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Metal-promoted reactions of nitriles with amino alcohols in aqueous and alcoholic solutions. Nickel(II) complexes of 2-pyridinyl-2-oxazolines*

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Abstract

The reaction of pyridine-2-carbonitrile with 2-amino-2-hydroxymethyl-1,3-propanediol in aqueous or alcoholic solutions of Ni(II) salts leads to the isolation of solid complexes containing 2-(2-pyridinyl)-4,4-bis(hydroxymethyl)-2-oxazoline. Analogous reactions of pyridine-2-carbonitrile with 2-amino-2-methyl-1,3-propanediol and 2-amino-2-methyl-1-propanol give complexes containing 2-(2-pyridinyl)-4-hydroxymethyl-4-methyl-2-oxazoline and 2-(2-pyridinyl)-4,4-dimethyl-2-oxazoline, respectively. The complexes can be obtained under mild reaction conditions. A new preparative method for these 2-oxazolines by direct reaction of a nitrile with amino alcohols in the presence of a catalytic amount of nickel bromide is also described. Based on an IR study of various aqueous solutions and solid complexes, some conditions for oxazoline formation and its hydrolysis have been specified.

Introduction

Increased reactivities of coordinated molecules in metal complexes have wide implications in chemistry. Over the past 25 years there has been considerable interest focused on the metal-catalyzed nucleophilic reactions of nitriles [1]. In particular, the activation of the nitrile group upon metal coordination has been exploited in addition reactions of nucleophiles such as water, alcohols and amines yielding amide [2–5], iminoether [6–9] or amidine [8, 10–12] complexes.

As was previously observed the reaction of pyridine-2-carbonitrile (2-CNpy) with some metal salts in aqueous or alcoholic solutions leads to the isolation of complexes which contain pyridine-2-carboxamide (piaH) or *O*-alkylpyridine-2-carboximidate (O-Rpii) [13–15].

The 2-oxazoline ring shows an interesting structure and is present in a wide variety of compounds which are of interest in many fields of applications. For example, optically active oxazolines have been extensively used as valuable auxiliaries in asymmetric syntheses [16]. Recently optically active oxazolines have been used as chiral ligands for transition metals in asymmetric catalyses [17–19]. Oxazolines have also been found in many microbial metal chelators such as vibriobactin, mycobactin and parabactin [20–22]. There are many ways in which 2-oxazolines may be formed [23]. The majority of them require strongly acidic, basic or thermal conditions. The formation of 2-oxazolines by reaction of nitriles with amino alcohols has been investigated only partially till now. Some 2-oxazolines have been prepared by heating a mixture of a nitrile with an amino alcohol to 130 °C in the presence of catalytic amounts of certain metal salts [24]. Similarly, dinitriles react with amino alcohols in chlorobenzene under zinc chloride catalysis to give bis(oxazolines). Moreover, treatment of some bis(oxazolines) with zinc dichloride in tetrahydrofuran results in the formation of solid complexes [25]. The synthesis of 2-oxazolines and their complexes by the reaction of nitriles with amino alcohols in the presence of other nucleophiles (water or alcohol) at room temperature or at moderate heating of the reaction mixture, have not been published.

This paper describes the synthesis and characterization of some new 2-pyridinyl-2-oxazolines (denoted as pyoxaL^1, pyoxaL^2 and pyoxaL^3) and their Ni(II) complexes. These were prepared by the reaction of 2-CNpy with 2-amino-2-hydroxymethyl-1,3-propanediol (AL^1), 2-amino-2-methyl-1,3-propanediol (AL^2) and 2-amino-2-methyl-1-propanol (AL^3), respectively, in aqueous or alcoholic solutions of some Ni(II) salts (Scheme 1).

A kinetic study of the reaction of 2-CNpy with AL^1 in aqueous solutions by means of electronic spectra

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*The name 'oxazoline' which refers to dihydro-1,3-oxazole, is not recommended by I.U.P.A.C., but is retained here for an easier comparison with the literature.

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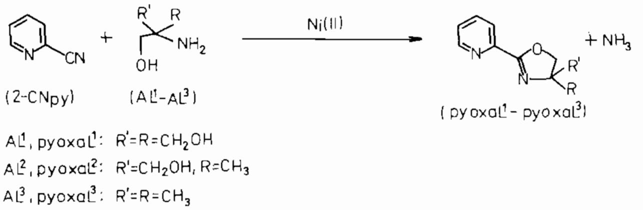


Scheme 1. Formation of 2-pyridinyl-2-oxazolines and their Ni(II) complexes by the reactions of pyridine-2-carbonitrile with amino alcohols.

has been presented in part [26]. Some new kinetic aspects of this reaction were obtained from an IR study of aqueous solutions and are also described in the present paper.

Experimental

Starting chemicals

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), 2-amino-2-methyl-1,3-propanediol (AL^2), 2-amino-2-methyl-1-propanol (AL^3) and pyridine-2-carboxylic acid (pycH) were used without further purification. The purity of the samples was checked by IR spectra.

Hydrates and anhydrous nickel(II) salts were prepared according to previously described procedures [27]. Methanol and ethanol were dried by standard methods [28].

Analysis and measurements

Nickel was determined by EDTA titration; carbon, hydrogen and nitrogen by microanalytical methods (Carlo Erba Instruments EA 1108).

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 on a Cary 2400 spectrophotometer at room temperature. A Radelkis OK-104 conductometer was used for conductivity measurements of complexes in nitrobenzene and in acetonitrile at 298 K. Analytical data, magnetic moments, electronic spectral data and molar conductivity values of solid samples are given in Tables 1 and 2.

^{1}H NMR spectra of the organic compounds were recorded on a Varian VX-300 spectrometer in CDCl$_3$ and CD$_3$COCD$_3$ solutions with TMS as the reference. Mass spectra were recorded on a MS 902 S spectrometer by AEI.

IR spectra in the range 4000–400 cm^{-1} were recorded on a Philips Analytical PU 9800 FTIR spectrometer at room temperature with 4 cm^{-1} resolution. The spectra of solid samples were obtained in KBr pellets (1 wt.%) as well as in mulls (nujol and hexachlorobutadiene) while those of aqueous solutions were measured in 0.02 mm calcium fluoride cells. The IR spectra of solutions were recorded at regular time intervals. pH measurements of the aqueous solutions were made at 293 K with a OP-208 pH meter (fy Radelkis), by the use of a combined glass electrode.

TABLE 1. Analytical data[a]

No.	Compound	Calculated (%) Found (%)			
		Ni	C	H	N
	pyoxaL^1		57.68	5.81	13.45
			57.30	5.82	13.40
	pyamL^1		53.09	6.24	12.38
			53.27	6.37	12.41
	pyoxaL^2		62.49	6.29	14.57
			62.04	6.39	14.36
	pyoxaL^3		68.16	6.87	15.90
			67.96	6.84	16.10
I	$[NiCl_2(pyoxaL^1)_2]$	10.75	43.99	4.43	10.26
		10.55	43.54	4.60	10.24
II	$[NiBr_2(pyoxaL^1)_2]$	9.25	37.83	3.81	8.82
		9.06	38.25	4.02	8.79
III	$[Ni(H_2O)_2(pyoxaL^1)_2]$-$(ClO_4)_2 \cdot H_2O$	8.06	32.99	4.15	7.69
		8.01	32.81	4.03	7.62
IV	$[Ni(NCS)_2(pyoxaL^1)_2]$	9.93	44.69	4.09	14.21
		10.17	44.61	4.10	14.24
V	$[Ni(NCS)_2(pyoxaL^2)_2]$	10.50	47.24	4.33	15.03
		10.60	47.16	4.30	15.11
VI	$[Ni(NCS)_2(pyoxaL^3)_2]$	11.13	50.11	4.59	15.94
		10.97	49.72	4.62	16.16
VII	$[Ni(H_2O)_2(pyc)_2] \cdot 2H_2O$	15.66	38.44	4.30	7.47
		15.60	38.28	4.37	7.57

[a] Microanalysis results obtained with maximum deviations: Ni, ±0.24; C, ±0.45; H, ±0.21; N, ±0.22.

Preparation of ligands

All of the 2-pyridinyl-2-oxazolines under study can be prepared by a new method in the presence of a catalytic amount of nickel bromide as described for the preparation of pyoxaL^2. Moreover, pyoxaL^1 and pyoxaL^3 were also prepared by other methods (see below). 2-Pyridinyl-2-oxazolines denoted as pyoxaL^1 and pyoxaL^2, as well as the amide pyamL^1, are new prepared compounds.

2-(2-Pyridinyl)-4,4-bis(hydroxymethyl)-2-oxazoline (pyoxaL^1) and pyridine-2-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]carboxamide (pyamL^1)

pyoxaL^1 was also prepared according to a conventional method previously described in the literature [23] for the preparation of 2-phenyl-4,4-bis(hydroxymethyl)-2-oxazoline. A mixture of equimolar quantities of AL^1, pycH (200 mmol) and 100 cm^3 xylene were refluxed

TABLE 2. Magnetic moments, electronic spectral data and molar conductivities for solid complexes

No.	Complex	μ_{eff} (BM)	Maxima of absorption bands (cm^{-1})			Λ_M[a]	Λ_M[b]
						(Ω^{-1} cm^2 mol^{-1})	
I	$[NiCl_2(pyoxaL^1)_2]$	3.06	9700	15700		1	32
II	$[NiBr_2(pyoxaL^1)_2]$	2.99	9700	16000		2	95
III	$[Ni(H_2O)_2(pyoxaL^1)_2](ClO_4)_2 \cdot H_2O$	3.12	10100	16800		45	281
IV	$[Ni(NCS)_2(pyoxaL^1)_2]$	3.11	10500	17200	25500–27000	1	13
V	$[Ni(NCS)_2(pyoxaL^2)_2]$	3.15	10000	17100		2	54
VI	$[Ni(NCS)_2(pyoxaL^3)_2]$	3.10	10200	17100	26000–27500	2	62
VII	$[Ni(H_2O)_2(pyc)_2] \cdot 2H_2O$	3.05	10500	16700		c	c

[a] In nitrobenzene (concentration 10^{-3} M). [b] In acetonitrile (concentration 10^{-3} M). [c] Not measured.

in a flask equipped with a moisture trap, until no more reaction water (removing as a xylene azeotrope) was collected in the trap (20 h). The reflux mixture was cooled and filtered. The recrystallization of crude product from acetone gave purified pyoxaL^1 (50%, m.p. 143–145 °C).

Mass spectrum (EI, 70 eV): m/z (%) = 208(1) [M^+], 177(100), 147(52), 106(24), 105(28), 79(17), 78(62).

^{1}H NMR ($CDCl_3$/TMS): $\delta = 3.10$ (s(br), 2H, OH); 3.68–3.89 (m, 4H, CH_2OH); 4.50 (s, 2H, H-5); 7.33–7.49 (m, 1H, py-5-H), 7.68–7.75 (m, 1H, py-4-H); 7.84–7.89 (m, 1H, py-3-H); 8.62–8.66 (m, 1H, py-6-H).

The filtrate left after isolation of pyoxaL^1 was slowly evaporated and finally white crystals of pyamL^1 (20%, m.p. 127 °C) were separated from the concentrated solution.

IR spectrum: $\tilde{\nu} = 3300$ (ν(NH)), 1643 (amide I), 1520 (amide II) and 1253 (amide III) cm^{-1}.

Mass spectrum (EI, 70 eV): m/z (%) = 226(1) [M^+], 195(63), 178(23), 161(10), 147(8), 106(73), 79(33), 78(100).

^{1}H NMR (CD_3COCD_3/TMS): $\delta = 2.99$ (s, 3H, OH); 3.81 (d, 6H, $J = 6$ Hz, CH_2OH); 7.60–7.64 (m, py-5-H); 8.01–8.06 (m, 1H, py-4-H); 8.15–8.18 (m, 1H, py-3-H); 8.63–8.65 (m, 1H, py-6-H); 8.96 (s(br), 1H, NH).

2-(2-Pyridinyl)-4-hydroxymethyl-4-methyl-2-oxazoline (pyoxaL^2)

pyoxaL^2 was only prepared by the reaction of equimolar quantities of 2-CNpy with AL^2 (40 mmol) in a dry methanolic solution of $NiBr_2$ (5 mmol were dissolved in 50 cm^3 of methanol). The mixture was heated under reflux for 30 h. The solvent was removed under reduced pressure to give an oily residue, which was extracted three times with 40 cm^3 of diethyl ether. The product deposited from the solution on standing for 5 h was collected by filtration and washed with petroleum ether. White crystals (60%, m.p. 76–77 °C).

Mass spectrum (EI, 70 eV); m/z (%) = 192(1) [M^+], 161(42), 105(20), 92(10), 78(16), 74(100).

^{1}H NMR ($CDCl_3$/TMS): $\delta = 1.37$ (s, 3H, CH_3); 3.03 (s(br), 1H, OH); 3.52 (d(AB), 1H, $J = 11.4$ Hz, CH_2OH); 3.83 (d(AB), 1H, $J = 11.4$ Hz, CH_2OH); 4.18 (d(AB), 1H, $J = 8.4$ Hz, H-5); 4.59 (d(AB), 1H, $J = 8.4$ Hz, H-5); 7.34–7.38 (m, 1H, py-5-H); 7.71–7.77 (m, 1H, py-4-H); 7.92–7.95 (m, 1H, py-3-H); 8.65–8.67 (m, 1H, py-6-H).

2-(2-Pyridinyl)-4,4-dimethyl-2-oxazoline (pyoxaL^3) [29]

pyoxaL^3 was also prepared according to the method given in a previous paper [25]. To a mixture of 2-CNpy (30 mmol), AL^3 (90 mmol) and nickel bromide (1.5 mmol), 90 cm^3 of chlorobenzene were added and the mixture was then heated under reflux for 24 h. The solvent was removed under reduced pressure to give an oily residue, which was dissolved in 90 cm^3 of dichloromethane. The solution was extracted three times with 60 cm^3 of water and the aqueous phase with 90 cm^3 of dichloromethane. The combined organic phases were dried with sodium sulfate and the solvent was removed in vacuum. The resulting oil was purified by distillation. Colorless crystals (80%, m.p. 31 °C).

^{1}H NMR ($CDCl_3$/TMS): $\delta = 1.39$ (s, 6H, CH_3); 4.18 (s, 2H, H-5); 7.34–7.39 (m, 1H, py-5-H); 7.72–7.78 (m, 1H, py-4-H); 7.98–8.03 (m, 1H, py-3-H); 8.67–8.71 (m, 1H, py-6-H).

Preparation of complexes

(a) From pyridine-2-carbonitrile

$[NiCl_2(pyoxaL^1)_2]$ (I) and $[NiBr_2(pyoxaL^1)_2]$ (II)

Solid complexes **I** and **II** were prepared in aqueous solutions by the reaction of equimolar quantities of 2-CNpy and AL^1 (20 mmol) with 10 mmol of hydrates of Ni(II) chloride and anhydrous Ni(II) bromide, respectively. The mixture was heated for 20 min at 60 °C. The aqueous solution was slowly evaporated at room temperature giving an oily residue. This was recrystallized from a 1:1 methanol–acetone mixture. The green crystals deposited were collected by filtration and washed with acetone and finally dried in vacuum; yields of **I** and **II** were 75 and 80%, respectively.

[Ni(H_2O)$_2$(pyoxaL^1)$_2$](ClO$_4$)$_2$·H_2O (III) and [Ni(NCS)$_2$(pyoxaL^1)$_2$] (IV)

Ni(II) perchlorate hydrates and anhydrous Ni(II) thiocyanate were used as starting compounds for the preparation of complexes **III** and **IV**, respectively. The aqueous reaction mixtures were prepared in the same way as described above. However, from these solutions, complexes **III** and **IV** started to precipitate after about 10 min. Blue crystals were filtered and washed with ethanol; yields of **III** and **IV** were 80 and 90%, respectively.

Ni(NCS)$_2$(pyoxaL^2)$_2$] (V) and [Ni(NCS)$_2$(pyoxaL^3)$_2$] (VI)

The analogous reactions of 2-CNpy with more basic AL^2 and AL^3 in aqueous solutions of Ni(NCS)$_2$ led to the isolation of solid complexes **V and VI** together with hydrolytic products of Ni(II) only. To minimize hydrolysis of Ni(II), complexes **V** and **VI** were prepared by the reaction of 20 mmol 2-CNpy with AL^2 and AL^3 (20 mmol) in an ethanolic solution of Ni(NCS)$_2$ (10 mmol). Blue complexes were precipitated after 20 min; yields of **V** and **VI** were 85 and 90%, respectively.

[Ni(H_2O)$_2$(pyc)$_2$]·2H_2O (VII)

The blue complex [Ni(H_2O)$_2$(pyc)$_2$]·2H_2O, where pyc is the anion of pyridine-2-carboxylic acid, was prepared when 50 cm^3 of an aqueous solution of 2-CNpy (20 mmol), AL^1 (20 mmol) and NiCl$_2$ (10 mmol) were directly refluxed for up to 50 h. The complex that deposited from the aqueous solution was collected by filtration, washed with ethanol and dried in vacuum (yield 75%).

(b) From 2-pyridinyl-2-oxazolines

Complexes I–VI

Solid complexes **I–VI** were also prepared directly by the reaction of Ni(II) salts (5 mmol were dissolved in 40 cm^3 of dry ethanol) with the appropriate 2-pyridinyl-2-oxazolines (10 mmol). The crystals deposited after 5 min were collected by filtration and washed with dry ethanol (yields about 95%).

Analytical and spectral data of the complexes prepared directly from 2-pyridinyl-2-oxazolines, are almost identical with those prepared from 2-CNpy. Therefore in this paper only the data for the complexes prepared from 2-CNpy are presented.

Complex VII

10 mmol of complexes [NiCl$_2$(pyoxaL^1)$_2$] when refluxed in 50 cm^3 of water for 50 h, gives after isolation the solid compound [Ni(H_2O)$_2$(pyc)$_2$]·2H_2O. The complex was filtered off and washed with ethanol (yield 85%). The aqueous filtrate was evaporated on a steam bath and the solid residue was extracted three times with 30 cm^3 of hot ethanol. After cooling of the filtrate white crystals of AL^1 were isolated in 75% yield.

Results and discussion

The compositions and structures of the organic ligands in the complexes studied were determined on the basis of IR data. The spectra of the solid complexes no longer exhibit the most characteristic bands assigned to the valence vibration ν(C≡N) of the nitrile group in 2-CNpy (at 2235 cm^{-1}) and the deformation vibration δ(NH$_2$) of the amino group in amino alcohols (about 1600 cm^{-1}). At the same time, however, there appear several new, often very intense, characteristic bands. In elucidating these spectral changes it is necessary at first to characterize the spectra of the prepared 2-oxazolines.

IR spectra of 2-pyridinyl-2-oxazolines

A few IR spectra of 2-aryl-2-oxazolines have been published [30–32], but there have been neither a previous systematic investigation nor a sufficient assignment of the characteristic bands. Some maxima of the characteristic absorption bands in the range 1800–900 cm^{-1} of the 2-pyridinyl-2-oxazolines under study are given and assigned in Table 3. Moreover, these compounds exhibit several bands belonging to typical vibrations of the 2-pyridinyl ring [33]. Similarly, pyoxaL^1 and pyoxaL^2 also show strong bands in the range 1070–1030 cm^{-1}, which are attributed to C–OH stretching vibrations of hydroxymethyl substituents coupled with other ring vibrations of 2-oxazolines.

The −C=N− stretching mode in these five-membered heterocyclic compounds (Table 3) lies well within the range usually cited for 2-oxazolines [34]. Assignments for the −C−N= stretching of 2-oxazolines have not yet been reported. All 2-pyridinyl-2-oxazolines under study show a strong band at about 1360 cm^{-1} which is shifted to higher frequencies in the complexes. We conclude that this band corresponds mainly to the −C−N= vibration of the 2-oxazoline ring.

Further characteristic bands for the 2-oxazolines are usually described [25, 30, 31] at approximately 1200 cm^{-1} and are assigned to −C−O−C= ring stretching. Lundquist and Ruby [34] also assigned another band at 1040 cm^{-1} to C−O−C stretching of some 2-methyl-2-oxazolines. We observed at least three bands in the region 1200–1040 cm^{-1} which can unambiguously be assigned to ring stretching vibrations and be associated mainly with the C−O−C group.

TABLE 3. Characteristic IR bands (in cm^{-1}) of solid 2-pyridinyl-2-oxazolines and their Ni(II) complexes^a

No.	Compound	CN stretching		CH$_2$ deformation^b		Ring stretching ν(C−O−C)			Region 900–1000 cm^{-1}
		ν(C=N−)	ν(C−N=)	δ_{sc}(CH$_2$)	δ_w(CH$_2$)				
	pyoxaL^1	1659m 1638s	1367s,br	1475m	1318w 1338m	1147m	1105m	1073m	977m 966s 951w 939w
	pyoxaL^2	1657m 1638s	1363s	1473m	1334m,br	1143m	1097m	1067s	963s 936m
	pyoxaL^3	1653s,br	1358s	1468m	1323m	1151w	1111m 1085s	1068m	966s 925m
I	[NiCl$_2$(pyoxaL^1)$_2$]	1655s,br	1395s,br	1487m	1338m	1153s,br	1110w	1062m	957s,br
II	[NiBr$_2$(pyoxaL^1)$_2$]	1650s,br	1403s	1490m	1340m	1154s	1105w	1063m	959s,br
III	[Ni(H$_2$O)$_2$(pyoxaL^1)$_2$]-(ClO$_4$)$_2$·H$_2$O	1644s	1406s	1492m	1324m,br	1154s		^{c}	984m 968m 950s
IV	[Ni(NCS)$_2$(pyoxaL^1)$_2$]	1648s	1394s,br	1486m,br	1320w 1342m,br	1153s		1061m	957s 941s 926m
V	[Ni(NCS)$_2$(pyoxaL^2)$_2$]	1650s	1395s	1488m	1336m	1149s	1132m	1072w	962m 941s
VI	[Ni(NCS)$_2$(pyoxaL^3)$_2$]	1652s	1398s	1482m	1332m	1157m	1139m	1091m	947s

^{a}s, strong; m, medium; w, weak; br, broad. $^b\delta_{sc}$(CH$_2$), scissoring vibration of CH$_2$ in 2-oxazoline ring; δ_w(CH$_2$), wagging vibration of CH$_2$ in oxazoline ring. ^{c}Other vibrations are overlapped by a very strong band of ν_3(ClO$_4^-$).

Another characteristic region for 2-oxazolines which is not sufficiently well described in the literature [30, 31, 34], is that from 1000 to 900 cm^{-1}. According to the IR study of similar compounds [35, 36], we suggest the strong or medium bands observed in this region be attributed to another ring stretching or especially to the ring breathing mode of 2-oxazolines. Thus the number and positions of bands in the region 1200–900 cm^{-1} give support to the conclusion that the C−O−C fragment of the studied 2-oxazoline ring is probably of acetal character [35, 37].

The 2-oxazolines studied in the present paper contain a various number of CH$_2$ and CH$_3$ groups. At the same time, CH$_2$ groups are bonded to oxygen atoms in two modes. It seems that the CH$_2$ group in the ring of 2-oxazolines always exhibits the methylene scissoring vibration at a higher frequency than that found for the hydroxymethyl group [34, 36]. Similarly we conclude that a medium band at about 1330 cm^{-1} corresponds only to the wagging vibration of the CH$_2$ group in the 2-oxazoline ring. Moreover, pyoxaL^2 and pyoxaL^3 show CH$_3$ deformation vibrations at expected normal positions.

Properties and structure of solid complexes

The values of magnetic moments, molar conductivities and electronic spectral data for the solid complexes are given in Table 2. All of the complexes under consideration are paramagnetic (μ_{eff} = 2.99–3.12 BM). In the electronic spectra the complexes exhibit two single absorption bands in the ranges 9700–10 500 and 15 700–17 200 cm^{-1}. The third band in the range 25 500–27 500 cm^{-1} is usually overlapped by intense ligand absorption or charge transfer bands. Based on electronic spectra and magnetic moment values [27], an octahedral configuration of the Ni(II) atom was assigned to all the solid complexes under investigation. Molar conductivity values in nitrobenzene (Λ_M = 1–2 Ω^{-1} cm^2 mol^{-1}) and acetonitrile (Λ_M = 13–95 Ω^{-1} cm^2 mol^{-1}) show that, except for complex **III**, all of the complexes are non-electrolytes [38] and contain only coordinated anionic ligands. The molar conductivities of complex **III** in nitrobenzene (Λ_M = 45 Ω^{-1} cm^2 mol^{-1}) and acetonitrile (Λ_M = 281 Ω^{-1} cm^2 mol^{-1}) are typical for those of 1:2 electrolytes [38] with non-coordinated perchlorate groups. The conductivities of complex **VII** were not measured.

Some characteristic IR bands of complexes **I**–**VI** are given in Table 3. Moreover, all thiocyanate complexes show a very strong and considerably broad band (partly split) in the region 2090–2070 cm^{-1}. The position of this band due to ν(C≡N) indicates the presence of monodentate NCS groups which are coordinated through the nitrogen atoms only [39]. Similarly, all of the complexes **I**–**VII** show that the 2-pyridinyl ring in organic ligands is always coordinated through the nitrogen atom [39]. The IR spectra observed for complexes **I**–**VI** prepared by the reaction of 2-CNpy with amino alcohols, when compared with those of the complexes prepared directly with 2-pyridinyl-2-oxazolines, give evidence that complexes **I–VI** contain coordinated pyoxaL[1], pyoxaL[2] or pyoxaL[3] molecules as organic ligands only. The most significant spectral changes after coordination of 2-pyridinyl-2-oxazolines molecules (Table 3) were observed as shifts of the bands due to $\nu(-C-N=)$ and $\delta_{SC}(CH_2)$ to higher frequencies. Other significant changes were observed in the region 1200–900 cm^{-1} for absorption bands which are attributed to various ring stretching vibrations associated mainly with the C–O–C group. In the spectra of the complexes some of these bands are stronger, the others are weaker or not observed. At the same time, small shifts of these bands to either higher or lower frequencies were observed. We conclude that the above discussed spectral changes correspond mainly to a loss of acetal character of the C–O–C group in the 2-oxazoline ring after its coordination to the Ni(II) atom. The present knowledge of IR spectra do not allow the precise coordination mode of the 2-oxazoline ring to be determined unambiguously.

The spectral and magnetic properties of compound **VII**, $Ni(pyc)_2 \cdot 4H_2O$, are identical with those given [40] for the same compound prepared directly with pycH. It has been found that this monomeric octahedral complex contains two anions of pyridine-2-carboxylic acid (as N,O-coordinated chelates) and only two coordinated molecules of water.

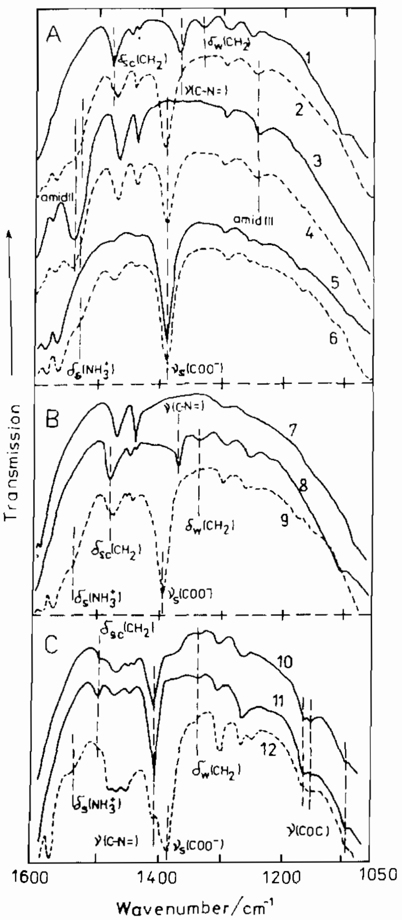


Fig. 1. IR spectra of aqueous solutions. Numbers in the figure represent spectrum numbers in Table 4. For denotation of vibrations see Table 3.

IR spectra of aqueous solutions

One of the more interesting properties of 2-oxazolines is their decomposition in aqueous solution to give various non-cyclic products [23, 41]. On the other hand, the complexes containing pyoxaL[1] as a ligand could be prepared by the reactions of aqueous or alcoholic solutions of Ni(II) salts with 2-CNpy and AL[1]. Therefore some kinetic aspects of these reactions have been studied in aqueous solutions.

The IR spectra of different solutions have been quite helpful in understanding some of these aspects. Although water absorbs strongly in some regions, it is relatively transparent in calcium fluoride cells between 1550–1200 cm^{-1}, particularly if thin layers are used. Some spectra of aqueous solutions under study in this region are illustrated in Fig. 1. Solid curves represent the spectra of solutions prepared at room temperature and, except for 8 and 11, were measured immediately after their preparation. Dashed curves, however, were obtained for aqueous solutions which were refluxed for up to 50 h. The composition of the starting solutions, the time and temperature, which were used for the preparation of measured solutions, as well as the pH of measured solutions and the dominant components observed in their IR spectra are given in Table 4.

The spectra of pyoxaL[1] itself and its decomposition products in aqueous solutions are illustrated in Fig. 1A. pyoxaL[1] is quite stable for a long time at room temperature, however, its gradual decomposition during reflux is observed. At first, amide pyamL[1] is quickly formed and later its mixture with pycH and AL[1]. The final mixture (spectrum 2) consists of pycH in the anionic form, AL[1] mainly in the cationic form denoted as AL[1]H (the $\delta_S(NH_3{}^+)$ vibration has appeared) and, partially of pyamL[1]. The latter non-cyclic amide itself is relatively stable for a long time at room temperature (spectrum 3). If the solution of pyamL[1] is refluxed for up to 50 h an incomplete decomposition of this amide to ionic forms of pycH and AL[1] is also observed. Spectrum 5, representing aqueous solutions of pycH in the range pH 7–10, is not changed during reflux. Similarly, the IR spectrum 6 of the aqueous solution of pycH and AL[1] is not affected by refluxing. This result leads to the conclusion that neither pyamL[1] nor pyoxaL[1] is formed in aqueous solutions of pycH and AL[1] at pH about 7.

Unlike the latter solution, in the spectra of aqueous solutions of 2-CNpy and AL[1] the slow formation of pyoxaL[1] is already observed at room temperature. At

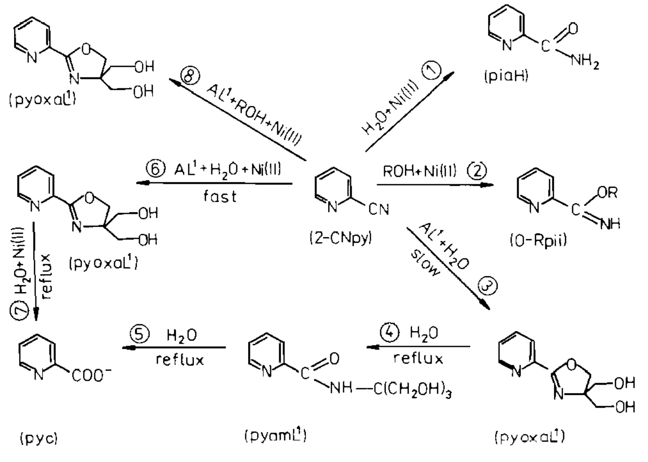
TABLE 4. Composition of aqueous solutions

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^{1}H, pyamL^1
3	pyamL^1	r.t.	5 min	6.1	pyamL^1
4	pyamL^1	reflux	50 h	6.0	pyamL^1, pyc, AL^1, AL^{1}H
5	pycH	r.t.	5 min	7–10	pyc
6	pyc + AL^1	reflux	50 h	6.8	pyc, AL^1, AL^{1}H
7	2-CNpy + AL^1	r.t.	5 min	10.6	2-CNpy, AL^1
8	2-CNpy + AL^1	r.t.	14 days	11.3	pyoxaL^1
9	2-CNpy + AL^1	reflux	50 h	8.0	pyc, AL^1, AL^{1}H
10	2-CNpy + AL^1 + NiCl$_2$	r.t.	5 min	8.4	complex of pyoxaL^1
11	2-CNpy + AL^1 + NiCl$_2$	r.t.	120 min	9.4	complex of pyoxaL^1
12	2-CNpy + AL^1 + NiCl$_2$	reflux	50 h	6.7	AL^1, AL^{1}H, complex of pyc and pyoxaL^1

[a]Solutions 1–11: the concentrations of organic compounds and NiCl$_2$ were 0.50 and 0.25 M, respectively; solution 12: the concentrations of organic compounds and NiCl$_2$ were 1.00 and 0.50 M, respectively. [b]r.t. = room temperature. [c]Structural species observed in IR spectra.

the same time, the band at 2246 cm^{-1}, assigned to the ν(C≡N) vibration of the nitrile group, was not observed in spectrum 8. A comparison of the latter spectrum with that of pyoxaL^1 shows that pyoxaL^1 is formed in the aqueous solution of 2-CNpy and AL^1 only to a certain extent. If the same solution is refluxed for up to 50 h, the presence of pyc, AL^1 and its ionic form is only confirmed in IR spectrum 9.

In the presence of Ni(II) ions formation of the complexes was indicated by significant spectral changes (Fig. 1C). Moreover, none of these solutions exhibit the strong band due to ν(C≡N) of 2-CNpy at 2246 cm^{-1}. At the same time, the pH values of the measured solutions depend strongly on the experimental conditions (see Table 4). In agreement with these spectral and pH changes we conclude that fast nucleophilic reactions on 2-CNpy take place immediately after preparation of the solutions to give Ni(II) complexes with pyoxaL^1 and other, probably non-cyclic initial addition products of 2-CNpy. The latter products are gradually changed at room temperature finally to pyoxaL^1 which is very strongly bonded to the Ni(II) ion (spectrum 11 is not changed during several days). This result is also confirmed by a comparison of the spectral changes for pyoxaL^1 itself (spectra 1 and 2) with those of the Ni(II) solutions (spectra 11 and 12). The latter solution after refluxing consists mainly of Ni(II) complexes, containing picolinate anion and, in a significant amount, also pyoxaL^1. A cationic form of AL^1, as a product of the decomposition of pyoxaL^1, was also confirmed in the final solution (see spectrum 12).



Scheme 2. Formation of different organic products or their Ni(II) complexes by the reactions of pyridine-2-carbonitrile with some nucleophiles.

Reactions of pyridine-2-carbonitrile and formation of 2-pyridinyl-2-oxazolines

The reactions of pyridine-2-carbonitrile with different nucleophilic reagents (water, dry or wet methanol and ethanol, 2-amino-2-hydroxymethyl-1,3-propanediol) and Ni(II) salts under our experimental conditions are outlined in Scheme 2 (see also Fig. 1 and Table 4). Some of these reactions can also take place in the presence of other amino alcohols under study (denoted as AL^2 and AL^3), but the present paper has been mainly directed to the influence of AL^1 on addition reaction products of 2-CNpy. Moreover, the surprising formation of 2-oxazolines in water containing solutions forced us to extend our study to the kinetic aspects of the hydrolysis of 2-CNpy and pyoxaL^1 in aqueous solutions.

Conclusions

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

1. While nearly neutral aqueous, methanolic or ethanolic solutions of 2-CNpy remain unchanged for a long period, the presence of Ni(II) salts yields [13, 15, 42] different addition products (reactions (1) and (2)). The composition of these products is not limited by reaction temperatures or isolation times.
2. No reaction of 2-CNpy with AL^1 in the neutralized aqueous solution (pH 7.7) has been observed at room temperature, but a slow reaction (3) in this mixture takes place at pH 10.6 and the formation of only $pyoxaL^1$ is, in part, observed. The reflux of both solutions, however, always leads to a gradual hydrolysis and the presence of pycH and AL^1 in the reaction mixtures has been confirmed.
3. When an aqueous solution of $pyoxaL^1$ itself is refluxed, the formation of $pyamL^1$ is already observed after a few hours (reaction (4)). Finally, pycH and AL^1 have been mainly observed in the mixture obtained after 50 h. Similarly the mixture of pycH and AL^1 has been observed in an aqueous solution of $pyamL^1$ itself when it is refluxed for long periods of time (reaction (5)).
4. The reaction of 2-CNpy with AL^1 in aqueous solutions of Ni(II) salts at room temperature (reaction (6)) leads to the fast formation of Ni(II) complexes containing $pyoxaL^1$ only. The cyano group of the nitrile ligand is attacked by the oxygen atom of the hydroxyl group of amino alcohol at subsequent ring closure and elimination of ammonia gives the final complex of $pyoxaL^1$ [43]. Other kinetic and mechanistic aspects of the 2-pyridinyl-2-oxazoline complex formation will be reported [44] later.
5. If aqueous solutions of Ni(II) complexes containing $pyoxaL^1$ are refluxed (reaction (7)), a gradual hydrolysis of the ligand to pycH and AL^1 is observed and complex $[Ni(H_2O)_2(pyc)_2]\cdot 2H_2O$ is isolated. On the other hand, this complex could also be prepared when an aqueous solution of 2-CNpy, AL^1 and $NiCl_2$ is directly refluxed for up to 50 h. Nevertheless, the reflux of aqueous solutions of Ni(II) salts and 2-CNpy for long periods in the absence of AL^1 leads to isolation of complexes containing piaH only. Therefore, unlike aqueous solutions of Cu(II) salts and 2-CNpy [44, 45], no further hydrolysis of piaH to pycH is observed under the described experimental conditions.
6. The reactions of 2-CNpy with AL^1 in methanolic and ethanolic solutions of Ni(II) salts (reaction (8)) lead to isolation of solid complexes containing $pyoxaL^1$. Similarly, the reaction of 2-CNpy with AL^2 and AL^3 gives complexes containing $pyoxaL^2$ and $pyoxaL^3$, respectively. This finding has also been proved by the reaction of $NiBr_2$ in methanolic solution with a considerable excess of 2-CNpy and AL^2 when pure $pyoxaL^2$ was separated (see 'Experimental'). The analogous reaction of 2-CNpy with AL^1 or AL^3 also leads to isolation of appropriate 2-oxazolines in good yields.

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