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Metal(II)-promoted hydrolysis of pyridine-2-carbonitrile to pyridine-2-carboxylic acid. The structure of [Cu(pyridine-2-carboxylate)$_2$]·2H$_2$O

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Abstract—Pyridine-2-carbonitrile (2-CNpy) undergoes Cu(II) or Co(II)-promoted hydrolysis to pyridine-2-carboxamide (piaH) and/or pyridine-2-carboxylic acid (pycH). The pathway of pycH formation depends on the presence of 2-amino-2-hydroxymethyl-1,3-propanediol (AL^1) and on the central atom. In the absence of AL^1, Co(II) or Cu(II) ions mediate piaH formation under mild reaction conditions in the first hydrolytic step. Cu(II) ions assist in piaH transformation to pycH by subsequent reflux. In the presence of AL^1 and Co(II), a Co(II) complex containing pyoxaL^1 (2-(2-pyridinyl)-4,4-bis(hydroxymethyl)-2-oxazoline) is formed in the first stage; subsequent decomposition of pyoxaL^1 under the reflux yields pycH. Under similar conditions, no solid Cu(II) complex with pyoxaL^1 can be isolated, but a Cu(II) complex with coordinated pyc$^-$ anions precipitates from the reaction mixture. The synthesis, spectral and magnetic properties of the complexes [Co(H$_2$O)$_2$(piaH)$_2$]Cl$_2$, [Co(H$_2$O)$_2$(pyc)$_2$]·2H$_2$O, [Cu(H$_2$O)$_2$(piaH)$_2$]Cl$_2$, [Cu(pyc)$_2$] and [Cu(pyc)$_2$]·2H$_2$O, including the structure determination of the latter one, are described. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: pyridine-2-carbonitrile; hydrolysis; copper(II) complexes; cobalt(II) complexes; crystal structure.

INTRODUCTION

Organic nitriles can coordinate to transition metal ions via their nitrile group (three bonding modes have been described so far; for a review see [1]) or by another donor atom of the organic moiety. In the chemistry of pyridinecarbonitriles, the former mode is typical for pyridine-2-carbonitrile (further denoted as 2-CNpy) while the latter for pyridine-3-carbonitrile and pyridine-4-carbonitrile. It should be pointed out, however, that the coordination of 2-CNpy through the pyridine nitrogen cannot be excluded, at least for kinetically inert complexes [2].

Either mode of 2-CNpy coordination to electron-withdrawing transition metal ions results in enhanced electrophilicity of the nitrile carbon, thus making it susceptible to nucleophiles such as OH$^-$, H$_2$O, ROH, and R–NH$_2$ [1,3].

As it has previously been observed [4–7], the reaction of 2-CNpy with some metal(II) salts in aqueous or alcoholic solutions leads to formation of solid complexes containing pyridine-2-carboxamide (piaH) and *O*-alkylpyridine-2-carboximidate (*O*-Rpii), respectively. It is worth mentioning that a similar metal(II) promoted hydrolysis of the nitrile group to amide was observed in the systems containing 2-carbonitrile-1,10-phenanthroline instead of 2-CNpy [8] for which, based on a kinetic analysis, the authors showed that its mechanism involved an external attack of a non-coordinated OH$^-$ ion to the nitrile group of coordinated ligand.

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In the presence of amino alcohols (AL^1–AL^3 in Scheme 1) and 2-CNpy, Ni(II) salts yield solid complexes containing 2-pyridinyl-2-oxazolines (pyoxaL^1-pyoxaL^3) [9] under mild reaction conditions both in water and alcohols. However, Cu(II) and most Co(II) complexes containing oxazolines could be prepared only from ethanolic solution. For example, solid complexes $[CoX_2(pyoxaL^1)_2]$ (X = Cl, Br or NCS) and $[CuX(pyoxaL^1)_2]X \cdot 0.5H_2O$ (X = Cl or Br) have been prepared by the reaction of 2-CNpy with AL^1 in ethanolic solutions of the corresponding Co(II) and Cu(II) salts. Also, solid complexes containing different hydrolytic products of 2-CNpy [10] have been isolated from aqueous solutions. The complexes were not, however, characterized in more detail.

In this paper the results on the hydrolytic reactions of 2-CNpy in the presence or absence of AL^1 in aqueous solutions of copper(II) and cobalt(II) salts are given. The course of the reactions was monitored by a solution IR study. Moreover, the synthesis and characterization of the solid pyc^- or piaH-containing complexes isolated from the above mentioned aqueous solutions are also described. The X-ray molecular and crystal structure of one of the products, $[Cu(pyc)_2] \cdot 2H_2O$, is presented. The paper summarizes results obtained within the study of metal(II)-facilitated hydrolysis of 2-CNpy and offers general conclusions relating to this field.

2. EXPERIMENTAL

2.1. *Chemical reagents*

All the chemicals used were of reagent grade. Solid pyridine-2-carbonitrile (2-CNpy) was purified by distillation under reduced pressure. 2-Amino-2-hydroxymethyl-1,3-propanediol (AL^1) was used without further purification. Water was double distilled prior to use. The other chemicals were used as received.

2.2. *Analysis and physical measurements*

Copper, cobalt and nickel were determined by EDTA titration; carbon, hydrogen and nitrogen by microanalytical methods (Carlo Erba Instruments EA 1108) with maximum deviations (in %): M, ±0.2; C, ±0.4; H, ±0.3; and N, ±0.2. The water content in hydrates was determined by thermogravimetry. The yields of products are related to the metal contents in reacting mixtures.

Magnetic moments were measured with a Gouy balance for the powdered solid at 293 K. Electronic spectra of the powdered samples in nujol mulls and diffuse reflectance spectra in MgO were recorded at room temperature on a Specord M 40 and a Magna 750 spectrophotometer, respectively. Magnetic moments, electronic and IR spectral data of solid complexes are gathered in Table 1.

Measurements of IR spectra (in solid state and aqueous solution) as well as pH measurements of the aqueous solutions are described elsewhere [9].

2.3. *X-ray structure determination*

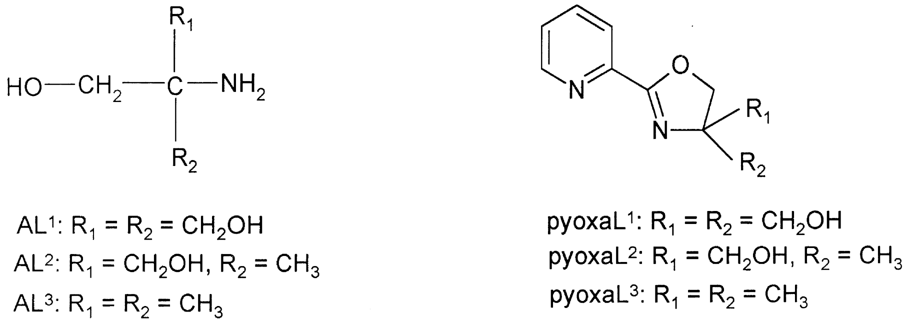
Data collection and cell refinement were carried out using KUMA (1991) KM4 diffractometer software [11]. Intensity data were corrected for Lorentz and polarization effects. The structure was solved by standard heavy atom procedures with SHELX86 [12], and subsequent Fourier synthesis using SHELXL93 [13]. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Geometrical analysis was performed using SHELXL93 [13]. The structures were drawn using ORTEP [14]. The final refined parameters are summarized in Table 2. Selected bond lengths and angles are collected in Table 3.

Supplementary material including non-hydrogen and hydrogen atomic coordinates ($\times 10^4$), anisotropic displacement parameters for non-hydrogen atoms ($Å^2 \times 10^3$) have been deposited at the Cambridge Crystallographic Data Centre. Observed and calculated structural factors are available from P. S.

2.4. *Preparation of complexes*

Copper(II) complexes

$[Cu(H_2O)_2(piaH)_2]Cl_2$ (**I**) and $[Cu(pyc)_2]$ (**II**). 50 cm^3



AL^1: $R_1 = R_2 = CH_2OH$
AL^2: $R_1 = CH_2OH$, $R_2 = CH_3$
AL^3: $R_1 = R_2 = CH_3$

pyoxaL^1: $R_1 = R_2 = CH_2OH$
pyoxaL^2: $R_1 = CH_2OH$, $R_2 = CH_3$
pyoxaL^3: $R_1 = R_2 = CH_3$

Scheme 1. Structures and abbreviations of ligands.

Table 1. Magnetic moments, electronic spectral data, characteristic IR bands and stereochemistry of solid complexes containing pyridine-2-carboxamide (piaH) or pyridine-2-carboxylic acid (pycH)

No.	Complex	μ_{ef} (B.M.)	Electronic spectra[a], maxima of absorption band (cm^{-1})	Infrared spectra[a] $\nu_a(CXO)$[b]	$\nu_s(CXO)$[b]	Stereo-chemistry[c]
I	$[Cu(H_2O)_2(piaH)_2]Cl_2$	1.90	15100	1663vs	1440s	O
II	$[Cu(pyc)_2]$	1.98	16800br 27000sh	1637s	1343s	S
III	$[Cu(pyc)_2]\cdot 2H_2O$	1.96	17000br 27000sh	1644s	1348s	S
IV	$[Co(H_2O)_2(piaH)_2]Cl_2$	4.90	8850 20500 21500	1657vs	1434s	O
V	$[Co(H_2O)_2(pyc)_2]\cdot 2H_2O$	4.79	8700 18800 19800 22100	1622s	1383s	O

[a] vs, very strong; s, strong; sh, shoulder; br, broad.

[b] For complexes **I** and **IV** is X = N and for complexes **II**, **III** and **V** is X = O.

[c] O, octahedral; S, square-planar.

Table 2. Crystal data and structure refinement for $[Cu(pyc)_2]\cdot 2H_2O$ (complex **III**)

Crystal data	
Empirical formula	$C_{12}H_{12}CuN_2O_6$
Formula weight	343.78
Crystal size (mm)	0.50 × 0.30 × 0.20
Crystal system	triclinic
Space group	$P\bar{1}$
Z	1
Unit cell dimensions	$a = 5.172(1)$ Å, $\alpha = 74.92(3)^\circ$ $b = 7.654(2)$ Å, $\beta = 84.22(3)^\circ$ $c = 9.175(2)$ Å, $\gamma = 71.69(3)^\circ$
Volume ($Å^3$)	332.9(1)
Density (calc.) ($Mg\,m^{-3}$)	1.715
$F(000)$	175
Linear absorption coefficient (μ) (mm^{-1})	2.622
Data collection	
Diffractometer	KUMA KM 4
Radiation type	Cu Kα $\lambda = 1.54180$ Å
Temperature (K)	293(2)
Θ range for data collection (°)	4.99–81.34
Index ranges	h −6–3, k −9–9, l −11–11
Number of data collected	2408
Independent reflections	1362 ($R_{int} = 0.0525$)
Absorption correction	no
Solution and refinement	
Refinement method	full-matrix, least-squares on F
Data/restraints/parameters	1307/0/98
Goodness-of-fit on F^2	0.897
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0429$, $wR_2 = 0.1011$
R indices (all data)	$R_1 = 0.0488$, $wR_2 = 0.1279$
Extinction coefficient	0.019(4)
Largest diff. peak and hole ($e\,Å^{-3}$)	0.910/−0.675

of an aqueous solution of copper(II) chloride dihydrate (10 mmol) was mixed with 2-CNpy (20 or 40 mmol). The resulting solution was left to slowly evaporate at room temperature. Pale blue crystals of **I** started to crystallize from the reaction solution after several hours. The crystals were filtered off, washed with ethanol and finally dried *in vacuo* (yield 80%).

Complex **II** was deposited as a blue solid when the

Table 3. Selected bond lengths (Å) and angles (°) for $[Cu(pyc)_2] \cdot 2H_2O$ (complex **III**)

Cu–O(1)	1.941(2)	Cu–N	1.979(2)
O(1)–C(6)	1.289(2)	O(2)–C(6)	1.239(3)
N–C(1)	1.343(3)	N–C(5)	1.340(3)
C(1)–C(2)	1.383(3)	C(1)–C(6)	1.510(2)
C(2)–C(3)	1.394(3)	C(3)–C(4)	1.374(4)
C(4)–C(5)	1.389(4)		
O(1)–Cu–N	82.9(1)	O(1)#1–Cu–N	97.1(1)
C(6)–O(1)–Cu	115.9(1)	C(1)–N–C(5)	119.6(2)
C(1)–N–Cu	112.2(1)	C(5)–N–Cu	128.1(2)
N–C(1)–C(2)	122.3(2)	N–C(1)–C(6)	114.6(2)
C(2)–C(1)–C(6)	123.1(2)	C(1)–C(2)–C(3)	118.1(2)
C(4)–C(3)–C(2)	119.3(2)	C(3)–C(4)–C(5)	119.7(2)
N–C(5)–C(4)	120.9(2)	O(2)–C(6)–O(1)	126.3(2)
O(2)–C(6)–C(1)	119.8(2)	O(1)–C(6)–C(1)	113.9(2)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z$.

above reaction mixture was refluxed for up to 20 h. The crystals were separated from the cool solution by filtration, washed with ethanol and dried *in vacuo* (yield 95%).

In addition to the above method, the complex $[Cu(H_2O)_2(piaH)_2]Cl_2$ was prepared directly from piaH and $CuCl_2$ [15]. No hydrolysis of piaH to pycH was also observed.

$[Cu(pyc)_2] \cdot 2H_2O$ (**III**). Method A. 20 mmol of 2-amino-1,3-propanediol (AL^1) was dissolved in 50 cm^3 of an aqueous solution of $CuCl_2$ (10 mmol). 2-CNpy (20 mmol) was then added to the system and the resulting solution was left to slowly evaporate at room temperature. A mixture of solid complexes containing piaH or pyc^- ligands was deposited after several days. Upon adjusting pH of the above resulting solution to 3.5, complex **I** was precipitated within 15 min. When an aqueous solution of 2-CNpy, AL^1 and $CuCl_2$ was refluxed for 32 h and then cooled down, the only compound, formed in 95% yield, was pure blue violet solid complex **III**. A well-shaped crystal of **III** was used for structure determination.

Method B. An aqueous solution (50 cm^3) of 10 mmol of $[CuCl(pyoxaL^1)_2]Cl \cdot 0.5H_2O$ [10] was left to slowly evaporate at room temperature. From the concentrated solution, complex **III** deposited upon several days standing (yield 95%).

Cobalt(II) complexes

$[Co(H_2O)_2(piaH)_2]Cl_2$ (**IV**) *and* $[Co(H_2O)_2(pyc)_2] \cdot 2H_2O$ (**V**). When 50 cm^3 of an aqueous solution of cobalt(II) chloride hexahydrate (10 mmol) was mixed with 2-CNpy (20 or 40 mmol), orange complex **IV** started to crystallize after several days. The crystals were filtered off, washed with ethanol and finally dried *in vacuo* (yield 80%). Contrary to its Cu(II) analogue (complex **I**), complex **IV** did not convert to the pyc-ligand containing complex even after 20 h reflux of the above reaction mixture, i.e. pure complex **IV** was isolated again as the only product in 75% yield. Compound **IV** was also prepared directly from $CoCl_2$ and piaH [15, 16] with no piaH hydrolysis observed.

The complex $[Co(H_2O)_2(pyc)_2] \cdot 2H_2O$ (**V**) was formed by 30 h reflux of a 50 cm^3 aqueous solution of 2-CNpy (20 mmol), AL^1 (20 mmol) and $CoCl_2$ (10 mmol). Orange crystals of **V** were filtered off and washed with ethanol (yield 80%). Complex **V** can also be synthesized by 30 h reflux of 10 mmol $[CoCl_2(pyoxaL^1)_2]$ [10] in water in a similar way as complex **III** in about 85% yield.

3. RESULTS AND DISCUSSION

3.1. *Stereochemistry of solid complexes*

The values of magnetic moments, electronic and IR spectral data for the studied complexes are listed in Table 1. The spectral and magnetic properties of complexes $[M(H_2O)_2(piaH)_2]Cl_2$ (**I** and **IV**) are identical to those prepared directly from piaH [15, 16] and consistent with their monomeric, hexacoordinated structure with two *N*,*O*-chelating piaH ligands and two water molecules present in the primary coordination sphere. The mode of piaH coordination has been proved by a single-crystal X-ray analysis of complex **I** [17].

The IR spectra of complex **III** show broad bands located in the region from 3100 to 3600 cm^{-1} attributable to the water molecules. Both copper(II) complexes **II** and **III** exhibit (Table 1) a band of the asymmetric stretch $\nu_a(COO^-)$ at 1637 and 1644 cm^{-1} together with a band of the symmetric stretch $\nu_s(COO^-)$ at 1343 and 1348 cm^{-1}, respectively. The difference $\nu_a(COO^-) - \nu_s(COO^-)$, being 294 and 296 cm^{-1} for complexes **II** and **III**, respectively, can be taken as a proof of unidentate coordination of the carboxylato group to the central atom [18]. The IR spectra of all complexes **I**–**V** provide an evidence of organic ligands coordination through the 2-pyridinyl ring nitrogen [19].

In general, room temperature magnetic measurements and spectral data do not provide sufficient information for a definite determination of the stereochemistry of Cu(II) complexes [20] and this relates also to complexes **II** and **III** previously prepared from pycH [21, 22, 23]. To eliminate the question on stereochemistry of **II** and **III**, an X-ray single-crystal analysis of complex **III** (the one with better evolved crystals) was performed.

The spectral and magnetic properties of $[Co(pyc)_2(H_2O)_2] \cdot 2H_2O$ (**V**) are identical to those given in [24] for a compound of the same composition synthesized directly with pycH. Moreover, the X-ray crystal study of **V** [25, 26] has revealed that the primary coordination sphere of this monomeric octahedral complex consists of two anions of pyridine-2-carboxylic acid (as *N*,*O*-coordinated chelates) and two molecules of water.

3.2. *Crystal structure description of complex* III

The crystal structure of $[Cu(pyc)_2] \cdot 2H_2O$ (**III**) consists of discrete $Cu(pyc)_2$ molecules and water molecules occupying lattice sites (Fig. 1). The $Cu(pyc)_2$ molecule, as a whole, is nearly planar. The Cu(II) atom has centrosymmetric square-planar coordination with *trans* positioned oxygen and nitrogen donor atoms of two *N*,*O*-chelating pyc^- ligands. The interatomic distances Cu–O(1) and Cu–N are 1.941(2) and 1.979(2) Å, respectively, and are consistent with the values reported for other copper(II) complexes [27]. The packing of $Cu(pyc)_2$ moieties in the crystal structure is shown in Fig. 1. The molecules $Cu(pyc)_2$ form parallel planes. There are weak interactions between copper atoms of one plane and O(2) atoms of neighboring planes (Cu · · · O(2aa) = 2.814(4) Å). The molecules of water are not coordinated to the central atom, they are bonded to O(2) atoms of pyc^- ligands by hydrogen bonds (O(2) · · · H(2) = 1.954(5) Å; O(3)–H(2) · · · O(2) = 172.1(6)°).

The similarity of the IR spectra for **II** and **III** (Table 1) led us to the conclusion of the square planar coordination of the central Cu(II) atom just like in **II**.

3.3. *IR spectra of aqueous solutions*

Owing to the known characteristic IR spectral features of 2-CNpy and the products of its transformation, the course of the reactions occurring in the investigated systems at various conditions can cosily be followed. The assignment of solid state and solution IR spectral bands in Fig. 2 to free and coordinated ligands is supported by the literature and our previous data [9,10,18].

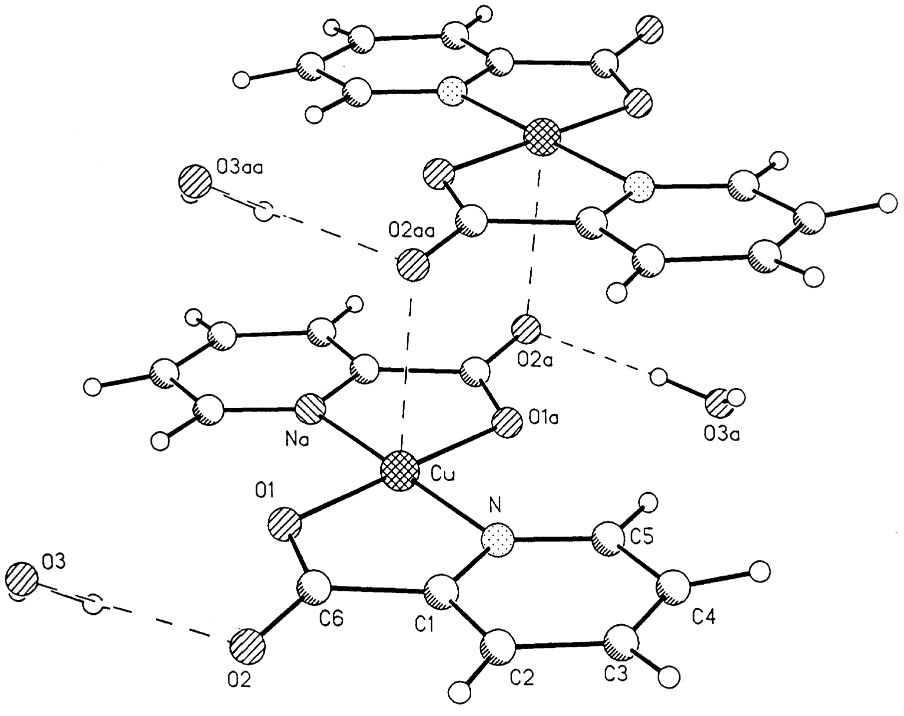


Fig. 1. Packing of $Cu(pyc)_2$ and H_2O in the crystal structure of $[Cu(pyc)_2] \cdot 2H_2O$ (complex **III**).

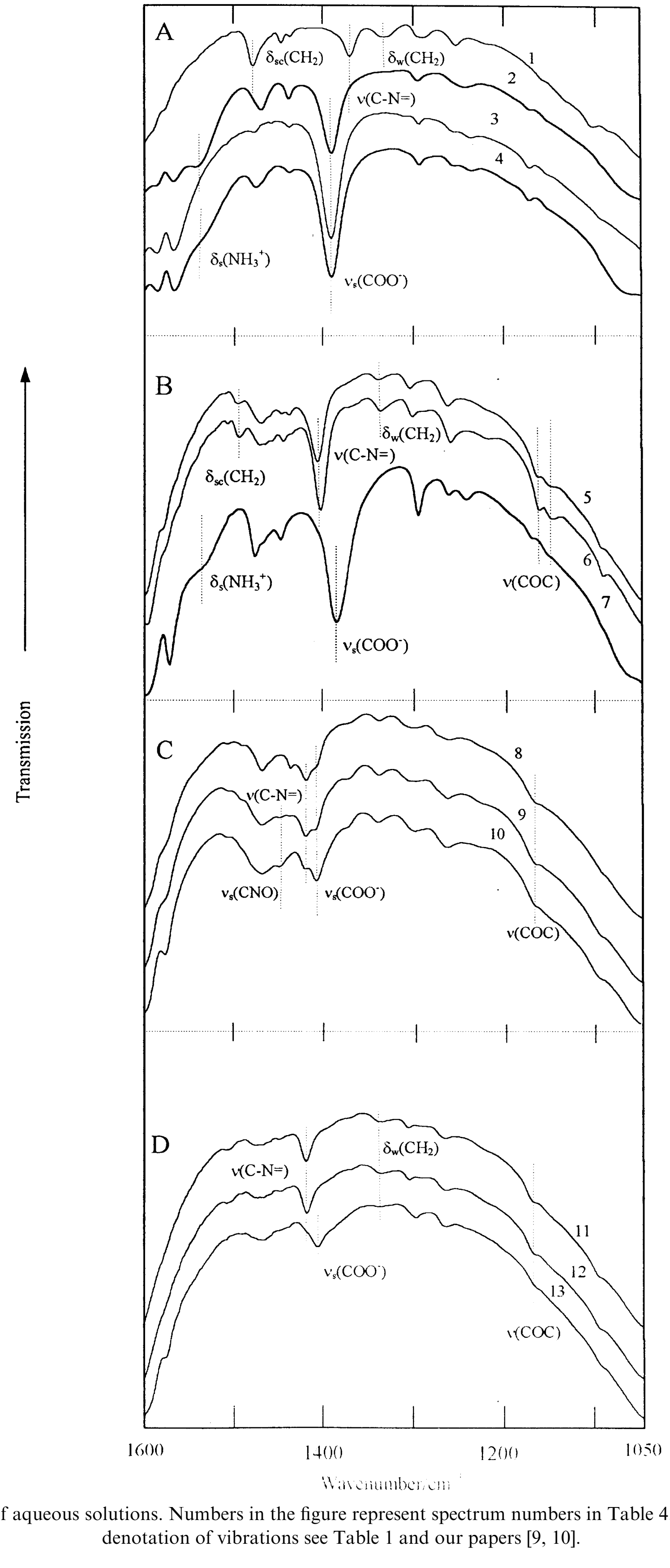


Fig. 2. IR spectra of aqueous solutions. Numbers in the figure represent spectrum numbers in Table 4. For assignment and denotation of vibrations see Table 1 and our papers [9, 10].

A kinetic study of the reaction of 2-CNpy with AL^1 in aqueous solutions of Ni(II) by means of electronic spectroscopy has been presented partly in [28]. Some new mechanistic information of this reaction was obtained from a solution IR study [9]. The IR spectra of $pyoxaL^1$ and its solid complexes of Ni(II), Co(II) and Cu(II) have been published, too [9, 10].

In this paper the results on the hydrolytic reactions of 2-CNpy in the presence or absence of AL^1 in aqueous solutions of copper(II) and cobalt(II) salts are given. Changes in solution IR spectra in the region from 1050 to 1600 cm^{-1} are for some of the studied systems illustrated in Fig. 2. The curves 1, 3, 5, 6, and 8–13 represent the spectra of solutions prepared at room temperature, thick solid curves 2, 4 and 7 were obtained after several-hours reflux of the solutions. The composition of the starting solutions, the time and temperature used in preparing the measured solutions, as well as the dominant components observed in the IR spectra are given in Table 4.

The spectra of $pyoxaL^1$ itself and its decomposition products in aqueous solution are illustrated in Fig. 2(A) [9]. Uncoordinated $pyoxaL^1$ (curve 1) is quite stable at room temperature for a long time. Under reflux it undergoes, however, a gradual hydrolysis to pycH, AL^1 and its protonated form AL^1H (spectrum 2). Curve 3 represents a solution IR spectrum of uncoordinated pycH, curve 4 relates to a aqueous solution of the 1:1 molar mixture of pycH and AL^1.

The room temperature IR spectra of aqueous solutions of 2-CNpy and AL^1 in the absence of metal(II) salts [9] showed that the rate of $pyoxaL^1$ formation is very low in comparison with that observed in the metal(II) salts containing systems.

Formation of the Co(II) complexes was indicated by significant spectral changes (Fig. 2(B)). Moreover, the IR spectrum of none of the systems related to Fig. 2(B) exhibits the strong band due to $\nu(C{\equiv}N)$ of 2-CNpy at 2246 cm^{-1}. At the same time, the pH values of the measured solutions depend strongly on the reaction time (see Table 4). In agreement with these spectral and pH changes we have concluded that a nucleophilic reaction on 2-CNpy takes place at room temperature yielding a Co(II) complex with $pyoxaL^1$ (spectrum 6 has not changed during several days). This conclusion is also confirmed by a comparison of the uncoordinated $pyoxaL^1$ spectrum (curve 1) with those of the Co(II) solutions containing $pyoxaL^1$ (spectra 5 and 6). However, in the presence of Co(II), $pyoxaL^1$ gradually hydrolyses when being refluxed for 30 h leading thus to the solution containing mainly pycH, AL^1 and its cationic form AL^1H (spectrum 7).

Unlike the solutions containing Co(II) ions, the presence of Cu(II) gives rise to different spectral changes (Fig. 2(C)). Stemming from the IR spectra evolution we have concluded that a nucleophilic reaction on the nitrile group proceeds in such solutions at room temperature (spectrum 8) and Cu(II) complexes with both $pyoxaL^1$ and pyc^- ligands are formed. Simultaneously, however, decomposition of $pyoxaL^1$ to pyc^- proceeds (spectrum 9) and after 24 h Cu(II) complexes with pyc^- ligand become dominant species in solutions (spectrum 10). Moreover, bands at 1445 cm^{-1} in spectra 9 and 10 are assigned to the

Table 4. Composition of aqueous solution

Spectrum No.	Starting solution[a]	Reaction temperature[b]	Reaction time	pH	Dominant species[c]
1	$pyoxaL^1$	r.t.	5 min	7.0	$pyoxaL^1$
2	$pyoxaL^1$	reflux	50 h	6.8	pyc, AL^1, AL^1H
3	pycH	r.t.	5 min	7–10	pyc
4	$pyc + AL^1$	reflux	50 h	6.8	pyc, AL^1, AL^1H
5	$2\text{-CNpy} + AL^1 + CoCl_2$	r.t.	5 min	8.3	complex of $pyoxaL^1$
6	$2\text{-CNpy} + AL^1 + CoCl_2$	r.t.	120 min	9.3	complex of $pyoxaL^1$
7	$2\text{-CNpy} + AL^1 + CoCl_2$	reflux	30 h	6.8	AL^1, AL^1H, complex of pyc
8	$2\text{-CNpy} + AL^1 + CuCl_2$	r.t.	5 min	6.9	complex of $pyoxaL^1$ and pyc
9	$2\text{-CNpy} + AL^1 + CuCl_2$	r.t.	120 min	7.8	complex of $pyoxaL^1$, pyc and pia
10	$2\text{-CNpy} + AL^1 + CuCl_2$	r.t.	24 h	8.3	complex of pyc, pia and $pyoxaL^1$
11	$[CuCl(pyoxaL^1)_2]\text{-}Cl \cdot 0.5H_2O$	r.t.	5 min	7.4	complex of $pyoxaL^1$
12	$[CuCl(pyoxaL^1)_2]\text{-}Cl \cdot 0.5H_2O$	r.t.	120 min	7.1	complex of $pyoxaL^1$
13	$[CuCl(pyoxaL^1)_2]\text{-}Cl \cdot 0.5H_2O$	r.t.	48 h	5.6	complex of pyc and $pyoxaL^1$

[a] Solutions 1–10: the concentrations of organic compounds and MCl_2 were 0.50 and 0.25 M, respectively; solutions 11–13: the concentration of complex $[CuCl(pyoxaL^1)_2]Cl \cdot 0.5H_2O$ was 0.25 M.

[b] r.t. = room temperature.

[c] Species observed in IR spectra.

symmetric valence vibration of the CNO group of pyridine-2-carboxamide (Table 1) which has appeared in the solution, too. PyoxaL^1 is present in solution after 24 h only in a small amount.

Curve 11 in Fig. 2(D) represents the IR spectrum of an aqueous solution of $[CuCl(pyoxaL^1)_2]Cl \cdot 0.5H_2O$ [10]. The spectral changes (curves 12 and 13) confirm a gradual room temperature hydrolysis of the coordinated pyoxaL^1 directly to pyc$^-$. Contrary to the solutions which are represented by spectra 9 and 10, no formation of piaH was observed in the solutions 12 and 13.

3.4. *Reactions of pyridine-2-carbonitrile and formation of pyridine-2-carboxylic acid*

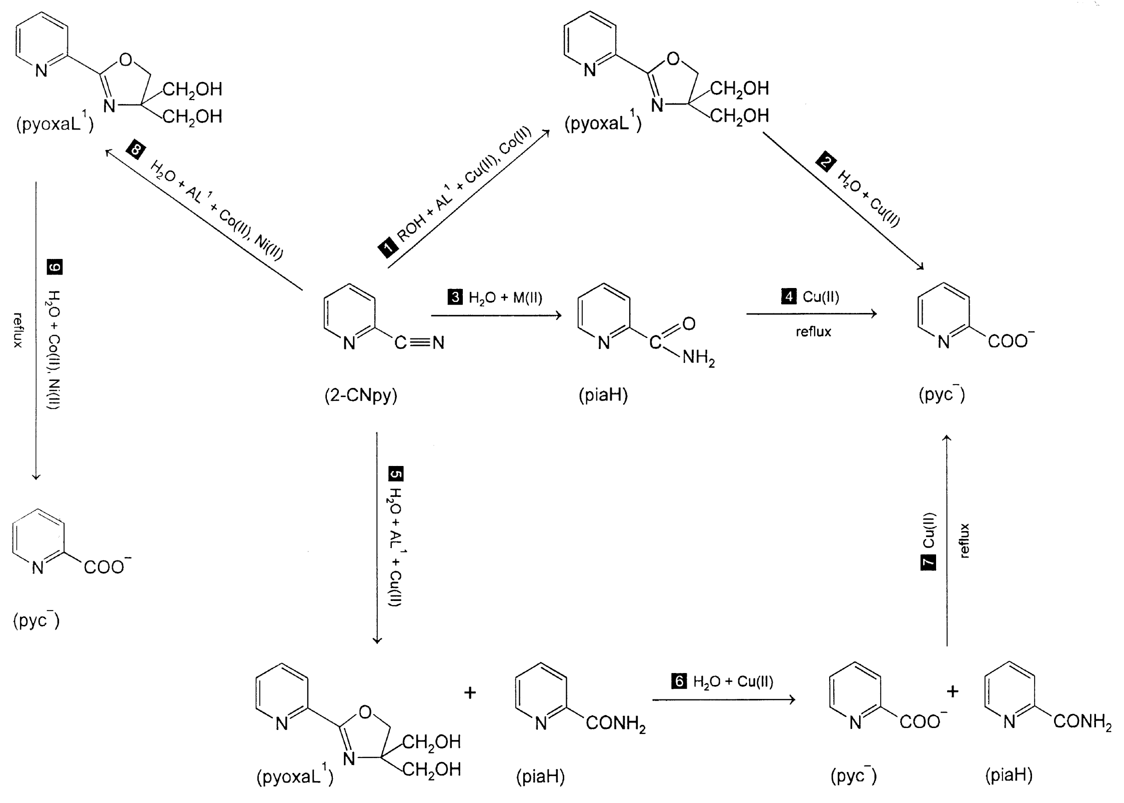
The reactions of 2-CNpy and pyoxaL^1 in aqueous solutions of Co(II) and Cu(II) salts under our experimental conditions are outlined in Scheme 2 (see also Section 2, Fig. 2 and Table 4). Moreover, the solid complexes of Co(II) and Cu(II) containing pyoxaL^1 have been prepared by the reaction of 2-CNpy with AL^1 [10]. For the sake of mutual comparability, Ni(II) complexes are included in Scheme 2, too.

All three transition metals M(II) mediate a pyoxaL^1 formation from 2-CNpy and AL^1. The process is, however, solvent and starting salt dependent. Solid Ni(II) complexes with pyoxaL^1 are formed both in water (reaction 8) and ethanol [9] regardless the counter anions. Halide complexes of Co(II) with pyoxaL^1 are formed only in ethanol (reaction 1) while pyoxaL^1 formation in water (reaction 8) was observed when starting with $Co(ClO_4)_2$ or $Co(NCS)_2$ [10]. Solid Cu(II)–pyoxaL^1 complexes [10] can be synthesized only in ethanolic solution (reaction 1). Some of these reactions can take place also in the presence of other amino alcohols (denoted in Scheme 1 as AL^2 and AL^3) but the present paper is focused mainly to the influence of AL^1 on addition reaction products of 2-CNpy. However, in this paper the results on the hydrolytic reactions of 2-CNpy in the presence or absence of AL^1 in aqueous solutions of copper(II) and cobalt(II) salts are described in detail.

4. CONCLUSIONS

The main conclusions of this paper can be summarized as follows.

1. The reaction of 2-CNpy with water or hydroxide ion in aqueous solution of metal(II) salts leads to the solid complexes containing piaH (reaction 3). The hydrolysis of piaH to pycH (reaction 4) was



Scheme 2. Formation of Cu(II), Ni(II) and Co(II) complexes containing different reaction products of pyridine-2-carbonitrile (2-CNpy).

observed only in refluxed solutions containing Cu(II).

2. The reaction of 2-CNpy with AL^1 in aqueous solution of Cu(II) salts at room temperature (reaction 5) leads to the fast formation of Cu(II) complexes containing pyoxaL^1. These complexes behave as intermediates and undergo a gradual decomposition to pyridine-2-carboxylic acid (reaction 6) already at room temperature. Simultaneously the nucleophilic attack of water or hydroxide on the nitrile group of coordinated 2-CNpy leads to the formation of copper complex with pyridine-2-carboxamide which is fully stable at room temperature in solution. This sequence of reaction steps is supported by a kinetic analysis of analogous systems containing 2-carbonitrile-1,10-phenanthroline instead of 2-CNpy, described in [8]. From that solution a mixture of solid complexes containing piaH or pyc^- ligands deposited after several days (see Section 2). When an aqueous reaction mixture of 2-CNpy, AL^1 and $CuCl_2$ is refluxed for a long time, well-shaped crystals of product **III** appeared (reaction 7).
3. Upon a reflux of aqueous solutions of $[CoCl_2(pyoxaL^1)_2]$ (reaction 9) a gradual hydrolysis of the pyoxaL^1 ligand to pycH and AL^1 is observed and complex $[Co(H_2O)_2(pyc)_2] \cdot 2H_2O$ is isolated. That complex can also be prepared by refluxing an aqueous solution of 2-CNpy, AL^1 and $CoCl_2$ for up 30 h.
4. The pure $[Cu(pyc)_2] \cdot 2H_2O$ was also prepared at room temperature directly from $[CuCl(pyoxaL^1)_2]Cl \cdot 0.5H_2O$ [9] via its decomposition in water (reaction 2).
5. Now the crystal and molecular structure of complex **III** fully confirms the conversion of the 2-CNpy to the coordinated pyc^- anions in aqueous solutions of $CuCl_2$. This complex is square-planar with two *N*,*O*-coordinated pyc^- ligands and two uncoordinated molecules of water. The same arrangement of donor atoms bonded to the central atom Cu(II) is supposed for complex **II**.

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