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HETEROGENEOUS REACTIONS OF SOLID NICKEL(II) COMPLEXES. XXII

Stoichiometry of thermal decomposition and stereochemistry of chloronickel(II) complexes with pyridine N-oxide and its methyl derivatives

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The stoichiometry of thermal decomposition was studied for the following compounds: $Ni(pyNO)Cl_2 \cdot H_2O$ (I), (pyNO = pyridine N-oxide), $Ni(2\text{-}MepyNO)Cl_2 \cdot 2H_2O$ (II), $Ni(3\text{-}MepyNo)Cl_2 \cdot 2H_2O$ (III) and $Ni(4\text{-}MepyNO)_2Cl_2 \cdot C_2H_5OH$ (IV). The heating of the compounds led first to the release of H_2O molecules (or C_2H_5OH molecules), with the formation of $Ni(pyNO)Cl_2$ (V), $Ni(2\text{-}MepyNO)Cl_2$(VI), $Ni(3\text{-}MepyNO)Cl_2$ (VII) and $Ni(4\text{-}MepyNO)_2Cl_2$ (VIII). In the next stage, decomposition of the heterocyclic ligands set in. The compositions and spectral and magnetic properties of these complexes indicate their dimeric (II, III, IV, VIII) of polymeric (I, V, VI, VII) structure with coordinated molecules of H_2O (or C_2H_5OH).

The thermal decomposition reactions of Ni(II) complexes with pyNO may be characterized mostly by two steps [1, 2]: the bonded solvent molecules (H_2O, C_2H_5OH) are released in the first step, while in the second step the complexes are completely decomposed, as shown by a marked exothermic peak (above 200°) in the DTA curve. According to [3], from halogenonickel(II) complexes with pyNO and its methyl derivatives, the organic ligands are released stepwise with the formation of defined intermediates; however, this is not in agreement with earlier results [1, 2]. Therefore, in the present paper we pay attention to the thermal, spectral and magnetic properties of chloronickel(II) complexes with pyNO and its methyl derivatives.

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Experimental

Preparation of starting compounds

$Ni(pyNO)Cl_2 \cdot H_2O$ (I): 0.02 mole $NiCl_2 \cdot 6H_2O$ was heated under constant stirring and dissolved in a mixture of ethanol and 2,2-diethoxypropane (mol. ratio 4 : 1). The obtained green solution was added to 0.06 mole pyNO in the said solvent. Stirring led to immediate precipitation of a yellow powdery complex.

An analogous procedure using 2-MepyNO gave $Ni(2\text{-}MepyNO)Cl_2 \cdot 2H_2O$ (II); with 3-MepyNO the complex $Ni(3\text{-}MepyNO)Cl_2 \cdot 2H_2O$ (III) was obtained; finally, 4-MepyNO resulted in the complex $Ni(4\text{-}MepyNO)_2Cl_2 \cdot C_2H_5OH$ (IV).

The complex compounds $Ni(pyNO)Cl_2$ (V), $Ni(2\text{-}MepyNO)Cl_2$ (VI), $Ni(3\text{-}MepyNO)Cl_2$ (VII) and $Ni(4\text{-}MepyNO)_2Cl_2$ (VIII) were obtained as intermediates in the decomposition on a derivatograph. The analytical results on compounds I–VII are listed in Table 1.

Analytical methods and equipment

The analytical methods and equipment used were described in [4]. The samples for thermal measurements had a mass of 100 mg. The rate of temperature increase was 2.5 deg/min. (The sensitivity for TG was 100 mg.) Measurements were made in air atmosphere; a platinum crucible with an upper diameter of 14 mm was used.

The infrared absorption spectra in the region 200–4000 cm^{-1} were measured in Nujol suspension between polyethylene sheets with a SP 3–300 Pye UNICAM spectrophotometer.

Results and discussion

Thermal properties

The data of the TG, DTG and DTA curves for complexes I–IV are given in Table 2. These data led to the following conclusions: Analogous as for thiocyanatonickel(II) complexes [2], the release of the bonded solvent molecules (H_2O, C_2H_5OH) and the decomposition of the organic can be distinguished. The release of H_2O and C_2H_5OH molecules takes place in well-defined steps, which can be clearly observed by means of the TG and DTG curves (Figs 1 and 2). The rate maxima of H_2O and C_2H_5OH escape (the temperatures of the 1st peak in the DTG curves) decrease in the sequence: pyNO > 2-MepyNO > 3-MepyNO > 4-MepyNO, i.e. in the same way as for thiocyanatonickel(II) complexes [2].

Table 1 Analytical data

No.	Complex	Ni, %		C, %		H, %		N, %	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
I	Ni(PyNO)$Cl_2 \cdot H_2O$	24.19	24.34	24.74	24.42	2.90	2.80	5.77	5.25
II	Ni(2-MePyNO)$Cl_2 \cdot H_2O$	21.37	21.52	26.23	25.80	3.30	3.52	5.10	5.31
III	Ni(3-MePyNO)$Cl_2 \cdot 2H_2O$	21.37	21.59	26.23	25.55	3.30	3.63	5.10	5.41
IV	Ni(4-MePyNO)$_2Cl_2 \cdot C_2H_5OH$	14.91	15.22	42.69	42.53	5.12	4.96	7.11	7.06
V	Ni(PyNO)Cl_2	26.13	26.06	26.73	26.53	2.24	2.37	6.23	5.94
VI	Ni(2-MePyNO)Cl_2	24.68	24.80	30.29	29.78	2.97	3.21	5.89	5.61
VII	Ni(3-MePyNO)Cl_2	24.68	24.76	30.29	29.84	2.97	3.18	5.89	5.70
VIII	Ni(4-MePyNO)$_2Cl_2$	16.88	16.99	41.44	40.94	4.06	4.15	8.05	8.08

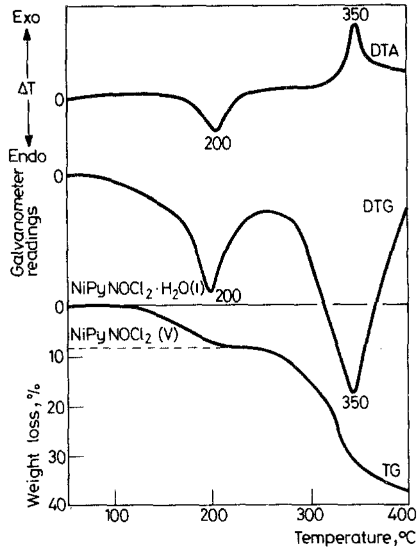

Fig. 1 Thermal curves of complex I

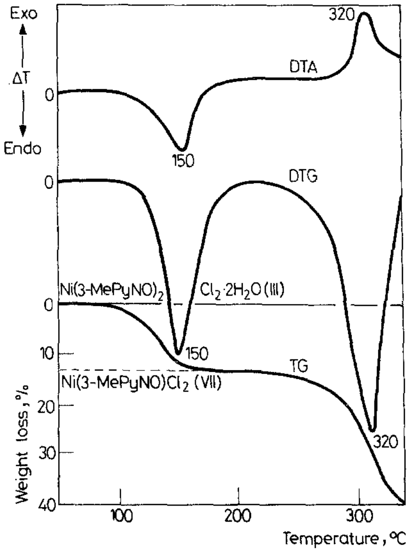

Fig. 2 Thermal curves of complex II

Table 2 Data from the TG, DTG and DTA curves

No.	Complex	The loss of H_2O (C_2H_5OH) molecules				The decomposition of heterocyklic molecules
		TG, %		DTG, °C	DTA, °C	DTA, °C
		Calcd.	Found			
I	$Ni(PyNO)Cl_2 \cdot H_2O$	8.0	7.4	200	200	350 (exo)
II	$Ni(2\text{-}MePyNO)Cl_2 \cdot 2H_2O$	12.0	13.0	150, 185	150, 185	330 (exo)
III	$Ni(3\text{-}MePyNO)Cl_2 \cdot 2H_2O$	12.5	13.0	150	150	320 (exo)
IV	$Ni(4\text{-}MePyNO)_2Cl_2 \cdot C_2H_5OH$	11.0	11.7	140	140	275 (exo)

The stoichiometry of thermal decomposition of complexes I–IV may be expressed as follows:

$$\underset{\text{light-yellow}}{Ni(pyNO)Cl_2 \cdot H_2O_{(s)}\ (I)} \xrightarrow{-H_2O} \underset{\text{dark-yellow}}{Ni(pyNO)Cl_{2(s)}} \rightarrow \text{decomposition of ligands} \tag{1}$$

$$Ni(2\text{-}MepyNO)Cl_2 \cdot 2H_2O_{(s)}\ (II) \xrightarrow{-H_2O,\,-H_2O} Ni(2\text{-}MepyNO)Cl_{2(s)} \rightarrow$$

yellow grey
→ decomposition (2)
of ligands

$$Ni(3\text{-}MepyNO)Cl_2 \cdot 2H_2O_{(s)}\ (III) \xrightarrow{-2H_2O} Ni(3\text{-}MepyNO)Cl_{2(s)} \rightarrow$$

greenish-yellow pink
→ decomposition (3)
of ligands

$$Ni(4\text{-}MepyNO)_2Cl_2 \cdot C_2H_5OH_{(s)}\ (IV) \xrightarrow{-C_2H_5OH} Ni(4\text{-}MepyNO)_2Cl_{2(s)} \rightarrow$$

yellow violet
→ decomposition (4)
of ligands

After the release of H_2O (or C_2H_5OH), the complexes under investigation showed a change in colour, indicating changes in their primary coordination sphere. This made us further study their spectral and magnetic properties.

Magnetic and spectral properties

The values of the magnetic moments (u_{eff} in B.M.) and the positions of the band maxima in the electronic absorption spectra (in cm^{-1}) of complexes I–VIII are given in Table 3.

Complexes I–V exhibit three bands in the measured region at $\approx$ 7000, 12,000 and 22,500 cm^{-1}, with a shoulder at 13,500 cm^{-1}. In accord with [5], these bands may be interpreted within O_h symmetry, and the shoulder of the band at $\approx$ 13,500 cm^{-1} corresponds to a triplet-singlet transition. As regards the heterogeneous coordination sphere, as follows from the IR spectra, the real symmetry will be lower, however.

The lower wavenumbers in the electronic spegtra of the complexes under study, compared with those of the analogous thiocyanatonickel(II) complexes [2], are due to the lower ligand field produced by the chloro ligands. From the electronic spectra and magnetic moments of complexes I–V, a pseudooctahedral configuration can be considered. (The complex $Ni(pyNO)Cl_2$ was also prepared from water-free solution [6]. There a distorted tetrahedral configuration was assumed; however, for complex V of the same composition, but prepared by the thermal dehydration of complex I, this was not confirmed.)

Table 3 Values of magnetic moments and maxima of absorption bands in electronic (d—d) spectra

No.	Complex	μ_{eff}, B. M.	Maxima of absorption bands, cm^{-1}
I	Ni(PyNO)$Cl_2 \cdot H_2O$	3.04	7100, 12,300, 13,600(sh)[a], 22,300
II	Ni(2-MePyNO)$Cl_2 \cdot 2H_2O$	3.13	7000, 12,100, 13,500(sh), 22,500
III	Ni(3-MePyNO)$Cl_2 \cdot 2H_2O$	2.94	7400, 12,400, 13,400(sh), 23,000
IV	Ni(4-MePyNO)$_2Cl_2 \cdot C_2H_5OH$	2.98	7000, 12,100, 13,500(sh), 22,400
V	Ni(PyNO)Cl_2	3.33	7000, 12,000, 13,200(sh), 22,000
VI	Ni(2-MePyNO)Cl_2	3.21	7200, 11,800, 15,000, 16,700(sh), 22,000
VII	Ni(3-MePyNO)Cl_2	3.22	7600, 11,100, 16,400, 20,100(sh), 21,500
VIII	Ni(4-MePyNO)$_2Cl_2$	3.13	8200, 11,200, 18,200, 20,800

a) sh – shoulder

Table 4 Maxima of absorption bands in IR spectra

No.	ν(OH)	δ(H—O—H)		ν(NO)	δ(NO)	ν(Ni—O')[a]	ν(Ni—O")	ν(Ni—Cl)
I	3420	1630	755	1205	840	420	320	245
	3300		700					220
II	3500	1600	750	1190[b]	840	400	350	260
	3200							
III	3340	1630	765(sh)[c]	1260	810	410	360	260(sh)
IV	3360	—	—	1210	860	415	360	255
				1180	840	375		
					830			
V	—	—	—	1200	830	415	—	260
								220
VI	—	—	—	1190	840	380	—	260
								230
VII	—	—	—	1250	810	420	—	260
								240(sh)
VIII	—	—	—	1210	860	410	—	270
				1180	840	375		
					830			

[a] Ni—O'(pyNO)
Ni—O"(H_2O or C_2H_5OH)
[b] in paper [14]: 1195 cm^{-1}
[c] sh — shoulder

For complexes VI–VIII (without H_2O or C_2H_5OH), there are marked changes in the electronic absorption spectra (Table 3). This also follows from the changes in colour. With a decreased number of neutral ligands coordinated to the Ni(II), a considerable distortion of the octahedron can occur [11], causing a lowering of the coordination number to 5.

The coordination mode of the ligands for the compounds under study was investigated via the IR spectra (Table 4). The presence of H_2O (or C_2H_5OH) in compounds I–IV is proved by the bands at 3500–3200 cm^{-1}, corresponding to the antisymmetric and symmetric valence vibrations of the O—H group, and the band at ≈1630 cm^{-1}, belonging to deformation vibrations of H—O—H. The presence of coordinated solvent molecules is proved by bands in the region 900–700 cm^{-1} [9] and at ≈350 cm^{-1} [11, 12], which do not occur for compounds V–VIII (without H_2O and C_2H_5OH).

The presence of oxygen bridges in compound I is indicated by a band assigned to ν(N—O) at 1205 cm^{-1}, characteristic of bridge-bonded pyNO molecules [10]. The broad bands of medium intensity at 260 cm^{-1} for complexes II–IV are in accordance with the presence of terminally bonded chloro ligands [8, 11, 12]. After the molecules of H_2O or C_2H_5OH are released, the hexacoordination in complexes V–VII is completed by the adjacent structural units, and consequently new bands occur below 250 cm^{-1} in their IR spectra (Table 4).

Two bands ν(N—O) and two band ν(Ni—O) were recorded for complex IV, apparently due to differently bonded 4-MepyNO molecules. These results support the presumption of a dimeric structure containing terminally and bridge-bonded molecules of 4-MepyNO.

Considering the factors stabilizing the coordination polyhedra in complex VIII after the coordinated C_2H_5OH has been released, pentacoordination seems to be more advantageous since hexacoordination is probably hindered by the steric effects of the bulky heterocyclic ligands [10].

Conclusions

The results obtained indicate that chloronickel(II) complexes with pyNO and its methyl derivatives, when thermally decomposed, first release H_2O and C_2H_5OH molecules. The decomposition of the heterocyclic ligands then takes place, analogous as found for thiocyanatonickel(II) complexes [2].

Study of the stereochemistry of the prepared compounds showed that a polymeric structure (with coordination number 6) is preferred for complexes I, V, VI and VII, while the others exhibit a dimeric structure with coordination number 6 (complexes II–IV) or 5 (complex VIII).

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Zusammenfassung — Die Stöchiometrie der thermischen Zersetzung folgender Verbindungen wurde untersucht: $Ni(pyNO)Cl_2 \cdot H_2O$ (I), (pyNO = Pyridin-N-oxid), $Ni(2\text{-}MepyNO)Cl_2 \cdot 2H_2O$ (II), $Ni(3\text{-}MepyNO)Cl_2 \cdot 2H_2O$ (III) und $Ni(4\text{-}MepyNO)_2Cl_2 \cdot C_2H_5OH$ (IV). Beim Erhitzen erfolgt zunächst die Abspaltung von Wasser bzw. C_2H_5OH unter Bildung von $Ni(pyNO)Cl_2$ (V), $Ni(2\text{-}MepyNO)Cl_2$ (VI), $Ni(3\text{-}MepyNO)Cl_2$ (VII) und $Ni(4\text{-}MepyNo)_2Cl_2$ (VIII). Im nächsten Schritt setzt die Zersetzung der heterozyklischen Liganden ein. Aus den Zersetzungsreaktionen und den spektralen und magnetischen Eigenschaften dieser Komplexe folgt deren dimere (II, III, IV, VIII) oder polymere (I, V, VI, VII) Struktur mit koordinierten Wasser- bzw. C_2H_5OH-Molekülen.

Резюме — Изучена стехиометрия термического разложения следующих соединений: $Ni(pyNO)Cl_2 \cdot H_2O$ (I), (pyNO = Н-окись пиридина), $Ni(2\text{-}MepyNO)Cl_2 \cdot 2H_2O$ (II), $Ni(3\text{-}MepyNO)Cl_2 \cdot 2H_2O$ (III) и $Ni(4\text{-}MepyNO)_2Cl_2 \cdot C_2H_5OH$ (IV). Нагревание приводит к потере молекулы воды (или спирта) и ка образованию соединений $Ni(pyNO)Cl_2$ (V), $Ni(2\text{-}MepyNO)Cl_2$ (VI), $Ni(3\text{-}MepyNO)Cl_2$ (VII) и $Ni(4\text{-}MepyNO)_2Cl_2$ (VIII). На следующей стадии разложения происходит разложение гетероциклических лигандов. Состав комплексов, их спектральные и магнитные свойства указывают на димерную (II, III, IV, VIII) или полимерную (I, V, VI, VII) структуру с координированными молекулами воды или спирта.