

THERMOCHEMICAL INVESTIGATION Ni(II)-3-pyridylcarbinol (ronicol) interactions in solid halogeno and thiocyanato complexes*

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(Received December 22, 1994; in revised form May 2, 1995)

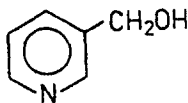
Abstract

The stoichiometry of the thermal decomposition and the stereochemistry of the following compounds was studied: NiR₄Cl₂ (I), NiR₄Br₂ (II), NiR₄I₂·2H₂O (III) and NiR₄(NCS)₂ (IV) (R=3-pyridylcarbinol, ronicol). In complexes I and II the loss of the volatile ligands (on the TG curves) occurs in three steps (-2R, -R, -R), in complex III in four steps (-2H₂O, -2R, -R, -R) and in complex (IV) in one step (-4R). According to the quasi-equilibrium decomposition temperatures, the thermodynamic stability of NiR₄X₂ complexes can be ordered in the sequence (according to X): Cl < Br > I < NCS. The spectral and magnetic data for all initial complexes indicated pseudooctahedral configuration.

Keywords: complexes

Introduction

It is well-documented that heterocyclic compounds play a significant role in many biological systems. Especially six-membered ring system being a component of several vitamins and drugs. In order to enhance understanding of drug-metal ion interactions, we have been studying the thermal properties of nickel(II) complexes with 3-pyridylcarbinol (ronicol):



* Part V in the series: "Thermal decomposition reactions of Nickel(II) complexes under quasi-equilibrium conditions". Part IV: J. Thermal Anal. 46 (1996) 129.

Ronicol contains pyridine ring and is used in the clinical treatment of analgesics which is believed to act as antiinflammatory analgesics.

This work is a continuation of previously reported studies [1–4] on the thermal properties of nickel(II) complexes with substituted pyridines. This paper describes the preparation of complexes formed by the chlorides, bromides, iodides and thiocyanates with ronicol along with thermal analyses and spectroscopic and magnetic investigation of prepared complexes.

Experimental

Preparation of the compounds

Halogeno complexes: To 0.04 mol of $\text{NiX}_2 \cdot 6\text{H}_2\text{O}$ ($X = \text{Cl}, \text{Br}, \text{I}$) in 100 ml of ethanol was added 0.16 mol of ronicol. At laboratory temperature, small blue-green crystals were formed within 2 to 3 days; they were washed with ethanol and dried in the air. For NiR_4Cl_2 (I), calculated: 10.37% Ni; 50.93% C; 4.99% H; 9.90% N; found: 10.54% Ni; 50.78% C; 4.80% H; 9.76% N. For NiR_4Br_2 (II), calculated: 8.96% Ni; 44.09% C; 4.31% H; 8.56% N; found: 9.28% Ni; 43.77% C; 4.20% H; 8.44% N. For $\text{NiR}_4\text{I}_2 \cdot 2\text{H}_2\text{O}$ (III) calculated: 7.48% Ni; 39.78% C; 4.11% H; 7.14% N; found: 7.62% Ni; 39.62% C; 4.09% H; 6.90% N.

Thiocyanato complex: $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.04 mole) was dissolved in ethanol (80 ml) under stirring. On dissolution, ground solid KNCS (0.08 mole) was added. Separated KCl was filtered off and ronicol (0.16 mole) was added into a pure solution of $\text{Ni}(\text{NCS})_2$. After about 2 days small purple crystals were separated. These were washed with ethanol and air-dried. For $\text{NiR}_4(\text{NCS})_2$ (IV), calculated: 9.60% Ni; 47.15% C; 4.62% H; 9.17% N; found: 9.79% Ni; 46.81% C; 4.50% H; 8.92% N.

Analytical methods and equipment

The analytical methods were described previously [1–4]. The thermal properties of the compounds were studied on a Derivatograph OD 102 instrument. In all thermal decompositions a sample weight of 100 mg was used and the rate of temperature increase was $2.5^\circ\text{C min}^{-1}$. The measurements were carried out in air using a platinum crucible. To study the decomposition process the Q-derivatograph under quasi-isobaric and quasi-isothermal conditions was used. This experimental technique results in stabilization of the decomposition temperature, i.e. experiment proceeds under quasi-isothermal conditions [5]. Using various sample holder types, it is possible to keep the pressure of the gaseous products to be almost constant (conical crucible ≈ 90 kPa).

To study the heats of decomposition reactions the Perkin-Elmer Differential Scanning Calorimeter DSC-7 on the null-balance power compensation principle was used (sample weight 7–8 mg, pure gas N₂, scanning rate 10°C min⁻¹). Calibration of the temperature axis and enthalpic change was made of pure indium with its melting point of 156.6°C and enthalpy of fusion $\Delta H = 28.47$ J/g.

The electronic spectra of the solid samples were measured on a Beckman UV 5240 spectrophotometer fitted with a reflectance attachment, using MgO as a reference. Magnetic susceptibilities of polycrystalline samples were measured Gouy method using a sensitive Cahn RM-2 electronic balance. Measurements were made at magnetic field strength 9.9 kOe. Mercury (tetrakis-thiocyanato) cobalt(II) was used as a susceptibility standard [6]. Corrections for diamagnetism of the complexes were calculated by use of Pascals constants.

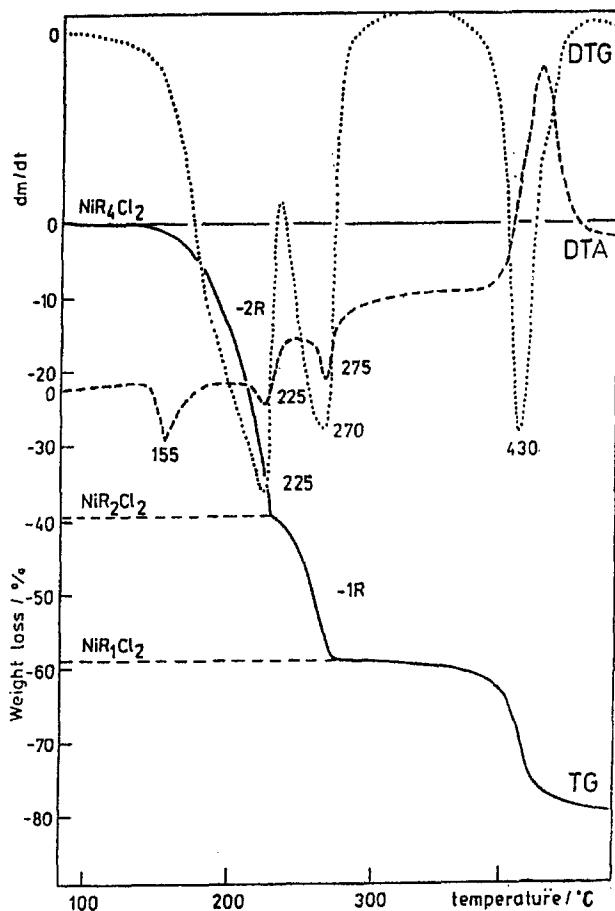


Fig. 1 TG, DTG and DTA curves of NiR₄Cl₂

Results and discussion

Thermal behaviour

Figures 1–4 show the DTA, DTG and TG curves obtained for NiR_4Cl_2 , NiR_4Br , $\text{NiR}_4\text{I}_2 \cdot 2\text{H}_2\text{O}$ and $\text{NiR}_4(\text{NCS})_2$ under static air atmosphere. Both theoretical and experimental weight losses are given in Table 1, along with their corresponding reactions, temperature ranges and temperatures at the peaks in the DTA, DTG, TG and Q-TG curves.

NiR_4Cl_2 (I). This blue-green compound is stable up to $\approx 110^\circ\text{C}$ (DTG); the first stage of decomposition takes place between 135 and 230°C . In this stage

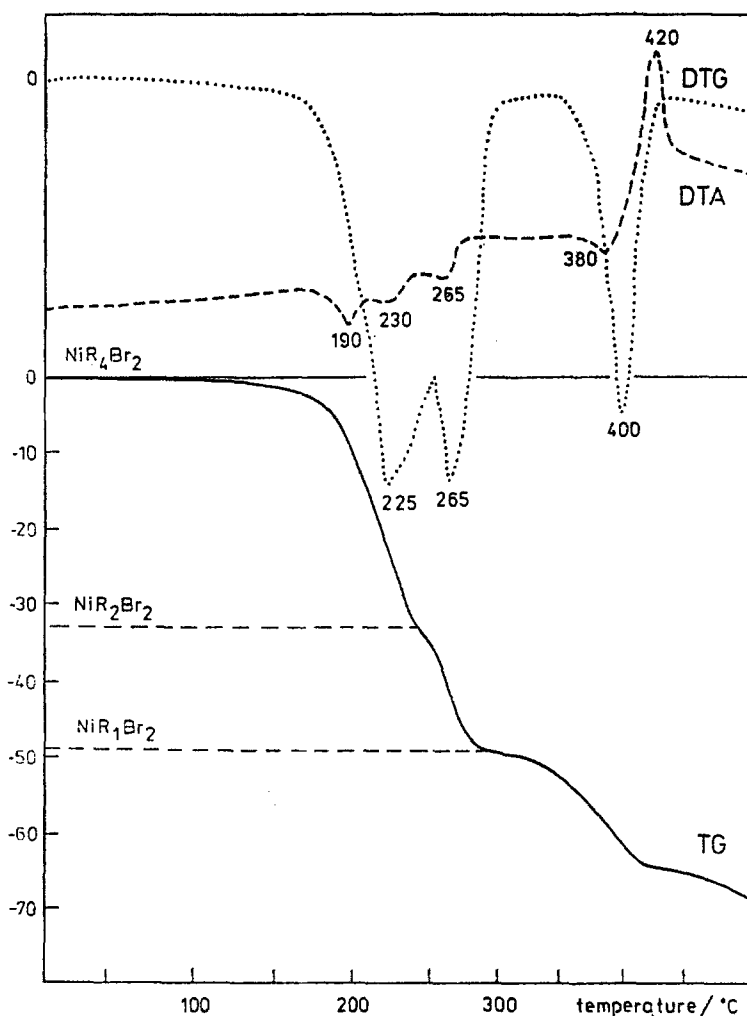


Fig. 2 TG, DTG and DTA curves of NiR_4Br_2

two moles of R is released to give NiR_2Cl_2 and two endothermic peaks are observed at ≈ 155 and 225°C (Fig. 1) attributed to the melting and the decomposition (-2R) respectively. NiR_2Cl_2 decomposes between 230 and 340°C (with minimum on the DTA and DTG curves at 275°C), giving NiR_1Cl_2 . The release of the last mole of R is accompanied by total decomposition of sample as shown by an expressive exothermic peak on the DTA curve at 450°C .

NiR_4Br_2 (II). This blue-green compound, which is stable up $\approx 80^\circ\text{C}$ (DTG), decomposes in temperature interval 20 – 500°C through three stages well dis-

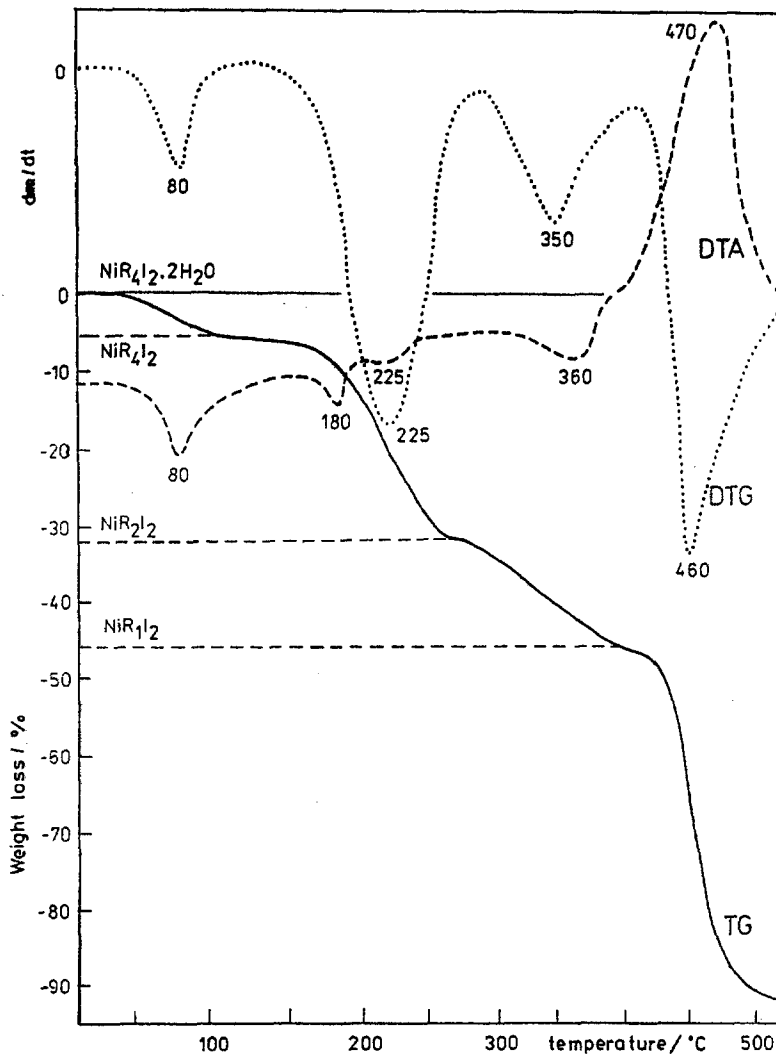


Fig. 3 TG, DTG and DTA curves of $\text{NiR}_4\text{I}_2 \cdot 2\text{H}_2\text{O}$

cernible in the DTG and TG curves (Fig. 2). In the first stage (between 80 and 250°C) it loses two moles of R to give NiR_2Br_2 . In the second stage the weight loss corresponds to one R (in the range 250–320°C) and NiR_1Br_2 is formed. The loss of the last mole of R is accompanied by total decomposition.

$\text{NiR}_4\text{I}_2 \cdot 2\text{H}_2\text{O}$ (III). This compound is stable up $\approx 100^\circ\text{C}$ (DTG). Between 100 and 150°C the loss of two moles of H_2O occurs through a well defined stage to give NiR_4I_2 . This compound loses a further molecule of R in three steps to give NiR_2I_2 and NiR_1I_2 . It should be noted that the release of the last mole of R is accompanied by their decomposition (exothermic peak on the DTA curve at $\approx 510^\circ\text{C}$).

$\text{NiR}_4(\text{NCS})_2$ (IV). This blue compound is stable up $\approx 140^\circ\text{C}$ (DTG) and the loss of the volatile ligands R occurs in one step (Fig. 4) (endothermic peaks on the DTA curves at 190°C (melting) and $\approx 260^\circ\text{C}$) to give $\text{Ni}(\text{NCS})_2$.

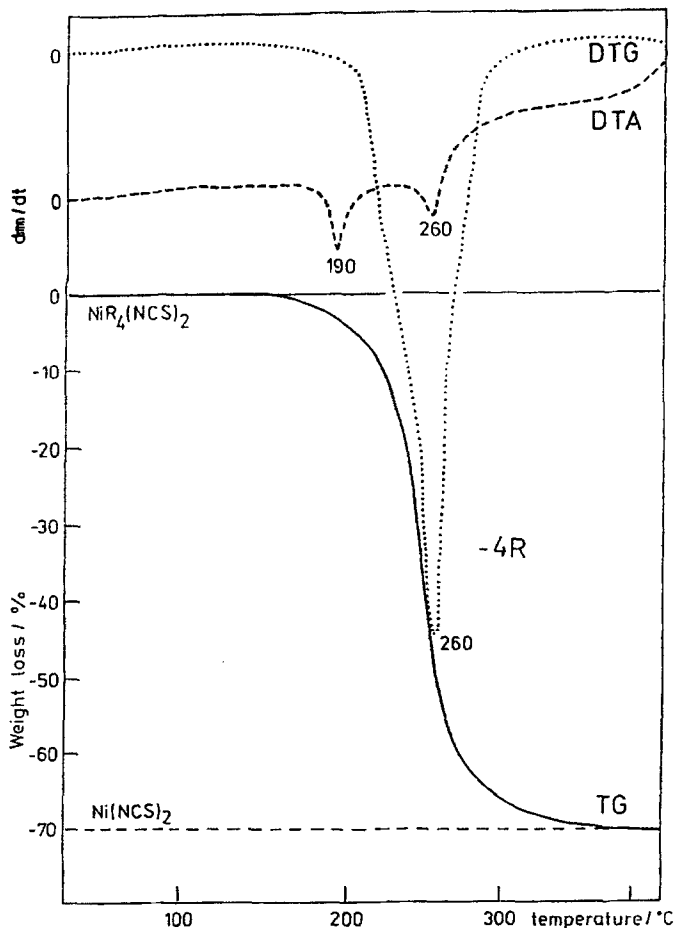


Fig. 4 TG, DTG and DTA curves of $\text{NiR}_4(\text{NCS})_2$

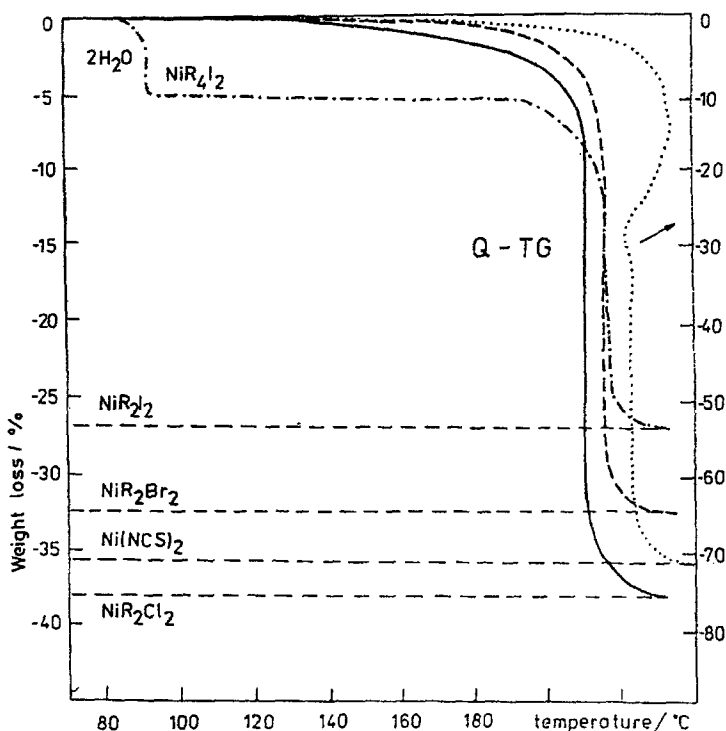
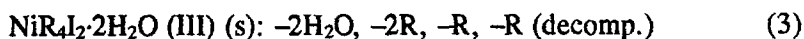
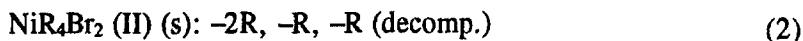


Fig. 5 Q-TG curves of $NiR_4X_2 \cdot nH_2O$ complexes

The loss of the volatile ligands R can be expressed briefly in terms of the following scheme:



The Q-TG curves (Fig. 5), which were traced under quasi-isothermal and quasi-isobaric conditions provide comprehensive information about the reaction stoichiometry as well as the decomposition temperatures [7]. The data listed in Table 1 show that the conditions used the complexes studied decompose according to schemes (1)–(4). The decomposition temperatures derived from the quasi-isothermal measurements can be used to set up qualitative sequence of the thermodynamic stabilities of the compounds in identical experimental conditions. According to the quasi-equilibrium decomposition temperatures,

Table 1 Data on thermal decomposition of complexes with ronicol ($R = \text{ronicol}$)

Decomposition reactions	Weight / %		$T_{\text{range}}(\text{TG}) / ^\circ\text{C}$		$T_{\text{peak}} / ^\circ\text{C}$	
	calc.	found(Q-TG)	found(TG)	$^\circ\text{C}$	DTG	Q-TG
$\text{NiR}_4\text{Cl}_2 \rightarrow \text{NiR}_2\text{Cl}_2 + 2\text{R}$	38.6	38.4	39.0	135-230	155(melt.)	212
$\text{NiR}_2\text{Cl}_2 \rightarrow \text{NiR}_1\text{Cl}_2 + \text{R}$	19.3	-	19.5	230-340	225(endo)	-
$\text{NiR}_1\text{Cl}_2 \rightarrow \text{decomp.}$	-	-	21.5	340-500	275(endo)	-
$\text{NiR}_4\text{Br}_2 \rightarrow \text{NiR}_2\text{Br}_2 + 2\text{R}$	33.3	32.5	33.0	80-250	450(exo)	216
$\text{NiR}_2\text{Br}_2 \rightarrow \text{NiR}_1\text{Br}_2 + \text{R}$	16.7	-	16.0	250-320	190(melt.)	-
$\text{NiR}_1\text{Br}_2 \rightarrow \text{decomp.}$	-	-	15.0	320-500	230(endo)	-
$\text{NiR}_4\text{I}_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{NiR}_4\text{I}_2 + 2\text{H}_2\text{O}$	4.6	4.4	5.0	100-150	265(endo)	92
$\text{NiR}_4\text{I}_2 \rightarrow \text{NiR}_2\text{I}_2 + 2\text{R}$	27.8	27.6	28.0	150-290	380(endo)	216
$\text{NiR}_2\text{I}_2 \rightarrow \text{NiR}_1\text{I}_2 + \text{R}$	13.9	-	14.0	290-450	420(exo)	-
$\text{NiR}_1\text{I}_2 \rightarrow \text{decomp.}$	-	-	45.0	450-550	180(melt.)	-
$\text{NiR}_4(\text{NCS})_2 \rightarrow \text{Ni}(\text{NCS})_2 + 4\text{R}$	71.0	70.5	71.0	140-430	80(endo)	223
					260(endo)	

corresponding the release of 2R moles (Table 1), the thermodynamic stability of NiR_4X_2 complexes can be ordered in the following sequence (according to X): $\text{Cl} < \text{Br} \approx \text{I} < \text{NCS}$.

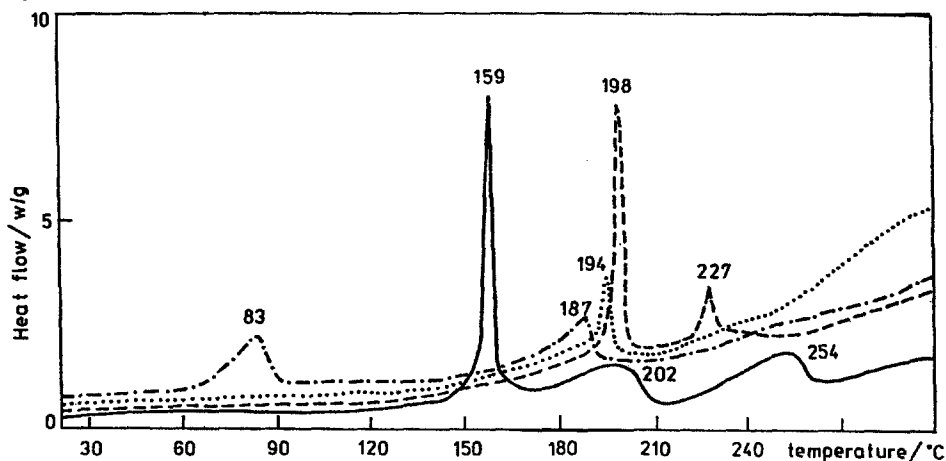


Fig. 6 DSC curves of $\text{NiR}_4\text{X}_2 \cdot n\text{H}_2\text{O}$ complexes — $\text{X}=\text{Cl}$, - - - $\text{X}=\text{Br}$, — · — $\text{X}=\text{I}$,
..... $\text{X}=\text{NCS}$

The complex III, however, obtain two moles of water. The differentiation of various types of water bonding (water bound by occlusion, by adsorption, zeolitic water, interlayer water, crystal water, etc.) by means of thermal analysis is rather difficult. The quasi-isothermal heating techniques are suitable for obtaining information on the features of water loss [8]. The loss of adsorbed water is not an equilibrium reaction and the dehydration curves are always essentially nonisothermal process, striving for equilibrium. This is in the agreement with the Differential Scanning Calorimeter (DSC) data (Fig. 6)(Table 2). The value of decomposition heat for release of H_2O molecules from complex III is comparable with ΔH_D , corresponding to the escape of ronicol molecules. For investigation the bond strength it would be correct to consider the dissociation heats in the gaseous state. As we suppose that the differences between the sublimation heats of starting and final decomposition products are approximately constant [9], then differences between the measured decomposition heats of solid complexes would be similar to those of gaseous complexes. Variations in the values of ΔH_D for studied complexes may be, however, attributed not only to changes in Ni-R bond strength, but also to recrystallisation processes and further effects in the solid state. The studied decomposition reactions are further complicated with melting of NiR_4X_2 complexes in temperature interval 146–202°C. According to melting heats (Table 2) the NiR_4X_2 complexes can be ordered in the following sequence: $\text{NCS} < \text{I} < \text{Cl} < \text{Br}$.

Magnetic and spectral properties

The susceptibility – temperature data for the all compounds were interpreted in terms of Curie-Weiss law. All possess a small positive Weiss constant (Table 3). All complexes studying in the higher temperature region 81–295 K indicated stable values of the magnetic moments characteristic for the monomeric form of the tetragonally distorted nickel(II) complexes [6]. Observed lowest temperatures ($T < 20$ K) informed that the doublet level lies above the singlet and the zero field splitting (ZFS) parameter D is positive. Because the EPR signal in the X-band even at 4.2 K was not observed the value of the ZFS should be large.

Table 2 DSC data of NiR_4X_2 complexes (temperature interval: 30–270°C)

Complex	Process	$T_{\text{interval}} / ^\circ\text{C}$	$T_{\text{peak}} / ^\circ\text{C}$	$\Delta H / \text{kJ mol}^{-1}$
NiR_4Cl_2 (I)	melting	146–164	159	73±2
	-2R	165–206	202	35±1
	-1R	217–261	254	33±1
NiR_4Br_2 (II)	melting	165–202	198	118±2
	-2R	202–247	227	46±1
$\text{NiR}_4\text{I}_2 \cdot 2\text{H}_2\text{O}$ (III)	-2H ₂ O	54–93	83	71±2
	melting	159–192	187	55±1
$\text{NiR}_4(\text{NCS})_2$ (IV)	melting	165–197	194	42±1

The complexes I–III in electronic absorption spectra (Table 3) exhibit weak but pronounced splitting of the first bands located in the region 8.000–11.500 cm^{-1} . In agreement with the results of the other authors [10] the absorption bands at 8.200 cm^{-1} and ≈ 11.000 cm^{-1} can be assigned to the transition ${}^3\text{B}_{1g} \rightarrow {}^3\text{E}_g^a$ and ${}^3\text{B}_{1g} \rightarrow {}^3\text{B}_{2g}$ respectively in a weak tetragonal field of D_{4h} symmetry. The electronic spectrum of $\text{NiR}_4(\text{NCS})_2$ (IV) contains three broad simple bands with relatively low intensity corresponding to the ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$ (P) (ν_1), ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (F) (ν_2) and $\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}$ (P) (ν_3) transitions in the O_h symmetry.

The ring vibrations of 3-pyridylcarbinol (ronicol) upon complex formation in the infrared spectra (1600–640 cm^{-1}) are not shifted appreciably, whereas those at 605 cm^{-1} (in-plane ring deformation) and 401 cm^{-1} (out-of-plane ring deformation) are shifted to higher frequencies (Table 4). This indicated [11], together with occurrence of bands in the region 240–210 cm^{-1} corresponding to the Ni–N stretching vibration, that 3-pyridylcarbinol in studied complexes is coordinated through the nitrogen atom of the heterocyclic ring. The presence of the water in $\text{NiR}_4\text{I}_2 \cdot 2\text{H}_2\text{O}$ (III) is confirmed by the broad band at 3161 cm^{-1} (OH stretching) and sharp band at 1635 cm^{-1} (HOH bending). In the low-frequency

Table 3 Magnetic data and band positions in reflectance spectra

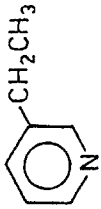
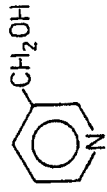
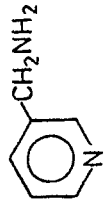
Complex	μ_{eff} (B. M.)	Weiss const./K	Band positions / cm^{-1}			
			ν_1	ν_2	ν_3	
NiR_4Cl_2 (I)	3.11(1)	0.4	8550	10850	16450	25950
NiR_4Br_2 (II)	3.06(3)	4.0	8260	11330	16050	25650
$\text{NiR}_4\text{I}_2 \cdot 2\text{H}_2\text{O}$ (III)	3.28(2)	6.0	8200	11050	16250	25850
$\text{NiR}_4(\text{NCS})_2$ (IV)	2.94(2)	6.3	10750	17540	25850	

Table 4 Important infrared bands ($4000\text{--}200\text{ cm}^{-1}$)

Assignment	Vibrational frequencies of compounds / cm^{-1}				
	R	I	II	III	IV
$\nu(\text{OH})$	3235	3217	3252	3278 3161	3368
$\nu(\text{CN})$	—	—	—	—	2087
$\delta(\text{HO})$	—	—	—	1635 ^a	—
$\nu(\text{CO})$	1057	1053	1052	1053	1059
	1599	1604	1604	1603	1604
	1581	1583	1583	1583	1583
	1028	1033	1033	1028	1034
		1024	1024		
		1010	1010	1009	1018
Ring	791	794	794	792	796
vibrations	708	704	704	711	707
	648	648	648	652	648
	605	619	619	620	625
	401	424	424	422	418
$\nu(\text{Ni-N}(\text{NCS}))$	—	—	—	—	280(sh)
$\nu(\text{Ni-N}(\text{ring}))$	—	230	229	237	241

region ($650\text{--}200\text{ cm}^{-1}$) lattice water exhibits 'librational modes' that are due to rotational oscillation of the water molecule, restricted by interactions with neighbouring atoms [11]. Coordinated water exhibits other modes (especially Ni-OH_2 stretching bands), which were observed at $300\text{--}450\text{ cm}^{-1}$ [12]. This band, however, is absent in the spectrum of complex III and that we can suppose that the water molecules are not coordinated to Ni(II).

Table 5 Thermal decomposition of NiL_4X_2 complexes

L	X	Starting compounds and isolated intermediates				Ref.	
	NCS	$NiL_4X_2 \rightarrow$	$NiL_2X_2 \rightarrow$	$NiLX_2 \rightarrow$	NiX_2	13, 14	
	Cl	$NiL_4X_2 \rightarrow$	$NiL_2X_2 \rightarrow$	$NiLX_2 \rightarrow$	$NiL_2X_3 \rightarrow$		NiX_2
	Br	$NiL_4X_2 \rightarrow$	$NiL_2X_2 \rightarrow$	$NiLX_2 \rightarrow$			
	I	$NiL_4X_2 \rightarrow$	$NiL_2X_2 \rightarrow$				
	NCS	$NiL_4X_2 \rightarrow$	\rightarrow	\rightarrow	NiX_2	This paper	
	Cl	$NiL_4X_2 \rightarrow$	$NiL_2X_2 \rightarrow$	$NiLX_2$			
	Br	$NiL_4X_2 \rightarrow$	$NiL_2X_2 \rightarrow$	$NiLX_2$			
	I	$NiL_4X_2 \cdot 2H_2O \rightarrow$					
	NCS	$NiL_4X_2 \rightarrow$	$NiL_2X_2 \rightarrow$	$NiLX_2$	NiX_2	15	
	Cl	$NiL_4X_2 \rightarrow$	\rightarrow	\rightarrow	$NiL_2X_2 \rightarrow$		NiX_2
	Br	$NiL_4X_2 \rightarrow$	$NiL_2X_2 \rightarrow$	$NiLX_2$			

Conclusions

The results obtained indicate that halogeno nickel(II) complexes with ronicol, when thermally decomposed, first release 2 mole and than 1 mole of R (iodocomplex first release 2 mole of water). The thermal decomposition of the $\text{NiR}_4(\text{NCS})_2$ complex proceeds in one step (-4R). This finding and its comparison with the results obtained for the complexes with the analogous $\text{R}-\text{CH}_2\text{py}$ ligands ($\text{R}=\text{CH}_3, \text{OH}, \text{NH}_2$) (Table 5) indicate the different stoichiometry of the starting complexes and the number of defined intermediates (first of all for $\text{R}=\text{NH}_2$ [15]). The stoichiometry of thermal decomposition can also be influenced by changes in the experimental conditions [16].

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