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HETEROGENEOUS REACTIONS OF SOLID NICKEL(II) COMPLEXES XXIII

The stoichiometry of thermal decomposition and stereochemistry of cyanatonickel(II) complexes with 3-Rpyridine derivatives (R = Et, Cl, Br, NH_2)

E. Jóna, M. Jamnický and *I. Kostelný*

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

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The thermal decompositions of the following compounds were studied: $Ni(NCO)_2(3\text{-}Etpy)_4$ (I), $Ni(NCO)_2(3\text{-}Clpy)_4$ (II), $Ni(NCO)_2(3\text{-}Brpy)_4$ (III), $Ni(NCO)_2(3\text{-}NH_2py)_4$ (IV), $Ni(NCO)_2(3\text{-}Clpy)_2 \cdot 2H_2O$ (V) and $Ni(NCO)_2(3\text{-}Brpy)_2 \cdot 2H_2O$ (VI). The release of volatile ligands (3-Rpy and H_2O) is a two-step process, $Ni(NCO)_2(3\text{-}Etpy)_2$ (VII), $Ni(NCO)_2(3\text{-}Clpy)_2$ (VIII), $Ni(NCO)_2(3\text{-}Brpy)_2$ (IX) and $Ni(NCO)_2(3\text{-}NH_2py)_2$ (X) being formed as intermediate complexes. The loss of the last molecules of volatile 3-Rpy ligands is accompanied by NCO ligand decomposition. The spectral and magnetic data indicated pseudooctahedral configuration for all complexes I–X.

In earlier papers [1–4] it was shown that the properties of nickel(II) thiocyanate complexes with pyridine derivatives depended on the type of the neutral ligand (primarily on the positions and types of the substituents).

In an effort to specify in detail the influence of the pseudohalide anion on the thermal properties and stereochemistry of solid nickel(II) complexes, attention has been paid in this paper to analogous cyanate complexes with derivatives of pyridine.

Experimental

Preparation of compounds

The basic synthesis was the reaction of an aqueous solution of $Ni(NO_3)_2$ (10 mmole) at room temperature with freshly prepared KNCO (20 mmole) in cold water, after which an aqueous-ethanolic solution of organic ligand was added to the reaction mixture in a ligand to nickel molar ratio of 8 : 1 for $Ni(NCO)_2L_4$ (L = 3-Brpy, 3-Clpy), 4.5 : 1 for $Ni(NCO)_2L_4$ (L = 3-Etpy, 3-NH_2py) and 2 : 1 for $Ni(NCO)_2L_2 \cdot 2H_2O$ (L = 3-Clpy, 3-Brpy).

The complexes obtained were purified by recrystallization from $CHCl_3$. Complexes of the type $Ni(NCO)_2(3\text{-}Rpy)_2$ (R = Et, Cl, Br, NH_2) were obtained as intermediates in the decomposition on a derivatograph. The analytical results are listed in Table 1.

Table 1 Analytical data

No.	Complex	Ni, % calcd.	Ni, % found.	C, % calcd.	C, % found.	H, % calcd.	H, % found.	N, % calcd.	N, % found.
I	$Ni(NCO)_2(3\text{-}Etpy)_4$	10.27	10.24	63.06	63.42	6.35	6.31	14.71	14.75
II	$Ni(NCO)_2(Clpy)_4$	9.84	10.04	44.27	43.81	2.70	2.83	14.08	14.18
III	$Ni(NCO)_2(3\text{-}Brpy)_4$	7.54	7.67	33.93	33.25	2.07	2.01	10.79	10.92
IV	$Ni(NCO)_2(3\text{-}NH_2py)_4$	11.31	11.38	50.89	50.23	4.66	4.68	26.98	26.78
V	$Ni(NCO)_2(3\text{-}Clpy)_2 \cdot 2H_2O$	14.47	14.52	35.51	34.87	2.98	2.93	13.80	13.70
VI	$Ni(NCO)_2(3\text{-}Brpy)_2 \cdot 2H_2O$	11.82	11.94	30.10	29.41	2.53	2.42	11.70	11.57
VII	$Ni(NCO)_2(3\text{-}Etpy)_2$	16.72	16.66	54.74	55.11	5.17	5.28	15.96	16.14
VIII	$Ni(NCO)_2(3\text{-}Clpy)_2$	15.74	15.78	38.97	38.10	2.18	2.01	15.15	14.98
IX	$Ni(NCO)_2(3\text{-}Brpy)_2$	12.74	12.54	31.28	30.31	1.75	1.66	12.16	12.38
X	$Ni(NCO)_2(3\text{-}NH_2py)_2$	17.74	17.56	43.55	42.71	3.65	3.64	25.39	25.35

Analytical methods and equipment

The analytical methods and equipment used were described in papers [1–4]. The samples for thermal decomposition always had a mass of 100 mg. The rate of temperature increase was 2.5 deg/min. Measurements were made in air atmosphere; a platinum polyplate crucible was used.

Results and discussion

Thermal properties

The following conclusions can be drawn from the data obtained from the TG, DTG and DTA curves for complexes I–VI, givesn in Table 2: Complex I is thermally stable up to 65°, complex II to 80°, complex III to 80°, complex IV to 125°, complex V to 75° and complex VI to 75° (according to the beginning of mass loss). Thus, the initiation of mass loss in the TG curves indicates that the thermal (kinetic [5]) stability of the complexes $Ni(NCO)_2(3\text{-}Rpy)_4$ increases according to the type of substituent R in the sequence $Et < Cl \approx Br < NH_2$, i.e. the same as for the

Table 2 Data from TG, DTG and DTA curves (20–250 °C)

No.	Compound	TG			DTG		DTA	
		T_0 (°C)[a]	1st step (%)		T_{max} (°C)[b] of steps		T_{max} (°C)[b] of steps	
			calcd.	found.	1st	2nd	1st	2nd
I	$Ni(NCO)_2(3\text{-}Etpy)_4$	65	37.0	37.5	120	180	125	180
II	$Ni(NCO)_2(3\text{-}Clpy)_4$	80	38.0	37.0	100	175	95	165
III	$Ni(NCO)_2(3\text{-}Brpy)_4$	80	41.0	40.0	100	175	100	170
IV	$Ni(NCO)_2(3\text{-}NH_2py)_4$	125	36.2	37.1	190	220	180	210
V	$Ni(NCO)_2(3\text{-}Clpy)_2 \cdot 2H_2O$	75	9.0	10.0	95	155	95	150
VI	$Ni(NCO)_2(3\text{-}Brpy)_2 \cdot 2H_2O$	75	9.0	8.0	90	185	90	190

[a] T_0 corresponds to the temperature of beginning of mass loss on the TG curve

[b] T_{max} corresponds to the tempesature of maximal deviations on the DTA or DTG curve

complexes $(Ni(NCS)_2(3\text{-}Rpy)_4$ [2]. The TG, DTG and DTA curves for complexes I–VI show that the release of the volatile ligands (3-Rpy or H_2O) is a two-step process (Table 2) according to the equations:

$$Ni(NCO)_2(3\text{-}Rpy)_{4(s)} \rightarrow Ni(NCS)_2(3\text{-}Rpy)_{2(s)} + 2\ (3\text{-}Rpy)_{(g)} \tag{1}$$

$$(R = \text{Et, Cl, Br, NH}_2)$$

$$Ni(NCO)_2(3\text{-}Rpy)_2 \cdot 2H_2O_{(s)} \rightarrow Ni(NCS)_2(3\text{-}Rpy)_{2(s)} + 2\ H_2O_{(g)} \tag{2}$$

$$(R = \text{Cl, Br})$$

$$\begin{aligned} Ni(NCO)_2\ (3\text{-}Rpy)_{2(s)} \rightarrow Ni(NCO)_2(\text{partial decomp.})_{(s)} + \\ + 2\ (3\text{-}Rpy)_{(g)} \end{aligned} \tag{3}$$

The release of the last molecules of the volatile ligands 3-Rpy is accompanied by partial decomposition of the NCO ligands. For this reason, $Ni(NCO)_2$ was not prepared as a pure compound by thermal decomposition of the studied complexes (in the temperature range 20 to 250°). $Ni(NCO)_2$ decomposes completely above 250°, as shown by a marked exothermic peak in the DTA curves (Figs 1 and 2). This is not in agreement with the thermal decomposition of $Ni(NCO)_2py_4$ [6]. The final products of decomposition (to 400°) are NiO and Ni_3N_2 [7]. The existence of definite intermediates was proved by phase analysis (by means of X-ray powder patterns).

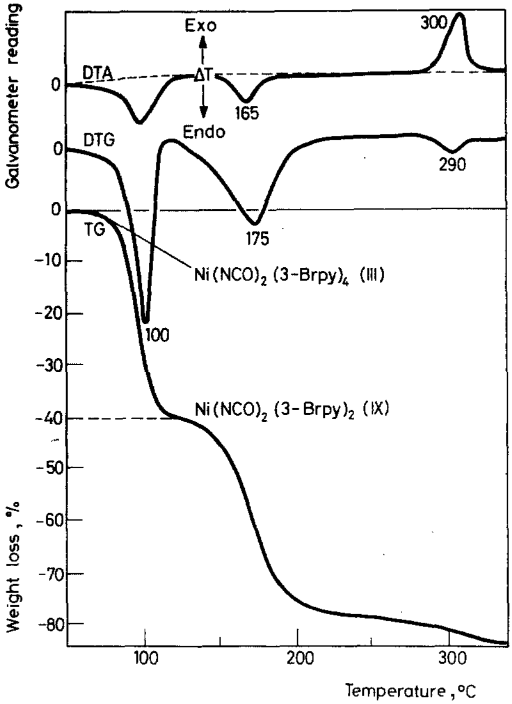


Fig. 1 Thermal curves of complex III

Magnetic and spectral properties

On the basis of the magnetic moments (Table 3), it can be concluded that all the complexes under study are paramagnetic and the values are in the range usually given for octahedral nickel(II) complexes [8]. All the complexes contain two or three relatively low-intensity bands in their electronic absorption spectra. Some complexes with the composition $Ni(NCO)_2(3\text{-}Rpy)_4$ (I, II, III and IV) exhibit only single bands in their electronic spectra, which are typical of monomolecular octahedral complexes with ligands coordinated through a nitrogen atom [8, 9]. The electronic spectra of the complexes $Ni(NCO)_2(3\text{-}Rpy)_2 \cdot 2H_2O$ (V and VI) display broader bands (some of them with distinct shoulders). It may be assumed that the complexes are monomolecular, with a distorted octahedral configuration [9], apparently due to the presence of oxygen atoms from water molecules in the coordination sphere of the Ni(II). The complexes $Ni(NCO)_2(3\text{-}Rpy)_2$ (VII, VIII, IX and X) also show broader bands (Table 3). This feature of the spectra lends support to the assumption that the complexes have a polymeric (greatly distorted) octahedral configuration, analogous to that observed for thiocyanatonickel(II) complexes [2].

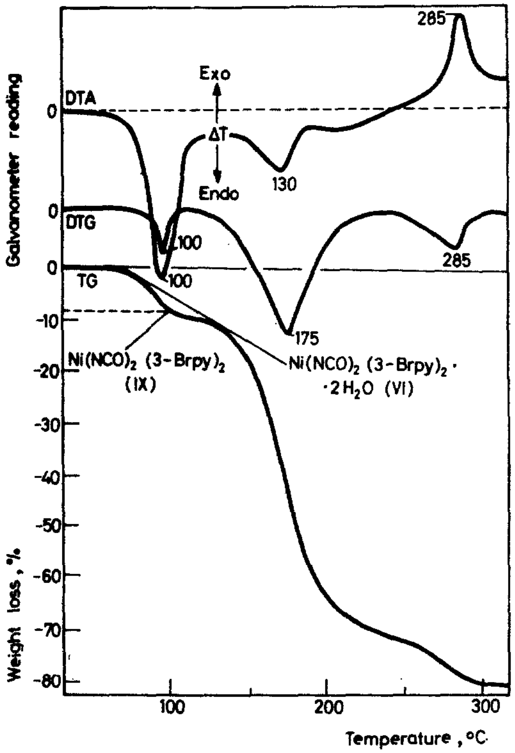


Fig. 2 Thermal curves of complex VI

Table 3 Values of magnetic moments and maxima of absorptions bands in electronic (d–d) spectra

No.	Complex	μ_{eff} B.M.	Maxima of absorption band cm^{-1}		
I	$Ni(NCO)_2(3\text{-}Etpy)_4$	3.12	10300	16190	25–27000
II	$Ni(NCO)_2(3\text{-}Clpy)_4$	3.21	9700	16100	26300
III	$Ni(NCO)_2(3\text{-}Brpy)_4$	3.15	10000	16400	25500–26500
IV	$Ni(NCO)_2(3\text{-}NH_2py)_4$	3.18	9600 10100(sh)	15600 13800(sh)	26100
V	$Ni(NCO)_2(3\text{-}Clpy)_2 \cdot 2H_2O$	3.26	10100 8200(sh)	15600 13800(sh)	26100
VI	$Ni(NCO)_2(3\text{-}Brpy)_2 \cdot 2H_2O$	3.28	9700 8500(sh)	15700 14000(sh)	26300
VII	$Ni(NCO)_2(3\text{-}Etpy)_2$	3.16	9100(br)	15200	25400
VIII	$Ni(NCO)_2(3\text{-}Clpy)_2$	3.20	8600(br)	14700	25000
IX	$Ni(NCO)_2(3\text{-}Brpy)_2$	3.22	8800(br)	15100	25100
X	$Ni(NCO)_2(3\text{-}NH_2py)_2$	2.93	9200	15900	—

sh = shoulder; br = broad

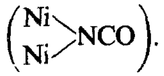
The characteristic vibrations of the NCO^- anion in the complexes under investigation, and of the H_2O molecules in complexes V and VI, are given in Table 4. The ν_s values provide evidence that the NCO^- anions are bonded through the nitrogen atoms in all these compounds. Two reasonably separated bands (δ_{NCO} more than 30 cm^{-1}) are observed for complexes VII, VIII and IX, which can be explained [10–12] by a pseudobridging coordination of NCO ligands  $\left(\begin{matrix}Ni\\Ni\end{matrix}\!\!>\!NCO\right)$. The other complexes exhibit a single band only (or split by less than 15 cm^{-1}), and this may suggest that the NCO groups are coordinated as monodentate ligands. The proved hexacoordination in complex X, however, requires that the 3-NH_2py molecules are bonded as bidentate ligands (through the nitrogen atoms of the pyridine ring and amino groups). Since complexes V and VI contain both monodentate NCO groups and R-py molecules, the octahedral configuration can be completed by the coordination of water molecules. In fact, complexes V and VI show bands at around 816 cm^{-1} (Table 4), which can be assigned to the vibrations of coordinated water molecules [13].

Table 4 Maxima of absorption band in IR spectra

No. ν_{as}	ν_s	δ_{NCO}	δ_{OH}	δ_{H_2O}	Coord. H_2O
I 2193vs[a]	1313m	620m	—	—	—
II 2220vs	1311m	627m	—	—	—
III 2189vs	1299m	629m	—	—	—
IV 2207vs	1300[b]	626m			
		613sh			
V 2228vs	1302m	608m	3460m	1630vs	816w
			3410m		
VI 2231vs	1288m	609m	3430m	1630vs	816w
			3375m		
VII 2220sh	1299m	665m	—	—	—
2188vs		625m			
VIII 2210sh	1298m	670	—	—	—
2190vs		630			
IX 2224s	1298m	668m	—	—	—
2191vs		622m			
X 2232vs	≈1300[b]	614m	—	—	—

[a] vs = very strong, s = strong, m = medium, w = weak, sh = shoulder

[b] overlapped by ligand absorption

Conclusions

The results obtained indicate that cyanatonickel(II) complexes with 3-Rpy, when thermally decomposed, first release 2 mole of 3-Rpy (complexes I, II, III and IV) or 2 mole of H_2O (complexes V and VI). The release of the remaining molecules of 3-Rpy, together with the decomposition of the NCO ligands, then takes place. This finding and its comparison with the results obtained for the analogous thiocyanatonickel(II) complexes [2] indicate the different influences of the anionic ligands (NCO or NCS) on the thermal properties of the systems under investigation.

All the studied complexes are pseudooctahedral. The hexacoordination can be achieved through the bonding of:

i) NCO and 3-Rpy as monodentate ligands (complexes I, II, III and IV);

ii) NCO, 3-Rpy and H_2O as monodentate ligands (complexes V and VI);

iii) NCO as a bridging bidentate ligand and 3-Rpy as a monodentate ligand (complexes VII, VIII and IX).

In the case of complex X, NCO and 3-NH_2py are presumed to behave as monodentate and bidentate ligands, respectively.

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Zusammenfassung — Die thermische Zersetzung der folgenden Verbindungen wurde untersucht: $Ni(NCO)_2(3\text{-}Etpy)_4$ (I), $Ni(NCO)_2(3\text{-}Clpy)_4$ (II), $Ni(NCO)_2(3\text{-}Brpy)_4$ (III), $Ni(NCO)_2(3\text{-}NH_2py)_4$ (IV), $Ni(NCO)_2(3\text{-}Clpy)_2 \cdot 2H_2O$ (V) und $Ni(NCO)_2(3\text{-}Brpy)_2 \cdot 2H_2O$ (VI). Die flüchtigen Liganden (3-Rpy und H_2O) werden in zwei Schritten abgegeben, wobei $Ni(NCO)_2(3\text{-}Etpy)_2$ (VII), $Ni(NCO)_2(3\text{-}Clpy)_2$ (VIII), $Ni(NCO)_2(3\text{-}Brpy)_2$ (IX) und $Ni(NCO)_2(3\text{-}NH_2py)_2$ (X) als intermediäre Komplexe gebildet werden. Die Abgabe der letzten Moleküle der flüchtigen 3-Rpy-Liganden geht mit der Zersetzung des NCO-Liganden einher. Die spektrometrischen und magnetischen Daten weisen auf eine pseudooktaedrische Konfiguration aller Komplexe (I–X) hin.

Резюме — Изучено термическое разложение следующих соединений: $Ni(NCO)_2(3\text{-}Etpy)_4$ (I), $Ni(NCO)_2(3\text{-}Clpy)_4$ (II), $Ni(NCO)_2(3\text{-}Brpy)_4$ (III), $Ni(NCO)_2(3\text{-}NH_2py)_4$ (IV), $Ni(NCO)_2(3\text{-}Clpy)_2 \cdot 2H_2O$ (V) и $Ni(NCO)_2(3\text{-}Brpy)_2 \cdot 2H_2O$ (VI). Выделение летучих лигандов (3-Rpy и H_2O) является двухстадийным процессом, протекающим с образованием промежуточных соединений $Ni(NCO)_2(3\text{-}Etpy)_2$ (VII), $Ni(NCO)_2(3\text{-}Clpy)_2$ (VIII), $Ni(NCO)_2(3\text{-}Brpy)_2$ (IX) и $Ni(NCO)_2(3\text{-}NH_2py)_2$ (X). Потеря оставшихся молекул замещенных пиридинов сопровождается разложением цианатового лиганда. Спектральные и магнитные данные для всех комплексов указывают на их псевдооктаэдрическую структуру.