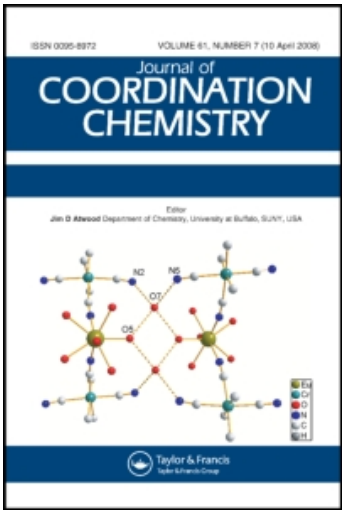

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FORMATION OF *N*-HYDROXYALKYLPYRIDINE-2-CARBOXAMIDINES AND 2-PYRIDINYL-2-OXAZOLINES IN THE COORDINATION SPHERE OF NICKEL(II)

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Condensation of pyridine-2-carbonitrile (2-CNpy) with 2-aminoethanol (L^1), 1-amino-2-propanol (L^2) and 2-amino-1-butanol (L^3) in ethanolic solutions of Ni(II) salts proceeded readily at room temperature to form stable complexes, which contain the amino form of *N*-hydroxyalkylpyridine-2-carboxamidines (amL-NH_2). The crystal structure of complex $[Ni(N\text{-}2\text{-hydroxyethylpyridine-2-carboxamidine})_2]Cl_2 \cdot 3.5H_2O$ and IR data confirm *N,N,O*-coordination of *N*-hydroxyalkylpyridine-2-carboxamidines (*via* the nitrogen atom of the pyridine ring, the nitrogen atom of the C=N– group and the oxygen atom of the hydroxyl group). The electron density distribution and structure of the amino form of amL-NH_2 are suitable for cyclization accompanied by ammonia elimination and formation of the appropriate oxazoline. On the other hand, substituted 2-amino-2-ethyl-1,3-propandiol (L^4) formed in alcoholic solutions of Ni(II) complexes containing 2-(2-pyridinyl)-4-ethyl-4-hydroxymethyl-2-oxazoline (oxaL^4) only. The influence of amino alcohols and nickel(II) salts, as well as reaction conditions on amidine or oxazoline formation is discussed.

Keywords: Nickel(II) complexes; nucleophilic reaction; *N*-hydroxyalkylpyridine-2-carboxamidines; 2-pyridinyl-2-oxazolines; crystal structure

* Corresponding author.

INTRODUCTION

Organic nitriles have applications in several industries. Usage is conditioned in many cases by complexation with a central atom. As an example, the use of copper(II) chloride–pyridine-2-carbonitrile–alcohol systems in the catalytic decomposition of sarin and soman[1] can serve.

Coordination of nitriles to electron-withdrawing transition metal ions results in enhanced electrophilicity of the nitrile carbon, thus making it susceptible to addition reactions of protic nucleophiles such as water, alcohols and amines to generate the corresponding amide, imino ether and amidine complexes, respectively.[2] As expected, most of these studies have been concerned with kinetically inert hexacoordinated Co(III), Rh(III), Ir(III), Ru(III) or square-planar Pt(II) and Pd(II) complexes. For example, nucleophilic attack of 1,2-diaminoethane on the carbon atom of the nitrile group of aminoacetonitrile in the coordination sphere of Co(III) leads to the formation of a terdentate *N*-alkylamidine ligand.[3] An X-ray study[4] indicated the presence of the amino form for that amidine ligand in the coordination sphere of Co(III).

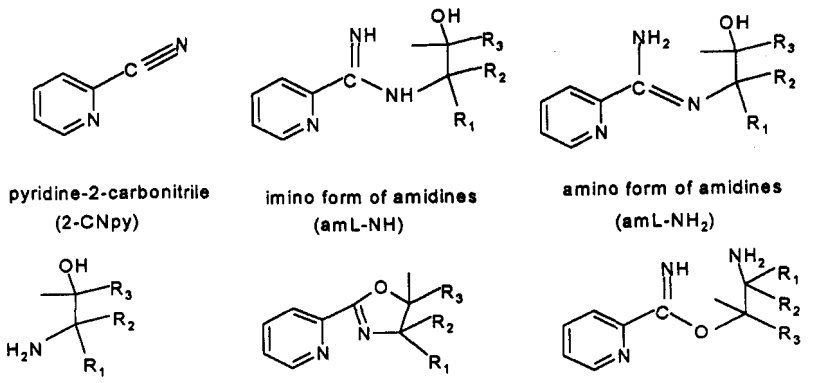
Following previous studies, a detailed investigation on the cyclization reactions of the nitrile ligands in Pt(II) complexes by nucleophilic attack of the oxygen atom of haloalcohols $HO-(CH_2)_n-Cl$ ($n=2,3$) to afford *N,O*-heterocycles has recently been reported.[5] Such attack has also been explored in the reaction of $HOCH_2CH_2Cl$ with *cis*- and *trans*-$[PtCl_2(NCR)_2]$ (R = alkyl and aryl groups), in which the steric and electronic properties of the R groups varied over a wide range, to afford 2-oxazoline complexes.[6] The attacking haloalkoxide ion can be generated by reaction of 2-chloroethanol with base.

There are many other ways in which 2-oxazolines may be formed.[7] The majority of them require strongly acidic or basic or thermal conditions. The formation of 2-oxazolines by reaction of nitriles with amino alcohols in the presence of certain metal(II) salts has been investigated only partially to now. In the presence of Ni(II), Co(II) or Cu(II) salts[8,9] the reaction of pyridine-2-carbonitrile with some substituted amino alcohols led to the formation of solid complexes containing 2-pyridinyl-2-oxazolines under mild reaction conditions both in water and alcohols. Amino alcohols are able to act as nucleophiles through two different atoms, *i.e.*, through the hydroxyl group oxygen or the amino group nitrogen. It is considered that the oxazoline formation could proceed *via* imino ethers or amidines although the reactive intermediate has not been isolated.[8,9] Moreover, molecules containing oxazoline moieties play an important role in several naturally occurring biological processes and, due to their ligation to various

metal centres related to treatment of neurological dysfunctions, bone disorders or iron overloading, these chelators are also of a biomedical interest.[10]

As part of systematic research on metal-promoted inner-sphere reactions of organic ligands, attention has been paid in our laboratory to the synthesis and structure of transition metal complexes with organic nitriles and their transformation to oxazolines and other products.[8,9] This paper describes the synthesis and structural characterization of some new nickel(II) complexes containing *N*-hydroxyalkylpyridine-2-carboxamidines or 2-pyridinyl-2-oxazolines. All complexes were formed in alcoholic solutions of nickel(II) salts, pyridine-2-carbonitrile and amino alcohols with varying electronic and steric properties. One of the goals of this work was to determine which of the above intermediates is formed preferentially. To answer this question, along with an IR study, the X-ray crystal structure of one of the complexes, $[Ni(N\text{-}2\text{-hydroxyethylpyridine-2-carboxamidine})_2]Cl_2 \cdot 3.5H_2O$, was solved. The influence of amino alcohols, nickel(II) salts and reaction conditions on the nucleophilic reactions is briefly discussed.

The structures of the ligands investigated in this paper are as follows (Scheme 1).



L^1: $R_1 = R_2 = R_3 = H$
L^2: $R_1 = R_2 = H$; $R_3 = CH_3$
L^3: $R_1 = R_3 = H$; $R_2 = C_2H_5$
L^4: $R_1 = CH_2OH$; $R_2 = C_2H_5$; $R_3 = H$

SCHEME 1 Structures and abbreviations of pyridine-2-carbonitrile and products of its metal(II) promoted transformations.

EXPERIMENTAL

Starting Chemicals

All the chemicals used were of reagent grade. Solid pyridine-2-carbonitrile (2-CNpy) was obtained from Sigma and purified by distillation under reduced pressure; 2-aminoethanol (L^1), 1-amino-2-propanol (L^2), 2-amino-1-butanol (L^3) and 2-amino-2-ethyl-1,3-propandiol (L^4) were used without further purification. All amino alcohols were purchased from Aldrich; their purity was checked by IR spectra and ^{1}H NMR spectra.

Anhydrous nickel(II) salts were prepared according to previously described procedures.[11] Methanol and ethanol were dried by standard methods.[12]

Analyses and Measurements

Nickel was determined by EDTA titration; carbon, hydrogen and nitrogen by microanalytical methods (Carlo Erba Instruments EA 1108). Water and acetone contents in the hydrates and/or solvates were determined, along with the elemental analysis, from thermogravimetrical curves. Analytical data for solid complexes are given in Table I.

Electronic spectra of the powdered samples in nujol mulls and diffuse reflectance spectra in MgO were recorded at room temperature on a Specord M40 and a Magna 750 spectrophotometer, respectively. A Radelkis OK 104 conductometer was used for conductivity measurements of complexes (concentration 1.0×10^{-3} M) in acetonitrile and dimethylformamide at 298 K. IR spectra were recorded on a Philips Analytical PU 9800 FTIR spectrometer at room temperature with 4 cm^{-1} resolution. Spectra of solid samples were obtained in nujol mulls and KBr pellets (1 wt%).

^{1}H NMR spectra of organic compounds were recorded on a Varian VX-300 spectrometer in $CDCl_3$ solution with TMS as internal reference. Thermogravimetrical measurements were performed on a Paulik-Paulik-Erdey Derivatograph (type OD 102, MOM) in air. Standard platinum crucibles, a sample mass of 100 mg and heating rate of 5°C min^{-1} were used.

X-ray Structure Determination

Cell refinement and diffraction data collection have been performed on a SYNTEX $P2_1$ diffractometer using MoK_α radiation and SYNTEX $P2_1$ software. Intensity data were corrected for Lorentz, polarization and absorption effects. The structure was solved by Patterson methods using XFPS[13] and subsequent Fourier difference maps. Anisotropic thermal parameters

TABLE I Analytical data[a] for the complexes

	Calculated (*Found*) (%)			
	Ni	*C*	*H*	*N*
oxaL[1]		64.9 (64.4)	5.4 (5.6)	18.9 (18.7)
$[Ni(amL^1\text{-}NH_2)_2]Cl_2 \cdot 3.5H_2O$	11.2 (11.2)	36.7 (37.1)	5.6 (5.2)	16.1 (16.0)
$[Ni(amL^1\text{-}NH_2)_2]Br_2 \cdot CH_3COCH_3$	9.7 (9.5)	37.6 (37.5)	4.6 (4.8)	13.8 (13.5)
$[Ni(amL^1\text{-}NH_2)_2](NCS)_2 \cdot CH_3COCH_3$	10.4 (10.5)	44.8 (44.4)	5.0 (4.6)	19.9 (20.2)
$[Ni(amL^2\text{-}NH_2)_2]Cl_2 \cdot 2CH_3COCH_3 \cdot 2H_2O$	9.2 (9.0)	45.0 (44.6)	6.6 (6.2)	13.1 (13.1)
$[Ni(amL^3\text{-}NH_2)_2]Cl_2 \cdot CH_3COCH_3 \cdot 4H_2O$	9.1 (9.4)	42.7 (43.1)	6.9 (6.5)	13.0 (13.0)
$[Ni(NCS)_2(oxaL^1)_2]$	12.5 (12.6)	45.9 (45.5)	3.4 (3.6)	17.8 (18.0)
$[Ni(NCS)_2(oxaL^2)_2]$	11.8 (11.5)	48.1 (48.1)	4.0 (4.4)	16.8 (17.0)
$[Ni(NCS)_2(oxaL^3)_2]$	11.1 (11.4)	50.1 (50.5)	4.6 (4.4)	15.9 (16.2)
$[NiCl_2(oxaL^4)_2] \cdot H_2O$	10.5 (10.3)	47.2 (47.4)	5.4 (5.2)	10.0 (9.9)
$[NiBr_2(oxaL^4)_2]$	9.3 (9.2)	41.9 (42.0)	4.5 (4.9)	8.9 (8.6)
$[Ni(NCS)_2(oxaL^4)_2]$	10.0 (9.8)	49.1 (48.9)	4.8 (5.0)	14.3 (14.2)

[a]Microanalysis results obtained with maximum deviations: M, ±0.3; C, ±0.5; H, ±0.4; N, ±0.3.

were refined for all non-hydrogen atoms. All hydrogen atoms except those of water molecules were found from a difference Fourier map and their positional parameters refined. Geometrical analysis was performed using SHELXL93[14] and PARST.[15] The structure of the cationic moiety was drawn by ORTEP[16] (Figure 1). Basic crystallographic data are summarized in Table II. Final positional and equivalent isotropic displacement parameters are given in Table III.

Supplementary material, including anisotropic displacement parameters of non-hydrogen atoms and positional parameters of hydrogen atoms, has been deposited at the Cambridge Crystallographic Data Centre. Observed and calculated structure factors are available on request from the authors.

Preparation of Complexes

The new complexes were obtained directly from methanolic or ethanolic solutions of nickel(II) salts by reaction of 2-CNpy with amino alcohols depending on the salt used as well as on temperature and reaction time. Some complexes can be isolated as solvates with water and acetone. Unfortunately, attempts to dehydrate them usually resulted in total decomposition.

$[Ni(amL^1\text{-}NH_2)_2]Cl_2 \cdot 3.5H_2O$ (1), $[Ni(amL^1\text{-}NH_2)_2]Br_2 \cdot CH_3COCH_3$ (2) *and* $[Ni(amL^1\text{-}NH_2)_2](NCS)_2 \cdot CH_3COCH_3$ (3)

A filtered solution of the nickel(II) salt (5 mmol) in ethanol (40 cm^3) was mixed with an ethanolic solution (10 cm^3) containing 2-CNpy (10 mmol)

TABLE II Crystal data and structure refinement details for $[Ni(amL^1\text{-}NH_2)_2]Cl_2 \cdot 3.5H_2O$ (complex **1**)

Empirical formula	$C_{16}H_{29}Cl_2N_6NiO_{5.5}$
Formula weight	523.06
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 8.701(2)$ Å $b = 16.481(3)$ Å, $\beta = 93.99(3)°$ $c = 16.476(3)$ Å
Volume	2357.0(8) Å^3
Z	4
Density (calculated)	1.474 Mg m^{-3}
Absorption coefficient	1.090 mm^{-1}
$F(000)$	1092
Crystal size	0.55 × 0.15 × 0.15 mm
ϑ range for data collection	1.75–25.09°
Index ranges	$0 \leq h \leq 10$, $0 \leq k \leq 19$, $-19 \leq l \leq 19$
Reflections collected	4151
Independent reflections	3870 [$R(int) = 0.0767$]
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	0.880 and 0.690
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3870/0/277
Goodness-of-fit on F^2	0.786
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0472$, $wR2 = 0.0954$

and 2-aminoethanol (10 mmol). The resulting solutions were left to slowly evaporate at room temperature. Well-shaped green crystals of (**1**), suitable for X-ray structure analysis were collected from the concentrated solution by filtration and washed with ethanol and finally dried *in vacuo* (yield was 60%). In isolating complexes (**2**) and (**3**), it was necessary to add acetone to the concentrated reaction solution. The deposited compounds (**2**) and (**3**) were collected by filtration, washed with ethanol and finally dried in a desiccator over P_2O_5; yields of grey (**2**) and blue (**3**) were 70% and 75%, respectively. Refluxing the above reaction mixture for up to 20 h did not result in any observable conversion of (**1**) and (**2**) to oxazoline complexes.

$[Ni(amL^2\text{-}NH_2)_2]Cl_2 \cdot 2CH_3COCH_3 \cdot 2H_2O$ (**4**) *and* $[Ni(amL^3\text{-}NH_2)_2]Cl_2 \cdot CH_3COCH_3 \cdot 4H_2O$ (**5**)

Ethanolic reaction mixtures were prepared in the same way as described above using L^2 and L^3 instead of L^1. The solid compounds (**4**) and (**5**) deposited following addition of acetone to the concentrated solutions and slow evaporation at room temperature. Green crystals were filtered off,

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[Ni(amL^1\text{-}NH_2)_2]Cl_2 \cdot 3.5H_2O$ (complex **1**). U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor

	x/a	y/b	z/c	U(eq)
Ni	4135(1)	1899(1)	778(1)	34(1)
Cl(1)	8065(2)	1396(1)	2705(1)	58(1)
Cl(2)	421(2)	1184(1)	−1099(1)	50(1)
O(1)	5460(4)	995(2)	1471(2)	38(1)
O(2)	2819(4)	903(2)	266(2)	38(1)
N(11)	3552(5)	2686(3)	−160(3)	38(1)
N(12)	5883(5)	1768(3)	100(3)	35(1)
N(13)	7171(6)	2269(3)	−966(3)	59(2)
N(21)	4763(6)	2832(3)	1577(3)	39(1)
N(22)	2354(5)	1959(3)	1431(2)	35(1)
N(23)	1047(6)	2669(3)	2398(3)	48(1)
C(11)	2275(7)	3130(4)	−283(4)	49(2)
C(12)	2042(8)	3649(4)	−918(4)	60(2)
C(13)	3179(9)	3734(4)	−1443(4)	61(2)
C(14)	4486(8)	3282(4)	−1327(4)	55(2)
C(15)	4645(7)	2773(4)	−680(3)	37(2)
C(16)	6007(7)	2234(4)	−506(3)	41(2)
C(17)	7077(7)	1203(4)	363(3)	44(2)
C(18)	6370(7)	592(4)	911(3)	44(2)
C(21)	6036(7)	3259(4)	1624(4)	53(2)
C(22)	6268(8)	3917(4)	2122(4)	74(2)
C(23)	5129(9)	4127(4)	2602(5)	80(3)
C(24)	3782(8)	3693(4)	2571(4)	62(2)
C(25)	3641(7)	3045(4)	2055(3)	40(2)
C(26)	2246(7)	2524(4)	1963(3)	39(2)
C(27)	1101(7)	1395(4)	1242(4)	45(2)
C(28)	1812(7)	664(3)	864(3)	42(2)
O(33)	−212(5)	172(3)	−2713(3)	82(2)
O(34)	9739(10)	1004(6)	5787(4)	229(5)
O(35)	7753(9)	460(6)	4497(5)	220(4)
O(36)	5000	0	5000	325(10)

washed with ethanol and finally dried in a desiccator over P_2O_5; yields of (**4**) and (**5**) were 80% and 75%, respectively. Similarly as above, only the pure amidine complexes (**4**) and (**5**) were prepared (with no oxazoline complexes formed) even when the reaction mixtures were refluxed for up to 20 h.

$[Ni(NCS)_2(oxaL^1)_2]$ (6), $[Ni(NCS)_2(oxaL^2)_2]$ (7) *and* $[Ni(NCS)_2(oxaL^3)_2]$ (8)

Solid complexes were prepared in ethanolic solutions of $Ni(NCS)_2$ (5 mmol) by the reaction of equimolar quantities of 2-CNpy and appropriate amino alcohol (10 mmol). The reaction solutions were further refluxed for 20 h. Different amounts of complexes started to precipitate from solution during

reflux. After cooling to room temperature, blue crystals were collected by filtration, washed with ethanol and dried *in vacuo*; yields of (**6**), (**7**) and (**8**) were 20%, 70% and 85%, respectively.

$[NiCl_2(oxaL^4)_2] \cdot H_2O$ (9), $[NiBr_2(oxaL^4)_2]$ (10) *and* $[Ni(NCS)_2(oxaL^4)_2]$ (11)

Solid complexes (**9**), (**10**) and (**11**) were prepared by the reaction of 2-CNpy with L^4 (10 mmol) in solution of Ni(II) salts (5 mmol dissolved in 40 cm^3 of dry ethanol). The mixtures were refluxed for 2 h. Green (**9**) and blue (**10**) were isolated by addition of acetone to the concentrated solution. Deposition of blue complex (**11**), however, started during refluxing of the reaction solution. All deposited complexes were collected by filtration, washed with dry ethanol and dried *in vacuo* (yields about 95%).

Preparation of 2-(2-pyridinyl)-2-oxazoline ($oxaL^1$)

Pure $oxaL^1$ was prepared according to a general procedure described previously.[8] Equimolar quantities of 2-CNpy and 2-aminoethanol (40 mmol) were added to a methanolic solution of $Ni(NCS)_2$ (5 mmol in 50 cm^3 of dry methanol). The mixture was heated under reflux for 24 h. A small amount of solid Ni(II) complexes deposited during the reaction was collected by filtration. The filtrate was concentrated under reduced pressure to give an oily residue which was dissolved in 60 cm^3 of chloroform. The solution was extracted three times with 40 cm^3 of water and, subsequently, the aqueous phase with 60 cm^3 of chloroform. The combined organic phases were dried with sodium sulphate and the solvent was removed *in vacuo*. The resulting oil was purified by chromatography on SiO_2 gel (diethylether/*n*-hexane 1 : 1) to afford a clean product. ^1H NMR ($CDCl_3$/TMS): $\delta = 4.12$ (t, 2H, $J = 19.5$ Hz, 5H); 4.52 (t, 2H, $J = 18.6$ Hz, 4H); 7.37–7.41 (m, 1H, py-5-H); 7.75–7.81 (m, 1H, py-4-H); 8.03–8.05 (m, 1H, py-3-H); 8.69–8.71 (m, 1H, py-6-H). ^{13}C NMR ($CDCl_3$/TMS): $\delta = 54.4$ (t); 67.6 (t); 123.1 (d); 124.9 (d); 136.0 (d); 146.0 (d); 149.0 (d); 163.1 (s).

RESULTS AND DISCUSSION

The reaction of 2-CNpy with substituted amino alcohol (having complete substitution on the carbon atom to which the amino group is attached) in aqueous and alcoholic solutions of Ni(II), Co(II) and Cu(II) salts led only to

the formation of pure solid complexes containing 2-(2-pyridinyl)-4,4-disubstituted-2-oxazolines.[8,9] Substituted amino alcohols of particular interest were 2-amino-2-hydroxymethyl-1,3-propanediol, 2-amino-2-methyl-1,3-propanediol and 2-amino-2-methyl-1-propanol. High yields of complexes can be obtained under mild reaction conditions. Moreover, we have also succeeded in obtaining high yields of pure 2-(2-pyridinyl)-4,4-disubstituted-2-oxazolines from methanolic reaction mixtures containing nickel(II) salts and a considerable excess of the starting 2-CNpy and appropriate amino alcohol.[8]

Stereochemistry of Solid Complexes

Solid complexes (**1**)–(**5**) contain terdentate *N,N,O*-coordinated *N*-hydroxyalkylpyridine-2-carboxamidines and complexes (**6**)–(**9**) contain bidentate *N,N*-coordinated 2-pyridinyl-2-oxazolines ligands (see crystal structure of complex (**1**) and IR spectra). In agreement with this finding and based on the values of molar conductivities and electronic spectroscopic data, composition and stereochemistry were assigned to the complexes under investigation.

Electronic spectroscopic data for the solid amidine complexes (**1**)–(**5**) and molar conductivities of their solutions are given in Table IV. In the visible and near IR region, complexes exhibit two broad LF absorption bands centred at 10 200–10 400 cm^{-1} and 17 200–17 900 cm^{-1}. The third spin-allowed LF band located around 25 000–27 000 cm^{-1} is partly overlapped by more intense intraligand or charge transfer bands. Electronic spectra of (**1**)–(**5**) are independent of the nature of the anionic ligands and are typical of octahedral nickel(II).[11] These findings confirm conclusions reached from conductivity measurements. The molar conductivity of (**1**) in dimethylformamide ($\Lambda_M = 147\ \Omega^{-1}\,cm^2\,mol^{-1}$) and complexes (**2**)–(**5**) in acetonitrile ($\Lambda_M = 205–310\ \Omega^{-1}\,cm^2\,mol^{-1}$) are characteristic of 1 : 2 electrolytes,[17] *i.e.*, the anionic ligands are outside the primary coordination sphere.

Two LF absorption bands located at 9550–10 800 cm^{-1} and 15 800–17 700 cm^{-1} in the electronic absorption spectra of all oxazoline complexes (**6**)–(**9**) (Table V) are consistent with the octahedral environment of the central atom.[11] Contrary to (**1**)–(**5**), complexes (**6**)–(**9**) are non-electrolytes[17] and the anionic ligands lie in the primary coordination sphere.

Crystal Structure of (1)

The crystal structure of (**1**) consists of discrete cationic moieties $[Ni(amL^1\text{-}NH_2)_2]^{2+}$, Cl^- counter-anions and water molecules, involved in a system of

TABLE IV Characteristic infrared bands of amidine groups, electronic spectroscopic data and molar conductivities of solid complexes with *N*-alkylpyridine-2-carboxamidines (amL-NH_2)

	Infrared spectra[a]				*Electronic spectra*[a]			Λ_M
	ν_{as}(NCN)	ν_s(NCN)	δ_{sc}(NH_2)	ν(C–O)	ν_{max} (10^{-3} cm^{-1})			(Ω^{-1} cm^2 mol^{-1})
$[Ni(amL^1\text{-}NH_2)_2]Cl_2 \cdot 3.5H_2O$	1667s	1422s	1630m	1022s	10.30br	17.20br	25.00–27.00	147[b]
$[Ni(amL^1\text{-}NH_2)_2]Br_2 \cdot CH_3COCH_3$	1659s,br	1410m	1630m	1017s	10.40br	17.90br	25.00–27.00	272[c]
$[Ni(amL^1\text{-}NH_2)_2](NCS)_2 \cdot CH_3COCH_3$	1655s	1402m	1634s	1019m	10.50br	17.90br	25.00–27.00	310[c]
$[Ni(amL^2\text{-}NH_2)_2]Cl_2 \cdot 2\ CH_3COCH_3 \cdot 2H_2O$	1665s	1404s	1632s	1020s	10.20br	17.80br	25.00–27.00	205[c]
$[Ni(amL^3\text{-}NH_2)_2]Cl_2 \cdot CH_3COCH_3 \cdot 4H_2O$	1661s,br	1401s	1628s	1017s	10.40br	17.90br	25.00–27.00	262[c]

[a]s – strong, m – medium, br – broad. [b]In acetonitrile. [c]In dimethylformamide.

TABLE V Characteristic infrared bands of oxazoline groups, electronic spectroscopic data and molar conductivities of solid complexes with 2-pyridinyl-2-oxazolines (oxaL)

	Infrared spectra[a]				*Electronic spectra*	Λ_M
	ν(C=N–)	ν(C–N=)	$\delta_{sc}(CH_2)$	$\delta_w(CH_2)$	$\nu_{max}(10^{-3}\,cm^{-1})$	$(\Omega^{-1}\,cm^2\,mol^{-1})$
oxaL^1	1647s	1366s	1472m	1335m		
[Ni(NCS)$_2$(oxaL^1)$_2$]	1657s	1399s	1489m	1352m	10.60 17.70	10[b]
[Ni(NCS)$_2$(oxaL^2)$_2$]	1657s	1399s	1487m	1346m	10.80 17.70	5[c]
[Ni(NCS)$_2$(oxaL^3)$_2$]	1663s	1397s	1489m	1341m	10.50 17.20	20[b]
[NiCl$_2$(oxaL^4)$_2$]·H$_2$O	1655s	1401s	1489m	1343m	9.55 15.80	13[b]
[NiBr$_2$(oxaL^4)$_2$]	1655s	1401s	1487m	1348m	10.15 16.70	45[d]
[Ni(NCS)$_2$(oxaL^4)$_2$]	1653s	1395s	1489m	1354m 1331w	10.25 16.80 25.0–27.0	2[b]

[a]s – strong, m – medium, w – weak. [b]In acetonitrile. [c]In dimethylformamide. [d]In acetone.

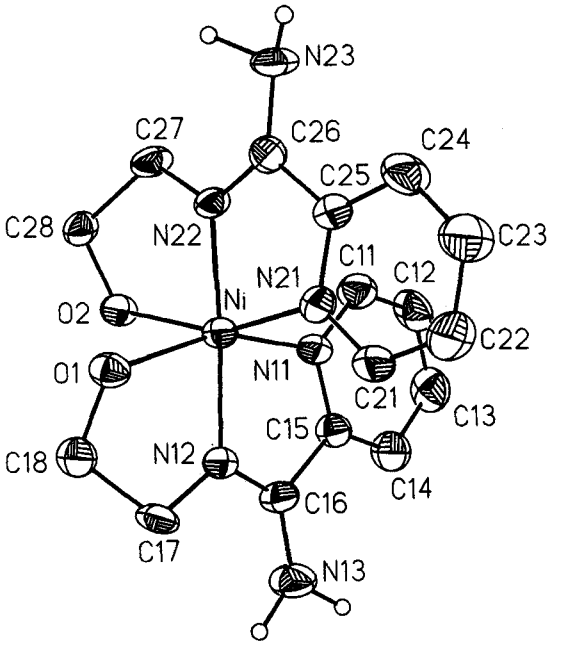


FIGURE 1 ORTEP plot of the [Ni(amL^1)$_2$]$^{2+}$ cation in complex (**1**); thermal ellipsoids are shown at the 50% probability level.

hydrogen bonds. As shown in Figure 1, the Ni(II) atom is six-coordinated by two pairs of nitrogen atoms (N11, N12 and N21, N22) and two oxygen atoms (O1 and O2) of the two respective *N*-hydroxyethylpyridine-2-carboxamidine (amL^1-NH$_2$) ligands to form a distorted octahedron. Thus

both amL^1-NH_2 molecules are *N,N,O*-coordinated as terdentate chelate ligands. Donor atoms of each of the two molecules form two fused five-membered metallocycles with the nickel atom.

Selected interatomic distances and bond angles are given in Table VI. The N–C distances of the NCN amidine group N12–C16 (1.270(6) Å) and N22–C26 (1.287(6) Å) as well as N13–C16 (1.309(6) Å) and N23–C26 (1.327(7) Å), respectively, suggest a bond order between 1 and 2 and indicate

TABLE VI Selected bond lengths (Å) and angles (°) for $[Ni(amL^1\text{-}NH_2)_2]Cl_2 \cdot 3.5H_2O$ (complex **1**)

Ni–N(22)	1.950(4)	Ni–N(12)	1.960(4)
Ni–N(11)	2.054(5)	Ni–N(21)	2.072(5)
Ni–O(2)	2.142(4)	Ni–O(1)	2.161(4)
O(1)–C(18)	1.422(6)	O(2)–C(28)	1.420(5)
N(11)–C(15)	1.331(6)	N(11)–C(11)	1.334(7)
N(12)–C(16)	1.270(6)	N(12)–C(17)	1.439(6)
N(13)–C(16)	1.309(6)	N(21)–C(21)	1.310(7)
N(21)–C(25)	1.343(6)	N(22)–C(26)	1.287(6)
N(22)–C(27)	1.451(6)	N(23)–C(26)	1.327(7)
C(11)–C(12)	1.356(8)	C(12)–C(13)	1.366(8)
C(13)–C(14)	1.362(8)	C(14)–C(15)	1.356(7)
C(15)–C(16)	1.493(8)	C(17)–C(18)	1.512(7)
C(21)–C(22)	1.366(8)	C(22)–C(23)	1.355(8)
C(23)–C(24)	1.371(8)	C(24)–C(25)	1.364(8)
C(25)–C(26)	1.486(8)	C(27)–C(28)	1.508(7)
N(22)–Ni–N(12)	176.3(2)	N(22)–Ni–N(11)	102.7(2)
N(12)–Ni–N(11)	78.6(2)	N(22)–Ni–N(21)	78.3(2)
N(12)–Ni–N(21)	105.2(2)	N(11)–Ni–N(21)	92.9(2)
N(22)–Ni–O(2)	80.4(2)	N(12)–Ni–O(2)	96.1(2)
N(11)–Ni–O(2)	95.2(2)	N(21)–Ni–O(2)	158.3(2)
N(22)–Ni–O(1)	99.1(2)	N(12)–Ni–O(1)	79.5(2)
N(11)–Ni–O(1)	158.1(2)	N(21)–Ni–O(1)	94.0(2)
O(2)–Ni–O(1)	85.96(14)	C(18)–O(1)–Ni	106.3(3)
C(28)–O(2)–Ni	106.1(3)	C(15)–N(11)–C(11)	117.9(5)
C(15)–N(11)–Ni	113.7(4)	C(11)–N(11)–Ni	128.3(4)
C(16)–N(12)–C(17)	121.9(5)	C(16)–N(12)–Ni	119.5(4)
C(17)–N(12)–Ni	118.2(3)	C(21)–N(21)–C(25)	118.1(5)
C(21)–N(21)–Ni	128.4(4)	C(25)–N(21)–Ni	113.4(4)
C(26)–N(22)–C(27)	121.4(5)	C(26)–N(22)–Ni	120.7(4)
C(27)–N(22)–Ni	117.6(3)	N(11)–C(11)–C(12)	122.8(6)
C(1l)–C(12)–C(13)	118.5(6)	C(14)–C(13)–C(12)	119.3(6)
C(15)–C(14)–C(13)	119.1(6)	N(11)–C(15)–C(14)	122.3(6)
N(11)–C(15)–C(16)	113.9(5)	C(14)–C(15)–C(16)	123.7(6)
N(12)–C(16)–N(13)	126.4(6)	N(12)–C(16)–C(15)	113.7(5)
N(13)–C(16)–C(15)	119.9(5)	N(12)–C(17)–C(18)	107.2(5)
O(1)–C(18)–C(17)	110.1(5)	N(21)–C(21)–C(22)	123.4(6)
C(23)–C(22)–C(21)	118.0(7)	C(22)–C(23)–C(24)	120.2(7)
C(25)–C(24)–C(23)	118.1(6)	N(21)–C(25)–C(24)	122.2(6)
N(21)–C(25)–C(26)	114.3(5)	C(24)–C(25)–C(26)	123.5(6)
N(22)–C(26)–N(23)	126.5(6)	N(22)–C(26)–C(25)	112.9(5)
N(23)–C(26)–C(25)	120.6(5)	N(22)–C(27)–C(28)	106.1(5)
O(2)–C(28)–C(27)	110.8(4)		

delocalized π-bonding. However, slightly longer distances N23–C26 and N13–C16 than N22–C26 and N12–C16, respectively, indicate that the amidine ligand is present predominantly in its amino form (amL^1-NH_2) and not in its tautomeric imino form (amL^1-NH). Moreover, the two hydrogen atoms of each of the two NH_2 groups (Figure 1) have been clearly found from the Fourier difference synthesis.

The prevailingly amino form of the non-deprotonized amL^1-NH_2 ligand seems to be stabilized by nearly linear hydrogen bonds O1–H···Cl1 (3.011(4) Å), O2–H···Cl2 (2.996(4) Å), and weak hydrogen bonds N13–H···Cl2 (3.365(6) Å), N23–H···Cl1 (3.402(5) Å), respectively. Therefore, based on the above X-ray diffraction study of complex (**1**) the formation of an imino ether (imL-NH) as coordinated ligand can be ruled out.

Structure of Solid Complexes

Amino alcohols are able to act as nucleophiles through two different atoms, *i.e.*, through the hydroxyl group oxygen or amino group nitrogen. Consequently, the formation of imino ethers (imL-NH) or amidines (amL-NH) can be expected. IR spectra have been useful to characterize the complexes. The presence of water and/or acetone of crystallization in all complexes containing amidines ((**1**)–(**5**)) was recognized from IR spectra. Solid state IR spectra of amidine complexes in the region 3000–4000 cm^{-1} are complicated by the presence of water and acetone of crystallization. Some characteristic IR bands of complexes (**1**)–(**5**) are given in Table IV. There are two characteristic strong bands (with maxima at about 1660 and 1410 cm^{-1}) which are assigned to the ν_{as}(NCN) and ν_s(NCN) modes, respectively, of the amidine groups. Similarly, amidine complexes also show a strong band at about 1020 cm^{-1}, attributed to C–OH stretching vibrations of hydroxyalkyl substituents. Now the crystal and molecular structure of complex (**1**) fully confirms the formation of the new organic ligand, *i.e.*, the nitrile to amidine conversion. IR spectra of other amidine complexes ((**2**)–(**5**)), when compared with that of complex (**1**), provide evidence that the nucleophilic addition of amino alcohols (L^1–L^3) to the nitrile group of 2-CNpy leads to the formation of complexes containing *N*-substituted amidines (amL-NH, or amL-NH_2) as the only organic ligands, and not to the isomeric imidate compounds (imL-NH). Thus properties already described define the amidine compounds as salts of six-coordinate complex ions in which two ligand molecules amL are coordinated. On the other hand, the ligands amL are capable of existing in two tautomeric forms – imino (amL-NH) and amino (amL-NH_2) (see also Scheme 1).

IR spectra of amL^1-NH_2 in complex (**1**) show two ν(NH) bands at 3520 and 3441 cm^{-1}. The observed frequencies are in close agreement with those

found for the asymmetrical and symmetrical valence vibrations in formamide[18] at 3533 and 3411 cm^{-1}, respectively, which indicates that amL^1-NH_2 contain a terminal amino group. The appearance of the band attributed to the $\delta(NH_2)$ mode (at about 1630 cm^{-1}) provides additional evidence for the presence of terminal amino groups in amL-NH_2 in complexes (**1**)–(**5**). Simultaneously, there was no "amidine II" band characteristic for the imino form of amL-NH. Moreover, the existence of the NH_2 groups have also been confirmed by the structure analysis in complex (**1**). Accordingly, the structure of amL containing the terminal amino group was accepted in complexes (**1**)–(**5**). The above conclusions are also in good agreement with the IR study of the amino and imino form of various *N*-substituted benzamides.[19]

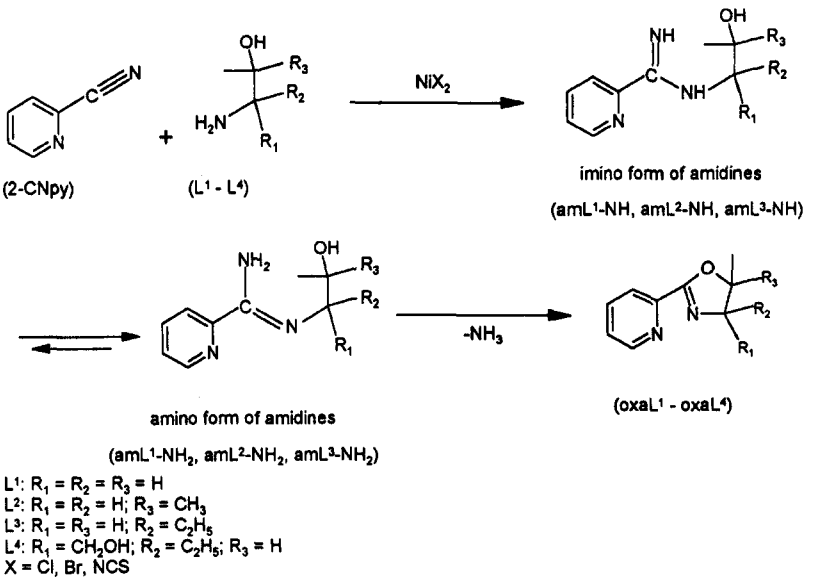
The thiocyanate complex (**3**) shows a strong band at 2054 cm^{-1} (ν(CN)) which is typical for non-coordinated (ionic) NCS groups.[20] IR spectra of all complexes show that the 2-pyridinyl ring in organic ligands is always coordinated through the nitrogen atoms.[20] Thus both knowledge of the crystal structure of complex (**1**) and IR data of complexes (**1**)–(**5**) confirm *N,N,O*-coordination of *N*-hydroxyalkylpyridine-2-carboxamidines (*via* the nitrogen atom of the pyridine ring, the nitrogen atom of the C=N– group and the oxygen atom of the hydroxyl group).

In previous reports,[8,9] the IR spectra of some 2-pyridinyl-2-oxazolines and their Ni(II), Co(II) and Cu(II) complexes were interpreted in detail. The crystal and molecular structures of some of those complexes evidenced only *N,N*-coordination of 2-pyridinyl-2-oxazolines molecules in solid complexes. IR spectra of complexes (**6**)–(**11**) under study (Table V), when compared with those of complexes containing similar oxazolines,[8,9] provide evidence that all the complexes (**6**)–(**11**) contain *N,N*-coordinated 2-pyridinyl-2-oxazoline (oxaL) molecules as the only organic ligands.

Thiocyanate complexes (**6**)–(**8**) and (**11**) show a very strong and broad band in the region 2090–2070 cm^{-1}. The position of this ν(C≡N) band indicates the presence of monodentate NCS groups coordinated exclusively through the nitrogen atom.[20]

Transformations of 2-CNpy to Amidines and Oxazolines Mediated by Ni(II) Salts

It is obvious that 2-CNpy coordination is due to the positive charge localized on the nitrile carbon which, in turn, facilitates a nucleophilic attack of the amine nitrogen lone pair at the carbon atom. A simplified reaction pathway of 2-CNpy transformations giving rise to amidines and oxazolines is shown in Scheme 2. Substituted amino alcohol L^4 (having complete



SCHEME 2 Pathway for oxazoline formation from pyridine-2-carbonitrile mediated by Ni(II).

substitution on the carbon atom containing the NH_2 group) as well as other similar substituted amino alcohols[8,9] formed in alcoholic solutions of Ni(II) only complexes containing oxaL^4; the corresponding amidine has not been isolated. Probably, this type of amidine is unstable and at room temperature fast intramolecular cyclization to 2-(2-pyridinyl)-4,4-disubstituted-2-oxazoline is accompanied by ammonia elimination. Similarly, the reaction of aliphatic and aromatic acids with this type of amino alcohol proceeds smoothly through the corresponding amide to the oxazoline[7] with elimination of water. On the other hand, unsubstituted amino alcohol (L^1) as well as monosubstituted amino alcohols (L^2 and L^3) formed stable complexes readily at room temperature containing the imino form of amidines (amL-NH), by nucleophilic addition of amino alcohol to the nitrile group of 2-CNpy. C–N bond formation is associated with the transfer of an amine hydrogen atom to the nitrile nitrogen. The imino form of amidines, generated in the first step, comes to equilibrium with its tautomeric amino form (amL-NH_2). The electron density distribution and structure of the amino form are suitable to accomplish the cyclization accompanied by ammonia elimination. The oxazoline can leave the primary coordination sphere and the process can be repeated. The central atom acts thus as a catalyst which open a new synthetic way for the preparation of oxazolines.

We used this method for the synthesis of 2-(2-pyridinyl)-2-oxazoline (oxaL^1).

The observed necessity to maintain solutions at higher temperature (reflux) for several hours in order to prepare oxazoline complexes (comparison of conditions for the synthesis of (**3**) and (**6**)) suggests that the cyclization is a process with a higher activation energy than that of amidine C–N bond formation. It should be pointed out, however, that different behaviour found for Cl^-, Br^- and NCS^- salts, as well as that for individual amino alcohols, may be a consequence of several simultaneously operating factors (*e.g.*, steric hindrance of the alcohol functional groups, different electron donating or withdrawing effects of the functional groups and acido anions, distribution of complexes in solution and dependence on relative permitivity of the solvent used, different solubility of complexes in solution), whose effects cannot be explicitely evaluated.

Acknowledgements

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