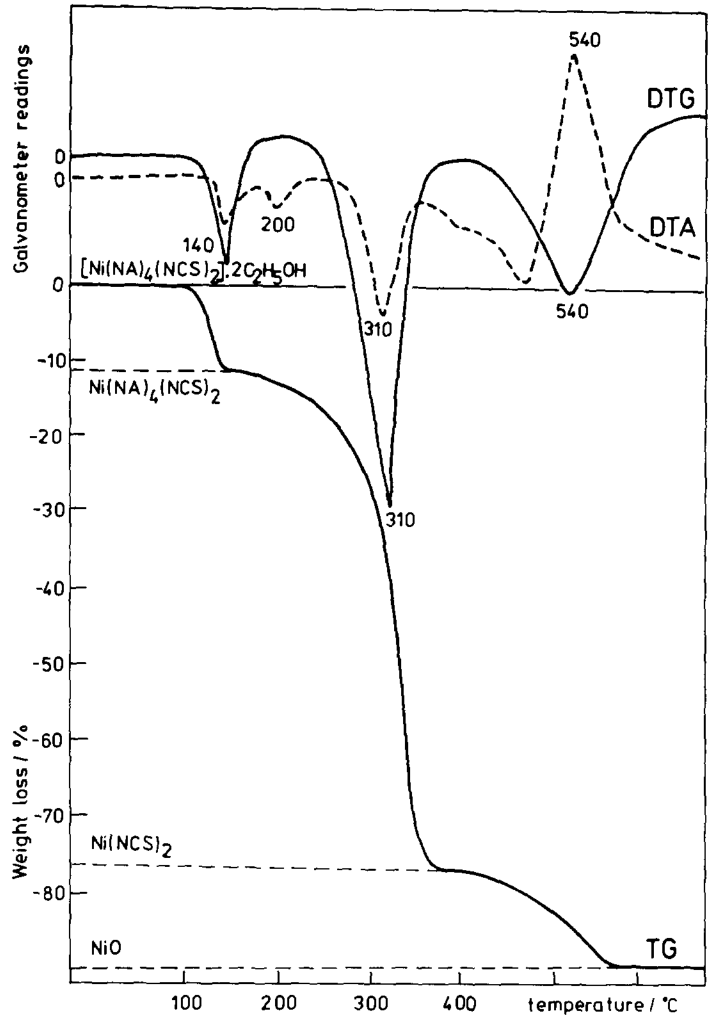

Fig. 4. Thermal curves of Ni $(NA)_4(NCS)_2 \cdot 2C_2H_5OH$.

Infrared absorption spectra can provide more information about the nature of the bonding between nicotinamide and solvent molecules in the complexes.

The presence of solvent molecules is shown by a broad band at about 3550–3200 cm^{-1} corresponding to ν(OH) stretching vibrations in H_2O or C_2H_5OH molecules [8]. However, bands in this region can also belong to $\nu(NH_2)$ stretching vibrations. Because the vibrations are absent in the spectra of the desolvated products I′–IV′, they can be assigned to the vibrations of solvent molecules.

The vibrations ν(CO) and δ(NH) in the pure solid nicotinamide are almost identical with those observed for nicotinamide bonded in the complexes. However, some

Table 3
Magnetic moments and reflectance spectra of the starting Ni(II) complexes (**I–IV**) and their desolvated products (**I′–IV′**)

Complex	μ_{eff}/B.M.	Maxima of absorption bands/cm^{-1}		
		1	2	3
I	3.25	8450	14100 12300	24500 22700
I′	3.24	8440	14080 12400 sh	24690 22730 sh
II	3.28	8700	16600	25800
II′	3.29	8600	16300 14400 sh	24000
III	2.90	8100 11800 sh	16200 13500 sh	25300
III′	2.86	8060 11250	16200 13700 sh	25300
IV	3.05	10400	17000	27400
IV′	3.02	10300	17200	27700

differences in the spectra are observed in the region of 3500–3100 cm^{-1} for $\nu(\mathrm{NH})_2$ bands and for ring vibrations at about 1600 and 650 cm^{-1}. While two intense bands are observed in the spectrum of free nicotinamide in the region of $\nu(\mathrm{NH_2})$ frequencies, their maxima being separated by about 200 cm^{-1}, two, three or four bands are registered in this region for nicotinamide complexes. The bands assigned to $\nu(\mathrm{NH_2})$ vibrations occur at about 3510 and 3357 cm^{-1} for nicotinamide in benzene solution [9] and solid nicotinamide, respectively. The lowering of the frequency by 153 cm^{-1} has been explained by the presence of hydrogen bonds in the solid nicotinamide [3]. Consequently, the occurrence of the respective bands in the region of 3407–3295 cm^{-1} may indicate the presence of hydrogen bonds in the complexes under investigation as well. The ring vibrations of coordinated nicotinamide at about 1600 and 640 cm^{-1} are evidently shifted to higher frequencies (Table 4). The latter shift and occurrence of bands in the region of 300–200 cm^{-1} indicate [8] that nicotinamide is coordinated through the nitrogen atom of its heterocyclic ring. However, two intense bands are observed in this region for complex **II**. The difference between the frequency values is smaller (100 cm^{-1}) in this case and indicates [9] that nicotinamide in complex **II** could also be bonded to nickel(II) atom through the nitrogen atom of its amide group.

For monomeric octahedral complexes of the type $\mathrm{Ni(NA)_xX_2}$, only one $\nu(\mathrm{Ni{-}N_{ring}})$ band and one $\nu(\mathrm{Ni{-}X})$ band are predicted to occur in the low frequency region (600–200 cm^{-1}) of their infrared spectra, while one $\nu(\mathrm{Ni{-}N_{ring}})$ band and two $\nu(\mathrm{Ni{-}X})$ bands are expected for complexes with a polymeric chain structure [8]. This assumption is in agreement with results obtained for nicotinamide nickel (II) complexes. The bands at 272–282 cm^{-1} can undoubtedly be assigned to $\nu(\mathrm{Ni{-}N_{ring}})$ vibrations. The

Table 4
Important vibrations (cm^{-1}) in infrared spectra of the solvated (**I–IV**) and desolvated (**I′–IV′**) complexes

Vibrations	NA[a]	**I/I′**	**II/II′**	**III/III′**	**IV/IV′**
ν(OH)	–	3407/–	3405/–	3407/–	3521/–
$\nu_{as}(NH_2)$	3357	3308/3303	3295/–	3349/3347	3404/3407
$\nu_s(NH_2)$	3150	3265/3265	3195/3196	–/3233	3297/3297
		3213/–		3169/–	3164/3164
		3196/3194		–/3146	
ν(CN)	–	– –	– –	– –	2087/2077
ν(CO)	1679	1667/1667	1653/–	1678/1674	1669/1655
δ(NH)	1617	1626/1624	1635/1635	1634/1638	1631/1622
			–/1614		
ν(ring)	1598	1605/1605	1599/1599	1599/1611	1607/1609
	1580	1580/1580	1570/1570	1570/1568	1578/1580
		1449/–	–/1427		1406/1421
γ(ccc)	644	654/654	648/648	648/650	651/656
	621	627/627	627/627	629/627	612/639
γ(Ni-NCS)	–	– –	– –	– –	297/291
$\gamma(Ni\text{-}N_{ring})$	–	284/282	274/274	280/278	272/271
Others in the region of 300 – 200 cm^{-1}	251	–/245	– –	– –	–/254
	237	230/230	233/233	224/228	231/237
	214	–/–	–/212	–/216	226/216
	206	203/203	206/206	210/210	–/210
					206/206

[a] Nicotinamide.

assignment of ν(Ni–X) frequencies to particular bands is, however, a more complicated problem because the bands are overlapped by those of nicotinamide.

In this region, lattice water exhibits "vibrational modes" due to rotational oscillations of the water molecule restricted by interactions with neighbouring atoms [8]. However, coordinated water shows other vibrations, especially $\nu(Ni\text{–}OH_2)$, which are observed, for example, at 405 and 332 cm^{-1} for complexes $[Ni(H_2O)_6]Cl_2$ [10] and $[Ni(H_2O)_2(quinoline)_2(NCS)_2]\cdot 2(quinoline)$ [11], respectively. The coordination of water in the latter compounds was proved by X-ray structure analysis. However, similar bands are absent in the spectra of complexes **I–IV** and thus the assumption that solvent molecules are not coordinated to Ni(II) atom in the complexes under study [3] has a real basis. Moreover, the assumption was confirmed by the X-ray structure analysis of compound **IV** [12]. The compound is monomeric with a tetragonal bipyramidal environment around the central Ni(II) atom (mean interatomic distances: Ni–N′ = 216.1 pm; and Ni–N″ = 204.7 pm) and chromophore $NiN'_4N''_2$ (N′…N(NA), N″…N(NCS), with ethanol molecules not being bonded to the Ni(II) atom.

3.3. Thermochemical investigation of the thermal desolvation processes

There is a variety of possibilities as to how solvent molecules, especially water, can be bonded in the complex compounds. For example, water molecules can be bound by occlusion and adsorption or in the form of a solid solution; and they can be present in the solid compound as zeolitic water, interlayer water, crystal water and structural water (bound in the form of hydroxyl groups). In our particular case the bonding modes of water were studied by means of thermal analysis methods [13]. Nevertheless, the differentiation of these various types of bonding is rather difficult because, on heating, solvent molecules are evolved at various temperatures and in rather wide temperature domains which overlap to different extents.

Quasi-isothermal and quasi-isobaric thermogravimetry (Q-TG) is suitable for obtaining information on the details of water loss in nicotinamide complexes. The loss of water from complex **I** is not an equilibrium reaction and the Q-TG curve is essentially non-isothermal (Fig. 5, a: adsorbed water). In contrast, the loss of crystal water or ethanol from complexes **II**–**IV** is an isothermal process tending to equilibrium. Deformation of the Q-TG curve in the case of complex **III** is typical for overheating of the sample (see Fig. 5).

The values of the decomposition enthalpies ($\Delta_{dec}H$) of the solid complexes (DSC data) can be used in the investigation of some bond strengths in the complexes (Fig. 6). Naturally, it would be correct to consider the dissociation heats in the gaseous state only. We assume [14] that the differences between the sublimation heats of the hydrated and dehydrated compounds are approximately constant and thus, differences

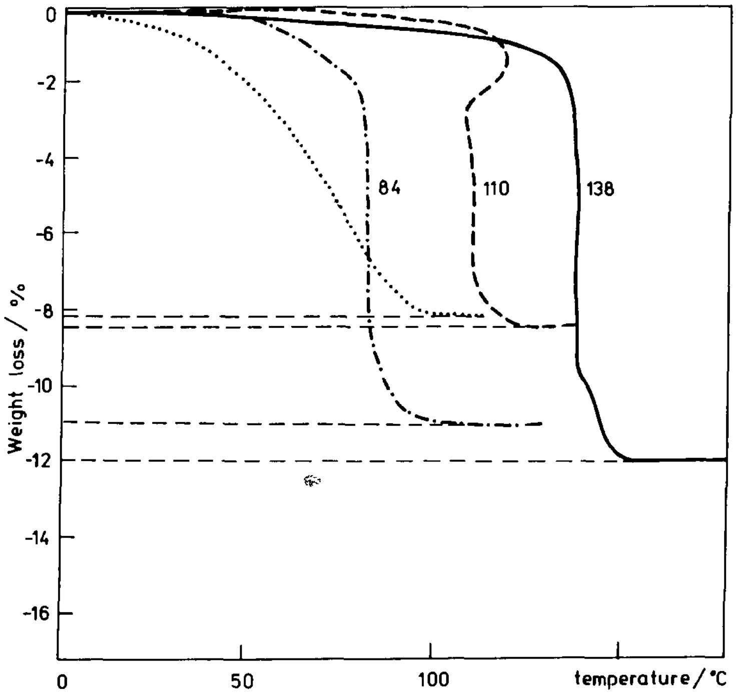

Fig. 5. Q-TG curves of release of solvent molecules: · · · ·, complex **I**; –·–·–, complex **II**; – – – –, complex **III**; ———, complex **IV**.

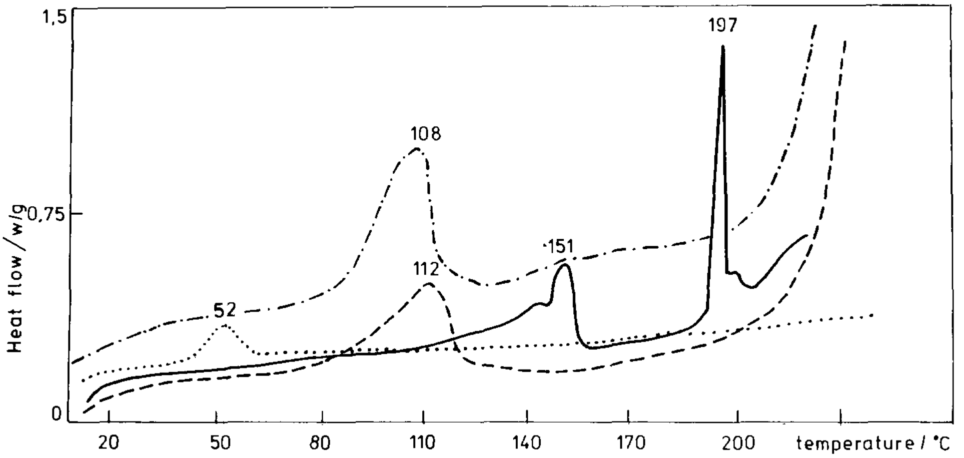

Fig. 6. DSC curves of $[Ni(NA)_nX_2]\cdot nG$ complexes: · · · ·, X is Cl, $nG = 2H_2O$; —·—·—, X is Br, $nG = 2H_2O$; – – – –, X is I, $nG = 4H_2O$; ————, X is NCS, $nG = 2C_2H_5OH$.

Table 5
DSC data of solvent molecules released from some nicotinamide Ni(II) complexes

Complex	Temperature interval/°C	T_p/ °C	$\Delta_{dec}H/(kJ mol^{-1})$	$\Delta_{dec}H$/moleS
$Ni(NA)_2Cl_2\cdot 2H_2O$	35–64	52	18.4 ± 0.4	9.0
$Ni(NA)_3Br_2\cdot 4H_2O$	78–135	108	131 ± 3	32.8
$Ni(NA)_4I_2\cdot 4H_2O$	54–147	112	189 ± 4	47.3
$Ni(NA)_4(NCS)_2\cdot 2C_2H_5OH$	96–155	151	96 ± 2	48.0

between the measured $\Delta_{dec}H$ would be similar to those of the gaseous complexes. Variations in the values of $\Delta_{dec}H$ registered for the studied complexes with various X may, however, be attributed not only to changes in bond strengths (especially to hydrogen bonds in these systems), but also to recrystallization processes, polarization effects, and especially to crystal lattice energy. The $\Delta_{dec}H$ values corresponding to release of water molecules from nicotinamide complexes of the type $Ni(NA)_xX_2$ fall in the order (according to X): I > Br > Cl. The small value of $\Delta_{dec}H$ when X is Cl (Table 5), as compared with those for the other complexes, is evidently a consequence of a different bonding mode for the water molecules in the chloride complex.

4. Conclusions

When the compositions of the complexes, positions of the absorption bands, as well as X-ray crystal analysis results for analogous complexes, are considered one can conclude that: solvent molecules are not coordinated to Ni(II) in the complexes under study; complexes **I** and **I′** with chromophores of NiN_2Cl_4 have a chain structure, bridges being formed by Cl atoms; complexes **III**, **III′**, **IV** and **IV′** possess a monomeric pseudo-octahedral configuration with chromophores NiN_4I_2 (**III**, **III′**) and $NiN'_4N''_2$ (**IV**, **IV′**); and complexes **II** and **II′** are pseudo-octahedral with polymeric structure and NiN_4Br_2 chromophore.

Thermal analysis results obtained for the Ni(II) nicotinamide complexes indicate that the complexes under study, when thermally decomposed, release water or ethanol molecules at first; the release of nicotinamide molecules is a three-step (**II′**, **III′**), two-step (**I′**) or one-step (**IV′**) process; quasi-isothermal thermogravimetry and DSC data are sufficient to differentiate the bonding modes of solvent molecules (adsorbed or crystal water).

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