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PYRIDINE-TYPE COMPLEXES OF TRANSITION METAL HALIDES

IV. Preparation and thermal studies on some new complexes of nickel(II)-halides formed with 2-, 3-, and 4-methyl-pyridines

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Formation of nitrogen ligated complexes of types NiL_6X_2, NiL_4X_2, NiL_2X_2 and NiL_1X_2 (where L = pyridine, 2-, 3- and 4-methyl-pyridine and X = F, Cl, Br, I) have been studied by traditional preparative methods, i.e. from solutions and by solid–gas phase chemisorption. Quaternary mixed complexes were obtained by chemisorption from heated intermediates. The complexes thus formed were further analysed by simultaneous TG-DTG-DTA. Effects of the ligands on stoichiometry and thermal properties of the complexes are discussed.

Keywords: complexes, pyridine-type complexes, transition metal halides

Introduction

In previous papers [1–3] we have described the preparation and thermal, spectroscopic and structural properties of cobalt(II) halide complexes of picolines (2-, 3- and 4-methyl-pyridines). This study deals with similar complexes of nickel(II) halides.

While the method of preparation is well-known for the pyridine and substituted pyridine complexes of nickel halides [4–9], relatively few papers have been published on conditions of preparation. It has been reported by different authors that the thermal intermediates can be obtained by thermal treatment [5–7, 10–13]. In one of our previous papers [1] we reported on the solid–gas chemisorption ability of these coordinatively unsaturated intermediates. Ligand sorption was observed from the vapour phase on the solid compounds. This sorp-

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tion leads either to quaternary mixed complexes or ternary tetrakis-compounds by total ligand exchange.

The thermal decomposition of pyridine and picoline ternary mixed complexes of nickel(II)-chlorides, bromides and iodides has been described [4, 14–18]. Although the effects of the halides are discussed in the literature, there are no results on fluoride complexes; this is probably due to preparation problems.

Experimental

In the preparative procedure four different solvents were tested. 0.05 moles of the nickel halides were dissolved in 20 cm^3 ethanol (method A), acetonitrile (method B), water or an excess of picoline (method C). The nickel halides were used as unhydrates; however, in the case of the preparation in acetonitrile the hexahydrates were also used (method D). The mixture was heated to the boiling point under intensive stirring. The Ni:ligand molar ratio was changed from 1:10 to 3:1. The appropriate amount of the ligand was dissolved in 20 cm^3 of solvent and added dropwise. The reaction mixture was boiled for an hour and then cooled slowly. The solid precipitate thus formed was filtered and washed with the solvent. The final products were dried in air and stored in a desiccator over calcium chloride. Complexes of nickel fluoride and α-picoline derivatives were prepared by solid-gas phase chemisorption (method E). The dehydrated nickel halides were placed in a desiccator over the vapour of the ligands. The reaction process was followed by changes in colour related to the chemical changes in the environment of the central ion. Solid samples were thoroughly powdered.

The thermal intermediates were prepared in a high-temperature furnace (method F) under vacuum at the temperature determined from thermal studies.

Quaternary mixed complexes were obtained by solid-gas phase chemisorption from these intermediates in a desiccator over the atmosphere of different picolines [1].

Nickel contents of the samples were determined by complexometric titration. Compositions of the complexes were also checked by thermogravimetry.

Thermoanalytical curves were recorded using a MOM OD2 Derivatograph with a sample weight of 100 mg and a heating rate of 5 $deg \cdot min^{-1}$. Platinum crucibles and a nitrogen atmosphere were used. 100 mg of α-aluminium-oxide was used as reference material.

Results

Preparation

Ternary mixed complexes prepared either from solution or by solid-gas phase chemisorption are listed in Table 1.

Table 1 Preparation of the complexes

Compounds	Method	Ni:ligand molar ratio	Ni content theor.	Ni content found	Ligand number	Colour
[Ni(α-pic)$_n$F$_2$]	E	–	30.9	31.1	1	green
[Ni(β-pic)$_n$F$_2$]	E	–	20.8	21.2	2	l. blue
[Ni(γ-pic)$_n$F$_2$]	E	–	20.8	20.6	2	l. blue
[Ni(α-pic)$_n$Cl$_2$]	E	–	18.6	17.9	2	l. blue
[Ni(β-pic)$_n$Cl$_2$]	A	1:10	11.7	12.0	4	blue
	A	1:3	18.6	18.5	2	l. blue
	B	1:10–1:3	11.7	12.1	4	blue
	B	1:2–3:1	18.6	18.0	2	l. blue
	C	1:40	11.7	11.3	4	blue
[Ni(γ-pic)$_n$Cl$_2$]	A	1:10–1:3	11.7	11.9	4	blue
	B	1:10–1:2	11.7	11.6	4	blue
	B	1:1–3:1	18.6	17.9	2	l. blue
	C	1:40	11.7	11.0	4	blue
[Ni(α-pic)$_n$Br$_2$]	E	–	14.5	14.1	2	l. blue
[Ni(β-pic)$_n$Br$_2$]	A	1:10–3:1	9.9	10.2	4	blue
	B	1:10–3:1	9.9	9.7	4	blue
	C	1:40	9.9	10.0	4	blue
[Ni(γ-pic)$_n$Br$_2$]	A	1:10–3:1	9.9	9.7	4	blue
	B	1:10–1:2	9.9	10.0	4	blue
	B	1:1–3:1	14.5	14.4	2	l. blue
	C	1:40	9.9	10.0	4	blue
[Ni(α-pic)$_n$I$_2$]	E	–	14.5	14.3	1	green
[Ni(β-pic)$_n$I$_2$]	A	1:10–1:3	8.6	8.4	4	l. blue
	B	1:10–3:1	8.6	8.8	4	l. blue
	C	1:40	8.6	8.6	4	l. blue
	D	1:10	6.7	6.5	6	blue
[Ni(γ-pic)$_n$I$_2$]	B	1:10–1:3	8.6	8.5	4	l. blue
	C	1:40	8.6	9.0	4	l. blue

We could not obtain nickel fluoride complexes and α-picoline derivatives from solution due to solubility and crystallization problems. These compounds were thus prepared by solid-gas phase chemisorption. α-picoline complexes of nickel fluoride and iodide contain one mole of the ligand while we obtained bis-complexes with nickel chloride and bromide. The β- and γ-picoline derivatives of nickel fluoride have two ligands in the inner coordination sphere.

The β- and γ-picoline complexes of nickel chloride, bromide and iodide were prepared from solution. The solvent has no influence on the complexation; mainly tetrakis-picoline derivatives were formed. Bis-complexes were obtained at low metal: ligand molar ratios. Water was not built into the coordination sphere of the complexes when the hexahydrates were used (method D), but hexakis-β-picoline compound formed with nickel iodide.

Thermal intermediates and quaternary mixed complexes prepared from these compounds by solid-gas chemisorption are listed in Table 2.

Table 2 Thermal intermediates and quatemary mixed complexes

Thermal	Temp. of	Compound formed in the vapour of		
intermediates	prep./°C	α–picoline	β–picoline	γ–picoline
$[Ni(\beta{-}pic)_2Cl_2]$	140	$[Ni(\beta{-}pic)_2Cl_2]$	$[Ni(\beta{-}pic)_4Cl_2]$	$[Ni(\gamma{-}pic)_4Cl_2]$
$[Ni(\beta{-}pic)_1Cl_2]$	160	$[Ni(\beta{-}pic)_1Cl_2]$	$[Ni(\beta{-}pic)_4Cl_2]$	$[Ni(\gamma{-}pic)_4Cl_2]$
$[Ni(\beta{-}pic)_{2/3}Cl_2]$	240	$[Ni(\beta{-}pic)_{2/3}Cl_2]$	$[Ni(\beta{-}pic)_4Cl_2]$	$[Ni(\gamma{-}pic)_4Cl_2]$
$[Ni(\gamma{-}pic)_2Cl_2]$	150	$[Ni(\gamma{-}pic)_2(\alpha{-}pic)_2Cl_2]$	$[Ni(\gamma{-}pic)_2(\beta{-}pic)_2Cl_2]$	$[Ni(\gamma{-}pic)_4Cl_2]$
$[Ni(\gamma{-}pic)_1Cl_2]$	200	$[Ni(\gamma{-}pic)_1(\alpha{-}pic)_1Cl_2]$	$[Ni(\gamma{-}pic)_1(\beta{-}pic)_3Cl_2]$	$[Ni(\gamma{-}pic)_4Cl_2]$
$[Ni(\gamma{-}pic)_{2/3}Cl_2]$	250	$[Ni(\gamma{-}pic)_{2/3}(\alpha{-}pic)_{1/3}Cl_2]$	$[Ni(\gamma{-}pic)_{2/3}(\beta{-}pic)_{4/3}Cl_2]$	$[Ni(\gamma{-}pic)_4Cl_2]$
$[Ni(\beta{-}pic)_2Br_2]$	150	$[Ni(\beta{-}pic)_2(\alpha{-}pic)_2Br_2]$	$[Ni(\beta{-}pic)_4Br_2]$	$[Ni(\gamma{-}pic)_4Br_2]$
$[Ni(\beta{-}pic)_1Br_2]$	200	$[Ni(\beta{-}pic)_1(\alpha{-}pic)_1Br_2]$	$[Ni(\beta{-}pic)_4Br_2]$	$[Ni(\gamma{-}pic)_4Br_2]$
$[Ni(\beta{-}pic)_{2/3}Br_2]$	240	$[Ni(\beta{-}pic)_{2/3}(\alpha{-}pic)_{1/3}Br_2]$	$[Ni(\beta{-}pic)_4Br_2]$	$[Ni(\gamma{-}pic)_4Br_2]$
$[Ni(\gamma{-}pic)_2Br_2]$	140	$[Ni(\gamma{-}pic)_2Br_2]$	$[Ni(\gamma{-}pic)_2(\beta{-}pic)_2Br_2]$	$[Ni(\gamma{-}pic)_4Br_2]$
$[Ni(\gamma{-}pic)_1Br_2]$	180	$[Ni(\gamma{-}pic)_1Br_2]$	$[Ni(\gamma{-}pic)_1(\beta{-}pic)_1Br_2]$	$[Ni(\gamma{-}pic)_4Br_2]$
$[Ni(\gamma{-}pic)_{2/3}Br_2]$	250	$[Ni(\gamma{-}pic)_{2/3}Br_2]$	$[Ni(\gamma{-}pic)_{2/3}(\beta{-}pic)_{4/3}Br_2]$	$[Ni(\gamma{-}pic)_4Br_2]$

Bis- and mono-complexes and the intermediates of chlorides and bromides containing two-thirs of the maximum amount of ligand were prepared by heating from the appropriate tetrakis derivates in a high-temperature furnace. Thermal intermediates of nickel-iodide decompose easily in air; thus quaternary mixed complexes were not prepared from these compounds. α-picoline derivatives cannot be used for the preparation of quaternary mixed complexes. Either β- or γ-picoline exchanges α-picoline from the solid sample. The resulting material was found to be tetrakis-β- or -γ-picoline complex.

α-picoline sorption was found on the thermal intermediates of nickel-γ-picoline chlorides and nickel-β-picoline bromides. The other compounds remain unchanged.

In β-picoline, vapour ligand sorption was observed on γ-picoline intermediates and the saturation of β-picoline derivatives to yield tetrakis-complexes.

γ-picoline sorption was observed on the intermediates. Tetrakis-γ-picoline complexes were formed either by a total ligand exchange from the intermediates of β-picoline or the completion of the γ-picoline complexes.

The existence of quaternary mixed complexes was checked by infrared spectroscopy as described previously [1–2]. In the far region of the sepctra, characteristic ring deformation vibrations occur for picolines. Results of spectroscopic studies will be published soon [19].

Thermal studies

The thermal decomposition pattern of the parent ligand complexes can be described by the following equations:

$$[\mathrm{Ni(L)_6X_2}] \rightarrow [\mathrm{Ni(L)_4X_2}] + 2\mathrm{L} \quad (1)$$

$$[\mathrm{Ni(L)_4X_2}] \rightarrow \mathrm{NiX_2} + 4\mathrm{L} \quad (2)$$

$$[\mathrm{Ni(L)_4X_2}] \rightarrow [\mathrm{Ni(L)_1X_2}] + 3\mathrm{L} \quad (3)$$

$$[\mathrm{Ni(L)_4X_2}] \rightarrow [\mathrm{Ni(L)_2X_2}] + 2\mathrm{L} \quad (4)$$

$$[\mathrm{Ni(L)_2X_2}] \rightarrow [\mathrm{Ni(L)_1X_2}] + 1\mathrm{L} \quad (5)$$

$$[\mathrm{Ni(L)_1X_2}] \rightarrow \mathrm{NiX_2} + 1\mathrm{L} \quad (6)$$

$$[\mathrm{Ni(L)_1X_2}] \rightarrow [\mathrm{Ni(L)_{2/3}X_2}] + 1/3\mathrm{L} \quad (7)$$

$$[\mathrm{Ni(L)_{2/3}X_2}] \rightarrow \mathrm{NiX_2} + 2/3\mathrm{L} \quad (8)$$

The mechanism and temperature of the DTG peak maxima are in good agreement with literature data [18] for chlorides, bromides and iodides (Table 3).

The thermal decomposition of the nickel fluoride complexes is of interest (Fig. 1). These compounds have been prepared for the first time. Two ligands are bound from the vapour phase for pyridine, β- and γ-picoline, while the mono-complex was formed with α-picoline. The decomposition scheme can be represented by Eqs(5) and (6) for bis-complexes and Eq.(6) for the mono-α-picoline compound of nickel fluoride.

Degradation of the quaternary mixed complexes can be described by the following equations:

$$[\mathrm{Ni(L)_2(M)_2X_2}] \rightarrow [\mathrm{Ni(L)_2X_2}] \quad +2\mathrm{M} \tag{9}$$

$$[\mathrm{Ni(L)_1(M)_3X_2}] \rightarrow [\mathrm{Ni(L)_1(M)_1X_2}] \quad +2\mathrm{M} \tag{10}$$

$$[\mathrm{Ni(L)_1(M)_1X_2}] \rightarrow [\mathrm{Ni(L)_1X_2}] \quad +1\mathrm{M} \tag{11}$$

$$[\mathrm{Ni(L)_{2/3}(M)_{4/3}X_2}] \rightarrow [\mathrm{Ni(L)_{2/3}(M)_{1/3}X_2}] \quad +1\mathrm{M} \tag{12}$$

$$[\mathrm{Ni(L)_{2/3}(M)_{1/3}X_2}] \rightarrow [\mathrm{Ni(L)_{2/3}X_2}] \quad +1/3\mathrm{M} \tag{13}$$

Decomposition of quaternary mixed complexes starts with the release of the ligand bound from the vapour phase (Fig .2). Subsequent steps are identical with those of the thermal degradation of the intermediates (Table 3).

Table 3 Decomposition (DTG peak temperatures) of the complexes in °C

Eq.	No.	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
$\mathrm{NiF_2}$	py	–	–	–	–	85	145	–	–
	α–pic	–	–	–	–	–	140	–	–
	β–pic	–	–	–	–	75	140	–	–
	γ–pic	–	–	–	–	70	140	–	–
$\mathrm{NiCl_2}$	py	–	–	–	130	175	–	275	315
	α–pic	–	–	–	–	90	–	155	275
	β–pic	–	–	–	135	185	–	245	315
	γ–pic	–	–	180	–	–	–	270	315
$\mathrm{NiBr_2}$	py	–	–	–	135	195	290	–	–
	α–pic	–	–	–		–	190	–	–
	β–pic	–	–	–	165	140	–	225	290
	γ–pic	–	–	–	180	200	–	285	305
$\mathrm{NiI_2}$	py	155	225	–	–	–	–	–	–
	α–pic	–	–	–	–	–	170	–	–
	β–pic	155	225	–	150	185	230	–	–
	γ–pic	–	–	–	185	265	245	–	–

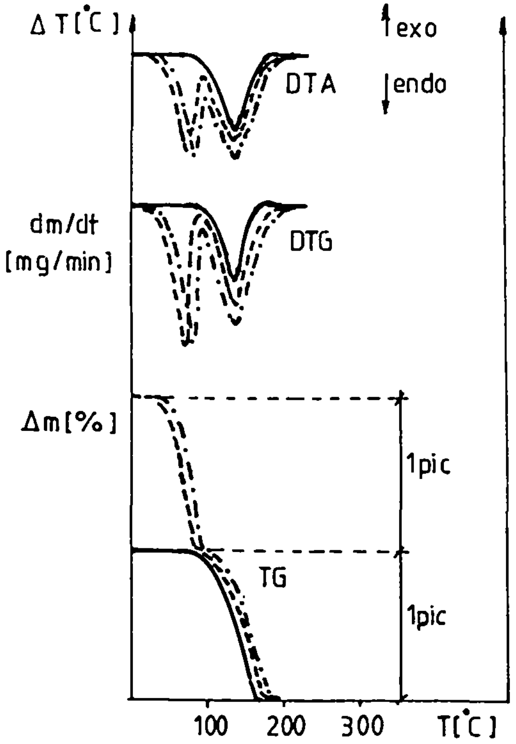

Fig. 1 Thermoanalytical curves of $[Ni(\alpha\text{-pic})_1F_2]$ (——) $[Ni(\beta\text{-pic})_2F_2]$ (- - -)$[Ni(\gamma\text{-pic})_2F_2]$ – · – · –

Discussion

The number of the coordinated nitrogen bases in the compounds prepared either from solution or by solid–gas chemisorption depends above all on the nature of the ligands and the steric effect of the methyl substituent in the pyridine ring. The quality of the solvent does not infuence, or plays only a minor role in the composition of the complexes; however, bis-compounds were obtained instead of tetrakis derivatives on decreasing the nickel:ligand molar ratio. The water content of the hexahydrates has no influence on the complexation, although nickel-hexakis-β-picoline iodide was obtained with preparation method D. The more polar reaction mixture is probably favourable for displacing the readily polarizable iodide ion from the inner coordination sphere.

The effect of the anions is unambiguous. While fluoride forms only bis complexes with pyridine, β- and γ-picoline, in the case of nickel chloride and bromide tetrakis derivatives were obtained. The composition of nickel iodide complexes formed with pyridine and β-picoline differs from those of the former analogous compounds on account of the greater space requirement of the iodide ion.

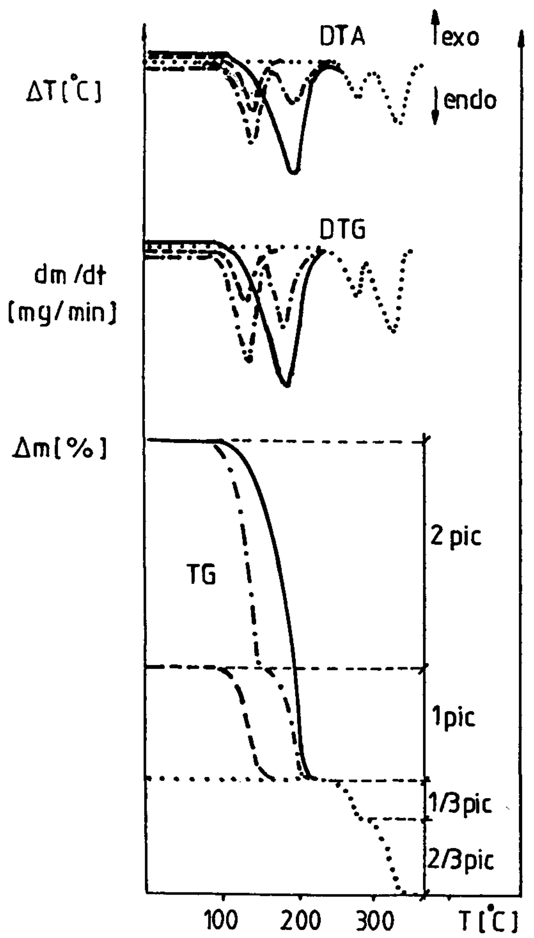

Fig. 2 Thermal decomposition of [Ni(γ-pic)$_4$Cl$_2$] (—) [Ni(γ-pic)$_1$(α-pic)$_1$Cl$_2$ (- - -) [Ni(γ-pic)$_1$(β-pic)$_3$Cl$_2$] (– · – · –) [Ni(γ-pic)$_1$Cl$_2$] (·······)

With nickel ion occupying a medium position with respect to polarizability, the electron density and the polarizability of the anions can take effect simultaneously. Increasing numbers of pyridine and picolines may enter the inner coordination sphere with increasing ionic radii and decreasing electronegativity of the halides. The polarizability has no strong effect on the composition of the complexes.

α-picoline complexes contain one, two, two and one moles of ligand for nickel fluoride, chloride, bromide and iodide, respectively. The steric hindrance is the dominating factor in these cases.

The thermal stability determined by the strength of the metal–nitrogen (py) bond is infuenced by several – at least three – factors. With the same halides, the increasing order of decomposition DTG peak temperature is:

$$\alpha\text{-pic} < \beta\text{-pic} < \text{py} \leq \gamma\text{-pic}$$

The steric effect in the case of α-picoline is obvious.

The electron-releasing effect of the methyl substituent increases the electron density on the nitrogen in the pyridine ring, and thus the covalency of the metal-nitrogen bond will be stronger.

Pyridine-type complexes can stabilize by back donation (Ni $d\pi \rightarrow p\pi$ N(py)). These electrons may be localized on the second, fourth and sixth positions of the ring. These positions have the greatest electron density in the case of β-picoline, when the methyl group is in the meta-position; thus the back donation is inhibited. γ-picoline has the smallest electron density with respect to earlier-mentioned schemes; back-donation can stabilize the complexes in this case. A higher thermal stability of γ-picoline complexes compared to β-picoline compounds would be expected from the Hammet σ values. The elctron releasing effect is more operative from the para-, than from metaposition.

Thermal stability increases for complexes with the same quality and quantity of the ligands in the following order:

$$NiL_xF_2 \ll NiL_xCl_2 \leq NiL_xBr_2 < NiL_xI_2$$

With increasing polarizability of the anions, the high charge acquired by the central Ni ion further increases the stabilization by the previously described back-donation.

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Zusammenfassung — Mittels üblicher präparativer Methoden, wie z.B. aus Lösung und mittels Feststoff-Gasphasen-Chemisorption wurde die Bildung von Stickstoffkomplexen des Types NiL_6X_2, NiL_4X_2, NiL_2X_2 und NiL_1X_2 (mit L= Pyridin, 2-,3- und 4-Methylpyridin und mit X= F,Cl,Br,I) untersucht. Durch Chemisorption erhitzter Intermediäre erhält man quaternäre Mischkomplexe. Die auf diese Weise hergestellten Komplexe wurden ferner mittels simultane TG-DTG-DTA analysiert. Weiterhin wurde der Einfluß der Liganden auf Stöchiometrie und thermische Eigenschaften der Komplexe besprochen.