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THERMAL AND SOME OTHER PROPERTIES OF THE COMPLEXES CRYSTALLIZING FROM THE SYSTEM Ni(II)-en-$[Ni(CN)_4]^{2-}$-H_2O

J. Černák, J. Chomič and *I. Potočňák*

DEPARTMENT OF INORGANIC CHEMISTRY, P. J. ŠAFÁRIK UNIVERSITY,
CS–041 54 KOŠICE, CZECHOSLOVAKIA

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Seven complex compounds exhibiting the compositions $Ni(en)_3Ni(CN)_4 \cdot H_2O$ (I), $Ni(en)_3Ni(CN)_4$ (II), α-$Ni(en)_2Ni(CN)_4$ (III), $Ni(en)Ni(CN)_4 \cdot 2H_2O$ (IV), $Ni(en)Ni(CN)_4$ (V), $Ni(en)_2Ni(CN)_4 \cdot 2.5H_2O$ (VI) and β-$Ni(en)_2Ni(CN)_4$ (VII) were prepared from the system Ni-en-$[Ni(CN)_4]^{2-}$-H_2O. These compounds were examined by the methods of infrared spectroscopy, X-ray powder diffractometry, UV–VIS reflectance spectroscopy, and also by the measurement of magnetic moments. The thermal stability, the stoichiometry of thermal decomposition and the mutual transformations were investigated with a derivatograph. The reactions proceeding according to the following schemes were observed if the system was heated to appropriate temperature:

$$\text{(I)} \rightarrow \text{(II)} \rightarrow \text{(III)} \rightarrow \text{(V)} \rightleftharpoons \text{(IV) and}$$
$$\text{(VI)} \rightarrow \text{(VII)} \rightarrow \text{(III)} \rightarrow \text{(V)} \rightleftharpoons \text{(IV)}$$

Process (VII) →(III) represents isomerization. The reversibility of the process (V) $\rightleftharpoons$ (IV) is due to the high hygroscopicity of the anhydrous complex. The changes in structure in the course of the individual processes are discussed.

Nickel(II) cyanide dissolves in aqueous solutions of amines such as ammonia and ethylenediamine (en) to give different complex compounds [1]. Cambi et al. [2] first prepared such complex compounds containing en and investigated their magnetic properties [2]. The general formula they presented for these compounds is $Ni(CN)_2 \cdot en_x \cdot nH_2O$. The preparation and magnetic properties of the complex $Ni(en)_3Ni(CN)_4 \cdot H_2O$ have been described in [3]. The preparation and infrared spectrum of the interlamellar complex containing $Ni(CN)_2$ and en (without stoichiometric composition) have been described in papers [4, 5]. The thermal analysis of this complex is presented in [6], but without the calculated and measured values of mass loss. The authors of [7] repeated the preparation of this complex and obtained violet crystals, the composition of which could be expressed by the formula $Ni(en)_3Ni(CN)_4$. A concise scheme of thermal decomposition of

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$Ni(en)_3Ni(CN)_4 \cdot H_2O$ without any other information is given in [8]. These papers reveal the possibility of preparing different complexes from the system Ni-en-$[Ni(CN)_4]^{2-}$-H_2O. However, the published data are not always complete and are sometimes contradictory. They do not give sufficient information about the structures of these complexes.

The present work forms part of a wider program involving studies of preparation, structures and properties of the complexes crystallizing from the system Ni(II)-en-$[Ni(CN)_4]^{2-}$-H_2O. In the frame of this program, the crystal structures of the complexes α-$Ni(en)_2Ni(CN)_4$ [9] and $Ni(en)_2Ni(CN)_4 \cdot 2.16\ H_2O$ [10] have been solved.

Experimental

Synthesis and analysis

The synthesis was carried out with the following chemicals: $NiSO_4 \cdot 7H_2O$, KCN, and en. These chemicals were analytical grade reagents. En was redistilled before use (b.p. 117°). They were used to prepare a 1 $mol \cdot dm^{-3}$ solution of $NiSO_4$ and 2 $mol \cdot dm^{-3}$ solutions of KCN and en. The yellow solution of $K_2Ni(CN)_4$ formed by mixing 10 ml of the $NiSO_4$ solution and 20.5 ml of the KCN solution was mixed with a solution consisting of 10 mol of the $NiSO_4$ solution and the necessary volume of the en solution. Via the volume of the added en solution, the molar ratio $NiSO_4$: en : $NiSO_4$: KCN was varied from 1 : 1 : 1 : 4 to 1 : 5 : 1 : 4. The crystals that separated out were filtered off under suction, washed with ethanol and ether, and dried in air. The individual complexes were obtained under the following conditions:

The complex $Ni(en)Ni(CN)_4 \cdot 2H_2O$ separated out at a molar ratio of 1 : 1 : 1 : 4 and to a certain extent at a molar ratio of 1 : 2 : 1 : 4, provided the product was filtered off at once.

The complex α-$Ni(en)_2Ni(CN)_4$ separated out at a molar ratio of 1 : 2 : 1 : 4, provided the product was filtered off after stirring for 30 min in the mother liquor.

The complex $Ni(en)_2Ni(CN)_4 \cdot 2.5H_2O$ separated out at a molar ratio of 1 : 2.5 : 1 : 4.

The complex $Ni(en)_3Ni(CN)_4 \cdot H_2O$ separated out at a molar ratio of 1 : 4 : 1 : 4 and at higher ratios.

The products crystallizing out from the filtrates after separation of the first products were also investigated. They were usually a mixture of two complexes, which could be distinguished even optically according to the habit of the crystals. The quality of the crystals was appropriate for their use for the determination of their structures by the X-ray diffraction methods.

The complex $Ni(en)_3Ni(CN)_4$ was prepared by another method. The precipitate of $Ni(CN)_2$ was subjected to decantation until the SO_4^{2-} ions had disappeared, and it was then dissolved in a 50% solution of en. The solution was allowed to crystallize at 60°. The required product separated out in the form of tiny crystals in the course of 24 hours.

We did not succeed in isolating the complexes $Ni(en)Ni(CN)_4$ and β-$Ni(en)_2Ni(CN)_4$ from this system. Nevertheless, they were prepared by dehydration of the complexes $Ni(en)Ni(CN)_4 \cdot 2H_2O$ and $Ni(en)_2Ni(CN)_4 \cdot 2.5H_2O$. The monoethylenediamine complex is very unstable in air because it is rather hygroscopic, and the temperature of dehydration is an important factor for the preparation of β-$Ni(en)_2Ni(CN)_4$.

The complexes prepared from the solutions were analysed for carbon, hydrogen and nitrogen with a Hewlett–Packard 185 analyzer.

Nickel in mineralized samples was determined complexometrically by using murexide. The results of the analyses are given in Table 1.

Table 1 Results of analyses

Complex	C		H		N		Ni		H_2O*	
	found	calc.	found	calc.	found	calc.	found	calc.	found	calc.
$Ni(en)_3Ni(CN)_4 \cdot H_2O$	28.36	28.61	6.34	6.24	33.70	33.37	28.15	27.97	5.0	4.3
$Ni(en)_3Ni(CN)_4$	29.59	29.89	6.08	6.02	34.39	34.86	28.90	29.22	—	—
$Ni(en)_2Ni(CN)_4 \cdot$ $\cdot 2.5H_2O$	24.12	24.84	5.51	5.17	29.05	28.97	30.89	30.36	12.0	11.6
α-$Ni(en)_2Ni(CN)_4$	28.50	28.12	4.83	4.72	32.76	32.79	33.53	34.36	—	—
β-$Ni(en)_2Ni(CN)_4$	27.94	28.12	4.68	4.72	32.56	32.79	34.05	34.36	—	—
$Ni(en)Ni(CN)_4 \cdot 2H_2O$	21.99	22.69	3.31	3.81	26.72	26.46	36.52	36.97	11.0	11.3

* From thermal analysis.

Infrared spectra

The infrared spectra of the prepared complexes and of the intermediates of their thermal decomposition were measured on a Specord 75 IR spectrophotometer in the range 4000–400 cm^{-1} by using the KBr technique or the nujol suspension technique. Owing to the significant hygroscopicity of $Ni(en)Ni(CN)_4$, the infrared spectrum of this compound was measured as follows: a KBr tablet of the dihydrate was dried in a drying oven at 105°, and the spectrum was recorded immediately after cooling of the sample.

Magnetic measurements

The magnetic susceptibilities were measured by the Faraday method. Corrections for diamagnetism [11] were applied in the calculations of the magnetic moments ($t = 22°$).

X-ray powder diffractometry

The X-ray diffraction patterns of the prepared complexes and the intermediates or products of their thermal decomposition were recorded on a Mikrometa II instrument (Chirana, Czechoslovakia) by using CuK_α radiation.

Thermal measurements

The thermal decompositions of the prepared complexes were measured under dynamic conditions by using an OD 102 derivatograph (MOM, Budapest). Ceramic crucibles and Pt/Pt–Rh thermocouples were used. The measurements were carried out under the following conditions: weighed amount 100 mg, rate of heating 6 deg per minute, air atmosphere, sensitivity of DTA 1/3, DTG 1/5. The intermediates of thermal decomposition were isolated by "freezing", i.e. when the chosen temperature was reached the heating was promptly stopped, or they were prepared by heating in an electric drying oven (up to 200°). The reactions of some intermediates of thermal decomposition with atmospheric humidity was investigated by means of a derivatograph: the sample was allowed to cool freely after the chosen temperature had been reached and the heating had been switched off. In the course of cooling, the T and TG curves were recorded.

Results and discussion

The measured infrared spectra are in line with the expected compositions of the prepared substances and reveal the presence of the individual functional groups (Table 2). The assignment of the observed absorption bands to individual types of vibration was made on the basis of [12–15]. The presence of the molecules of en is demonstrated by several characteristic absorption bands. The corresponding data are given in Table 2. Moreover, the absorption bands of the type ν(C–C) and ν(C–N) were observed in the region of 1100 and 1020 cm^{-1}, as were the bands corresponding to vibrations $\varrho(NH_2)$ in the region of 650 cm^{-1}. On the other hand, the chelate bonding is revealed by one or two strong absorption bands in the region 480–530 cm^{-1}, which may be attributed to the bending vibration of the chelate ring, δ(NCCN) [14, 15].

Table 2 Infrared (cm^{-1}) and reflectance (nm) spectral data and magnetic moments (B.M.)

Complex	ν(OH)	$\nu(NH_2)$	$\nu(CH_2)$	$\nu(C\equiv N)$	$\delta(NH_2)$	$\delta(CH_2)$	δ(NC–CN)	δ(Ni–CN)	μ_B	$^3T_1(P)\leftarrow{}^2A_2$	$^3T_1(F)\leftarrow{}^3A_2$
I	3495s	3360vs, 3335vs	2985w	2130vs	1583s	1463w	490m				
		3310vs, 3280vs	2965m	2120vs			510m	413s	3.01	328	544
	3430s	3185m	2895m								
II	—	3345vs, 3310vs	2980w	2120m			517s	400s			
		3267vs, 3177m	2940s		1585s	1460m			2.99	333	543
			2880s	2110vs			485m				
III	—	3340vs, 3305ssh	2975m	2147vs	1613s	1460w	527s	435s			
		3288vs, 3180m	2945w	2118vs	1584s	1447w		418s	3.09	325	541
			2910m								
			2867m								
IV	3655vs	3338s	2960w	2161vs							
	3580s	3280s, 3180m	2907w	2133msh	1600s	1448vw	513m	438s	3.06	319	562
			2867w								
V	—	3364s	2990vw	2147vs							
		3306s	2927m	2174sh, m	1580s	1453w	513m	433s	dia	[2]	[2]
		3144vw	2873w								
VI	[1]3407ssh	3341vs	2947w	2119vs							
	3443ssh	3290vs	2883w	2129vs	1580s	1453w	510m	427m	3.10	328	542
		3170msh		2147s							
				2154ssh							
VII	—	3366ssh	2937m	2113vs							
		3346vs	2883m	2130vs	1580s	1463w	519m	420s	2.92	322	532
		3293vs		2140s							
		3185ssh		2160msh							

v – very, s – strong, m – medium, w – weak, sh – shoulder; [1] – broad intense peak in the range 3630–3000 cm^{-1}; [2] – not measured because of hygroscopicity.

The strong and sharp absorption bands in the region 2100–2200 cm^{-1}, due to the stretching vibrations $\nu(C \equiv N)$ of the cyano groups, are significantly characteristic. They may serve for the identification of individual complexes in the mixtures, which is why they are also presented in Fig. 1. In the spectra of the complexes $Ni(en)_3Ni(CN)_4 \cdot H_2O$ (I) and $Ni(en)_3Ni(CN)_4$ (II), two absorption bands appear in the mentioned spectral region. On the basis of the isomorphism of complexes I and II with the complexes $Zn(en)_3Ni(CN)_4 \cdot H_2O$ and $Zn(en)_3Ni(CN)_4$, which exhibit an ionic structure [16], the existence of two absorption bands may be explained by the crystallochemical inequivalence of the terminal cyano groups. The spectrum of the complex α-$Ni(en)_2Ni(CN)_4$ (III) also exhibits two absorption bands in this spectral region. On the basis of the solved crystal structure of this complex (Fig. 2) [9], the band at 2118 cm^{-1} may be assigned to vibrations of the terminal cyano groups, and the band at 2147 cm^{-1} to vibrations of the bridging cyano groups. One absorption band with a small shoulder is to be observed at high wavenumbers in this region in the spectra of the complexes $Ni(en)Ni(CN)_4 \cdot 2H_2O$

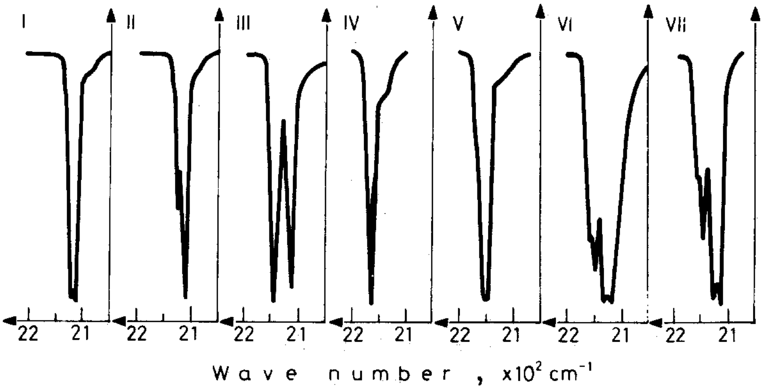

Fig. 1 Characteristic IR $\nu(C \equiv N)$ absorption bands of complexes I–VII in the range 2000–2200 cm^{-1}

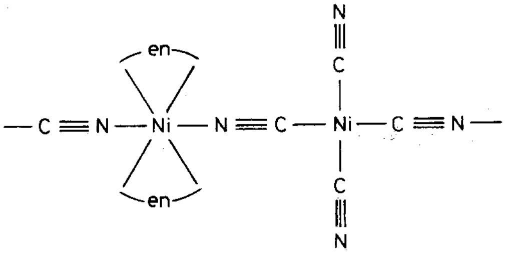

Fig. 2 Schematic chain structure of α-$Ni(en)_2Ni(CN)_4$

(IV) and $Ni(en)Ni(CN)_4$ (V), which suggests a bridging linkage of the cyano groups. Furthermore, four absorption bands in this region appear in the spectra of the complexes $Ni(en)_2Ni(CN)_4 \cdot 2.5H_2O$ (VI) and β-$Ni(en)_2Ni(CN)_4$ (VII). The existence of four absorption bands for complex VI may be explained on the basis of the solved crystal structure by the ineaquivalence of all the cyano groups, the two of which in the cis positions are bridging groups (Fig. 3) [10]. A similar situation may be expected for complex VII, formed from complex VI by dehydration.

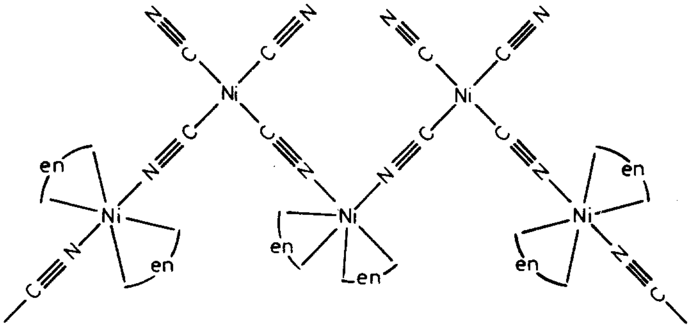

Fig. 3 Schematic chain structure of $Ni(CN)_2Ni(CN)_4 \cdot 2.24\,H_2O$

The characteristic absorption band in the region 400–440 cm^{-1}, which corresponds to the bending vibration δ(Ni–CN), indicates coordination of the cyano groups.

For complexes I, IV and VI, the absorption spectra likewise exhibit absorption bands which may be assigned to the stretching vibrations ν(OH). While these bands are strong and distinguishable for complexes I and IV, this is not the case for complex V. The solved crystal structure of this complex shows that the molecules of water occupy four crystallographic positions in the structure; they are not coordinated, but they are involved in the system of hydrogen-bonds [10]. Owing to this fact, a broad absorption band is to be observed in the region 3630–3000 cm^{-1} of the infrared spectrum.

The octahedral or pseudo-octahedral coordination of the nickel atom in the complex cation is reflected in the measured reflectance spectra of complexes I–IV, VI and VII. In all cases, two maxima (Table 2) were observed in the regions 319–333 nm ($^3T_1$ (P)$\leftarrow$ $^3A_2$) and 532–544 nm ($^3T_1$ (F)$\leftarrow$ $^3A_2$). They correspond to the chromophore NiN_6, as results from a comparison with the values measured in solution for the cation $[Ni(en)_3]^{2+}$ (344(1) nm and 543(1) nm) [17]. The presence of this chromophore was confirmed by solving the crystal structures of complexes III and VI. The reflectance spectrum of complex IV, in which the maximum due to the transition $^3T_1$ (F)$\leftarrow$ $^3A_2$ is observed at 562 nm, is an exception. The maximum due to this transition for the species $[Ni(en)_2(H_2O)_2]^{2+}$ in solution is at 570 nm [17]. These facts indicate the presence of the chromophore NiN_4O_2 in complex IV, and hence the coordination of the molecules of water to the Ni atom. As proved by comparison with the reflectance spectrum of $Zn(en)_3Ni(CN)_4 \cdot H_2O$, the maxima originating from the anion $[Ni(CN)_4]^{2-}$ appear in the region below 319 nm.

The experimental values of the magnetic moments vary within the range 2.92–3.10 B.M. These values indicate pseudo-octahedral coordination of the Ni atom in the complex cation, and square planar coordination of the Ni atom in the anion $[Ni(CN)_4]^{2-}$. This result is in agreement with the results obtained from the reflectance spectra and from structural analysis of complexes III and VI. Only the anhydrous complex $Ni(en)Ni(CN)_4$, which is diamagnetic, deviates, from this series; this means that both Ni atoms in complex V are square-coordinated.

The thermal decomposition curves (TG, DTG and DTA) of complexes I, VI and IV are presented in Figs 4–6. The temperature intervals and the calculated and observed mass losses are given in Table 3.

In the first stage of thermal decomposition of complex I, dehydration takes place. As shown by the infrared spectra and X-ray diffraction pattern, the resulting

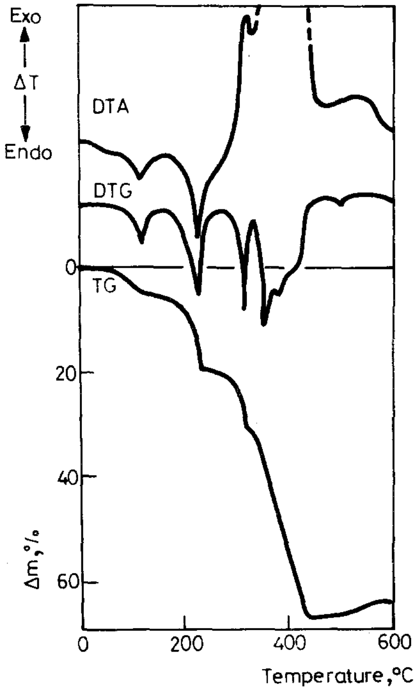

Fig. 4 Thermal curves of $Ni(en)_3Ni(CN)_4 \cdot H_2O$

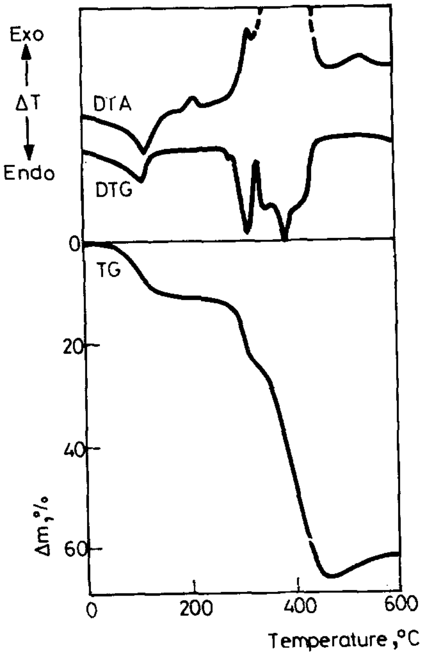

Fig. 5 Thermal curves of $Ni(en)_2Ni(CN)_4 \cdot 2.5H_2O$

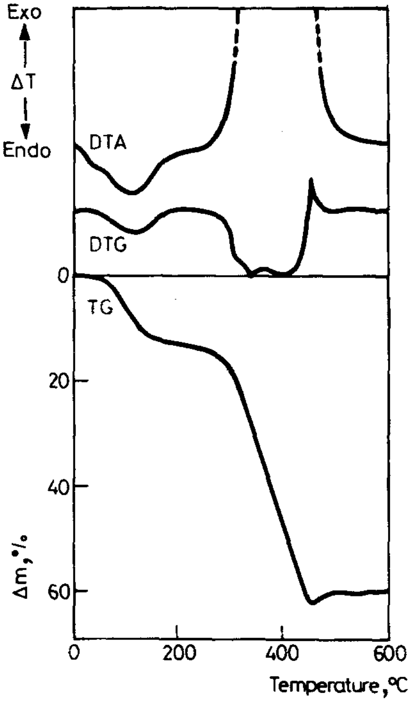

Fig. 6 Thermal curves of $Ni(en)Ni(CN)_4 \cdot 2H_2O$

Table 3 Data on thermal decompositions of the prepared complexes

Complex	Temperature, °C	Weight loss, %		Composition of product
		obs.	calc.	
$Ni(en)_3Ni(CN)_4 \cdot H_2O$	80–120 (endo)	5.5	4.3	$Ni(en)_3Ni(CN)_4$
	185–230 (endo)	15.0	14.3	α-$Ni(en)_2Ni(CN)_4$
	270–330 (exo)	14.0	14.3	$Ni(en)Ni(CN)_4$
	330–435 (exo)	37.0	39.1	NiO
		71.5	72.0	
$Ni(en)_2Ni(CN)_4 \cdot 2.5H_2O$	50–120 (endo)	11.5	11.6	β-$Ni(en)_2Ni(CN)_4$
	230 (exo)	0	0	α-$Ni(en)_2Ni(CN)_4$
	260–325 (exo)	15.0	15.5	$Ni(en)Ni(CN)_4$
	325–450 (exo)	41.5	42.4	NiO
		68.0	69.5	
$Ni(en)Ni(CN)_4 \cdot 2H_2O$	60–170 (endo)	10.5	11.3	$Ni(en)Ni(CN)_4$
	290–470 (exo)	47.0	47.0	NiO
		57.5	58.3	

anhydrous complex II is identical with the compound with the same stoichiometric composition obtained by crystallization at elevated temperature. On the basis of the isomorphism of complexes I and II with the complexes $Zn(en)_3Ni(CN)_4 \cdot H_2O$ and $Zn(en)_3Ni(CN)_4$ [16], the process

$$Ni(en)_3Ni(CN)_4 \cdot H_2O \rightarrow Ni(en)_3Ni(CN)_4 + H_2O$$

may be described as the liberation of a non-coordinated molecule of water from the crystal lattice of the monohydrate. In the course of this process, the nature of the coordination of the central Ni atoms does not change.

In the second stage of thermal decomposition, one molecule of en is released from the coordination sphere. This process may be expressed by the equation

$$Ni(en)_3Ni(CN)_4 \rightarrow \alpha\text{-}Ni(en)_2Ni(CN)_4 + en$$

In this connection, it is worth noting that the released material was not investigated; accordingly, the notation en need not exactly express the real composition of the outgoing component, which might vary, especially at higher temperatures. As shown by the infrared spectra and X-ray diffraction patterns, the product $Ni(en)_2Ni(CN)_4$ formed at laboratory temperature is identical with complex (III). The crystal structure of complex III is known (Fig. 2) [9]. Thus, two cyano groups pass from different anions $[Ni(CN)_4]^{2-}$ to vacated coordination sites about the Ni atom in the trans position after a molecule of en is released from the complex cation $[Ni(en)_3]^{2+}$. This process gives rise to the chain structure depicted in Fig. 2.

The third stage of thermal decomposition is characterized by the release of a further molecule of en from the coordination sphere of the Ni atom. In this process the intermediate $Ni(en)Ni(CN)_4$ is formed. This compound is converted to the dihydrate during cooling in humid air. This dihydrate is identical with complex IV obtained from solution. This process may be expressed by the equation

$$\alpha\text{-}Ni(en)_2Ni(CN)_4 \rightarrow Ni(en)Ni(CN)_4 + en$$

The results of indirect methods suggest that further cross-linking of the structure takes place in the course of this process.

In the last stage of thermal decomposition, the total decomposition of $Ni(en)Ni(CN)_4$ takes place to give NiO, which was proved by X-ray diffractometry. The formation of NiO may be responsible for the small increase in mass at 500°.

In the first stage of thermal decomposition, complex VI undergoes dehydration. This process may be expressed by the equation

$$2\,Ni(en)_2Ni(CN)_4 \cdot 2.5H_2O \rightarrow 2\,\beta\text{-}Ni(en)_2Ni(CN)_4 + 5\,H_2O$$

On the basis of the crystal structures of complex VI (Fig. 3) [10], we may assume that the nature of the coordination of the central Ni atoms does not change in the course of dehydration, but only the non-coordinated molecules of crystal water are released. In spite of the fact that the water molecules occupy four crystallographically independent positions in the structure of complex VI, the dehydration proceeds in a single step. A maximum which is not accompanied by any change in mass appears at 230° in the DTA curve. This maximum corresponds to a phase change. The infrared spectrum and X-ray diffraction pattern of the product of the phase change do not differ significantly from those of complex III. This process may be expressed by the equation

$$\beta\text{-Ni(en)}_2\text{Ni(CN)}_4 \rightarrow \alpha\text{-Ni(en)}_2\text{Ni(CN)}_4$$

This transformation is not reversible because the spectra and diffraction patterns were recorded at laboratory temperature. The simultaneous check measurement performed by using DSC indicated a phase change only for the heating of complex VII, and not for cooling. The chain structure of complex VI contains both cis and trans variants of $\text{Ni(en)}_2\text{N}_2$, and the bridging cyano groups in the anion $[\text{Ni(CN)}_4]^{2-}$ are in the cis position, while the bridging cyano groups in the structure of complex III are bonded to the cation as well as to the anion in the trans position. Accordingly, the presented phase change may be regarded as irreversible double cis-trans isomerization. This isomerization represents an essential impairment of the structure. The fact that the α-isomer exists as the anhydrous substance at laboratory temperature, while the β-isomer crystallizes as the hydrate, shows that the molecules of water contribute significantly to stabilization of the structure of the cis isomer. The isolation of pure complex VII (β-isomer) posed some difficulties, because residual bands corresponding to vibrations ν(OH), and also the bands corresponding to the α-isomer, appeared in the infrared spectrum. These results suggest that complex VII is in a metastable state. The further course of the thermal decomposition is analogous to that of complex I.

Complex IV decays in two stages. In the first stage it undergoes reversible dehydration, as revealed by the TG curves (Fig. 7), which indicate a mass decrease

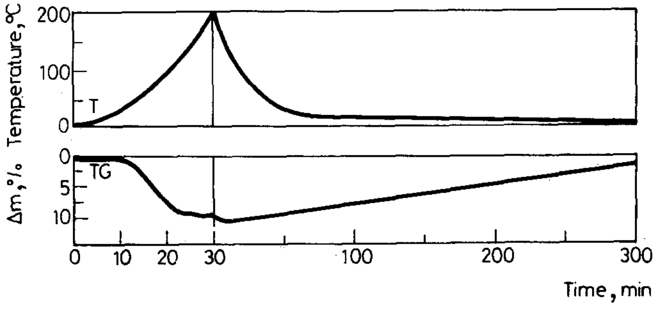

Fig. 7 Dehydration and hydration curves relating to $\text{Ni(en)Ni(CN)}_4 \cdot 2\text{H}_2\text{O}$

during heating and a mass increase to the original value during cooling in humid air. These processes may be described by the equation

$$\mathrm{Ni(en)Ni(CN)_4\cdot 2H_2O} \rightleftharpoons \mathrm{Ni(en)Ni(CN)_4} + 2\,\mathrm{H_2O}$$

A similar experiment with complex VI has shown that the dehydration is not reversible in this case. The paramagnetism of the dihydrate and the diamagnetism of anhydrous complex V suggest that the molecules of water in the dihydrate are bonded to the Ni atom in a similar manner as that assumed for hydrated nickel(II) cyanide [18]. The resulting complex V decomposes in the way described for complex I.

The results have shown that seven complex compounds with different stoichiometric compositions may be isolated from the system Ni(II)-en-$[\mathrm{Ni(CN)_4}]^{2-}$-H_2O. Investigations of their thermal, spectral and magnetic properties have shown that some of these complexes can be prepared by various methods. A scheme may be put forward for the transformations of these complexes:

$$\begin{tikzcd}
\mathrm{Ni(en)_3Ni(CN)_4\cdot H_2O} \arrow[d] & \\
\mathrm{Ni(en)_3Ni(CN)_4} \arrow[d] & \mathrm{Ni(en)_2Ni(CN)_4\cdot 2.5H_2O} \arrow[d] \\
\alpha\text{-}\mathrm{Ni(en)_2Ni(CN)_4} \arrow[d] & \beta\text{-}\mathrm{Ni(en)_2Ni(CN)_4} \arrow[l] \\
\mathrm{Ni(en)Ni(CN)_4} \arrow[d] \arrow[r, shift left] & \mathrm{Ni(en)Ni(CN)_4\cdot 2H_2O} \arrow[l, shift left] \\
\mathrm{NiO} &
\end{tikzcd}$$

The left side of this scheme is agreement with the scheme presented in [8].

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Zusammenfassung — Aus einem System Ni-en-$[Ni(CN)_4]^{2-}$-H_2O wurden sieben Komplexe der Formeln $Ni(en)_3Ni(CN)_4 \cdot H_2O$ (I), $Ni(en)_3Ni(CN)_4$ (II), α-$Ni(en)_2Ni(CN)_4$ (III), $Ni(en)Ni(CN)_4 \cdot 2H_2O$ (IV), $Ni(en)Ni(CN)_4$ (V), $Ni(en)_2Ni(CN)_4 \cdot 2.5H_2O$ (VI) und β-$Ni(en)_2Ni(CN)_4$ (VII) hergestellt. Diese Verbindungen wurden mittels IR-Spektroskopie, Röntgenpulverdiffraktometrie, UV-Reflexionsspektroskopie und durch Messungen des magnetischen Momentes untersucht. Die Wärmestabilität, die Stöchiometrie des thermischen Zerfalles und die gegenseitigen Umwandlungen wurden mittels eines Derivatographen untersucht. Wird das System auf geeignete Temperaturen erhitzt, kann der Reaktionsverlauf durch folgendes Schema dargestellt werden:

$$(I) \rightarrow (II) \rightarrow (III) \rightarrow (V) \rightleftharpoons (IV) \text{ und}$$

$$(VI) \rightarrow (VII) \rightarrow (III) \rightarrow (V) \rightleftharpoons (IV).$$

Der Prozeß (VII) → (III) verkörpert eine Isomerisierung. Die Umkehrbarkeit von Prozeß (V) ⇌ (IV) ist auf die ausgeprägten Hygroskopieeigenschaften des wasserfreien Komplexes zurückzuführen. Es werden die im Ablaufe der einzelnen Prozesse vorgehenden Strukturveränderungen besprochen.

Резюме — Исходя из системы Ni-этилендиамин-$[Ni(CN)_4]^{2-}$-H_2O получено семь комплексов состава $Ni(en)_3Ni(CN)_4 \cdot H_2O$ (I), $Ni(en)_3Ni(CN)_4$ (II), α-$Ni(en)_2Ni(CN)_4$ (III), $Ni(en)Ni(CN)_4 \cdot 2H_2O$ (IV), $Ni(en)Ni(CN)_4$ (V), $Ni(en)_2Ni(CN)_4 \cdot 2{,}5H_2O$ (VI) и β-$Ni(en)_2Ni(CN)_4$ (VII). Полученные комплексы были изучены методом ИК спектроскопии, порошкового рентгеноструктурного анализа, спектроскопией отражения в УФ- и видимой области, а также измерением магнитных моментов. С помощью дериватографа изучена их термоустойчивость, стехиометрия термического разложения и общие превращения. При нагревании системы до соответствующей температуры реакции протекали по следующей схеме

$$(I) \rightarrow (II) \rightarrow (III) \rightarrow (V) \rightleftharpoons (IV) \text{ и}$$

$$(VI) \rightarrow (VII) \rightarrow (III) \rightarrow (V) \rightleftharpoons (IV).$$

Процесс (VII) → (III) представляет собой изомеризацию. Обратимость процесса (V) ⇌ (IV) обусловлена высокой гигроскопичностью безводного комплекса. Обсуждены изменения структуры соединений в ходе отдельных процессов.