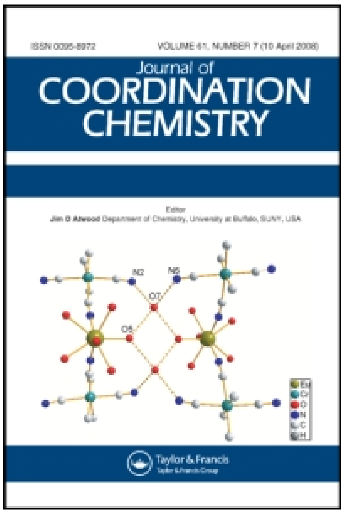

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Innersphere transformations of pyridine-2-carbonitrile mediated by copper(II), cobalt(II) and nickel(II). Crystal structures of <i>bis</i>(nitrato)-<i>bis</i>(<i>N</i>-2-hydroxyethyl- pyridine-2-carboxamidine-<i>N,N</i>')copper(II) and bromo-bis(<i>N</i>-3-hydroxy-propylpyridine-2-carboxamidine-<i>N,N</i>')copper(II) bromide

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Innersphere transformations of pyridine-2-carbonitrile mediated by copper(II), cobalt(II) and nickel(II). Crystal structures of *bis*(nitrato)-*bis*(*N*-2-hydroxyethyl-pyridine-2-carboxamidine-*N*,*N*′)copper(II) and bromo-*bis*(*N*-3-hydroxy-propylpyridine-2-carboxamidine-*N*,*N*′)copper(II) bromide

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Condensation of pyridine-2-carbonitrile (2-CNpy) with 2-aminoethanol (L^1) or 1-amino-3-propanol (L^2) in alcohol solutions of CuX_2 ($X = NO_3^-$, ClO_4^-, Cl^- and Br^-) proceeds readily under mild conditions to form stable solid complexes $[Cu(NO_3)_2(amL^1\text{-}NH)_2]$, $[Cu(amL^1\text{-}NH)_2](ClO_4)_2$, $[Cu(amL^2\text{-}NH)_2](ClO_4)_2$, $[CuCl_2(amL^2\text{-}NH_2)]\cdot H_2O$, $[CuCl_2(amL^2\text{-}NH)_2]$ and $[CuBr(amL^2\text{-}NH)_2]Br$, which contain the imino form of *N*-2-hydroxyethylpyridine-2-carboxamidine (amL^1-NH) and imino or amino forms of *N*-3-hydroxypropylpyridine-2-carboxamidine (amL^2-NH or $amL^2\text{-}NH_2$). Crystal structures of $[Cu(NO_3)_2$(*N*-2-hydroxyethyl-pyridine-2-carboxamidine-*N*,*N*′$)_2]$ and [CuBr(*N*-3-hydroxypropylpyridine-2-carboxamidine-*N*,*N*′$)_2$]Br and IR data confirm bidentate *N*,*N*-coordination of *N*-hydroxyalkylpyridine-2-carboxamidines (via the nitrogen atom of the pyridine ring as well as the nitrogen atom of the terminal imino group). The structure of $[Cu(NO_3)_2(amL^1\text{-}NH)_2]$ consists of well-separated centrosymmetrical $Cu(amL^1\text{-}NH)_2(NO_3)_2$ entities, including two independent kinds of molecules (molecule $[Cu(NO_3)_2(amL^1\text{-}NH)_2]$ and molecule $[Cu(amL^1\text{-}NH)_2](NO_3)_2$) with central atoms Cu1 and Cu2 located at two crystallographically independent symmetry centres. $[CuCl_2(amL^2\text{-}NH_2)]\cdot H_2O$ contains only a terdentate *N*,*N*,*O*-coordinated amino form of *N*-3-hydroxypropylpyridine-2-carbox-amidine ($amL^2\text{-}NH_2$). The analogous reaction of 2-CNpy with L^2 and $M(NCS)_2$ ($M = Ni$ and Co) in ethanol leads to the solid complexes $[Co(NCS)_2(oxaL^2)_2]\cdot 2H_2O$ and $[Ni(NCS)_2(oxaL^2)_2]$, which contain 2-pyridinyl-1,3-oxazine ($oxaL^2$). Based on the molecular structure, electronic and IR spectroscopic data are discussed.

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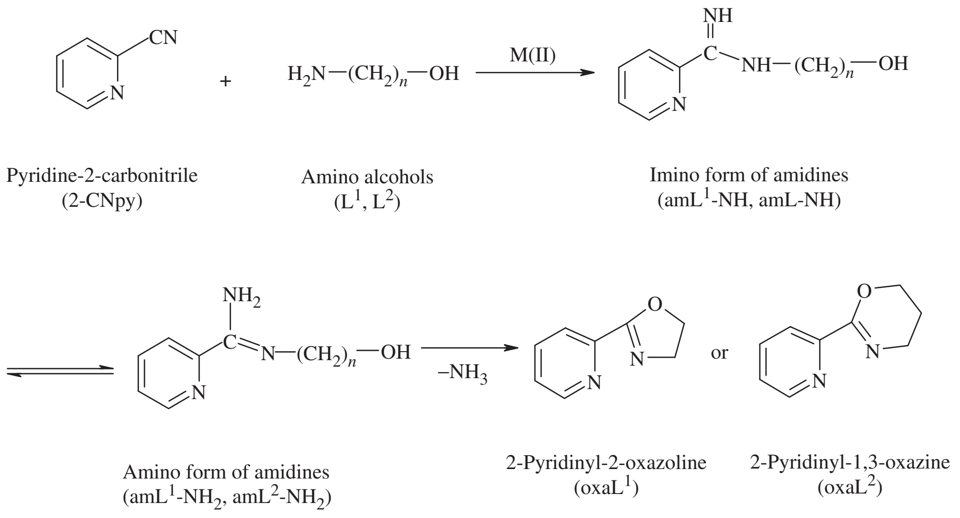
1. Introduction

Transformations of organonitriles play an important role in both laboratory and industry due to their well-recognized chemical versatility. In particular, in organic chemistry the addition of nucleophiles [1] or electrophiles [2], or asymmetric dipolar cycloaddition [3] to the C≡N triple bond offers an attractive route for the creation of novel C–C, C–N, C–O, and C–S bonds. 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 [4].

Synthesis of oxazolines (or 4,5-dihydrooxazoles) [5, 6] and oxazoline type monomers for further polymerization [7] has already been reviewed. The most developed synthetic approaches to furnish these heterocycles include dehydration and cyclization of some carboxamides (e.g., hydroxyamides), reaction between halocarboxamides and strong bases, addition of oxiranes to nitriles and amino alcohols to carboxylic acids or imino esters, and, eventually, two routes involving metal centres. The latter involve addition of halo alcohols/base or oxirane/Cl^- systems to Pt(II)-bonded nitriles [8] and reactions between nitriles and amino alcohols in the presence of certain metal(II) salts. The synthesis of the oxazolines from nitriles and amino alcohols has been performed at highly labile metal centres, and it is not surprising that intermediates in the conversion were not isolated or even detected *in situ* [9].

The reaction of pyridine-2-carbonitrile (2-CNpy) with substituted amino alcohols (having complete substitution on the carbon atom containing the NH_2 group;



L^1, amL^1-NH, amL^1-NH_2, oxaL^1: $n = 2$
L^2, amL^2-NH, amL^2-NH_2, oxaL^2: $n = 3$

Scheme 1. Pathway of *N*-hydroxyalkylpyridine-2-carboxamidines (amL), oxazolines (oxaL^1) and oxazines (oxaL^2) formation from pyridine-2-carbonitrile (2-CNpy) mediated by Ni(II), Co(II) and Cu(II).

for example 2-amino-2-hydroxymethyl-1,3-propandiol) in aqueous and alcohol solutions of MX_2 (M = Ni, Co and Cu; X = Cl, Br, NCS and ClO_4) led to formation of solid complexes containing 2-pyridinyl-2-oxazolines or their decomposition products [10]. On the other hand, condensation of 2-CNpy with another amino alcohol, 2-aminoethanol or 1-amino-2-propanol in ethanol solutions of MX_2 (M = Ni and Cu; X = Cl and Br) leads to formation of stable solid complexes, which contain imino or amino forms of *N*-hydroxyalkylpyridine-2-carboxamidines or 2-pyridinyl-2-oxazolines [11] (scheme 1).

This article describes synthesis and structural characterization of new complexes containing *N*-hydroxyalkylpyridine-2-carboxamidines (amL) or 2-pyridinyl-1,3-oxazine (oxaL). All complexes were formed in alcohol solutions of CuX_2 (X = NO_3, ClO_4, Cl and Br) or $M(NCS)_2$ (M = Ni and Co), pyridine-2-carbonitrile and aminoalcohols (L^1 = 2-aminoethanol or L^2 = 1-amino-3-propanol). One of the goals of this work is to determine which of the tautomeric intermediates (imino or amino form of amidines) or oxazines is formed preferentially as a consequence of several simultaneously operating factors (e.g., influence of central atom, steric hindrance of amino alcohol functional groups, different electron donating or withdrawing effects of functional groups and acido anions). To answer this question, along with an IR study, the X-ray crystal structures of two complexes, $[Cu(NO_3)_2$(*N*-2-hydroxyethylpyridine-2-carboxamidine-*N*,*N*′$)_2]$ and [CuBr(*N*-3-hydroxypropylpyridine-2-carboxamidine-*N*,*N*′$)_2$]Br, have been solved. Abbreviations and structures of the ligands investigated in this article are indicated in (scheme 1).

2. Experimental

2.1. *Starting chemicals*

All chemicals used were of reagent grade. Solid pyridine-2-carbonitrile (2-CNpy) was purified by distillation under reduced pressure; 2-aminoethanol (L^1) and 1-amino-3-propanol (L^2) were used without further purification. Commercial hydrates $Cu(NO_3)_2 \cdot 2.5H_2O$, $Cu(ClO_4)_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ were of reagent grade. Anhydrous $M(MCS)_2$ (M = Ni and Co) and $CuBr_2$ were prepared according to previously described procedures [12].

2.2. *Analyses and measurements*

Nickel and cobalt were determined by EDTA titration. Copper was determined by electrolysis and carbon, hydrogen and nitrogen by microanalytical methods (Carlo Erba Instrument EA 1108). Water in the hydrates was determined from thermogravimetric curves. Measurements of electronic and IR spectra in the solid state as well as thermogravimetric measurements are described elsewhere [11a].

2.3. *Preparation of the complexes*

2.3.1. General procedure. A filtered solution of anhydrous or hydrated metal(II) salt (5 mmol) in methanol or ethanol (20 cm^3) was mixed with an alcohol solution (15 cm^3)

containing pyridine-2-carbonitrile and an appropriate amino alcohol (L^1 or L^2) in equimolar quantities (10 mmol). The resulting solution was then refluxed. Crystals or precipitates of the complexes were collected by filtration, washed with ethanol and dried *in vacuo*. Some special conditions used in preparing the complexes are described below.

2.3.2. $[Cu(NO_3)_2(amL^1\text{-}NH)_2]$ (1) and $[Cu(amL^1\text{-}NH)_2](ClO_4)_2$ (2). The ethanol reaction mixture prepared according to the general procedure was refluxed for 1 h for the preparation of both complexes. Resulting solutions were left to slowly evaporate at room temperature. Well-shaped dark violet crystals of **1** suitable for X-ray structure analysis as well as dark blue to violet crystals of **2** were collected after several days from the concentrated solutions. Refluxing the above reaction mixture for up to 20 h did not result in any observable conversion of **1** or **2** to oxazoline complexes. Complex **1**: Anal. Calcd for $C_{16}H_{22}CuN_8O_8$ (%): C, 37.1; H, 4.3; N, 21.6; Cu, 12.3. Found: C, 37.3; H, 4.3; N, 21.6; Cu, 11.9. IR (cm^{-1}): 3358(s) (ν(OH)), 3284(s) (ν(NH)), 1633(s) (amidine I), 1573(s) (amidine II), 1243(s) (amidine III). Electronic data (cm^{-1}): 17,800(br), 24,700(sh). Complex **2**: Anal. Calcd for $C_{16}H_{22}CuCl_2N_6O_{10}$ (%): C, 32.4; H, 3.7; N, 14.2; Cu, 10.7. Found: C, 32.8; H, 3.8; N, 14.0; Cu, 10.4. IR (cm^{-1}): 3473(s) (ν(OH)), 3363(s) (ν(NH)), 1634(s) (amidine I), 1566(s) (amidine II), 1244(s) (amidine III). Electronic data (cm^{-1}): 17,200(br), 25,300(sh).

2.3.3. $[Cu(amL^2\text{-}NH)_2](ClO_4)_2$ (3), $[CuCl_2(amL^2\text{-}NH_2)]\cdot H_2O$ (4), $[CuCl_2(amL^2\text{-}NH)_2]$ (5) and $[CuBr(amL^2\text{-}NH)_2]Br$ (6). Alcohol reaction mixtures were prepared in the same way as described above using L^2 instead of L^1 and an appropriate copper(II) salt. Ethanol reaction mixtures were refluxed for 1 and 5 h, respectively, for the preparation of **3** and **6**. Deposition of blue complexes **3** and **6** started during refluxing. Well-shaped crystals of **6** separated after several days from the filtrate, which had been left to stand after the isolation of **6**. The methanol reaction mixture was refluxed for 1 h for the preparation of the green precipitate **4**. Blue crystals of **5** were collected after several days from the concentrated filtrate. Similarly, only the pure amidine complexes **3**, **4** and **6** could be prepared (with no oxazine complexes formed) even when the mixtures were refluxed for up to 20 h. Complex **3**: Anal. Calcd for $C_{18}H_{26}CuCl_2N_6O_{10}$ (%): C, 34.8; H, 4.2; N, 13.5; Cu, 10.2. Found: C, 35.3; H, 4.3; N, 13.2; Cu, 10.0. IR (cm^{-1}): 3470(s) (ν(OH)), 3360(s) (ν(NH)), 1633(s) (amidine I), 1563(s) (amidine II), 1250(m) (amidine III). Electronic data (cm^{-1}): 16,900(br). Complex **4**: Anal. Calcd for $C_9H_{15}CuCl_2N_3O_2$ (%): C, 32.6; H, 4.6; N, 12.7; Cu, 19.2. Found: C, 32.1; H, 5.0; N, 12.4; Cu, 18.9 IR (cm^{-1}): 3331(s) ($\nu_{as}(NH_2)$), 3146(s) ($\nu_s(NH_2)$), 1658(s) (ν_{as}(NCN)), 1630(m) ($\delta_{sc}(NH_2)$), 1422(s) (ν_s(NCN)). Electronic data (cm^{-1}): 13,700, 11,400(sh), 24,000(sh). Complex **5**: Anal. Calcd for $C_{18}H_{26}CuCl_2N_6O_2$ (%): C, 43.9; H, 5.3; N, 17.1; Cu, 12.9. Found: C, 43.4; H, 5.3; N, 17.1; Cu, 12.5. IR (cm^{-1}): 3294(s) (ν(OH)), 3235(s) (ν(NH)), 1627(s) (amidine I), 1565(s) (amidine II), 1242(m) (amidine III). Electronic data (cm^{-1}): 13,700, 16,700(sh). Complex **6**: Anal. Calcd for $C_{18}H_{26}CuBr_2N_6O_2$ (%): C, 37.2; H, 4.5; N, 14.4; Cu, 10.9. Found: C, 37.2; H, 4.5; N, 14.5; Cu, 10.5. IR (cm^{-1}): 3500(s) (ν(OH)), 3227(s) (ν(NH)), 1626(s) (amidine I), 1557(m) (amidine II), 1243(m) (amidine III). Electronic spectrum (cm^{-1}): 16,100, 14,000(sh).

2.3.4. [Co(NCS)$_2$(oxaL^2)$_2$]·2H$_2$O (7) and [Ni(NCS)$_2$(oxaL^2)$_2$] (8). Solid complexes were prepared in ethanolic solutions of M(NCS)$_2$ by reaction of 2-CNpy with L^2. The reaction solutions were refluxed for 2 h. Pink and blue precipitates of **7** and **8** started to deposit during refluxing. Complex **7**: Anal. Calcd for $C_{20}H_{24}CoN_6O_4S_2$ (%): C, 44.9; H, 4.5; N, 15.7; Co, 11.0. Found: C, 44.4; H, 4.4; N, 15.5; Cu, 10.7. IR (cm^{-1}): 1655(s) (ν(C=N–)), 1469(m) (δ_{sc}(CH$_2$)), 1394(m) (ν(C–N=)), 1363(m) (δ_w(CH$_2$)).

Electronic data (cm^{-1}): 10,400(br), 21,000(br). Complex **8**: Anal. Calcd for $C_{20}H_{20}NiN_6O_2S_2$ (%): C, 48.1; H, 4.0; N, 16.8; Ni, 11.8. Found: C, 47.9; H, 4.0; N, 16.6; Ni, 11.4. IR (cm^{-1}): 1658(s) (ν(C=N–)), 1469(m) (δ_{sc}(CH$_2$)), 1394(m) (ν(C–N=)), 1363(m) (δ_w(CH$_2$)). Electronic spectrum (cm^{-1}): 11,100(br), 17,900(br).

2.4. *X-ray crystallography*

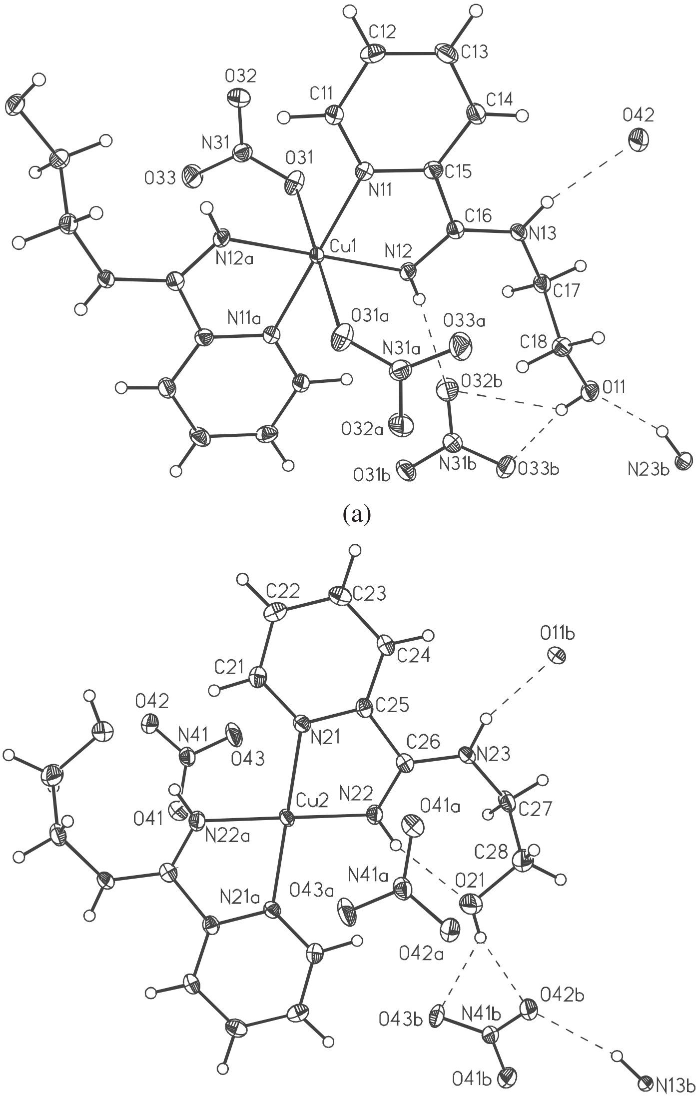
Cell refinement and data collection were performed on SYNTEX *P*2$_1$ **1** and KUMA KM4 diffractometers **6**. Diffraction intensities were corrected for Lorentz-polarization effects. The structures were solved by Patterson methods using XFPS [13] and subsequent Fourier difference maps. Anisotropic thermal parameters were refined for all non-hydrogen atoms. All hydrogen atoms were found from different Fourier maps and their positional and displacement parameters freely refined. Geometrical analysis was performed using SHELX97 [14]. Structures of **1** and **6** were drawn using ORTEP 15] (figures 1 and 2). Basic crystallographic data are summarized in table 1.

3. Results and discussion

3.1. *Crystal structure of [Cu(NO$_3$)$_2$(N-2-hydroxyethylpyridine-2-carboxamidine-N,N′)$_2$] (1)*

The structure consists of well-separated centrosymmetrical Cu(amL^1-NH)$_2$(NO$_3$)$_2$ entities, including two independent kinds of molecules shown in figure 1(a) (molecule 1A, [Cu(NO$_3$)$_2$(amL^1-NH)$_2$]) and figure 1(b) (molecule 1B, [Cu(amL^1-NH)$_2$](NO$_3$)$_2$) with central atoms Cu1 and Cu2 located at two crystallographically independent symmetry centres. Selected interatomic distances, bond and torsion angles are listed in table 2.

In molecule 1A the arrangement around Cu1 can be described as tetragonal bipyramidal (4 + 2) with four strongly bonded equatorial N-donors of two amL^1-NH and two axial *O*-ligands of two nitrato groups at a considerably longer distance. The equatorial positions are occupied by pyridine nitrogen atoms (Cu1–N11 = 2.014(2) Å) and imine nitrogen atoms (Cu1–N12 = 1.954(2) Å) of two chelating pyamL^1-NH molecules. The two axial sites are filled by oxygen atoms of unidentate nitrato ligands (Cu1–O31 = 2.573(2) Å). This type of tetragonal (4 + 2) coordination is widespread in chemistry of copper(II), a d^9 metal centre with a non-spherical d-shell particularly sensitive to the Jahn–Teller effect [16]. A similar all-*trans* arrangement has been observed [17] for [Cu(ethylenediamine)$_2$(H$_2$O)$_2$]$^{2+}$, in which water molecules occupy axial positions. In molecule 1B two chelating pyamL^1-NH molecules coordinate to the central atom Cu2 in a manner analogous to molecule 1A, but the nearest oxygen atom (O43) of a nitrato group is too far (Cu2–O43 = 3.218(2) Å) from Cu2 to be considered



(a)

(b)

Figure 1. An ORTEP view of $[Cu(NO_3)_2(N\text{-2-hydroxyethylpyridine-2-carboxamidine-}N,N')_2]$ (**1**); (a) molecule 1A, $[Cu(NO_3)_2(pyamL^1\text{-}NH)_2]$; (b) molecule 1B, $[Cu(pyamL^1\text{-}NH)_2](NO_3)_2$.

as being coordinated. Therefore, the coordination arrangement around Cu2 is square planar with one bond distance slightly longer (Cu2–N21 = 2.023(2) Å) and one shorter (Cu2–N22 = 1.915(2) Å) compared with those in 1A.

Both *N*-2-hydroxyethylpyridine-2-carboxamidine and nitrato groups are involved in hydrogen bonding. While the imino nitrogen N12 of 1A forms a rather weak hydrogen bond to oxygen O32 (O32b in figure 1a) of the nitrato group (N12 ··· O32 = 3.318 Å) of a neighbouring 1A molecule, the imino nitrogen N22 of 1B forms a strong intramolecular hydrogen bond with oxygen O21 of the

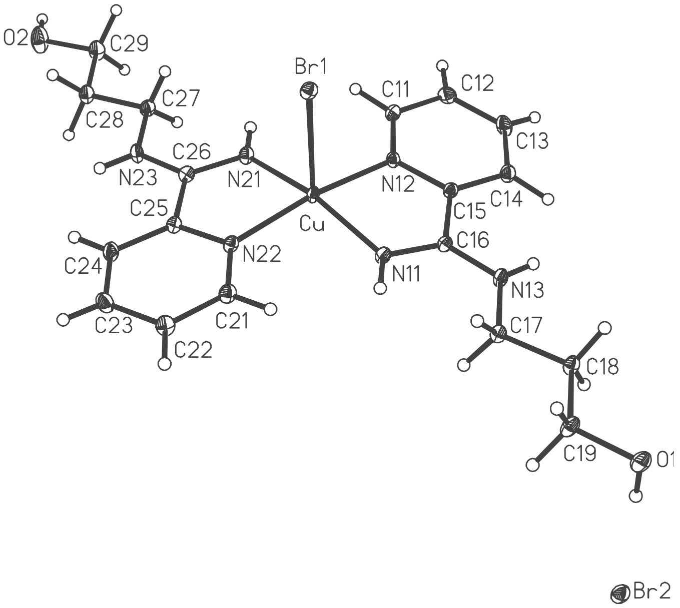


Figure 2. An ORTEP view of [CuBr(*N*-3-hydroxypropylpyridine-2-carboxamidine-*N*,*N*′)$_2$]Br (**6**).

Table 1. Crystal data and structure refinement details.

Compound	[Cu(NO$_3$)$_2$(pyamL^1-NH)$_2$] (**1**)	[CuBr(pyamL^2 - NH)$_2$]Br (**6**)
Formula	$C_{16}H_{22}CuN_8O_8$	$C_{18}H_{26}Br_2CuN_6O_2$
Formula weight	517.96	581.81
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
Z	4	4
a (Å)	20.695(4)	9.195(1)
b (Å)	12.725(3)	19.240(1)
c (Å)	7.583(2)	12.153(1)
β (°)	93.99(3)	95.53(4)
V (Å^3)	1992.1(8)	2140(2)
Density (Calcd) (Mg m^{-3})	1.727	1.806
$F(000)$	1068	1164
μ (mm^{-1})	1.164	4.782
Temperature (K)	293(2)	293(2)
θ range for data collection (°)	3.23–28.69	3.53–28.42
Index ranges	$-28 \le h \le 27$; $-16 \le k \le 17$; $-6 \le l \le 10$	$-12 \le h \le 11$; $-25 \le k \le 24$; $-15 \le l \le 12$
Reflections collected	13574	13296
Independent reflections	4792 [R(int) = 0.0345]	4913 [R(int) = 0.0656]
Refinement method	Full matrix, least-squares on F^2	Full matrix, least-squares on F^2
Data/restr./parameters	4792/0/389	4913/0/262
Goodness-of-fit on F^2	1.021	0.961
Final R indices ($I > 2\sigma(I)$)	$R = 0.0358$, $R_w = 0.0755$	$R = 0.0338$, $R_w = 0.0833$
R indices (all data)	$R = 0.0609$, $R_w = 0.0860$	$R = 0.0404$, $R_w = 0.0867$
Largest diff. peak and hole (e Å^{-3})	0.351/−0.479	1.869/−0.928

Table 2. Selected bond lengths (Å), angles and torsion angles (°) for $[Cu(NO_3)_2(pyamL^1\text{-}NH)_2]$ (**1**).

Molecule 1A		Molecule 1B	
Cu1–N12	1.9542(18)	Cu2–N22	1.9154(19)
Cu1–N11	2.0137(17)	Cu2–N21	2.0229(17)
Cu1–O31	2.5729(17)	Cu2$\cdots$O43	3.2178(18)
N12–Cu1–N11	80.88(7)	N22–Cu2–N21	81.39(7)
N12–Cu1–N11#1	99.12(7)	N22–Cu2–N21#2	98.61(7)
N12–Cu1–O31	90.90(7)		
N12–Cu1–O31#1	89.10(7)		
N11–Cu1–O31	86.15(6)		
N11#1–Cu1–O31	93.85(6)		
O11–C18	1.427(2)	O21–C28	1.427(3)
C18–C17	1.521(3)	C28–C27	1.508(3)
C17–N13	1.461(3)	C27–N23	1.460(3)
N13–C16	1.332(3)	N23–C26	1.328(3)
C16–N12	1.301(3)	C26–N22	1.309(3)
C16–C15	1.497(3)	C26–C25	1.495(3)
O11–C18–C17	110.92(17)	O21–C28–C27	111.5(2)
C18–C17–N13	111.35(17)	C28–C27–N23	115.70(19)
C17–N13–C16	123.38(18)	C27–N23–C26	123.35(18)
N13–C16–N12	126.46(19)	N23–C26–N22	125.39(19)
N13–C16–C15	118.71(18)	N23–C26–C25	119.54(18)
N12–C16–N13–C17	−1.0(3)	N22–C26–N23–C27	7.3(3)
C15–C16–N13–C17	−178.40(18)	C25–C26–N23–C27	−170.20(18)
C16–N13–C17–C18	−81.9(2)	C26–N23–C27–C28	−75.2(3)
N13–C17–C18–O11	−174.15(17)	N23–C27–C28–O21	77.5(3)

Symmetry transformations used to generate equivalent atoms are #1: $-x+1, -y+1, -z$; #2: $-x, -y+1, -z$.

hydroxyl group (N22$\cdots$O21 = 2.802 Å). The amidine nitrogen N13 of 1A forms a hydrogen bond with the oxygen atom O42 of a nitrato group belonging to 1B with N13$\cdots$O42 of 2.991 Å, whereas the amidine nitrogen N23 of 1B forms a relatively strong hydrogen bond with oxygen O11 of the hydroxyl group belonging to 1A with N23$\cdots$O11 of 2.812 Å. Both nitrato groups are bonded to the respective hydroxyl groups of $pyamL^1$-NH by asymmetrical bifurcated hydrogen bonds (with O11$\cdots$O33 of 2.794 and O11$\cdots$O32 of 3.076 Å for 1A, and O21$\cdots$O42 of 2.772 and O21$\cdots$O43 of 3.180 Å for 1B). Configurations of both *N*-2-hydroxyethylpyridine-2-carboxamidines are very similar except for different rotations of terminal C18–O11 and C28–O21 bonds around the C17–C18 and C27–C28 bonds, respectively, as indicated by the corresponding torsion angles (table 2). Thus, the different hydrogen bond systems for 1A and 1B and different configurations of terminal parts of *N*-2-hydroxyethylpyridine-2-carboxamidine molecules are the probable reason for different modes of coordination of the nitrato groups to Cu1 and Cu2.

In the series of copper(II) complexes, there exist several types of isomerism [18]. Included are distortion, *cis*-*trans*, polymerization, linkage and coordination number isomerism, of which the former is most common. Coordination number isomerism denotes compounds exhibiting the same empirical formula, but different coordination numbers. There are several examples of such isomers. However, $[Cu(NO_3)_2$ (*N*-2-hydroxyethylpyridine-2-carboxamidine-*N*,$N')_2]$ is the only example that contains within the same crystal two crystallographically independent molecules with different coordination numbers.

3.2. *Crystal structure of [CuBr(N-3-hydroxypropylpyridine-2-carboxamidine-N,N′)$_2$]Br (6)*

The crystal structure of **6** consists of [CuBr(amL^2-NH)$_2$]$^+$ cations and Br$^-$ counter-anions. The structure is shown in figure 2 and selected bond distances and angles are given in table 3. The Cu(II) atom is five-coordinate. Two molecules of *N*-3-hydroxypropylpyridine-2-carboxamidine (pyamL^2-NH) are coordinated via two nitrogen atoms N12 and N22 of the pyridine rings at distances of 2.018(2) and 2.006(2) Å, as well as nitrogen atoms N11 and N21 of the imino groups at distances of 1.985(2) and 1.983(2) Å, respectively. The *N*,*N*-coordinated bidentate chelates form a distorted square planar arrangement with two smaller N–Cu–N angles (N11–Cu–N12 80.39(9), N21–Cu–N22 80.70(9)°) and two greater angles (N11–Cu–N22 97.67(9), N21–Cu–N12 98.19(9)°). The donor atoms form two five-membered metallocycles with the copper atom. The fifth coordination site is occupied by the bromide anion completing a tetragonal pyramidal stereochemistry ($\tau = 0.09$) [19]. The Cu–Br1 distance is 2.7415(4) Å. The distance of Cu from the equatorial plane N11–N12–N21–N22 towards Br1 is 0.234(1) Å. While coordination of the oxygen atoms O1 and O2 of the hydroxyl groups is not observed, there is a strong hydrogen bond of the type O2–H $\cdots$ O1 between neighbouring molecules with the distance O2 $\cdots$ O1 equal to 2.764 Å. The hydrogen atom of the O1–H group takes part in a hydrogen bond O1–H $\cdots$ Br2 with O1 $\cdots$ Br2 equal to 3.199 Å. Amidine nitrogen atoms N13 and N23 are also involved in weak hydrogen bonding to the Br ions with N13 $\cdots$ Br2 3.516 and N23 $\cdots$ Br1 3.638 Å, respectively.

3.3. *IR and electronic spectra*

The ligands *N*-hydroxyalkylpyridine-2-carboxamidines (amL) are capable of existing in two tautomeric forms, imino (amL-NH) and amino (amL-NH$_2$) (scheme 1). IR spectra have been useful to characterize the complexes. Characteristic IR bands are given in the experimental section. IR spectra of **1**–**3**, **5** and **6** indicate that they exist predominantly in the form having a terminal imino group, –C(=NH)–NH–R. Strong bands with maxima at about 1630 and 1560 cm^{-1} are assigned to amidine I and amidine II (they consist mainly of ν(C=N–) and δ(NH), respectively). Moreover, the crystal and molecular structures of **1** and **6** fully confirm conversion of the nitrile group to the imino form of *N*-hydroxyalkylpyridine-2-carboxamidines. IR spectra of all complexes show that the 2-pyridinyl ring is always coordinated through the nitrogen atom [20]. IR spectra of **2**, **3** and **5**, when compared with those of **1** and **6**, give evidence that these complexes contain coordinated *N*-2-hydroxyethylpyridine-2-carboxamidine

Table 3. Selected bond lengths (Å) and angles (°) for [CuBr(pyamL^2-NH)$_2$]Br (**6**).

Cu–N21	1.983(2)	Cu–N12	2.018(2)
Cu–N11	1.985(2)	Cu–Br1	2.7415(4)
Cu–N22	2.006(2)		
N21–Cu–N11	163.81(10)	N22–Cu–N12	169.26(9)
N21–Cu–N22	80.70(9)	N21–Cu–Br1	95.71(7)
N11–Cu–N22	97.67(9)	N11–Cu–Br1	100.48(7)
N21–Cu–N12	98.19(9)	N22–Cu–Br1	95.65(7)
N11–Cu–N12	80.39(9)	N12–Cu–Br1	95.10(7)

(complex **2**) and *N*-3-hydroxypropylpyridine-2-carboxamidine (complexes **3** and **5**), respectively. Both organic ligands amL^1-NH and amL^2-NH are *N*,*N*-coordinated via the nitrogen atom of the pyridine as well as the nitrogen atom of the terminal imino group.

IR spectra of **4**, which contains the amino form, differs considerably from the spectra of the above imino complexes. In **4**, there are two characteristic strong bands with maxima at 1658 and 1422 cm^{-1} assigned to the ν_{as}(NCN) and ν_{as}(NCN), respectively, of the amidine group. The appearance of the band attributed to $\delta_{sc}(NH_2)$ at 1630 cm^{-1} provides additional evidence for the presence of terminal amino groups (amL^2-NH$_2$) in **4**. Simultaneously, there is no amidine II band characteristic of the imino form of amL-NH. The amino form is stabilized only in the pentacoordinate complex [CuCl$_2$(amL^2-NH$_2$)]$\cdot$H$_2$O, which contains a terdentate *N*,*N*,*O*-coordinated molecule (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 the IR spectrum of **1**, medium intensity bands at 1420 ($\nu_{as}(NO_2)$), 1305 ($\nu_s(NO_2)$) and 1008 cm^{-1} (ν(NO)) are typical for unidentate coordination of nitrato groups [20]. The nature of the perchlorate groups in **2** and **3** was established on the basis of IR spectra. Both complexes contain only ionic perchlorate groups (a very broad band with maximum at about 1080 cm^{-1} due to $\nu_3(ClO_4)$ [20]). Further support for this comes from analysis of the bands in the region 1000–900 cm^{-1} ($\nu_4(ClO_4)$) [20].

In previous reports [10], IR spectra of some 2-pyridinyl-2-oxazolines and their Ni(II), Co(II) and Cu(II) complexes were interpreted in detail. The very similar IR spectra observed for complexes **7** and **8** prepared by reaction of 2-CNpy with 1-amino-3-propanol (L^2) suggests that both complexes contain coordinated 2-pyridinyl-1,3-oxazine (oxaL^2) molecules. Thiocyanate complexes **7** and **8** show a very strong and broad band in the region 2090–2070 cm^{-1}. This indicates the presence of monodentate NCS groups coordinated exclusively through nitrogen [20].

Electronic spectra of complexes **1**, **2** and **3** show a broad band in the narrow range 17,800–16,900 cm^{-1}, typical of square planar or tetragonally distorted octahedral copper(II) with CuN$_2$O$_2$ or CuN$_2$O$_4$ chromophores [21]. This is consistent with the X-ray structure of **1**. Electronic spectra of complexes **4** and **6** in the visible and near IR regions exhibit a broad asymmetrical LF absorption with a maximum at about 13,700 and 16,100 cm^{-1} and shoulders on its low-energy side, typical of five-coordinate copper(II) complexes with almost square pyramidal structure [21]. The suggested composition and stereochemistry of complex [CuBr(amL^2-NH)$_2$]Br **6** is in good agreement with the crystal structure.

Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC 602860 for [Cu(NO$_3$)$_2$(*N*-2-hydroxyethyl-pyridine-2-carboxamidine-*N*,*N*′)$_2$] and CCDC 602861 for [CuBr(*N*-3-hydroxypropylpyridine-2-carboxamidine-*N*,*N*′)$_2$]Br. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.ukor: www.http://www.ccdc.ac.uk).

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References

[1] G.V. Boyd. In *The Chemistry of Amidines and Imidates*, S. Patai, Z. Rappoport (Eds), Vol. 2, p. 339, Wiley, Chichester (1991).

[2] I.D. Gridnev, N.A. Gridneva. *Russ. Chem. Coord.*, **64**, 1091 (1995).

[3] For a recent reviews on 1,3-dipolar cycloaddition see (a) S. Karlsson, H.E. Hodberg. *Org. Prep. Proced. Int.*, **33**, 103 (2001); (b) L. Raimondi, M. Benaglia. *Eur. J. Org. Chem.*, 1033 (2001); (c) P. De March, M. Figueredo, J. Font. *Heterocycles*, **50**, 1213 (1999).

[4] For reviews see (a) R.A. Michelin, M. Mozzon, R. Bertani. *Coord. Chem. Rev.*, **147**, 299 (1996); (b) V.Y. Kukushkin, A.J.L. Pombeiro. *Chem. Rev.*, **102**, 1771 (2002); (c) J.L. Eglin. *Comments Inorg. Chem.*, **23**, 23 (2002).

[5] J.A. Frump. *Chem. Rev.*, **71**, 483 (1971).

[6] S. Robin, G. Rousseau. *Tetrahedron*, **54**, 13681 (1998).

[7] B.M. Culbertson. *Prog. Polym. Sci.*, **27**, 579 (2002).

[8] (a) R.A. Michelin, U. Belluco, M. Mozzon, P. Berin, R. Bertani, F. Benetello, G. Bombieri, R.J. Angelici. *Inorg. Chim. Acta*, **220**, 21 (1994); (b) R.A. Michelin, M. Mozzon, P. Berin, R. Bertani, F. Benetello, G. Bombieri, R.J. Angelici. *Organometallics*, **13**, 1341 (1994); (c) R.A. Michelin, R. Bertani, M. Mozzon, G. Bombieri, F. Benetello, R.J. Angelici. *J. Chem. Soc., Dalton Trans.*, 959 (1993); (d) R.A. Michelin, R. Bertani, M. Mozzon, G. Bombieri, F. Benetello, R.J. Angelici. *Organometallics*, **10**, 1751 (1991).

[9] (a) K.M. Button, R.A. Gossage, R.K.R. Philips. *Synth. Commun.*, **32**, 363 (2002); (b) M.A. Stark, G. Jones, C.J. Richards. *Organometallics*, **19**, 1282 (2000); (c) H. Witte, W. Seeliger. *Liebigs Ann. Chem.*, 996 (1974); (d) C. Bolm, K. Weickhardt, M. Zehnder, T. Ranff. *Chem. Ber.*, **124**, 1173 (1991); (e) A.V. Makarycheva-Mikhailova, V.Y. Kukushkin, A.A. Nazarov, D.A. Garnovskii, A.J.L. Pombeiro, M. Haukka, B.K. Keppler, M. Galanski. *Inorg. Chem.*, **42**, 2805 (2003).

[10] (a) P. Segl'a, M. Jamnický. *Inorg. Chim. Acta*, **205**, 221 (1993); (b) P. Segl'a, M. Jamnický, M. Koman, T. Glowiak. *Polyhedron*, **17**, 2765 (1998); (c) P. Segl'a, M. Koman, T. Glowiak. *J. Coord. Chem.*, **50**, 105 (2000).

[11] (a) P. Segl'a, D. Mikloš, M. Jamnický, J. Šima. *J. Coord. Chem.*, **48**, 15 (1999); (b) D. Mikloš, P. Segl'a, T. Glowiak. *Inorg. Chem. Comm.*, **4**, 66 (2001).

[12] (a) D. Nichols. In *Comprehensive Inorganic Chemistry*, J.C. Bailar Jr (Ed.), Vol. 24, p. 1109, Pergamon, Oxford (1975); (b) A.G. Masey. In *Comprehensive Inorganic Chemistry*, J.C. Bailar Jr (Ed.). Vol. 17, p. 41, Pergamon, Oxford (1975).

[13] F. Pavelčík, C. Rizzoli, A.D. Andreetti. *Program for Automatic Structure Determination by Fourier, Patterson and Superposition Methods*, Comenius University, Bratislava, Slovakia, and University of Parma, Italy (1990).

[14] G.M. Sheldrick. *SHELX97*, *Program for the Refinement of Crystal Structures*, University of Göttingen, Germany (1997).

[15] C.K. Johnson. *ORTEP II, Report ORNL-5138*, Oak Ridge National Laboratory, Tennessee, USA (1976).

[16] L.R. Falvello. *J. Chem. Soc., Dalton Trans.*, 4463 (1997).

[17] P. Segl'a, M. Palicová, M. Koman, D. Mikloš, M. Melník. *Inorg. Chem. Comm.*, **3**, 120 (2000).

[18] M. Melník. *Coord. Chem. Rev.*, **47**, 239 (1982).

[19] A.W. Addison, T.N. Rao, R. Reedijk, J. Rijn, G.C. Verschoor. *J. Chem. Soc., Dalton Trans.*, 1349 (1984).

[20] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Part B, 5th Edn, pp. 23, 56, 79, Wiley, New York (1997).

[21] A.B.P. Lever *Inorganic Electronic Spectroscopy*, 2nd Edn, pp. 480, 554, Elsevier, Amsterdam (1984).