Journal of Thermal Analysis, Vol. 34 (1988) 1053–1072

THERMAL PROPERTIES OF SOLID NICKEL(II) COORDINATION COMPOUNDS[+]

Part B: Thermal octahedral ↔ square planar transformations

E. Jóna

DEPARTMENT OF INORGANIC CHEMISTRY, SLOVAK TECHNICAL
UNIVERSITY, 812 37 BRATISLAVA, CZECHOSLOVAKIA

(Received September 9, 1987)

The paper deals with the chemical and physical factors influencing the thermal octahedral ↔ square planar changes of nickel(II) complexes in the solid phase. The relationship between these transformations and the tetragonal distortion of the octahedral ligand field is discussed. Depending on the coordination of the ligands, these transformations can be divided into two groups: octahedral monomer ↔ square planar monomer, and octahedral polymer ↔ square planar monomer changes. Attention is directed only to octahedral and square planat Ni(II) complexes (square planar complexes with chromophores [NiN_4], [NiN_2O_2] and [NiO_4]), which can be isolated in the solid state before and after heating. The possibility of such a configurational change seems to be dependent upon the thermal stabilities of the initial and final complexes, the electronic and steric properties of the ligands, the complexing ability of the central atom, and particularly the equatorial–axial interactions of the ligands via the central atom.

The development of catalysis during the past two decades has been characterized by the wide application of metal complexes as catalysts. With unchanged catalytic technologies, coordination compounds have been used as solid heterogeneous catalysts (anchored complexes on inorganic supports, surface complexes, etc.) [1]. It is known [2] that the catalytically active complexes possess at least one free position in their coordination spheres, and they therefore, have often an energetically less advantageous arrangement of the ligands around the central ion. The nickel(II) ion forms complexes with various configurations (mainly octahedral and square planar [3]), between which thermal mutual transformations can occur. From this aspect, attention has been paid to theoretical suggestions and experimental data concerning the thermal octahedral ↔ square planar changes of solid nickel(II)

[+] Part A: J. Thermal Anal., 16 (1979) 213.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

complexes (square planar complexes with [NiN_4], [NiN_2O_2] and [NiO_4]) chromophores).

Recent studies of Ni(II) complexes by means of thermal analysis indicated that there are two types of thermal reactions involving the configurational change described above [4, 5]. One type is thermal decomposition (TD), when the complexes lose volatile ligands and configurational changes occur. Another type is thermal isomerization (TI), involving transformation without the liberation of any ligands. On the other hand, the octahedral ↔ square planar changes may be further divided with regard to the coordination mode of the ligands into octahedral monomer ↔ square planar monomer and octahedral polymer ↔ square planar monomer. The following study considers both of these types of thermal transformation of Ni(II) complexes which can be isolated in the solid state before and after heating.

Tetragonal distortion in solid pseudo-octahedral nickel(II) complexes

The transition from one type of coordination polyhedron (e.g. octahedron) to another (square plane) may be judged with regard to the tetragonal distortion of the octahedral ligand field (Fig. 1). The simple ligand field theory predicts that the triplet $^3A_2$ state (paramagnetic) must always lie below the singlet ^1E state (the latter state would impose diamagnetism) for all values of the ligand field strength (Δ_0). All regular octahedral complexes of Ni(II) must therefore show a paramagnetism corresponding to the presence of two unpaired electrons. The situation changes, however, whenever axial distortion is applied to the originally regular octahedral field. Such distortion lowers the symmetry from O_h to D_{4h} and is accompanied by a further loss in degeneracy of the d orbitals (Fig. 2). When this tetragonal distortion is large, the energy of separation between the $d_{x^2-y^2}$ and d_{z^2} orbitals (Δ_1) or between the $d_{x^2-y^2}$ and d_{xy} orbitals (Δ_2) may exceed the electron-pairing energy (E_π). In this case there will be a change in magnetic moment from ca. 3.0 B.M. to zero. It is clear

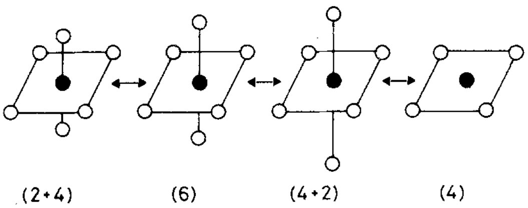


Fig. 1 Scheme of coordination polyhedra of nickel(II) complexes (with corresponding coordination number) with regard to the tetragonal distortion of the octahedral ligand field

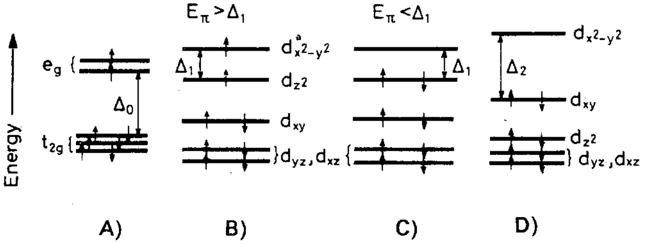


Fig. 2 Splitting of orbitals in octahedral, tetragonal and square planar ligand fields for Ni(II) complexes; A: octahedral complex [NiL_6]; B, C: tetragonal complex (NiL_4X_2]; D: square planar complex [NiL_4]

that tetragonal distortion leads, in the limit, to square planarity and a coordination number of four. Proceeding in the reverse direction for a square planar complex [NiL_4] which interacts along the z axis with two ligands X, there will be a reduction in the energy of separation (Δ_1 or Δ_2) of the two highest-energy orbitals. For weak interactions, such as would be caused by ligands low in the spectrochemical series (e.g. ClO_4^- and BF_4^-) [3], Δ_2 may still exceed the pairing energy. On the other hand, if the separation of the ligands L and X in the spectrochemical series is relatively small (e.g. py and NCS^-), then Δ may be less than the pairing energy and a change in spin multiplicity will occur. The distorted octahedral and square planar Ni(II) complexes may then be high or low-spin, depending on Δ and E_π. The square planar complexes, however, have large values of Δ and are diamagnetic, and pseudo-octahedral Ni(II) complexes are mostly paramagnetic.

In the solid state, however, there are many further factors which influence the interatomic distances and configurational transformations. Therefore, useful correlations must be based on a great many structural results, and a statistical elaboration of the data is necessary [6]. The mean value of the central atom—ligand distances in the equatorial plane is denoted by R_e and that for the distances in the axial direction by R_a.

The correlations between the values of R_a and R_e have been found individually for several chromophores (Fig. 3). Increase in R_a results in a shortening in R_e and vice versa. This correlation has been classified as an equatorial—axial influence of the ligands [6, 7]. This term expresses the collective interaction of ligands in the equatorial plane versus that of those in the axial positions through the central atom. Figure 3 demonstrates a higher rigidity of Ni(II) complexes in comparison with Cu(II) complexes, manifested by the configurational change (octahedral to square planar) and usually by a change in the spin state.

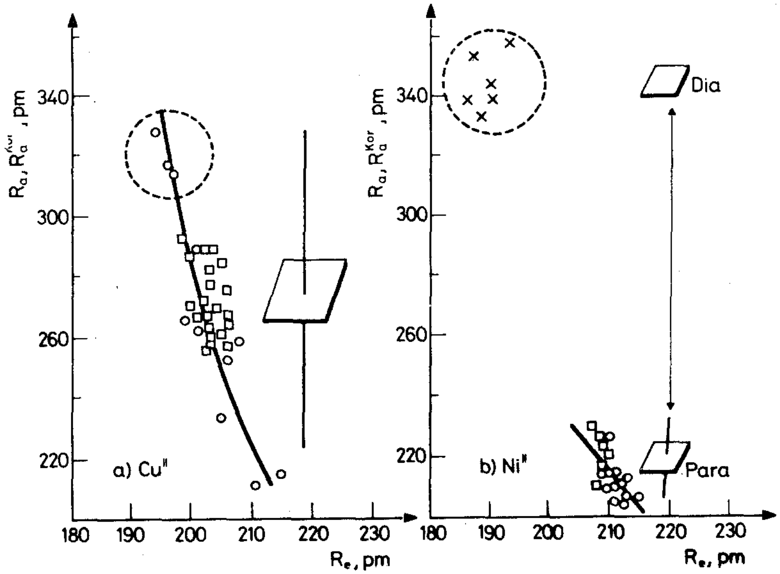


Fig. 3 Plot of R_a *vs.* R_e for Cu(II) and Ni(II) complexes: ○ — $[MN_6]$ chromophore; □ — $[MN_4O_2]$ chromophore; × — $[MN_4]$ chromophore

Classification of thermal octahedral ↔ square planar transformations

These stereochemical changes may be divided (with regard to the coordination mode of the ligands) into octahedral monomer ↔ square planar monomer and octahedral polymer ↔ square planar monomer transformations.

The octahedral monomer (Oh) ↔ square planar monomer (Sq) changes can be represented by the following schemes (Oh' = anated octahedron):

1
$$\underset{\text{(Oh)}}{[Ni(H_2O)_2L_n]X_2} \xrightarrow[-2H_2O]{\text{TD}} \underset{\text{(Sq)}}{[NiL_n]X_2} \xrightarrow{\text{TI}} \underset{\text{(Oh')}}{[NiL_nX_2]} \qquad (1)$$

(L = unidentate or bidentate neutral ligand, X = uncoordinated anion or unidentate anionic ligand.)

2
$$\underset{\text{(Oh)}}{[Ni(H_2O)_2L_nX_2]\cdot mL} \xrightarrow[\substack{-2H_2O \\ -mL}]{\text{TD}} \underset{\text{(Sq)}}{[NiL_nX_2]} \qquad (2)$$

(L = unidentate neutral ligand, X = unidentate anionic ligand.)

3
$$\underset{(Oh)}{[NiL_2(\overset{\frown}{XX})_2]} \xrightarrow[-2L]{TD} \underset{(Sq)}{[Ni(\overset{\frown}{XX})_2]} \tag{3}$$

(L = unidentate neutral ligand, X X = bidentate anionic ligand.)

4
$$\underset{(Oh)}{[Ni(H_2O)_2L(\overset{\frown}{XX})]Y} \xrightarrow[-2H_2O]{TD} \underset{(Sq)}{[NiL(\overset{\frown}{XX})]Y} \tag{4}$$

(L = bidentate neutral ligand, $\overset{\frown}{XX}$ = bidentate anionic ligand, Y = uncoordinated anion.)

The square planar monomer →octahedral polymer (Oh(p)) changes can be expressed by the following reactions:

1
$$\underset{(Sq)}{n(NiL_mX_2)} \xrightarrow[-n(mL)]{TD} \underset{(Oh(p))}{[NiX_2]n} \tag{5}$$

[L = unidentate neutral ligand, X = monodentate anionic ligand ($m=2$) or uncoordinated anion ($m=4$) in initial complex.]

2
$$\underset{(Sq)}{n[Ni(\overset{\frown}{XX})_2]} \xrightarrow{TI} \underset{(Oh(p))}{[Ni(\overset{\frown}{XX})_2]_n} \tag{6}$$

($\overset{\frown}{XX}$ = bidentate anionic ligand. The initial square planar complex is transformed to a polymeric pseudo-octahedral complex without the liberation of any ligands.)

Thermal octahedral monomer ↔ square planar monomer transformations

1. Reactions of the type

$$\underset{(Oh)}{[Ni(H_2O)_2L_n]X_2} \xrightarrow{TD} \underset{(Sq)}{[NiL_n]X_2} \xrightarrow{TI} \underset{(Oh')}{[NiL_nX_2]}$$

The studied changes are summarized in Table 1.

i) *L = unidentate neutral ligand:* This stereochemical change has been observed in Ni(II) complexes with pyridine and imidazole derivatives (Table 1). The coordinating ability of anionic axial ligands generally gives rise to pseudo-

Table 1 Thermal configurational changes of the type: $[Ni(H_2O)_2L_n]X_2$ (Oh) $\rightarrow [NiL_n]X_2$ (Sq) $\leftrightarrow$ $[NiL_nX_2]$(Oh′)

Initial octahedral complex (Oh)	X	Square planar complex (Sq)	Final octahedral complex (Oh′)	Ref.
$[Ni(H_2O)_2(3\text{-Mepy})_4]X_2$	ClO_4, BF_4	$[Ni(3\text{-Mepy})_4]X_2$	—	8
$[Ni(H_2O)_2(imd)_4]X_2$	Br	$[Ni(imd)_4]X_2$	—	9
—	I, NO_3	$[Ni(bimd)_4]X_2$	$[Ni(bimd)_4X_2]$	10
—	Cl, Br, NO_3	$[Ni(abi)_4]X_2 \cdot nH_2O$	—	11
$[Ni(H_2O)_2(en)_2]X_2$	ClO_4	$[Ni(en)_2]X_2$	—	12
$[Ni(H_2O)_2(N\ N\text{-dmen})_2]X_2 \cdot 2H_2O$	I	$[Ni(N\ N\text{-dmen})_2]X_2$	—	13
$[Ni(H_2O)_2(N\ N\text{-deen})_2]X_2 \cdot H_2O$	Br	$[Ni(N\ N\text{-deen})_2]X_2$	—	14
$[Ni(H_2O)_2(N\ N\text{-deen})_2]X_2$	ClO_4	$[Ni(N\ N\text{-deen})_2]X_2$	—	13
$[Ni(H_2O)_2(pn)_2]X_2$	ClO_4	$[Ni(pn)_2]X_2$	—	15
$[Ni(H_2O)_2(phenen)_2]X_2$	NO_3	$[Ni(phenen)_2]X_2$	$[Ni(phenen)_2X_2]$	15
—	Cl	$[Ni(i\text{-bn})_2]X_2$	$[Ni(i\text{-bn})_2X_2]$	5
—	NO_3	$[Ni(m\text{-bn})_2]X_2$	$[Ni(m\text{-bn}))_2X_2]$	5, 16
$[Ni(H_2O)_2(dl\text{-bn})_2]X_2$	Cl, Br	$[Ni(dl\text{-bn})_2]X_2$	$[Ni(dl\text{-bn})_2X_2]$	5, 16
$[Ni(H_2O)_2(dl\text{-bn})_2]X_2$	NO_3, ClO_4	$[Ni(dl\text{-bn})_2]X_2$	—	5,16
$[Ni(H_2O)_2(dl\text{-stien})_2]X_2$	Cl, r, NO_3	$[Ni(dl\text{-stien})_2]X_2$	$[Ni(dl\text{-stien})_2X_2]$	17

py = pyridine; N N-dmen = N,N-dimethylethylenediamine; phenen = 1-phenyl-1,2- ethanediamine;
imd = imidazole; N N-deen = N,N-diethylethylenediamine; dl-bn = dl-2,3-butanediamine;
en = ethylenediamine; pn = 1,2-propanediamine; dl-stien = dl-1,2-diphenyl-1,2-ethanediamine.

Table 2 Stereochemistry of the solid NiL_4X_2 complexes

L	pK_a	Stereochemistry				
		Cl	Br	I	ClO_4	BF_4
py	5.17	Oh	Oh	Oh	Oh	Oh
3-Mepy	5.68	Oh	Oh	Oh	Oh Sq	Oh Sq
4-Mepy	6.02	Oh	Oh	Oh	Sq	Sq
3,4-Me_2py	6.46	Oh	Oh	Sq	Sq	Sq
4-NH_2py	9.17	Oh Sq	Oh Sq	Sq	Sq	Sq

Table 3 Possibility of thermal Sq →Oh transformation of $NiL_4X_2 \cdot nH_2O$ complexes

X	L	
	bimd	abi
Cl	—	Sq →Oh
Br	—	Sq →Oh
I	Sq →Oh	decomposed
NO_3	Sq →Oh	Sq →Oh
ClO_4	decomposed	decomposed
SO_4	—	decomposed

(bimd = benzimidazole, abi = aminobenzimidazole)

octahedral or square planar complexes NiL_4X_2 (Table 2). with increasing basicity of the nitrogen-containing ligands and with decreasing coordination ability of anionic axial ligands, the probability of formation of square planar complexes increases [8].

The possibilities of the transformation from a square planar configuration to an octahedral one on the isothermal treatment of benzimidazole and 2-aminobenzimidazole complexes (Eq. (7)) are summarized in Table 3.

$$\underset{(Sq)}{[NiL_4]X_2 \cdot nH_2O} \xrightarrow[170\text{–}230^\circ]{-nH_2O} \underset{(Oh')}{[NiL_4X_2]} \tag{7}$$

(L = bimd, abi).

The results suggest that the ionic radii of the anions in *bimd complexes* are important as a stereochemical requirement for the preparation of the starting complexes and for the configurational transformation. The formation of the square planar species in *abi complexes* seems to depend on steric hindrance by the amino group introduced and on the higher basicity of the abi ligands surrounding the nickel(II) ion. Another feature of the abi complex is that thermal configurational transformation favours tetragonal distortion in the products of heating relative to the bimd complexes [10, 11].

ii) *L = bidentate neutral ligand:* Table 4 summarizes the results of the thermal structural transformations of nickel(II) complexes with N- and C-substituted ethylenediamines. When the original species are octahedral, e.g. the diaquabis(diamine)nickel(II) complexes, they are denoted by Oh in this Table. When heated, they change in one of three ways: simple deaquation leading to a square planar species: Oh →Sq; single-step deaquation—anation (coordination of anionic ligands) leading to an octahedral dianiono species: Oh →Oh'; and two-step deaquation—anation: Oh →Sq →Oh' (Fig. 4). When the original species are

Table 4 Thermal structural changes in nickel(II) complexes with N- and C-substituted ethylenediamines of the type $[Ni(H_2O)_2(\widehat{NN})_2]X_2$

$\widehat{NN}$	X				
	Cl	Br	I	NO_3	ClO_4
N N-dmen	Oh →Oh′	Oh →Oh′	Oh →Oh′	Oh →Oh′	—
N N-deen	Oh →Oh′	Oh →Oh′	Oh →Oh′	Oh →Oh′	Oh →Sq[a]
N N-dmen	Oh →Oh′	Oh →Oh′	Oh →Sq	Oh →Oh′	—
N N-deen	Oh →Oh′	Oh →Sq	Sq[b]	Sq	Sq
pn[c]	Oh →Oh′	Oh →Oh′	—	Oh →Oh′	Oh →Sq
phenen	Oh →Oh′	Oh →Oh′	—	Oh →Sq →Oh′	Sq
i-bn	Sq →Oh′	Sq	Sq	Sq	Sq
m-bn	Sq	Sq	Sq	Sq →Oh′	Sq
dl-bn	Oh →Sq→Oh′	Oh →Sq→Oh′	—	Oh →Sq	Oh →Sq
m-stien	Sq	Sq	Sq	Sq	Sq
dl-stien	Oh →Sq→Oh′	Oh →Sq →Oh′	Sq	Oh →Sq →Oh′	Sq

[a] at 165 °C; at 130 °C: Oh →Oh

[b] only give the anhydrous square planar structure

[c] see Table 1

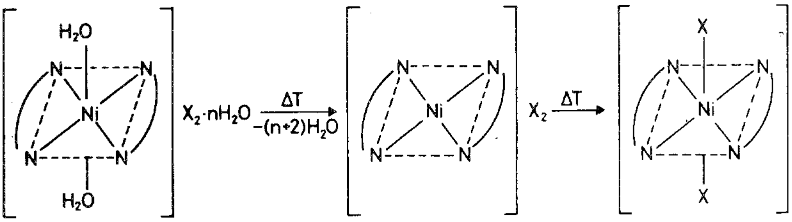


Fig. 4 Thermal reaction scheme of Oh →Sq →Oh′ transformation in nickel(II) diamine complexes

square planar, they may remain unchanged upon heating, or they may be converted into the octahedral dianiono species: Sq →Oh'.

The configurational change is dependent upon the positions to which the substituents are attached and upon the nature of the substituents. In the complexes containing *NN'-dmen and NN'-deen* (two methyl or ethyl groups are bonded to different nitrogen atoms), all the complexes undergo the coordination of anionic ligands X after liberating coordinated water (except for ClO_4^- together with NN'-deen ligands). On the other hand, in the complexes containing NN-dmen or NN-deen (two alkyl substituents are bonded to the same nitrogen atom), the configurational change Oh →Sq takes place (Table 4), while the iodide and perchlorate NN-deen complexes give only the anhydrous square planar complex. Such differences are probably due to the larger steric hindrance of the NN-disubstituent against the coordination of anionic ligands than that of the NN'-disubstituent. The difference in behaviour as concerns the configurational change between the NN-dmen and NN-deen complexes (the latter has been found to turn or assume a square planar configuration more easily) is possibly attributable to the bulkiness of the ethyl group relative to the methyl group [13, 14].

In the case of Ni(II) complexes with *C-substituted ethylenediamines,* it can be seen that pn and phenen complexes easily undergo deaquation—anation, either in one step or in two. An important reason for this easy anation is to be found in the structure of the planar complex $[\mathrm{Ni}(\overset{\frown}{\mathrm{N\,N}})_2]^{2+}$. It is clear that there is enough space above and below the plane to permit the anation of counter ions (the bulky phenyl groups can occupy the equatorial positions in the plane containing two diamines). On the other hand, in the complexes i-bn, m-bn or m-stien, at last two of their substituents are forced to occupy the axial positions and the Sq configuration is stabilized. For the Sq →Oh' transformation to occur, the ateric hindrance of the ligands should be intermediate [5, 15–17].

2. Reactions of the type

$$[\mathrm{Ni(H_2O)_2L}_n\mathrm{X_2}]\cdot m\mathrm{L} \xrightarrow[\substack{-2\mathrm{H_2O} \\ -m\mathrm{L}}]{\mathrm{TD}} [\mathrm{NiL}_n\mathrm{X_2}]$$

can be represented by reaction (8):

$$\underset{\text{(Oh)}}{[\mathrm{Ni(H_2O)_2L_2(NCS)_2}]\cdot 2\mathrm{L}} \xrightarrow{-2\mathrm{H_2O},\ -2\mathrm{L}} \underset{\text{(Sq)}}{[\mathrm{NiL_2(NCS)_2}]} \tag{8}$$

(L = qn [18–20], 4-Meqn [21] and 6-Meqn [22].)

It has been found [4, 20] that the initial complex with L = qn exhibits different courses of thermal decomposition for the coarse-crystalline (cc.) form and the powder (p.) form. In the decomposition of the starting compound in the cc. form, a quinoline solution is produced, from which the thermodynamically more stable square planar isomer crystallized. In the decomposition of the starting compound in the p. form, the liquid phase was not observed macroscopically. Due to this circumstance, the pseudo-octahedral isomer $Ni(qn)_2(NCS)_2$ was formed.

3. Reactions of the type $\underset{(Oh)}{[NiL_2(\overset{\frown}{XX})_2]} \xrightarrow[-2L]{TD} \underset{(Sq)}{[Ni(\overset{\frown}{XX})_2]}$

i) $\overset{\frown}{XX} = \overset{\frown}{NO}$: Structural changes and kinetic data for thermal pyridine (L = py) dissociation from the bis-pyridine adducts of bis(N-alkyl or aryl-substituted salicylindeneaminato)nickel(II) (abbreviated as [Ni(N-R-X-salam)$_2$py$_2$], Fig. 5) are summarized in Table 5 [23, 24]. On pyrolysis, these pyridine adducts of Ni(II) with an octahedral configuration liberated pyridine to leave products with the formula [Ni(N-R-X-salam)$_2$]. The products obtained from compounds 1, 2, 7–15 were square planar, while those from 3–6 were pseudo-octahedral. The values of the activation energy (E_a) increased with increase in the electron-withdrawing property of the substituents; these values were considered to reflect the kinetic bond stability between the central atom and the axial pyridine ligands [23]. The ΔH values of bis(pyridine)-bis(N-alkyl-substituted-salicylideneaminato)nickel(II) depend on the nature of R and X (products 7–13). The logarithmic values of the rate constants decreased linearly with increase in ΔH, indicating that the kinetic bond stability could be correlated with the thermodynamic bond stability with respect to the Ni(II)-pyridine linkage [20]. Whether pyridine dissociation gives rise to a square planar or octahedral complex is not determined purely by the E_a values. As far as the present complexes are concerned, the rater more bulky R seems to favour the pseudo-octahedral form (Table 5).

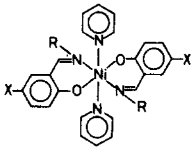


Fig. 5 Bis(pyridine)-bis(N-alkyl or aryl-substituted salicylideneaminato)nickel(II): [Ni(N-R-X-salam)$_2$py$_2$]

ii) $\overset{\frown}{XX} = \overset{\frown}{OO}$: Extensive investigations have been performed on the nickel(II) chelates of pentane-2,4-dione, of which bis(pentane-2,4-dionato)nickel(II) dihy-

Table 5 Thermal structural change and kinetic data of pyridine liberation reactions of [Ni(N-R-X-salam)$_2$py$_2$] complexes

No.	X	R	Structural change	E_a, kJ mol^{-1}		ΔH, kJ mol^{-1}
				izotherm.	dynam.	
1	H	C_6H_5	Oh → Sq	167 ± 4	—	—
2	H	F-C_6H_4	Oh → Sq	163 ± 4	—	—
3	H	MeO-C_6H_4	Oh → $Oh_{(p)}$[a]	97 ± 5	—	—
4	H	Me-C_6H_4	Oh → $Oh_{(p)}$	159 ± 14	—	—
5	H	Cl-C_6H_4	Oh → $Oh_{(p)}$	173 ± 12	—	—
6	H	Br-C_6H_4	Oh → $Oh_{(p)}$	172 ± 13	—	—
7	5-MeO	Me	Oh → Sq	73 ± 5	73 ± 0.2	115 ± 1
8	5-Me	Me	Oh → Sq	89 ± 11	80 ± 0.5	121 ± 1
9	H	Me	Oh → Sq	86 ± 3	82 ± 0.4	131 ± 2
10	5-F	Me	Oh → Sq	67 ± 10	69 ± 0.3	127 ± 3
11	5-Cl	Me	Oh → Sq	81 ± 4	83 ± 0.3	147 ± 3
12	5-Br	Me	Oh → Sq	84 ± 10	81 ± 0.5	140 ± 7
13	5-NO_2	Me	Oh → Sq	94 ± 4	96 ± 1.0	165 ± 2
14	H	Et	Oh → Sq	—	83 ± 0.7	125 ± 6
15	H	*n*-Pr	Oh → Sq	—	71 ± 0.6	118 ± 3

[a] monomeric octahedral → polymeric octahedral change

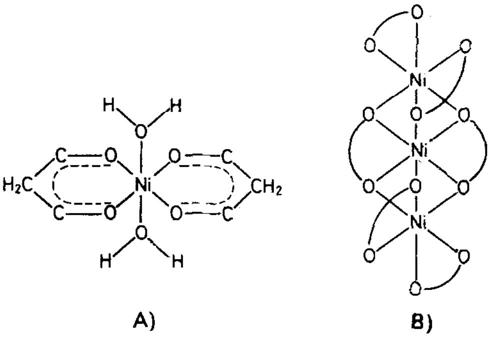


Fig. 6 Proposed pseudo-octahedral structure of bis(pentane-2,4-dionato)nickel(II) dihydrate (A) and anhydrous trimeric chelate (B)

drate can be obtained most easily. The structure of this dihydrate is similar to that of the cobalt(II) complex dihydrate [25] (Fig. 6, A).

The dehydration of this dihydrate affords the anhydrous trimeric chelate, in which Ni(II) is octahedrally coordinated [26] (Fig. 6, B). However, when the terminal methyl groups in pentane-2,4-dione are replaced by *t*-butyl groups, the steric hindrance between the substituents completely prevents trimerization, and the chelate is a spin-paired red planar chelate [27]. Similar observations have been made with the ligands R—CO—CH_2—CO—$C(CH_3)_3$ [28], where R is *p*-tolyl, *p*-anisyl, *p*-chlorobenzyl, *p*-bromobenzyl or *p*-nitrobenzyl. The octahedral → square planar transformation of these complexes seems to be connected with the steric hindrance of one substituent in the *p* position on the phenyl ring, and thus the formation of the trimeric chelate is more complicated.

4. Reactions of the type

$$\underset{\text{(Oh)}}{[Ni(H_2O)_2L(\overset{\frown}{XX})]Y} \xrightarrow[-2H_2O]{TD} \underset{\text{(Sq)}}{[NiL(\overset{\frown}{XX})]Y}$$

This kind of octahedral →square planar change was observed in studies of the mixed complexes $[Ni(H_2O)_2$ (tmen)(acac)]Y, which are dehyrated as follows on heating (29–31]:

$$\underset{\text{(blue, Oh)}}{[Ni(H_2O)_2(tmen)(acac)]Y} \xrightarrow[\Delta T]{-2H_2O} \underset{\text{(red, Sq)}}{[Ni(tmen)(acac)]Y} \tag{9}$$

(tmen = N,N,N,N-tetramethylethylenediamine, acac = acetylacetonate ion, Y = I, ClO_4). In this type of chelate, an anion with very poor coordination ability (e.g. ClO_4^-) acts as the counter ion, while the complex cation contains either two water molecules or a bidentate anion with relatively strong coordination ability (e.g. NO_3^-) in its coordination sphere [30]. When Y = Br, thermal decomposition occurs in the following way [31]:

$$\begin{aligned} 2[Ni(H_2O)_2(tmen)(acac)]Y &\xrightarrow[\Delta T]{-4H_2O} [Ni(tmen)(acac)_2]+ \\ &+[Ni(tmen)Y_2] \end{aligned} \tag{10}$$

Thermal square planar monomer ↔ octahedral polymer transformations

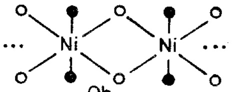
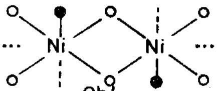
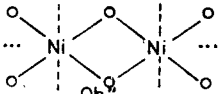
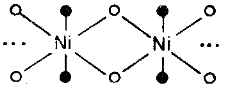
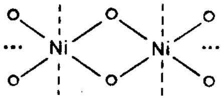
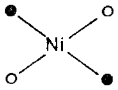
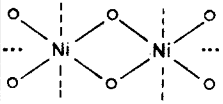
Reactions of the type $\underset{\text{(Sq)}}{n(NiL_mX_2)} \xrightarrow[-n(mL)]{TD} \underset{\text{(Oh(p))}}{[NiX_2]_n}$

i) $m = 2$; L = q-Rpy

The thermal structural changes of the complexes $[Ni(q\text{-}Rpy)_2(NCS)_2]$, depending on the various positions and nature of the substituents (q and R, respectively), are given in Table 6 [32–35]. These pseudo-octahedral complexes with the

Table 6 Structural change of $NiL_n(NCS)_2$ complexes in thermal decomposition reactions:

$$NiL_2(NCS)_2 \xrightarrow{-L} NiL(NCS)_2 \xrightarrow{-L} Ni(NCS)_2{}^a$$

L	n			References
	2	1	0	
4-Mepy 3-Mepy 3-Etpy	 $Oh_{(p)}$	 $Oh'_{(p)}$	 $Oh''_{(p)}$	32,33
4-Clpy 3-Clpy 3-Brpy 3-CNpy 3,4-Me_2py 2-Clpy 2-Brpy	 $Oh_{(p)}$ b)	—	 $Oh''_{(p)}$	32,33,35
2-Mepy 2-Etpy 2,4-Me_2py 2.5-Me_2py 2,6-Me_2py 2-Me, 5-Etpy	 Sq	—	 $Oh''_{(p)}$	34,37

[a] ○ — NCS; ● — Rpy.

[b] $Oh_{(p)}$ — polymeric octahedral (chain) structure; $Oh'_{(p)}$, $Oh''_{(p)}$ — more polymeric octahedral (net) structure.

substituent in the 4 or 3 position on the pyridine ring liberate Rpy molecules on heating and form products with the composition $(Ni(Rpy)_1(NCS)_2$ or $Ni(NCS)_2$ with a more polymeric octahedral structure (similar changes were observed for L = 2-Clpy and 2-Brpy). However, the complexes with an alkyl substituent in the 2 position (α position) show the configurational change square planar →more polymeric octahedral (Oh″(p)) (the hexacoordination is completed by thc adjacent structural units [36]).

The substituent in the 2 position on the pyridine ring leads to a steric interaction between the R and NCS groups, resulting in destabilization of the structure. Stabilization can be achieved by twisting of the pyridine ring out of the equatorial plane (Fig. 7).

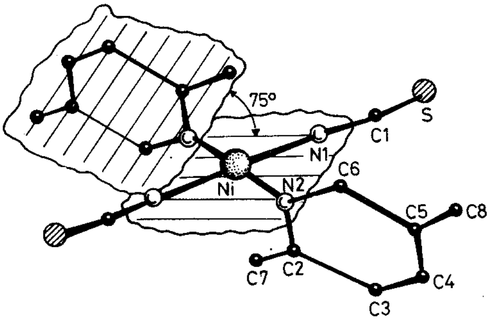


Fig. 7 The position of 2,5-Me_2py in relation to the $[NiN_4]$ plane

The 2 substituent of the twisted pyridine ring makes interaction in the axial position more difficult, and thus the formation of complexes with the coordination number four is understandable. With regard to the relatively strong ligand field of NCS groups (in contrast with the weaker ligand field of Cl^- and Br^-, for example), it is not surprising that the square planar configuration is preferred in the complexes $Ni(2\text{-}Rpy)_2(NCS)_2$ [37]. In the complexes with 2-Clpy and 2-Brpy, however, pseudo-octahedral configuration is achieved. This result can be explained by the different electronic properties of 2-Rpy. Alkyl substituents exhibit a positive inductive effect (+I), and consequently the basicity and σ-bonding ability of 2-alkyl substituents should be greater than those of halogenopyridines (the sequence of the base strengths is as follows: 2-Mepy = 2-Etpy > 2-Brpy > 2-Clpy, in accordance with the pK_a values: $5.97 = 5.97 > 0.90 > 0.72$, respectively) [37]. These properties of the 2-alkylpyridines are evidently sufficient for them to form stable square planar complexes. A similar influence of the 2-alkyl substituent on the structural changes was observed during the thermal decomposition of nickel(II) isothiocyanate complexes with dialkylpyridines (Table 6) [35]. Considerable steric hindrance may also be assumed in complexes with dialkylamines as neutral ligands [38, 39].

Table 7 Kinetic and thermodynamic data of thermal decomposition of $NiL_2(NCS)_2$ complexes

L	Reaction scheme[a]	Structural change	$E_a{}^b$, kJ mol^{-1}	ΔH, kJ mol^{-1}
py	A	$Oh_{(p)} \to Oh''_{(p)}{}^c$	123 ± 6	132 ± 7
3-Mepy	B	$Oh_{(p)} \to Oh'_{(p)} \to Oh''_{(p)}$	116 ± 6	123 ± 6
qn (II)	A	$Oh_{(p)} \to Oh''_{(p)}$	102 ± 5	116 ± 6
2-Mepy	A		95 ± 5	102 ± 5
2,5-Me_2py	A	$Sq \to Oh''_{(p)}$	117 ± 6	126 ± 6
qn(I)	A		128 ± 6	119 ± 6

[a] A: $NiL_2(NCS)_2 \xrightarrow{-2L} Ni(NCS)_2$

B: $NiL_2(NCS)_2 \xrightarrow{-L} NiL(NCS)_2 \xrightarrow{-L} Ni(NCS)_2$

[b] using the isothermal method [41–43]

[c] see Table 6

Kinetic and thermodynamic data on the thermal decompositions of the complexes $NiL_2(NCS)_2$ (L = pyridine and quinoline ligands) are given in Table 7 [40–44]. The values of E_a decrease in the following sequences:

a) $E_a(L = py) > E_a(L = 3\text{-Mepy}) > E_a(L = quin)$ for the Oh(p) →Oh″(p) transformations; and

b) E_a(L = quin(> E_a(L = 2,6-Mepy) > E_a(L = 2-Mepy) for the Sq →Oh″(p) transformation. The reaction rate increases in the same sequence. The observed increase in reaction rate for the initial pseudo-octahedral complexes (a) with more voluminous ligands permits the suggestion that the course of the reaction corresponds to dissociative activation [41, 43]. For initial square planar complexes (b), the contrary was found, indicating associative activation [42, 43]. With the exception of $[Ni(qu)_2(NCS)_2]$(II), the decomposition enthalpy (ΔH) is higher than the activation energy [44] in all cases, and it has to be assumed that intermediates are formed in all reactions (with coordination number 5).

ii) $m = 4$; L = imd:

This case of thermal square planar →octahedral change was observed in reactions (11):

$$\underset{(Sq)}{n[Ni(imd)_4]X_2} \xrightarrow[-4\,imd]{TD} \underset{(Oh(p))}{[NiX_2]_n} \tag{11}$$

(X = Br, I; imd = imidazole).

The compounds $[Ni(imd)_4]X_2$ with X = Br and I form square planar low-spin compounds with a very strong Ni—imidazole bond, in contrast with $[Ni(imd)_4Cl_2]$

and $[\mathrm{Ni(imd)_4(NCS)_2}]$, which are paramagnetic. This agrees with the observed decomposition enthalpies: for X = NCS, (ΔH = 98.4 kJ $\mathrm{mol^{-1}}$), X = Cl (ΔH = 102.2 kJ $\mathrm{mol^{-1}}$), X = Br (ΔH = 118.5 kJ $\mathrm{mol^{-1}}$), X = I (ΔH = 121.8 kJ $\mathrm{mol^{-1}}$) [9]. Comparison with the ΔH values of the corresponding pyridine compounds confirms that imidazole and pyridine are similarly bound to Ni(II). Observed differences are all within experimental error, except for $[\mathrm{Ni(imd)_4]X_2}$ (X = Br, I), which are square planar.

2. Reactions of the type

$$\underset{(\mathrm{Sq})}{n[\mathrm{Ni}(\widehat{XX})_2]} \xrightarrow{\mathrm{TI}} \underset{(\mathrm{Oh(p)})}{[\mathrm{Ni}(\widehat{XX})_2]_n}$$

i) $\widehat{XX} = \widehat{NO}$:

Thermal isomerizations in the solid phase have been found to occur for nickel(II) complexes having the formula $\mathrm{Ni(N\text{-}R\text{-}X\text{-}salam)_2}$ (where N-R-X-salam represents an anion of the Schiff bases derived from the ring-substituted salicylaldehydes X-sal and amine $\mathrm{R\text{-}NH_2}$) [45–47]. A kinetic investigation was carried out on two structural transformations in the solid phase (Fig. 8) [48]: square planar monomer to octahedral polymer for $\mathrm{Ni(N\text{-}ME\text{-}salam)_2}$ (E_a = 303 ± 11 kJ $\mathrm{mol^{-1}}$) and octahedral polymer to square planar monomer for $\mathrm{(Ni(N\text{-}Ph\text{-}salam)_2}$ (E_a = 78 ± 5 kJ $\mathrm{mol^{-1}}$). The polymerization of $\mathrm{Ni(N\text{-}Me\text{-}salam)_2}$, involving the alteration of the spin state of Ni(II), singlet (monomer) to triplet (polymer), has been considered to progress through the further coordination of the phenolato oxygen atoms in the complex molecule to a Ni(II) ion of adjacent molecules at the apical position, forming octahedral coordination geometry around the Ni(II). On the other hand, the monomerization of $\mathrm{Ni(N\text{-}Ph\text{-}salam)_2}$ involves the spin state alteration of Ni(II), triplet (polymer) to singlet (monomer). The larger E_a value for the polymerization of $\mathrm{Ni(N\text{-}Me\text{-}salam)_2}$ than that for the monomerization of $\mathrm{Ni(N\text{-}Ph\text{-}salam)_2}$ can be understood by speculating that the progress of the

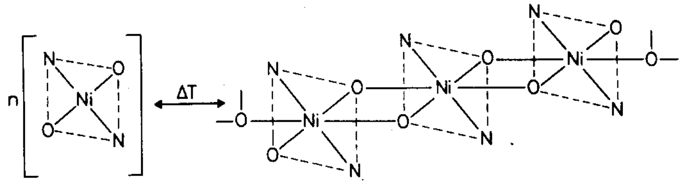


Fig. 8 Skeletal representation of monomer-to-polymer and polymer-to-monomer transformations for complexes $[\mathrm{Ni(N\text{-}R\text{-}X\text{-}salam)_2}]$

polymerization requires a more extensive movement of the molecules than that of the monomerization does.

ii) $\widehat{XX} = \widehat{OO}$:

Thermal isomarization has also been found for nickel(II) complexes with *t*-butyl-substituted *β*-diketones. While bis(dibenzoylmethanato)nickel(II) [49, 50] and bis(3-phenylacetylacetonato)nickel(II) [27] can change upon heating from planar monomer to octahedral trimer before the melting point, transformation of the analogous diamagnetic chelates [28] proceeds only in the melt. On rapid cooling of the melt, a paramagnetic green "glass" is formed, which melts during subsequent careful heating (but at a considerably lower temperature than the previously diamagnetic form) and slowly changes again into the red or brown starting material. Figure 9 shows the scheme of this cyclic process.

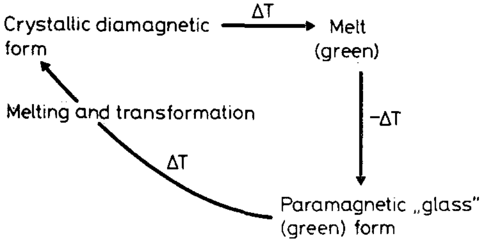
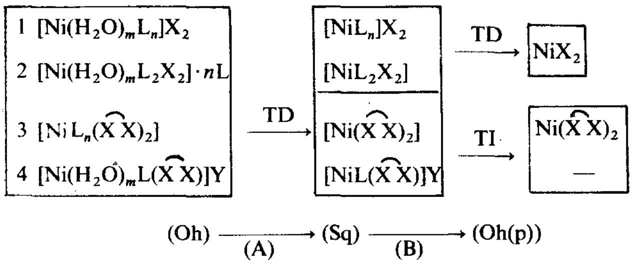


Fig. 9 Mutual transformation of diamagnetic (monomer) and paramagnetic (trimer) chelates with *t*-butyl-substituted *β*-diketones

Conclusions

The studied thermal octahedral ↔ square planar transformation of solid Ni(II) complexes (square complexes with $[NiN_4]$, $[NiN_2O_2]$ and $[NiO_4]$ chromophores) may be expressed by the following general scheme:



Step (A) represents octahedral monomer →square planar monomer changes (Oh →Sq). Step (B) represents square planar monomer →octahedral polymer changes (Sq →Oh(p)).

In the mechanism of both of these observed thermal transformations for Ni(II) complexes, a number of factors may play a role:

1) *The thermal properties of the starting complexes and the decomposed (or changed) products:* these properties influence the studied structural changes from two aspects:

i) the thermodynamic aspect (certain species, octahedral or square planar, are thermodynamically unstable, and this change is therefore not likely to be observed);

ii) the kinetic aspect (certain species are formed slowly, so that again there is little probability of identifying this change).

2) *The basicity of the ligands:* the basicity and the CFES of the ligands play a role in that the strengths of the M-N or M-O bonds are determined in part by the basic nature of the ligands (e.g. with increasing basicity of the pyridine ligands, the probability of formation of square planar complexes $[Ni(R\text{-}py)_4]X_2$ increases).

3) *The steric effects of the ligands:* steric factors play an important role. It has been observed that octahedral ↔ square planar transformations depend on the size of the substituents (e.g. the alkyl or aryl groups on the N,N and N,N′—disubstituted diamine complexes), on the positions and nature of the substituents on the heterocyclic ligands (e.g. the alkyl substituents in the 2 position on the pyridine ring), the changes in orientation of the ligands with changes in temperature, and their influence on the axial interactions.

4) *The nature of the anions:* the structural transformation is also seen to be related to the nature of the anion. For Ni(II) complexes with bimd and abi, the ionic radii of the anions are important for the above change (the smaller ion fits to a greater extent the packing of the trans sites of the coordination plane surrounded by the four bimd molecules). The probability of formation of square planar complexes $[Ni(Rpy)_4]X_2$ increases with decreasing coordination ability of the axial anionic ligands.

5) *The complexing ability of the central atom:* the complexing ability of the central atom is important as well. This factor is illustrated by the differences between Ni(II) and Cu(II) complexes (Fig. 3). In the case of pseudo-octahedral Ni(II) complexes, the tetragonal distortion does not change continuously to a square planar configuration; after a certain mean value of the central atom—ligand distance is reached, an octahedral ↔ square planar change proceeds. Thus, the determining factor in the integral redistribution of the bond strengths along the three axes of the octahedron, leading to the octahedral ↔ square planar transformation of Ni(II) complexes, is the equatorial—axial interactions of the

ligands *via the central atom* [6, 7]. The process, which is connected with weakening of the bonds on one axis and strengthening of the bonds on the remaining twó axes, and vice versa, strongly influences the catalytic properties of metal complexes [2].

References

1 Yu. I. Yermakov, B. N. Kuznetzov and V. A. Zakkarov, Catalysis by supported complexes. Elsevier, Amsterdam–Oxford–New York 1981.

2 G. V. Lisickhin and A. Ya. Yuffa, Heterogeneous metal complex catalysts. Khimiya 1981 (in Russian).

3 F. K. Barenfield, D. H. Busch and S. M. Nelson, Quart. Rev., 4 (1968) 497.

4 E. Jóna, T. Šramko and J. Gažo, J. Thermal Anal., 16 (1979) 213.

5 Y. Ihara, T. Kamishima and R. Tsuchiya, Thermochim. Acta, 67 (1983) 23.

6 J. Gažo, R. Boča, E. Jóna, M. Kabešová, Ľ. Macášková, J. Šima, P. Pelikán and F. Valach, Coord. Chem. Rev., 43 (1982) 87.

7 E. Jóna, F. Valach, J. Gažo, E. Fendrich and T. Šramko, Koord. Khim., 9 (1983) 86.

8 L. M. Vallarino, W. E. Hill and J. V. Quagliano, Inorg. Chem., 4 (1965) 1598.

9 J. C. Van Dam, G. Hakvoort, J. C. Jansen and J. Reedijk, J. Inorg. Nucl. Chem., 37 (1975) 713.

10 R. Tsuchiya, E. Kyuno, A. Uehara, S. Joba and S. Ohba, Chem. Lett., (1976) 911.

11 Y. Ihara and R. Tsuchiya, Bull. Chem. Soc. Jpn, 53 (1980) 1614.

12 M. E. Farago, J. M. James and V. C. G. Trew, J. Chem. Soc. (A), (1967) 820.

13 Y. Ihara, E. Izumi, A. Uehara, R. Tsuchiya, S. Nakagawa and E. Kyuno, Bull. Chem. Soc. Jpn, 55 (1982) 1028.

14 R. Tsuchiya, S. Joba, A. Uehara and E. Kyuno, Bull. Chem. Soc. Jpn, 46 (1973) 1454.

15 Y. Ihara, Bull. Chem. Soc. Jpn, 58 (1985) 3248.

16 H. Nishimoto, T. Yoshikumi, A. Uehara, E. Kyuno and R. Tsuchiya, Bull. Chem. Soc. Jpn, 51 (1978) 1068.

17 Y. Ihara and R. Tsuchiya, Bull. Chem. Soc. Jpn, 57 (1984) 2829.

18 J. Kohout, M. Kohútová and E. Jóna, Z. Naturforsch., 25 (1970) 1054.

19 E. Jóna, T. Šramko, J. Kohout, A. Sirota and J. Gažo, Chem. Zvesti, 25 (1971) 241.

20 T. Šramko and E. Jóna, Collect. Czech. Chem. Commun., 37 (1972) 1645.

21 E. Jóna, M. Jamnický, T. Šramko and J. Gažo, Collect. Czech. Chem. Commun., 37 (1972) 3679.

22 E. Ďurčanská, M. Koman and E. Jóna, Z. Chem., 16 (1976) 453.

23 K. Miyokawa, H. Hirashima and I. Masuda, Bull. Chem. Soc. Jap., 55 (1982) 104.

24 H. Masuda, T. Kawarada, K. Miyokawa and I. Masuda, Thermochim. Acta, 63 (1983) 307.

25 R. H. Holm and F. A. Cotton, J. Phys. Chem., 65 (1961) 321.

26 G. J. Bullen, R. Mason and P. Pauling, Nature, 189 (1961) 291.

27 F. A. Cotton and J. P. Facler, Jr. J. Amer. Chem. Soc., 83 (1961) 2818.

28 F. Dietze, E. Butter and E. Uhlemann, Z. Anorg. Allg. Chem., 400 (1973) 51.

29 Y. Fukuda and K. Sone, Bull. Chem. Soc. Jpn, 43 (1970) 2282.

30 Y. Fukuda and K. Sone, J. Inorg. Nucl. Chem., 34 (1972) 2315.

31 N. Hoshino, Y. Fukuda and K. Sone, Chem. Lett. (Jpn) (1979) 437.

32 M. Jamnický and E. Jóna, Z. Anorg. Allg. Chem., 487 (1982) 225.

33 M. Jamnický and E. Jóna, Collect. Czech. Chem. Commun., 47 (1982) 651.

34 E. Jóna and M. Jamnický, J. Thermal Anal., 27 (1983) 359.

35 E. Jóna, M. Jamnický and T. Šramko, Z. Anorg. Allg. Chem., 447 (1978) 207.

36 A. Reller and H. R. Oswald, J. Solid State Chem., 62 (1986) 306.
37 M. Jamnický and E. Jóna, Inorg. Chim. Acta, 88 (1984) 1.
38 E. Jóna, B. Vojtas, T. Šramko and J. Gažo, Chem. Zvesti, 30 (1976) 100.
39 E. Jóna, B. Vojtas and T. Šramko, Chem. Zvesti, 30 (1976) 107.
40 E. Jóna, T. Šramko and J. Gažo, J. Thermal Anal., 4 (1972) 61.
41 E. Jóna, V. Jesenák, T. Šramko and J. Gažo, J. Thermal Anal., 5 (1973) 57.
42 E. Jóna, V. Jesenák, T. Šramko and J. Gažo, J. Thermal Anal., 5 (1973) 389.
43 E. Jóna, V. Jesenák and T. Šramko, J. Thermal Anal., 5 (1973) 315.
44 E. Jóna, T. Šramko, P. Ambrovič and J. Gažo, J. Thermal Anal., 4 (1972) 153.
45 H. C. Clark and R. J. O'Brien, Can J. Chem., 39 (1961) 1030.
46 L. Sacconi, P. Paoletti and R. Cini, J. Amer. Chem. Soc., 80 (1958) 3583.
47 C. M. Harris, S. L. Lencer and R. I. Martin, Aust. J. Chem., 11 (1958) 331.
48 K. Miyokawa, H. Hirashima and I. Masuda, Bull. Chem. Soc. Jpn, 54 (1981) 3361.
49 L. Wolf, E. Butter and H. Weinelt, Naturwissenschaften, 48 (1961) 378.
50 H. Hennig, U. Eckelmann and E. Uhlemann, Z. Chem., 8 (1968) 232.

Zusammenfassung — Vorliegende Arbeit befasst sich mit den chemischen und physikalischen Faktoren, die den thermischen Übergang oktaedrisch-rechteckig planar der Festkörperphase von Nickel(II) komplexen beeinflussen. Es werden die Beziehungen zwischen dieser Transformation und der tetragonalen Verzerrung oktaedrischer Ligandenfelder besprochen. Entsprechend der Koordinierung der Liganden können diese Transformationen in zwei Gruppen eingeteilt werden: monomer oktaedrisch-monomer rechteckig planar sowie polymer oktaedrisch-monomer rechteckig planare. Hier werden nur solche oktaedrische und rechteckig planare Ni(II)komplexe (rechteckig planare Komplexe mit (NiN_4)-, (NiN_2O_2)- und (NiO_4)-Chromophoren) betrachtet, die sowohl vor als auch nach dem Erhitzen in fester Form isoliert werden können. Die Möglichkeit solcher Konfigurationsübergange scheint von der thermischen Stabilität der Ausgangs- und Produktekomplexe, von elektronischen und sterischen Eigenschaften der Liganden, von der Komplexbildungsstärke des Zentralatomes und hauptsächlich von den äquatorial-axialen Wechselwirkungen der Liganden gegenüber dem Zentralatom abzuhängen.

Резюме — Статья касается химических и физических факторов, затрагивающих термическое структурное превращение октаэдр ↔ плоский квадрат для твердых комплексов никеля. Обсуждена взаимосвязь между этим превращением и тетрагональным искажением октаэдрического поля лигандов. Согласно координации лигандов, эти превращения могут быть разделены на две группы: мономерная октаэдрическая структура ↔ мономерная плоская квадратная структура и полимерная октаэдрическая структура ↔ мономерная плоская квадратная структура. Основное внимание уделено октаэдрическим и плоско-квадратным комплексам двухвалентного никеля (плоские квадратные комплексы с хромофорами [NiN_4], [NiN_2O_2] и [NiO_4]), которые могут быть выделены в твердом состоянии перед и после нагрева. Представляется, что возможность такого конфигурационного изменения зависит от термоустойчивости исходного и конечного комплексов, электронных и стерических свойств лиганда, комплексообразующей способности центрального иона металла и, главным образом, от экваториального—аксиального взаимодействия лигандов через центральный ион металла.