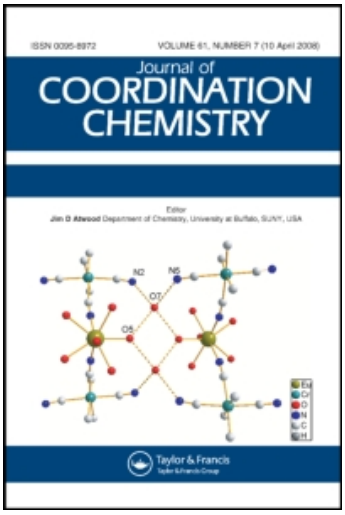

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FORMATION OF 2-PYRIDINYL-2-OXAZOLINES AND PYRIDINE-2-CARBOXAMIDINE IN THE COORDINATION SPHERE OF COPPER(II)

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The reaction of pyridine-2-carbonitrile (2-CNpy) with 2-amino-2-hydroxymethyl-1,3-propanediol (L^1) and 2-amino-2-methyl-1-propanol (L^2) in methanolic solutions of anhydrous copper(II) chloride at room temperature led to the formation of solid complexes containing 2-(2-pyridinyl)-4,4-bis(hydroxymethyl)-2-oxazoline (pyoxaL^1) and 2-(2-pyridinyl)-4,4-dimethyl-2-oxazoline (pyoxaL^2), respectively. With copper(II) bromide instead of copper(II) chloride, along with the oxazoline complexes, the complex dibromo-bis(pyridine-2-carboxamidine)copper(II) was isolated. Under several hour reflux, the complexes dihalogenobis(pyridine-2-carboxamidine)copper(II) are the only isolable products both for chloride and bromide starting salts. The stereochemistry of the complexes and the mode of ligand coordination have been determined by spectroscopic and conductometric measurements. The crystal structure of bromobis[(2-(2-pyridinyl)-4,4-dimethyl)-2-oxazoline]copper(II) bromide hydrate was solved by X-ray diffraction techniques. The mechanism of 2-CNpy transformation to the final products is proposed.

Keywords: Copper(II) complexes; pyridine-2-carbonitrile; 2-pyridinyl-2-oxazolines; pyridine-2-carboxamidine; crystal structure

INTRODUCTION

It has previously been found[1–3] that the ability of pyridine-2-carbonitrile (2-CNpy) to participate in nucleophilic additions is enhanced by its coordination and influenced by the solvent and the nature of the central atom.

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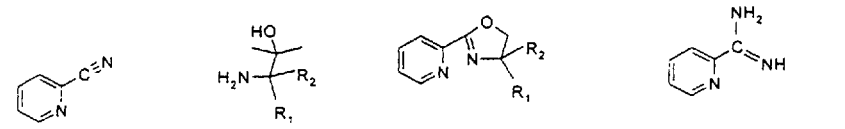


L^1: pyoxaL^1: $R_1 = R_2 = CH_2OH$
L^2: pyoxaL^2: $R_1 = R_2 = CH_3$

SCHEME 1 Structures and abbreviations of ligands.

With alcohols, complexes containing *O*-alkylpyridine-2-carboximidate were formed, whereas reactions in water led to pyridine-2-carboxamide. However, any attempts to bind ammonia to coordinated 2-CNpy failed.[4]

Amino alcohols react with 2-CNpy in the presence of Ni(II), Co(II) or Cu(II) salts to form solid complexes containing *N*-hydroxyalkylpyridine-2-carboxamidine or 2-pyridinyl-2-oxazoline[5–8] both in aqueous and ethanolic solutions regardless of the solution temperature. The course of the transformation was confirmed by time-dependent IR measurements;[6,8] for some of the final complexes their crystal structures were solved.[7,8]

As a part of our investigation of the central atom and solvent influence on the course of nucleophilic additions involving 2-CNpy, the synthesis and structural characterization of copper(II) complexes containing 2-pyridinyl-2-oxazoline (pyoxaL) and pyridine-2-carboxamidine (pycam) have been performed. The complexes were formed in methanolic solutions of copper(II) salts, pyridine-2-carbonitrile, and amino alcohols. As before, IR techniques were exploited to follow 2-CNpy transformations. The structure of one of the products, bromobis[(2-(2-pyridinyl)-4,4-dimethyl)-2-oxazoline]copper(II) bromide hydrate, was solved by single-crystal X-ray methods.

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

EXPERIMENTAL

Starting Chemicals

All chemicals used were of reagent grade. Anhydrous copper(II) chloride and bromide were prepared according to previously described procedures.[9] Methanol was dried by a standard method.[10] Pyridine-2-carboxamidinium hydrochloride (pycam · HCl) was synthesized as described[11] and its purity

checked by m.p. determination and its ^1H NMR spectrum. Solid pyridine-2-carbonitrile (2-CNpy) was obtained from Sigma and purified by distillation at reduced pressure; 2-amino-2-hydroxymethyl-1,3-propandiol (L^1) and 2-amino-2-methyl-1-propanol (L^2), both purchased from Aldrich, were used without further purification.

Analyses and Measurements

Copper was determined by EDTA titration; carbon, hydrogen and nitrogen by microanalytical methods (Carlo Erba Instruments EA 1108). Analytical data for solid complexes are given in Table I. The yields of products are related to the initial metal content in reacting mixtures.

Measurements of electronic and IR spectra of solid samples, and conductivity of dissolved complexes involved methods described elsewhere.[7]

X-Ray Structure Determination

The diffraction intensities for bromobis[(2-(2-pyridinyl)-4,4-dimethyl)-2-oxazoline]copper(II) bromide hydrate were collected with a KUMA KM4 diffractometer using graphite-monochromatized CuK_α radiation and were corrected for Lorentz, absorption and polarization factors. Basic crystallographic data are listed in Table II. The structure was solved by the Patterson method (SHELXS-86)[12] and refined using SHELXL-93.[13] The non-hydrogen atoms were refined anisotropically. Atomic scattering factors were taken from *International Tables for X-ray Crystallography*.[14] Final positional and equivalent isotropic displacement parameters are given in Table III. Positions of the hydrogen atoms of water molecules have not been determined.

Hydrogen atom coordinates, thermal parameters and lists of observed and calculated structure factors are available on request from the corresponding author.

TABLE I Analytical data[a] for the compounds

	Calculated (*found*) (%)			
	Cu	*C*	*H*	*N*
Pycam · HCl		45.7 (45.4)	5.1 (5.0)	26.6 (26.3)
$[CuCl(pyoxaL^1)_2]Cl \cdot 0.5H_2O$	11.4 (11.2)	42.9 (42.5)	4.5 (4.2)	10.0 (9.9)
$[CuCl(pyoxaL^2)_2]Cl \cdot H_2O$	12.6 (12.3)	47.6 (47.4)	5.2 (5.0)	11.1 (10.8)
$[CuBr(pyoxaL^1)_2]Br \cdot 0.5H_2O$	9.8 (9.9)	37.0 (37.1)	3.9 (3.7)	8.6 (8.5)
$[CuBr(pyoxaL^2)_2]Br \cdot H_2O$	10.7 (10.4)	40.5 (40.1)	4.4 (4.4)	9.4 (9.2)
$[CuCl_2(pycam)_2]$	16.9 (16.6)	38.3 (38.0)	3.8 (3.8)	22.3 (21.9)
$[CuBr_2(pycam)_2]$	13.7 (13.6)	31.1 (31.1)	2.6 (3.0)	18.1 (17.7)

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

TABLE II Crystal data and structure refinement details for $[CuBr(pyoxaL^2)_2]Br \cdot H_2O$ (complex (4))

Empirical formula	$C_{20}H_{26}Br_2O_3Cu$
Formula weight	593.81
Temperature	293(2) K
Wavelength	1.54180 Å
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	$a = 8.614(2)$ Å $\alpha = 90°$ $b = 18.954(4)$ Å $\beta = 90°$ $c = 28.232(6)$ Å $\gamma = 90°$
Volume	4609(2) Å^3
Z	8
Density (calculated)	1.711 mg m^{-3}
Absorption coefficient	5.639 mm^{-1}
$F(000)$	2376
Crystal size	0.30 × 0.25 × 0.40 mm
ϑ range for data collection	3.13–81.38°
Index ranges	$0\backslash h\backslash 11$, $0\backslash k\backslash 22$, $0\backslash l\backslash 36$
Reflections collected	4273
Independent reflections	3973[$R(int) = 0.0450$]
Absorption correction	Semi-empirical from psi-scans
Max. and min. transmission	0.750 and 0.540
Refinement method	Full-mat. least-squares on F^2
Data/restraints/parameters	3973/0/272
Goodness-of-fit on F^2	1.061
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.055$, $wR2 = 0.150$
Largest diff. peak and hole	0.730 and −0.913 eÅ^{-3}

Preparation of Complexes

The complexes containing 2-pyridinyl-2-oxazolines (pyoxaL) or pyridine-2-carboxamidine (pycam) were obtained directly from methanolic solutions of copper(II) salts by the reaction of 2-CNpy with amino alcohols depending on the salt used as well as on temperature and reaction time. Particular conditions are given in the descriptions of the complex preparations.

Analogous reactions of 2-CNpy with the same amino alcohols in methanolic solutions of Co(II) and Ni(II) salts under the same experimental conditions led to mixtures of solid complexes containing various adducts of 2-CNpy. These complexes were not characterized.

$[CuCl(pyoxaL^1)_2]Cl \cdot 0.5H_2O$ (1) and $[CuCl(pyoxaL^2)_2]Cl \cdot H_2O$ (2)

A filtered solution of copper(II) chloride (5 mmol) in methanol (30 cm^3) was mixed with a methanolic solution (10 cm^3) containing 2-CNpy and an appropriate amino alcohol in equimolar quantities (10 mmol). Using amino alcohol L^1, the blue-green complex (1) started to crystallize from the

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parametres ($Å^2 \times 10^3$) for $[CuBr(pyoxaL^2)_2]Br \cdot H_2O$ (complex (4)). $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

	x/a	y/b	z/c	U(eq)
Cu	−488(1)	465(1)	1210(1)	16(1)
Br(1)	2254(1)	289(1)	1308(1)	32(1)
Br(2)	2675(1)	−2313(1)	841(1)	44(1)
N(1)	−702(5)	−225(2)	666(1)	17(1)
N(2)	−2159(5)	998(2)	811(1)	19(1)
N(3)	−545(5)	1134(2)	1762(1)	16(1)
N(4)	−1981(5)	−123(2)	1686(1)	20(1)
O(1)	−3799(5)	814(2)	213(2)	37(1)
O(2)	−3211(6)	24(3)	2379(1)	43(1)
O(3)	2390(8)	−1431(4)	1842(2)	68(2)
C(1)	69(7)	−815(3)	613(2)	24(1)
C(2)	−286(7)	−1278(3)	246(2)	28(1)
C(3)	−1442(7)	−1113(3)	−68(2)	28(1)
C(4)	−2251(7)	−489(3)	−10(2)	27(1)
C(5)	−1848(6)	−62(3)	359(2)	18(1)
C(6)	−2599(6)	607(3)	470(2)	21(1)
C(7)	−4256(9)	1502(4)	402(3)	47(2)
C(8)	−3193(6)	1625(3)	829(2)	25(1)
C(9)	−2228(9)	2281(4)	755(3)	44(2)
C(10)	−4057(8)	1647(4)	1287(3)	47(2)
C(11)	183(6)	1747(3)	1790(2)	24(1)
C(12)	64(8)	2175(3)	2179(2)	33(1)
C(13)	−790(7)	1952(3)	2563(2)	32(1)
C(14)	−1518(8)	1312(3)	2546(2)	33(1)
C(15)	−1388(6)	915(3)	2138(2)	20(1)
C(16)	−2191(6)	248(3)	2061(2)	23(1)
C(17)	−3954(9)	−594(4)	2163(2)	44(2)
C(18)	−2961(6)	−772(3)	1732(2)	26(1)
C(19)	−1870(9)	−1388(4)	1820(3)	47(2)
C(20)	−3911(7)	−880(4)	1297(2)	36(1)

solution after several days. With L^2, the solution turns oily within several weeks and from which oil blue-green crystals of (2) were deposited following addition of acetone. Both solids were washed with ethanol and dried *in vacuo*; yields of (1) and (2) were 95% and 85%, respectively.

$[CuBr(pyoxaL^1)_2]Br \cdot 0.5H_2O$ (3) and $[CuBr(pyoxaL^2)_2]Br \cdot H_2O$ (4)

Methanolic reaction mixtures were prepared in the same way as described above except that $CuBr_2$ was used instead of $CuCl_2$. Several days' crystallization of green oxazoline complexes (3) and (4) was accompanied by deposition of a small amount of blue complexes containing pyridine-2-carboxamidine (see later). Green crystals of (3) and (4) were selectively dissolved in a warm methanol–ethanol (1 : 1) mixture leaving the blue compounds undissolved. By cooling the warm solutions, well-shaped green

crystals of (3) and (4) deposited after several days. They were collected by filtration, washed with ethanol and finally dried *in vacuo*. Yields of (3) and (4) were 80% and 70%, respectively.

$[CuCl_2(pycam)_2]$ (5) and $[CuBr_2(pycam)_2]$ (6)

Method A Blue solid complexes (5) and (6) were prepared by the reaction of 2-CNpy (10 mmol) with equimolar quantities of appropriate amino alcohol (L^1 or L^2) in a solution of Cu(II) salts (5 mmol dissolved in 40 cm^3 of dry methanol). The final reaction mixtures were refluxed for 10 and 4 h, respectively. Both complexes started to deposit during reflux. Yields of (5) and (6) were 25% and 35%, respectively.

Method B Methanolic solutions of reagents were prepared in the same way as described above, but 20 mmol of 2-CNpy were used. The reaction mixtures containing $CuCl_2$ and $CuBr_2$ were heated at reflux for 10 and 4 h, respectively. Deposited complexes were filtered, washed with ethanol and dried *in vacuo*. Yields of (5) and (6) were 70% and 85%, respectively.

RESULTS AND DISCUSSION

Complexes with 2-Pyridinyl-2-oxazolines (pyoxaL)

The reaction of 2-CNpy with amino alcohols L^1 and L^2 in ethanolic solutions of Cu(II) salts proceeded to form solid complexes containing oxazoline pyoxaL^1 and pyoxaL^2 ligands as the only products of 2-CNpy transformation. Based on spectroscopic (electronic and IR) and molar conductivity data, the composition and stereochemistry of the complexes $[CuX(pyoxaL^1)_2]X \cdot 0.5H_2O$ and $[CuX(pyoxaL^2)_2]X \cdot H_2O$ (where X = Cl and Br) have been suggested.[7] The spectroscopic, magnetic and conductometric properties for pyoxaL-containing Cu(II) complexes prepared both in methanol and ethanol are identical. However, along with solid Cu(II) complexes containing oxazolines (pyoxaL), solid complexes with pycam were isolated also in high yields from methanolic solutions.

Crystal Structure of (4)

The crystal structure of (4) consists of $[CuBr(pyoxaL^2)_2]^+$ cations, Br^- counter-anions and water molecules, involved in a system of hydrogen bonds. The structure of the $[CuBr(pyoxaL^2)_2]^+$ cation is shown in Figure 1 and selected bond distances and angles are given in Table IV. Moreover, the

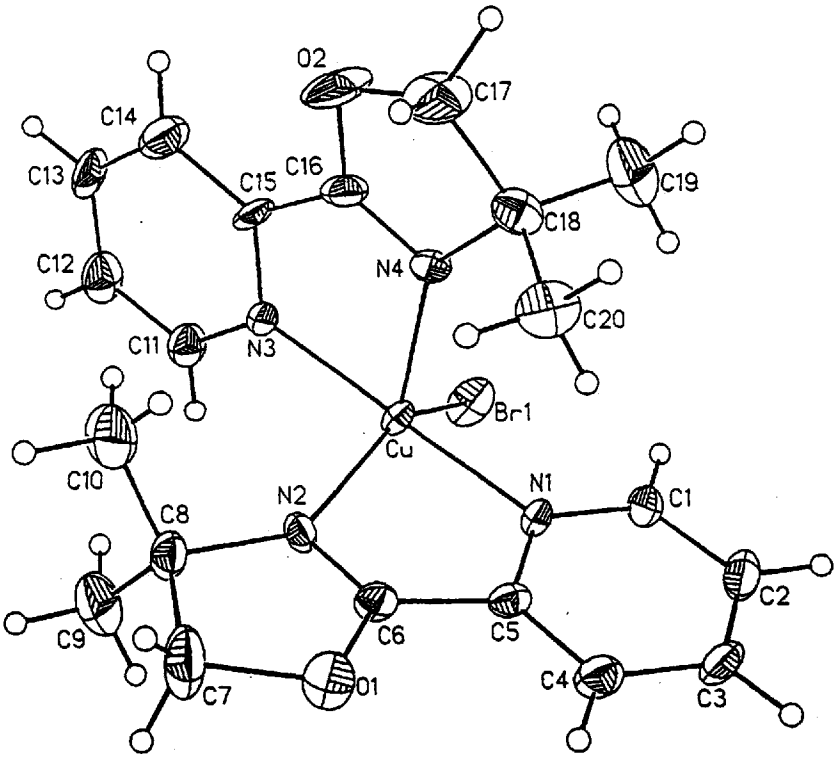


FIGURE 1 ORTEP plot of $[CuBr(pyoxaL^2)_2]^+$ cation in complex (4) (thermal ellipsoids are shown at 50% probability level).

X-ray crystal structure of the complex $[CuBr(pyoxaL^1)_2]Br \cdot 0.5H_2O$ prepared in ethanolic solutions has been previously determined[7] and is very similar to that of complex (4).

The Cu(II) atom is five-coordinate. Two bidentate $pyoxaL^2$ ligands are attached to the central atom *via* nitrogen atoms N1 and N3 of the pyridine rings and nitrogen atoms N2 and N4 of the oxazoline rings. Dimensions of the oxazoline ring indicate double bond character of both C–O and C–N bonds (Table IV). Thus both $pyoxaL^2$ groups are *N,N*-coordinated as bidentate chelate ligands. The fifth coordination site of the Cu(II) atom is occupied by the bromide anion. The Cu–Br1 interatomic distance in the coordination polyhedron is 2.401(1) Å and is nearly identical with the Cu–Br1 interatomic distances (2.403(1) Å) in $[CuBr(pyoxaL^1)_2]Br \cdot 0.5H_2O$.[7] The coordination polyhedron in these compounds can be described as being intermediate between square pyramidal and trigonal bipyramidal. The

TABLE IV Bond lengths (Å) and angles (°) for $[CuBr(pyoxaL^2)_2]Br \cdot H_2O$ (complex (4))

Cu–Br(1)	2.4014(10)	Cu–N(1)	2.025(4)
Cu–N(3)	2.011(4)	Cu–N(2)	2.087(4)
Cu–N(4)	2.169(4)	N(1)–C(1)	1.310(7)
N(1)–C(5)	1.350(6)	N(2)–C(6)	1.275(6)
N(2)–C(8)	1.487(6)	N(3)–C(11)	1.324(7)
N(3)–C(15)	1.350(6)	N(4)–C(16)	1.283(7)
N(4)–C(18)	1.497(7)	C(5)–C(4)	1.363(7)
C(5)–C(6)	1.457(7)	O(2)–C(16)	1.327(6)
O(2)–C(17)	1.467(8)	C(1)–C(2)	1.392(7)
C(2)–C(3)	1.369(8)	C(3)–C(4)	1.382(8)
O(1)–C(6)	1.323(6)	O(1)–C(7)	1.463(7)
C(7)–C(8)	1.532(8)	C(8)–C(10)	1.493(9)
C(8)–C(9)	1.510(9)	C(11)–C(12)	1.368(8)
C(12)–C(13)	1.377(9)	C(13)–C(14)	1.367(9)
C(14)–C(15)	1.380(7)	C(15)–C(16)	1.458(8)
C(17)–C(18)	1.525(8)	C(18)–C(20)	1.492(8)
C(18)–C(19)	1.519(9)		
N(3)–Cu–N(1)	173.2(2)	N(3)–Cu–N(2)	95.5(2)
N(1)–Cu–N(2)	80.9(2)	N(3)–Cu–N(4)	80.1(2)
N(1)–Cu–N(4)	94.8(2)	N(2)–Cu–N(4)	100.0(2)
N(3)–Cu–Br(1)	91.26(12)	N(1)–Cu–Br(1)	95.02(12)
N(2)–Cu–Br(1)	143.89(13)	N(4)–Cu–Br(1)	116.11(12)
C(1)–N(1)–C(5)	119.5(4)	C(1)–N(1)–Cu	126.3(4)
C(5)–N(1)–Cu	114.0(3)	C(6)–N(2)–C(8)	108.2(4)
C(6)–N(2)–Cu	109.4(3)	C(8)–N(2)–Cu	141.5(3)
C(11)–N(3)–C(15)	118.5(4)	C(11)–N(3)–Cu	126.0(3)
C(15)–N(3)–Cu	115.4(3)	C(16)–N(4)–C(18)	107.4(4)
C(16)–N(4)–Cu	108.2(3)	C(18)–N(4)–Cu	144.2(3)
N(1)–C(5)–C(4)	122.7(5)	N(1)–C(5)–C(6)	112.7(4)
C(4)–C(5)–C(6)	124.6(5)	C(16)–O(2)–C(17)	105.2(4)
N(1)–C(1)–C(2)	120.8(5)	C(3)–C(2)–C(1)	119.8(5)
C(2)–C(3)–C(4)	119.0(5)	C(5)–C(4)–C(3)	118.1(5)
C(6)–O(1)–C(7)	106.0(4)	N(2)–C(6)–O(1)	118.3(5)
N(2)–C(6)–C(5)	122.5(4)	O(1)–C(6)–C(5)	119.2(4)
O(1)–C(7)–C(8)	105.2(5)	N(2)–C(8)–C(10)	110.5(5)
N(2)–C(8)–C(9)	108.9(5)	C(10)–C(8)–C(9)	111.8(6)
N(2)–C(8)–C(7)	102.1(4)	C(10)–C(8)–C(7)	112.9(6)
C(9)–C(8)–C(7)	110.2(6)	N(3)–C(11)–C(12)	122.1(5)
C(11)–C(12)–C(13)	119.4(6)	C(14)–C(13)–C(12)	119.3(5)
C(13)–C(14)–C(15)	118.4(6)	N(3)–C(15)–C(14)	122.2(5)
N(3)–C(15)–C(16)	113.8(4)	C(14)–C(15)–C(16)	124.0(5)
N(4)–C(16)–O(2)	118.5(5)	N(4)–C(16)–C(15)	122.2(4)
O(2)–C(16)–C(15)	119.3(5)	O(2)–C(17)–C(18)	105.2(4)
C(20)–C(18)–N(4)	110.5(5)	C(20)–C(18)–C(19)	111.6(6)
N(4)–C(18)–C(19)	107.3(5)	C(20)–C(18)–C(17)	112.3(5)
N(4)–C(18)–C(17)	101.8(5)	C(19)–C(18)–C(17)	112.8(6)

crystal and molecular structures of the complexes $[CuBr(pyoxaL^1)_2]Br \cdot 0.5H_2O$[7] and $[CuBr(pyoxaL^2)_2]Br \cdot H_2O$ as well as spectroscopic data fully confirm that conversion of coordinated 2-CNpy to oxazolines proceeds both in methanol and ethanol.

Complexes with Pyridine-2-carboxamidine (Pycam)

To take advantage of IR spectroscopy in tracing the pathways of 2-CNpy transformation in our systems, IR spectra of all possible products should be reliably interpreted. In this connection our attention has been focussed on pycam · HCl since its IR spectrum has not been unambiguously characterized. IR bands of the other products have previously been interpreted to a sufficient extent.

For the structure of the pyridinamidinium ion, two possible tautomeric forms can be suggested, as shown below.

In the spectrum of pycam · HCl (see Table V), the $\nu_{as}(NH_2)$ and $\nu_s(NH_2)$ vibrations are assigned to absorption bands at 3335 and 3190 cm^{-1}, respectively. The spectrum does not exhibit the most characteristic bands of valence and deformation vibrations of NH; however, at the same time, several bands characteristic of the $=NH_2^+$ group[15] (*e.g.*, a band at 1607 cm^{-1} assigned to $\delta(NH_2^+)$) appear. Consequently, the IR spectrum of pycam · HCl, similarly to that of acetamidinium hydrochloride,[16] strongly favours the left-hand structure above.

IR spectra of solid (5) and (6) in the region 3400–3100 cm^{-1}(see Table V) show three bands at 3364, 3279, 3158 cm^{-1} and 3372, 3277, 3165 cm^{-1}, respectively. These bands may result from the $\nu_{as}(NH_2)$, $\nu_s(NH_2)$ or $\nu(NH)$, vibrations. The characteristic strong absorption bands at 1655 and 1653 cm^{-1} are attributed to $\nu_{as}(NCN)$ arising principally from the C=N mode. The medium intensity bands at 1615 cm^{-1} are associated with deformation of the NH_2 group.

IR spectra of (5) and (6), when compared to that of pycam · HCl, provide evidence that both complexes contain coordinated pycam molecules as the sole organic ligand. Moreover, similarity of the spectroscopic change caused by coordination of pycam and its protonization support a conclusion that the ligand is coordinated both through the nitrogen atoms of the pyridine ring and of the imino group (C=NH), and exclude its coordination *via* the nitrogen atom of the amino group or its presence in the complexes as a free molecule held in the structure by hydrogen bonds.

TABLE V Characteristic infrared bands of amidine group, electronic spectroscopic data and molar conductivities of solid compounds

	Infrared spectra[a]						*Electronic spectra*[a] ν_{max} (10^{-3} cm^{-1})		Λ_M[b] Ω^{-1} cm^2 mol^{-1}
	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\nu(NH)$	$\nu_{as}(NCN)$	$\delta(NH_2)$	$\delta(NH)$			
Pycam · HCl	3335s	3190s		1694s	1626m 1607m				
$[CuCl_2(pycam)_2]$	3364s	3279s	3158s,br	1655s	1615m	1472s	16.90br	24.50	64
$[CuBr_2(pycam)_2]$	3372s	3277s	3165s,br	1653s	1615m	1470s	17.30br	23.50	59

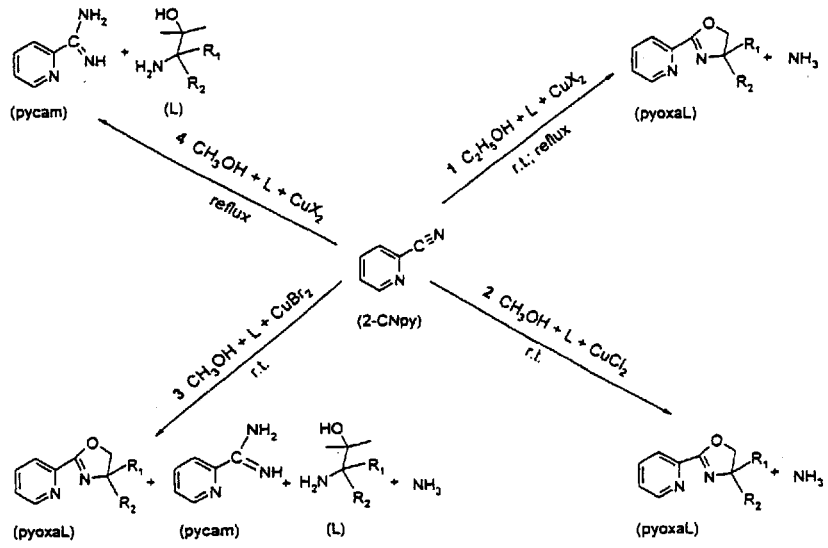
[a] s, strong; m, medium; br, broad. [b] In methanol (concentration 10^{-3} M).

A typical broad peak centred at about 17 000 cm^{-1} is observed in electronic absorption spectra of (**5**) and (**6**). There is also a charge transfer band at about 24 000 cm^{-1}. This type of d-d spectrum is typical of a tetragonally distorted octahedral environment for the Cu(II) central atom.[17] The presence of both halides in the primary coordination sphere of Cu(II) is supported also by conductivity measurements (Table V). Molar conductivity values in methanol for dissolved dihalogenobis(pyridine-2-carboxamidine)copper(II) complexes show that both complexes behave as non-electrolytes, *i.e.*, halide anion is always coordinated.[18]

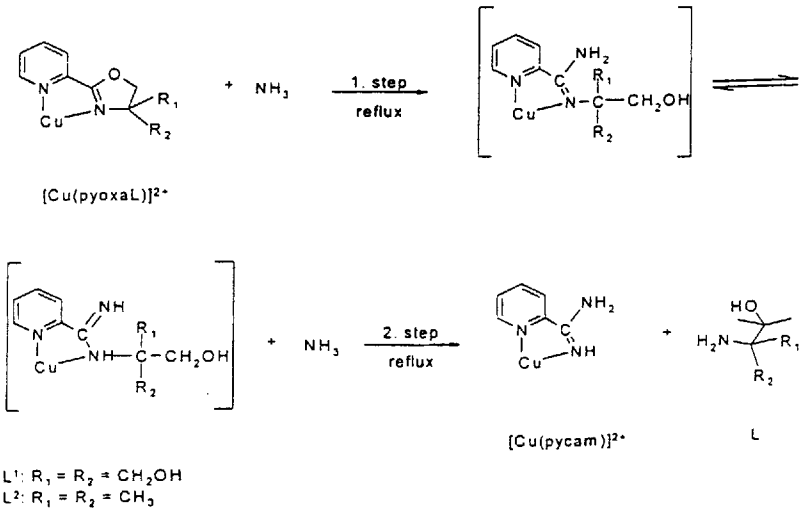
Reactions of 2-CNpy and Formation of Pycam

The pathways of 2-CNpy transformation in methanolic and ethanolic solutions of the CuX_2 salts under our experimental conditions are outlined in Scheme 2. Condensation of 2-CNpy with L^1 and L^2 in ethanolic solutions of Cu(II) (reaction 1) led, both at room temperature and at reflux, to the formation of solid complexes[7] containing only oxazoline (pyoxaL^1 and pyoxaL^2) ligands.

In methanolic solutions, oxazoline complexes were prepared only in the presence of $CuCl_2$ and at room temperature (reaction 2). In the presence of



SCHEME 2 Formation of Cu(II) complexes containing different reaction products of pyridine-2-carbonitrile (2-CNpy).



SCHEME 3 Proposed mechanism for pyridine-2-carboxamidine (pycam) formation from oxazolines (pyoxaL) mediated by Cu(II).

$CuBr_2$, solid complexes containing pyoxaL and complexes containing pycam were prepared (reaction 3). Pycam-containing solid complexes were isolated as the only products following several hours reflux of the methanolic reaction mixtures (reaction 4).

The proposed mechanism for pycam formation from oxazolines mediated by Cu(II) is outlined in Scheme 3. The first step is attack of ammonia to open the oxazoline ring (the oxazoline ring C–O bond is split) producing the amino form *N*-substituted amidines. The amino form comes subsequently to equilibrium with its tautomeric imino form which reacts in the second step with another ammonia molecule producing pycam associated with amino alcohol elimination. The only source of ammonia present in the methanolic reaction solutions is the condensation forming oxazoline. In agreement with the proposed mechanism (one mol of pyoxaL reacts with two mols of ammonia), the maximum yield of pycam formation can approach 50%. The yields of (5) and (6) reached 25% and 35%, respectively (*Method A*). When the mol ratio of 2-CNpy : L was 2 : 1 (*Method B*), the recovered L (Scheme 3) condenses with further 2-CNpy to oxazoline and eliminates ammonia which could participate in the process of additional pycam formation. In agreement with the above mechanism, the yields for (5) and (6) were 70% and 85%, respectively. Therefore, pycam formation from oxazolines in methanolic solutions is highly specific for Cu(II) and shows

some solvent dependence. It is worth mentioning that treatment of 2-aryl-4,4-disubstituted-2-oxazolines with ammonia or methylamine opens the oxazoline ring in a different way and benzamides are formed as main products.[19]

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