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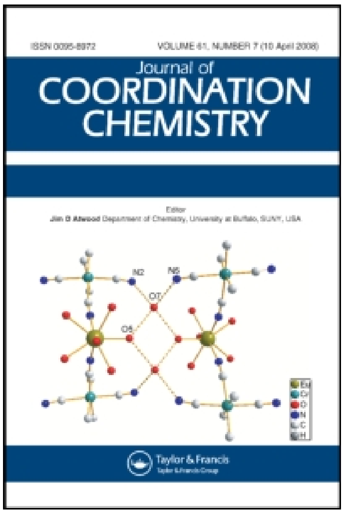

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Methanolysis of Pyrazinecarbonitrile in the Coordination Sphere of Copper(II). The Crystal Structure of Dichlorobis(*O*-Methylpyrazinecarboximidate)-Copper(II) Dihydrate

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METHANOLYSIS OF PYRAZINECARBONITRILE IN THE COORDINATION SPHERE OF COPPER(II). THE CRYSTAL STRUCTURE OF DICHLORO-BIS(*O*-METHYLPYRAZINECARBOXIMIDATE)-COPPER(II) DIHYDRATE

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Reaction of pyrazinecarbonitrile (pz-CN) with copper(II) in methanol solution led to formation of solid complexes containing *O*-methylpyrazinecarboximidate (pz-C(NH)OMe) as a ligand. The analogous reaction of pyrazinecarbonitrile in ethanol led to isolation of solid complexes containing unchanged pz-CN. Six novel copper(II) compounds have been obtained under various reaction conditions. Their stereochemistry and the mode of ligand coordination has been determined by spectroscopic and conductometric measurements. Moreover, the crystal structure of the complex [$CuCl_2$(*O*-methylpyrazinecarboximidate)$_2$]·$2H_2O$ has been determined by X-ray diffraction techniques.

Keywords: Copper(II) complexes; nucleophilic reaction; pyrazinecarbonitrile; *O*-methylpyrazinecarboximidate; crystal structure

INTRODUCTION

Nitriles, R–C≡N, isoelectronic with unsaturated ligands such as dinitrogen, carbon monoxide, isocyanides and alkynes, have been extensively used in the preparation of transition metal complexes. Activation of molecules

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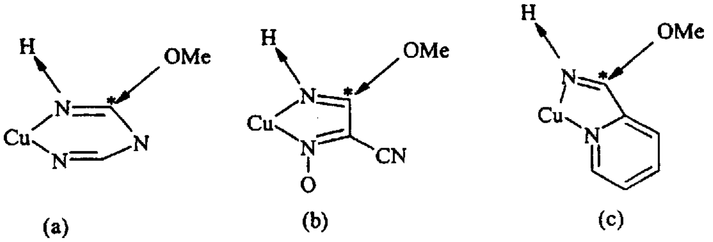

SCHEME 1 Examples of the nucleophilic addition: (a), methanol to a coordinated dicyanamide; (b), methanol to a coordinated nitrosodicyanmethanide; (c), methanol to a coordinated pyridine-2-carbonitrile. Asterisks denote the nucleophilic sites.

containing the nitrile group upon their coordination to a metal atom has been exploited in addition reactions of nucleophiles such as water, alcohols and amines.[1]

Reactions of some nitriles R–C≡N with methanol are outlined in Scheme 1. Some ligands having a linear R–C≡N group (*e.g.*, $N(CN)_2^-$ and $(NO)C(CN)_2^-$, as well as pyridine-2-carbonitrile) become bent upon coordination; the activated β-carbon atom, originally *sp*-hybridized, alters to sp^2-hybridized. This site becomes saturated by nucleophilic addition of solvent molecules such as water, methanol and ethanol.[2–4]

Reactions in which nucleophilic addition of water or alcohols to a ligand nitrile bond is promoted by chelation of the pyridine-2-carboxamide or *O*-alkylpyridine-2-carboximidate products to the metal atom are known to occur with pyridine-2-carbonitrile.[2,5–8] Similarly, we have found[9] that the reaction of pyrazinecarbonitrile (pz-CN) in the presence of some nickel(II) salts in dry methanolic and ethanolic solution led to the formation of solid complexes containing *O*-alkylpyrazinecarboximidate. Furthermore, a preparative method for free *O*-methylpyrazinecarboximidate (pz-C(NH)OMe) in the presence of Ni(II) chloride has been described.[9]

This paper describes the synthesis and structural characterization of some new copper(II) complexes prepared by the reaction of pz-CN in alcoholic solutions of Cu(II) salts. There are many structures that can be proposed for Cu(II)-pz-C(NH)OMe complexes because this potentially multidentate ligand can interact with a metal ion in several ways. In order to help solve the problem of pz-C(NH)OMe coordination, the X-ray crystal structure of one of the complexes, $[CuCl_2(O\text{-methylpyrazinecarboximidate})_2]\cdot 2H_2O$ was determined.

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EXPERIMENTAL

Chemical Reagents

All chemicals used were of reagent grade. Solid pyrazinecarbonitrile (Aldrich) was used without additional purification. Other chemicals were purchased from Lachema. Anhydrous Cu(II) chloride and bromide were prepared according to previously described procedures.[10] Methanol and ethanol were dried by standard methods.[11]

Analyses and Physical Measurements

Copper was determined by EDTA titration; carbon, hydrogen and nitrogen by microanalytical methods (Carlo Erba Instruments EA 1108). Analytical data, colours and yields of prepared complexes are given in Table I.

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

X-ray Structure Determination

The diffraction intensities for the complex $[CuCl_2(pz\text{-}C(NH)OMe)_2] \cdot 2H_2O$ (complex **4**) were collected with a KUMA KM 4 diffractometer using a graphite-monochromated MoK_α radiation. The space group $P\bar{1}$ was assumed throughout the structure analysis and was confirmed by successful refinement of the structure. Lorentz and polarization corrections were applied. The structure was solved by standard heavy atom procedures with SHELX86,[12] and subsequent Fourier synthesis using SHELXL93.[13] Anisotropic thermal parameters were refined for all non-hydrogen atoms. Geometrical analysis was performed using SHELXL93.[13] The structure was drawn using ORTEP[14] (Figure 1). A summary of crystal structure, experimental and refinement data are listed in Table II. Final positional and equivalent isotropic displacement parameters are given in Table III.

Supplementary material including non-hydrogen and hydrogen atomic coordinates ($\times 10^4$), anisotropic displacement parameters for non-hydrogen atoms ($Å^2 \times 10^3$) are available on request from the authors.

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TABLE I Analytical data[a], colours and yields for the complexes

	Colour	*Yield* g (%)	*Calculated* (*Found*) (%)			
			Cu	*C*	*H*	*N*
[$CuCl_2(pz\text{-}CN)_2$]	Green	1.55 (90)	18.4 (18.8)	34.9 (34.6)	1.8 (1.7)	24.4 (24.0)
[$CuBr_2(pz\text{-}CN)_2$]	Tawny	2.06 (95)	14.7 (14.4)	27.7 (27.4)	1.4 (1.2)	19.4 (19.0)
[$CuCl_2(pz\text{-}C(NH)OMe)$]	Light green	1.29 (95)	23.4 (23.0)	26.5 (26.9)	2.6 (2.5)	15.5 (15.8)
[$CuCl_2(pz\text{-}C(NH)OMe)_2$] · $2H_2O$	Dark green	0.33 (15)	14.3 (14.2)	32.4 (32.3)	4.1(4.0)	18.9 (18.7)
[$CuBr_2(pz\text{-}C(NH)OMe)$]	Greenish yellow	1.44 (80)	17.6 (18.0)	20.0 (19.7)	2.0 (1.7)	11.7 (11.9)
[$CuBr_2(pz\text{-}C(NH)OMe)_2$] · $2H_2O$	Dark green	1.73 (65)	11.9 (12.1)	27.0 (26.8)	3.4 (3.5)	15.8 (15.4)

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

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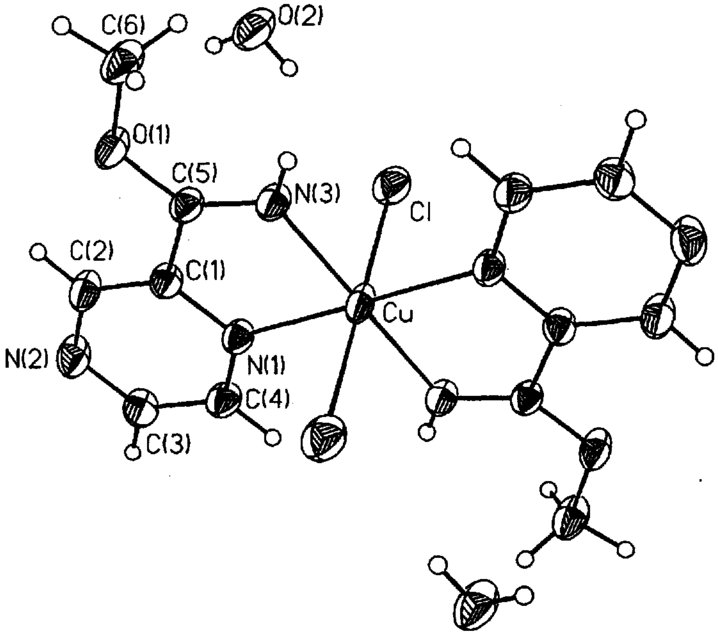

FIGURE 1 ORTEP plot of the [$CuCl_2$(*O*-methylpyrazinecarboximidate)$_2$] · $2H_2O$ (complex 4); thermal ellipsoids are shown at the 50% probability level.

TABLE II Crystal data and structure refinement details for [$CuCl_2$(pz-C(NH)OMe)$_2$] · $2H_2O$ (complex 4)

Empirical formula	$C_{12}H_{18}Cl_2N_6CuO_4$
Formula weight	444.76
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 7.3800(10)$ Å, $\alpha = 94.65(3)°$ $b = 8.028(2)$ Å, $\beta = 102.72(3)°$ $c = 8.349(2)$ Å, $\gamma = 114.71(3)°$
Volume	429.9(2) $Å^3$
Z	1
Density (calculated)	1.708 mg/m^3
Absorption coefficient	1.613 mm^{-1}
F(000)	227
Crystal size	0.40 × 0.30 × 0.25 mm
ϑ range for data collection	3.43–28.72°
Index ranges	−9*h*\\6, −10*k*\\10, −10*l*\\10
Reflections collected	2926
Independent reflections	1897 [*R*(*int*) = 0.0264]
Absorption correction	No
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1897/0/151
Goodness-of-fit on F^2	1.090
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0331$, $wR2 = 0.0879$
Largest diff. peak and hole	0.335 and −0.431 $eÅ^{-3}$

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters [$\text{Å}^2 \times 10^3$] for [$CuCl_2(pz\text{-}C(NH)OMe)_2$]$\cdot 2H_2O$ (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	0	0	0	31(1)
Cl	3543(1)	3081(1)	2064(1)	39(1)
O(1)	16(2)	3377(2)	−3428(2)	33(1)
O(2)	3350(3)	6306(3)	194(3)	45(1)
N(1)	1576(3)	162(2)	−1731(2)	26(1)
N(2)	3650(3)	825(3)	−4187(3)	38(1)
N(3)	−727(3)	1791(2)	−1239(2)	28(1)
C(1)	1473(3)	1362(3)	−2717(2)	26(1)
C(2)	2525(4)	1715(3)	−3927(3)	32(1)
C(3)	3738(4)	−370(3)	−3202(3)	34(1)
C(4)	2718(4)	−706(3)	−1960(3)	31(1)
C(5)	129(3)	2242(3)	−2401(2)	25(1)
C(6)	−1203(4)	4355(4)	−3214(4)	39(1)

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Preparation of Complexes

All the new complexes under study (**1**)–(**6**) can be prepared in reaction mixtures containing Cu(II) salts, pyrazinecarbonitrile and dry solvent (methanol or ethanol). Reflux of metal-free methanolic solution of pz-CN for 5 h did not induce any significant change in electronic spectra. Thus, no nucleophilic addition of solvent molecules in the absence of metal ions took place under our experimental conditions.

The complexes can be obtained in high yields under mild reaction conditions. The Cu(II) salt to pz-CN molar ratio was 1 : 2 or 1 : 4. The resulting solution was then worked up at two different temperatures, room temperature and boiling temperature of the solution. Some special conditions used in preparing the complexes are described below. Yields of the solid complexes are related to the initial metal contents in the reacting mixtures.

[$CuCl_2(pz\text{-}CN)_2$] (1) and [$CuBr_2(pz\text{-}CN)_2$] (2)

A filtered solution of $CuCl_2$ or $CuBr_2$ (5 mmol) in dry ethanol (40 cm^3) was mixed with an ethanolic solution (10 cm^3) of pz-CN (10 or 20 mmol). The solid complexes (**1**) and (**2**) started to crystallize from the solutions after several minutes; the yields of green (**1**) and tawny (**2**) were 90% and 95%. In the same way as above complexes (**1**) and (**2**) were obtained from methanolic solutions of CuX_2 (CuX_2 to pz-CN molar ratio was 1 : 2 and 1 : 4 for (**1**) or 1 : 2 for (**2**)) at room temperature in high yield (80%) for both complexes. The resulting fine microcrystals of products were filtered, washed with ethanol and dried *in vacuo*.

[$CuCl_2$(pz-C(NH)OMe)] (3) and [$CuCl_2$(pz-C(NH)OMe)$_2$] · $2H_2O$ (4)

Complex (3) was prepared by reaction in a stirred methanolic solution (40 cm^3) of $CuCl_2$ (5 mmol) and pz-CN (10 mmol). Light green precipitates were obtained from the solution after several days; the yield of (3) was about 95%. Well shaped dark green crystals of (4) were obtained in small yield (15%) from the methanolic filtrate ($CuCl_2$ to pz-CN molar ratio 1 : 2) been left at room temperature after the isolation of (1) (see above). The deposited complex (4) was filtered, washed with ethanol and dried *in vacuo* at room temperature.

[$CuBr_2$(pz-C(NH)OMe)] (5) and [$CuBr_2$(pz-C(NH)OMe)$_2$] · $2H_2O$ (6)

Complex (5) was prepared in dry methanolic solution (40 cm^3) of $CuBr_2$ (5 mmol) by reaction of pz-CN (20 mmol). Greenish yellow crystals of (5) were deposited during several days by slow evaporation of the solvent at room temperature; the yield of (5) was 80%. For the preparation of complex (6) a filtered methanolic solution of $CuBr_2$ (5 mmol) was mixed with a methanolic solution (10 cm^3) of pz-CN (10 or 20 mmol). The reaction solutions were further refluxed for 5 h. Dark green precipitates which started to deposit during reflux were collected by filtration, washed with dry ethanol and finally dried *in vacuo*; yields were 65% ($CuBr_2$ to pz-CN molar ratio 1 : 2) and 50% (CuX_2 to pz-CN molar ratio 1 : 4).

When methanolic solutions of Cu(II) salts containing pz-CN were heated under reflux for several hours to a few days, we isolated a mixture of solid complexes containing different condensation products of pz-CN and pz-C(NH)OMe. However, the resulting complexes were not characterized in more detail.

RESULTS AND DISCUSSION

Synthesis and Reactivity

While aqueous, methanolic or ethanolic solutions of pyrazinecarbonitrile remain unchanged for long periods, the presence of Cu(II) salts leads to the formation of solid complexes containing pyrazinecarbonitrile or its addition products as ligands. All solid complexes (1)–(6) were prepared only by the reaction of pz-CN with Cu(II) salts in methanol and ethanol.

The formation of *O*-methylpyrazinecarboximidate (pz-C(NH)OMe) and of their solid complexes (3)–(6) prepared by the reaction of pz-CN with

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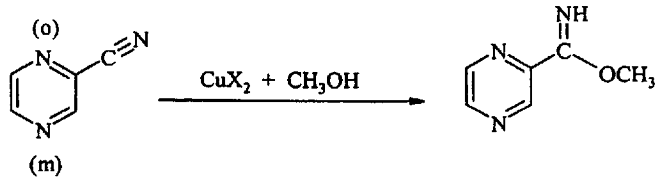

(pz-CN) (pz-C(NH)OMe)

(o) = nitrogen in *ortho* position to the nitrile group

(m) = nitrogen in *meta* position to the nitrile group

X = Br, Cl

SCHEME 2 Formation of Cu(II) complexes (3)–(6) which contain *O*-methylpyrazinecarboximidate (pz-C(NH)OMe).

Cu(II) salts in dry methanol is shown in Scheme 2. While solid complexes (3)–(5) containing addition product were isolated at room temperature, the pure complex (6) was isolated only from the reaction mixture containing $CuBr_2$ heated under reflux. The reaction of pz-CN in methanolic solution of $NiCl_2$ ($NiCl_2$ to pz-CN molar ratio 1 : 4) under reflux gives[9] free pz-C(NH)OMe, whereas from the methanolic solution of CuX_2 under the same experimental conditions only a mixture of solid complexes was isolated, containing different condensation products of pz-CN and pz-C(NH)OMe.

Pure solid complexes (1) and (2) containing unchanged pz-CN as ligand could be prepared when ethanolic solutions of $CuCl_2$ and $CuBr_2$, respectively, were either stirred at room temperature or heated under reflux. These complexes with pz-CN could be prepared in methanolic solution too, but only at room temperature.

As has previously been observed,[2,5,8] the reaction of pyridine-2-carbonitrile with alcohol (methanol or ethanol) in the presence of metal(II) salts leads predominantly to the formation of complexes containing *O*-alkylpyridine-2-carboximidate. Analogous nucleophilic reaction of pz-CN under the same experimental conditions in the presence of Cu(II) salts proceeds only with methanol.

Crystal Structure of (4)

Possible alternatives with respect to the structure were resolved by single-crystal X-ray analysis. A perspective view and the atom numbering of complex (4) is shown in Figure 1. The crystal structure of the complex

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TABLE IV Selected bond lengths (Å) and angles (°) for $[CuCl_2(pz\text{-}C(NH)OMe)_2] \cdot 2H_2O$ (complex 4)

Cu–N(3)	2.017(2)	O(1)–C(5)	1.316(2)
Cu–N(1)	2.025(2)	N(3)–C(5)	1.267(3)
Cu–Cl	2.800(3)	N(1)–C(4)	1.332(3)
N(1)–C(1)	1.332(3)	O(1)–C(6)	1.448(2)
N(2)–C(3)	1.326(3)	C(1)–C(2)	1.382(3)
N(2)–C(2)	1.341(3)	C(3)–C(4)	1.390(3)
C(1)–C(5)	1.491(2)		
N(3)–Cu–N(1)#1	99.33(7)	N(1)–C(1)–C(2)	121.5(2)
N(3)–Cu–N(1)	80.67(7)	N(3)–C(5)–O(1)	130.3(2)
C(5)–O(1)–C(6)	117.6(2)	C(5)–N(3)–Cu	114.47(14)
C(1)–N(1)–C(4)	117.6(2)	C(1)–N(1)–Cu	113.39(13)
C(4)–N(1)–Cu	129.0(2)	C(3)–N(2)–C(2)	116.6(2)

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

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$[CuCl_2(pz\text{-}C(NH)OMe)_2] \cdot 2H_2O$ (4) consists of discrete $[CuCl_2(pz\text{-}C(NH)\text{-}OMe)_2]$ units and water of crystallization linked by hydrogen bonding interactions. Bond distances and angles for complex (4) are listed in Table IV.

The copper(II) atom is six-coordinate. As shown in Figure 1, molecules of *O*-methylpyrazinecarboximidate (pz-C(NH)OMe) are coordinated to the Cu(II) atom *via* two N atoms (Cu-N(1) being 2.025(2) Å where N(1) is the nitrogen atom of the pyrazine ring, Cu-N(3) being 2.017 Å where N(3) is the nitrogen atom of the imino ether group) as *N*,*N*-coordinated bidentate chelate ligands to form a square planar arrangement. Donor atoms of each of the two molecules form two fused five-membered metallocycles with the copper atom. The pyrazine ring is coordinated through only one nitrogen atom. Coordination of the second nitrogen atom of the pyrazine ring is not observed in any case. The N(3)–C(5) and O(1)–C(5) distances of the imino ether group (N(3)=C(5)–O(1)–C(6)) suggest a bond order of between 1 and 2 and indicate delocalized π-bonding (see IR spectra). In addition, there are weak axial interactions between the copper and chlorine atoms in axial positions (Cl_{ax}) which allow formation of an elongated tetragonal bipyramid around the Cu(II) atom. The Cu–Cl_{ax} interatomic distances in the coordination polyhedron of complex (4) are 2.800(3) Å. The mean Cu–Cl_{ax} bond distance 2.85 Å for other complexes[15] with the chromophore $\{CuN_4Cl_2\}$ which have tetragonal bipyramidal configuration around Cu(II) atoms is very similar. This stereochemical finding is in good agreement with electronic spectra of complex (4) (see below).

Stereochemistry of Solid Complexes

Solid complexes (1) and (2) contain pyrazinecarbonitrile coordinated as a monodentate by the nitrogen of the pyrazine ring and complexes (3)–(6)

contain bidentate *N*,*N*-coordinated *O*-methylpyrazinecarboximidate ligands (see crystal structure of complex (**4**) and IR spectra). In agreement with this finding and based on the values of molar conductivities and electronic spectroscopic data, compositions and stereochemistries were assigned to the complexes under investigation.

Molar conductivities and electronic spectra data for the solid complexes under study are given in Table V. Molar conductivity values for complexes (**1**) and (**3**)–(**5**) in acetonitrile ($\Lambda_M = 31-95\,\Omega^{-1}\,cm^2\,mol^{-1}$), for complex (**2**) in dimethylformamide ($\Lambda_M = 38\,\Omega^{-1}\,cm^2\,mol^{-1}$) as well as for complex (**6**) in nitrobenzene ($\Lambda_M = 5\,\Omega^{-1}\,cm^2\,mol^{-1}$) show that all complexes are non-electrolytes[16] and all halide anionic ligands lie in the primary coordination sphere.

The electronic spectra of the solid complexes (**1**), (**2**), (**4**) and (**6**) are consistent with a tetragonally distorted octahedral Cu(II) complex.[17] Moreover, the determined composition and stereochemistry for complex (**4**) are in good agreement with its crystal structure determined by single-crystal X-ray diffraction. Complexes [CuX_2(pz-C(NH)OMe)] ((**3**) and (**5**)) exhibit in the electronic spectra a broad symmetrical absorption band at 14 700 and 14 400 cm^{-1}, respectively, consistent with a square planar structure.[17]

Structure of Solid Complexes

The structure of the organic ligand in the complexes was determined mainly on the basis of IR data. The principal infrared absorption bands of the precursor complexes (**1**) and (**2**) containing unchanged pz-CN and those of the free base are listed in Table VI. A small increase in ν(C≡N) for complexes (**1**) and (**2**) compared to that of free nitrile indicates[19] that in the above complexes the nitrile group nitrogen is not coordinated to Cu(II). We note,

TABLE V Electronic spectroscopic data, molar conductivities and stereochemistry of solid complexes with pyrazinecarbonitrile (pz-CN) and *O*-methylpyrazinecarboximidate (pz-C(NH)OMe)

	Maxima of absorption band[a] ν_{max} ($10^{-3}\,cm^{-1}$)		Λ_M[b,c,d] ($\Omega^{-1}\,cm^2\,mol^{-1}$)	*Stereochemistry*[e]
[$CuCl_2$(pz-CN)$_2$]	13.70	23.50–25.50	54[b]	O
[$CuBr_2$(pz-CN)$_2$]	13.50		38[c]	O
[$CuCl_2$(pz-C(NH)OMe)]	14.70br	24.00–26.00	33[b]	S
[$CuCl_2$(pz-C(NH)OMe)$_2$] · $2H_2O$	15.30	23.50–25.00	31[b]	O
[$CuBr_2$(pz-C(NH)OMe)]	14.40br	19.00–21.00	125[b]	S
[$CuBr_2$(pz-C(NH)OMe)$_2$] · $2H_2O$	16.00	25.00–27.00	5[d]	O

[a] br – broad. [b] In acetonitrile. [c] In dimethylformamide. [d] In nitrobenzene. [e] S – square-planar, O – octahedral.

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TABLE VI Characteristic IR bands[a] of solid complexes containing pyrazinecarbonitrile (pz-CN)

		Pyrazine ring[b]				
	$\nu(C{\equiv}N)$	ν_{8a}	ν_{8b}	ν_{12}	ν_{16b}	
pz-CN	2240m	1570w	1526w	1015s	410s	
[$CuCl_2(CNpz)_2$]	2251w	1582w	1525w	1020m	441s	491w
[$CuBr_2(CNpz)_2$]	2249m	1576m	1520w	1016m	440s	468w

[a] s – strong, m – medium, w – weak. [b] For assignment see Ref. [18].

moreover, that the strong pz-CN band (ν_{16b}) observed at 410 cm^{-1} for the free ligand is shifted to the significantly higher wave numbers at 441 and 440 cm^{-1}, respectively, for the complexes (1) and (2) and also that the shift is typical for monodentate coordination of the pyrazine ring in the above complexes. On the other hand the observation of a weak band at 491 cm^{-1} (complex (1)) and 468 cm^{-1} (complex (2)) indicates the presence of a small amount of complexes containing bidentate, bridging pyrazine ligands.[20,21] In the present paper the pyrazine ring nitrogen in the *ortho* position with respect to the nitrile group will be called the *ortho* nitrogen and the other nitrogen atom at the *meta* position will be called the *meta* nitrogen (see Scheme 2). It can be supposed that pz-CN is coordinated in the complexes (1) and (2) predominantly through the more basic pyrazine ring *meta* nitrogen and only in a few cases by the *ortho* nitrogen for bidentate bridging pyrazine ligands. Other pyrazine ring absorptions (ν_{8a}, ν_{8b} and ν_{12}) are shifted slightly from the free ligand values, but none of them appears to be sufficiently coordination sensitive to be of diagnostic value.

The mode of pz-CN coordination is important for its reactivity. Complexes containing pz-CN coordinated only by the *meta* nitrogen do not undergo addition reactions of nucleophiles such as methanol. On the other hand bidentate bridging coordination of pz-CN (see IR spectra) induces the addition of nucleophiles to the nitrile group. Similarly, addition reactions were observed only for pyridine-2-carbonitrile (which is more reactive than pyrazinecarbonitrile) but not for pyridine-3-carbonitrile[2,8] bonded by its *meta* nitrogen.

The spectra of the solid complexes (3)–(6) no longer exhibit the characteristic band at 2240 cm^{-1} assigned to the stretching vibration $\nu(C{\equiv}N)$ of the nitrile group in free pyrazinecarbonitrile. At the same time, however, several new, often very intense, characteristic bands appear. Now the crystal and molecular structure of complex (4) fully confirms formation of the new organic ligand, *i.e.*, conversion of the nitrile group to the imino ether.

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IR spectra of the complexes (3), (5) and (6) when compared with that of complex (4) provide evidence that these complexes contain coordinated *O*-methylpyrazinecarboximidate molecules as the only organic ligands. Characteristic absorption bands of the imino ether group for free and coordinated pz-C(NH)OMe are given in Table VII. IR spectra of pz-C(NH)OMe and of its Ni(II) complexes have been published.[9]

The most significant spectroscopic change following coordination of pz-C(NH)OMe molecules (Table VII) was observed as shifts of the band at 1085 cm^{-1} belonging to the ν_a(COC) vibration to higher wave numbers. The band attributed to ν(C=N) exhibits only a small shift. These results indicate that the "order" of the C=N bond, which might be expected to change on coordination through the nitrogen atom, is being maintained by drawing electrons from the C–O–C moiety. The fragment N=C–O–C of the imino ether group is more delocalized in the complexes and the "bond order" of the =C–O group is raised (see crystal structure of complex (4)).

For pz-C(NH)OMe (similar to pz-CN), a strong band (ν_{16b}) at 442 cm^{-1} as well as one at 1019 cm^{-1} for the free ligand is shifted to significantly higher wave numbers (about 460 and 1040 cm^{-1}, respectively) for all complexes which contain pz-C(NH)OMe. These shifts are typical of monodentate coordination of the pyrazine ring. All data are consistent with the conclusion that pz-C(NH)OMe in all complexes is coordinated as a chelate through the pyrazine ring nitrogen as well as the imino group nitrogen. Moreover, this type of *N,N*-coordination has been confirmed by the X-ray structure analysis of complex (4).

TABLE VII Characteristic IR bands[a] (in cm^{-1}) of the solid complexes containing *O*-methylpyrazinecarboximidate (pz-C(NH)OMe)

	Imidate group				*Pyrazine ring*[b]			
	ν(NH)	ν(C=N)	ν_{as}(COC)	ν_s(COC)	ν_{8a}	ν_{8b}	ν_{12}	ν_{16b}
pz-C(NH)OMe	3281s	1650s	1085s	952s	1574m	1527m	1019s	442s
[CuCl_2(pz-C(NH)OMe)]	3258s	1639s	1152s 1157sh	956s 946sh	1582s	1539w	1044s	457m
[CuCl_2(pz-C(NH)OMe)$_2$]· $2\text{H}_2\text{O}$	3227s	1650s 1640sh	1155s	955s	1582m	1539w	1049s	463s 441w
[CuBr_2(pz-C(NH)OMe)]	3298m	1648s	1154s	961s	1580m	1536w	1039s 1021w	453s 442m
[CuBr_2(pz-C(NH)OMe)$_2$]· $2\text{H}_2\text{O}$	3233s	1641s	1154s	956s	1578s	1537w	1047s	461s 441sh

[a] s – strong, m – medium, w – weak, sh – shoulder, ν – stretching. [b] For assignment see Ref. [18].

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References

[1] For a review see: R.A. Michelin, M. Mozzon and R. Bertani, *Coord. Chem. Rev.*, **147**, 299 (1996).
[2] M. Jamnický, P. Segl'a and M. Koman, *Polyhedron*, **14**, 1837 (1995).
[3] R. Boča, M. Hvastijová, J. Kožíšek and M. Valko, *Inorg. Chem.*, **35**, 4794 (1996).
[4] M. Hvastijová, J. Kohout, J. Kožíšek, R. Boča, J. Buchler and L. Jäger, *Coord. Chem. Rev.*, **175**, 17 (1998).
[5] P. Byers, M.G.B. Drew, M.J. Hudson, N.S. Isaacs and A. Upadhaya, *Polyhedron*, **13**, 345 (1994).
[6] A.R. Katritzky, R.J. Offerman, H.D. Durst, J.R. Ward, J.W. Hovanec and J.M. Albizo *J. Fluorine Chem.*, **44**, 121 (1989).
[7] Y.N. Belakon, V.I. Tarasov, T.F. Savel'eva, S.V. Vitt, A.E. Paskonova, S.Ch. Dotdayev, Y.A. Borisov, Y.T. Struchkov, A.S. Batasanov and V.M. Belikov, *Inorg. Chem.*, **27**, 4046 (1988).
[8] P. Segl'a and M. Jamnický, *Inorg. Chim. Acta*, **146**, 93 (1988).
[9] P. Segl'a and M. Palicová, *Synth. React Inorg. Met.-Org. Chem.*, **29**, 1843 (1999).
[10] A.G. ·Masey, in *Comprehensive Inorganic Chemistry*, Vol. 24, Ch. 27, 2nd edn., Eds. J.C. Bailar Jr. (Pergamon, Oxford, 1975), p. 41.
[11] A.I. Vogel, *Practical Organic Chemistry*, 3rd edn. (ELBS and Longman, London, 1965), p. 163.
[12] G.M. Sheldrick, SHELXS-86. *Crystallographic Computing*, Vol. 3 (Oxford University Press, Oxford, 1985), pp. 175-189.
[13] G.M. Sheldrick, SHELXL-93. Program for Refinement of Crystal Structure (University of Göttingen, Germany, 1994).
[14] C.K. Johnson, ORTEP. Report ORNL-3794 (Oak Ridge National Laboratory, TN, 1965).
[15] M. Melník, M. Kabešová, Ľ. Macášková and C.E. Holloway, *J. Coord. Chem.*, **45**, 31 (1998).
[16] W.J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
[17] A.B.P. Lever, *Inorganic Electronic Spectroscopy* (Elsevier, Amsterdam, 1984), p. 554.
[18] R.C. Lord, A.L. Marston and F.A. Miller, *Spectrochim. Acta*, **9**, 113 (1957).
[19] R.A. Walton, *J. Inorg. Nucl. Chem.*, **28**, 2229 (1966).
[20] J.S. Heynes, A. Kostikas, J.R. Sams, A. Simopoulos, R.C. Thompson, *Inorg. Chem.*, **26**, 2630 (1987).
[21] T. Otieno, S. Rettig, R.C. Thompson, J. Trotter, *Can. J. Chem.*, **67**, 1964 (1989).

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