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METHANOLYSIS OF PYRIDINE-2-CARBONITRILE IN THE COORDINATION SPHERE OF COPPER(II), COBALT(II) AND NICKEL(II). THE STRUCTURE OF [Ni(*O*-METHYLPYRIDINE-2-CARBOXIMIDATE)$_3$]Br$_2\cdot$4H$_2$O

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Abstract—The reaction of pyridine-2-carbonitrile with copper(II), cobalt(II) and nickel(II) salts in methanol solution led to the formation of solid complexes containing *O*-methylpyridine-2-carboximidate as a ligand (L). Seventeen compounds with general formulae [MX$_2$L], [MXL$_2$]X, [MX$_2$L$_2$] or [ML$_3$]X$_2$, where X = Br$^-$, Cl$^-$, NCS$^-$, ClO$_4^-$ and M = Cu^{II}, Co^{II}, Ni^{II}, have been obtained under various reaction conditions. Their stereochemistry and the mode of ligand coordination have been determined by spectral, magnetic and conductometric measurements. The crystal structure of [Ni(*O*-methylpyridine-2-carboximidate)$_3$]Br$_2\cdot$4H$_2$O was determined by X-ray diffraction techniques. The influence of the metal(II) atom on the composition and the stereochemistry of solid complexes is briefly discussed.

Increased reactivities of molecules coordinated in metal complexes have wide applications in chemistry. The activation of molecules 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 yielding amide,[1-3] imino ether[4,5] or amidine[4,6] complexes.

As has previously been observed, the reaction of pyridine-2-carbonitrile with water or an alcohol in the presence of some metal(II) salts leads to the formation of complexes which contain pyridine-2-carboxamide or *O*-alkylpyridine-2-carboximidate.[7-9] In preparing some chelates of the latter it was necessary, however, to add sodium methoxide, sodium hydroxide or various amines as a catalyst to the reaction mixtures.[7,8] However, several nickel(II) complexes of 2-pyridinyl-2-oxazolines have been isolated from the aqueous or alcoholic solutions of pyridine-2-carbonitrile in the presence of amino alcohols.[10]

This paper describes the synthesis and characterization of some copper(II), cobalt(II) and nickel(II) solid complexes which contain *O*-methylpyridine-2-carboximidate. The complexes are formed in systems containing metal(II) salts, pyridine-2-carbonitrile and dry methanol only; no base catalyst is needed. Based on the present knowledge the actual coordination mode of *O*-methylpyridine-2-carboximidate in the complexes cannot be determined unambiguously by IR spectroscopy. In order to help solve the problem of imino-ether coordination, the X-ray crystal structure of one of the complexes, [Ni(*O*-methylpyridine-2-carboximidate)$_3$]Br$_2\cdot$4H$_2$O, was determined.

EXPERIMENTAL

Chemical reagents

Anhydrous copper(II), cobalt(II) and nickel(II) salts were prepared according to previously described procedures.[11,12] Solid pyridine-2-carbonitrile was purified by distillation under reduced pressure. Methanol and acetone were dried by the

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standard method.[13] All other chemicals were of reagent grade.

Analyses and physical measurements

Copper, cobalt and nickel were determined by EDTA titration ; carbon, hydrogen and nitrogen by microanalytical methods (Carlo Erba Instruments EA 1108). Analytical data, colours and methods of the preparation for the complexes described here are given in Table 1.

Magnetic moments were measured with a Gouy balance for the powdered solid at 20°C. Electronic spectra of the powdered samples were recorded on a Perkin–Elmer Lambda 9 spectrometer at room temperature. A Radelkis OK-104 conductimeter was used for conductivity measurements of complexes (concentration 1.0×10^{-3} M) in nitrobenzene, acetonitrile and dimethylformamide at 25°C. IR spectra were recorded on a Philips Analytical PU 9800 FTIR spectrometer at room temperature with 4 cm^{-1} resolution. The spectra of solid samples were obtained in mulls (Nujol and hexachlorobutadiene) in the range 4000–200 cm^{-1} as well as in KBr pellets (1 wt%) in the range 4000–400 cm^{-1}.

Table 1. Analytical data, colours and methods of preparation

No.	Complex[a]	Colour Preparation	Calc. (found[b]) (%) M	C	H	N
I	$[CuBr_2L_1]$	Dark green A-2, A-4	17.7 (17.5)	23.4 (23.3)	2.2 (2.2)	7.8 (7.9)
II	$[CuBrL_2]Br$	Light blue C	12.8 (12.6)	33.9 (33.6)	3.3 (3.5)	11.3 (11.0)
III	$[CuBrL_2]Br \cdot 2H_2O$	Pale blue A-2, A-4	12.0 (11.8)	31.6 (31.9)	3.8 (3.6)	10.5 (10.6)
IV	$[CuCl_2L_1]$	Blue–green A-2	23.5 (23.4)	31.1 (31.5)	3.0 (3.2)	10.4 (10.6)
V	$[CuCl_2L_2]$	Light blue A-2	15.6 (15.6)	41.3 (41.1)	4.0 (4.1)	13.8 (13.7)
VI	$[CuCl_2L_2] \cdot 2H_2O$	Pale blue B-4	14.4 (14.4)	38.0 (38.1)	4.6 (4.8)	12.7 (12.8)
VII	$[CoBr_2L_1] \cdot 0.5(CH_3)_2CO$	Green A-1	15.4 (15.2)	26.6 (26.9)	2.9 (2.9)	7.3 (7.5)
VIII	$[CoBr_2L_2]$	Yellow C	12.0 (12.0)	34.2 (34.2)	3.3 (3.2)	11.4 (11.1)
IX	$[CoBr_2L_2] \cdot 2H_2O$	Orange A-2, B-2	11.2 (11.0)	31.9 (32.3)	3.8 (3.4)	10.6 (10.7)
X	$[CoL_3]Br_2 \cdot 2H_2O$	Reddish orange A-4	8.9 (9.1)	38.0 (38.1)	4.3 (3.9)	12.7 (12.6)
XI	$[CoCl_2L_1] \cdot H_2O$	Blue–green A-1	20.8 (20.6)	29.6 (29.4)	3.6 (3.3)	9.9 (9.7)
XII	$[CoCl_2L_2]$	Orange B-4	14.7 (14.5)	41.8 (41.4)	4.0 (4.0)	13.9 (13.8)
XIII	$[Co(NCS)_2L_1] \cdot CHCl_3$	Blue–green A-1	13.7 (13.8)	27.9 (28.1)	2.1 (2.3)	13.0 (12.8)
XIV	$[Co(NCS)_2L_2]$	Orange B-4	13.2 (13.0)	43.0 (43.3)	3.6 (3.8)	18.8 (18.6)
XV	$[NiL_3]Br_2 \cdot 4H_2O$	Pink B-4	8.4 (8.3)	36.1 (36.5)	4.6 (4.3)	12.0 (12.3)
XVI	$[Ni(ClO_4)L_2]ClO_4 \cdot 2H_2O$	Light blue B-2	10.4 (10.2)	29.7 (29.4)	3.6 (3.5)	9.9 (9.8)
XVII	$[NiL_3](ClO_4)_2$	Pink B-4	8.8 (8.7)	37.9 (37.9)	3.6 (3.8)	12.6 (12.3)

[a] *O*-methylpyridine-2-carboximidate is denoted by L.

[b] Microanalysis results obtained with maximum deviations: M, ±0.2; C, ±0.4; H, ±0.4; N, ±0.3.

The X-ray crystal structure of [Ni(*O*-methylpyridine-2-carboximidate)$_3$]Br$_2$·4H$_2$O (complex **XV**) was determined by single crystal X-ray diffraction. All data were collected at room temperature on a Syntex P2$_1$ diffractometer. The intensities of diffractions were corrected for Lorentz polarization factors. Complete crystal, experimental and refinement data are given in Table 2. The structure was solved by the use of the Patterson function to locate the nickel and bromine atoms, followed by successive application of difference Fourier maps and least-squares refinement to locate the remaining non-hydrogen atoms.[14] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms, except those in water molecules, were placed in calculated positions. Atomic scattering factors were taken from International Tables for X-ray Crystallography.[15] Selected interatomic distances and angles are listed in Table 3. Additional data for the structure of complex **XV** are included in the Supplementary material available (see later).

Table 2. Structure determination summary for the X-ray diffraction study of complex **XV**

Crystal data	
Empirical formula	NiBr$_2$(N$_2$O$_1$C$_7$H$_8$)$_3$·4H$_2$O
Formula weight	699.022
Crystal colour and habit	Pink Tetragonal bipyramid
Crystal dimensions (mm)	0.26 × 0.35 × 0.65
Crystal system	Monoclinic
Space group	$P2_1/c$
Z	4
Unit cell dimensions from 15 reflections	$8.28 \leqslant 2\theta \leqslant 17.60^\circ$
a (Å)	11.830(7)
b (Å)	13.448(19)
c (Å)	19.007(11)
β (°)	92.85(5)
Volume (Å^3)	3020.3(5)
Density (calc.) (g cm^{-3})	1.5373
F(000)	1416
Linear absorption coefficient (μ) (cm^{-1})	32.35
Data collection	
Diffractometer	Syntex P2$_1$
Radiation type	Mo-$K_\alpha \lambda = 0.71073$ Å
Temperature	Laboratory
Scan type	θ—2θ
2 θ Scan range (°)	$0 \leqslant 2\theta \leqslant 45$
Octants used	h − 13 to 13, k 0 to 13, l 0 to 21
Standard reflections	2 measured every 100
Number of data collected	3557
Observed reflections with $F_o \geqslant 3\sigma(F)$	1163
Absorption correction	No
Solution and refinement	
System used	SHELX76
Solution	Patterson
Refinement method	Full-matrix, least squares
Hydrogen atoms	Rigid model
Number of parameters refined	334
$R = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)/\Sigma\lvert F_o\rvert$	0.0747
$R_2 = \Sigma(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma w\lvert F_o\rvert^2]^{1/2}$ $w^{-1} = \sigma^2(F_o) + 0.003090\,(F_o)^2$	0.0794
Maximum shift/error	0.219/−0.304
Residual electron density (e Å^{-3})	0.47

Preparation of complexes

The solid complexes under study (**I**–**XVII**) can be prepared by three methods. Most of the complexes were obtained directly from methanolic solutions of metal(II) salts and pyridine-2-carbonitrile (abbreviated as Methods A-1, A-2, A-4, B-2 or B-4). Some complexes can be isolated as hydrates only. Unfortunately, attempts to dehydrate them usually resulted in total decomposition. Anhydrous complexes **II** and **VIII** can only be prepared by thermal decomposition of the corresponding hydrates (Method C).

General procedures for Methods A and B. A filtered solution of an anhydrous or hydrated metal (II) salt (5 mmol) in dry methanol (40 cm^3) was mixed with a methanolic solution (10 cm^3) of pyridine-2-carbonitrile. The metal to nitrile molar ratio was 1 : 1, 1 : 2 or 1 : 4. The resulting solution was then worked up at two different temperatures, i.e. at room temperature (Method A) or at boiling temperature of the solution (Method B). Owing to the metal to nitrile molar ratio used, both Methods are further divided into groups as follows:

Method A-1 (room temperature, molar ratio 1 : 1)
Method A-2 (room temperature, molar ratio 1 : 2)
Method A-4 (room temperature, molar ratio 1 : 4)
Method B-2 (boiling temperature, molar ratio 1 : 2)
Method B-4 (boiling temperature, molar ratio 1 : 4)

Methods A. The resulting solutions were left to slowly evaporate at room temperature in a desiccator over KOH.

Methods B. The reaction solutions were first heated under reflux usually for 8 h and then slowly cooled to room temperature. Solid complexes deposited from final solutions over several minutes or days. However, in preparing some solid complexes by Method B-4 it was usually necessary to add acetone to the final reaction solution.

The crystals or precipitates of complexes were

Table 3. Selected interatomic distances (Å) and angles (°) for complex **XV**

Ni—N(1)	1.975(32)	Ni—N(2)	2.064(20)
Ni—N(3)	2.018(24)	Ni—N(4)	2.097(20)
Ni—N(5)	2.003(20)	Ni—N(6)	2.085(20)
N(1)—Ni—N(2)	80.4(9)	N(1)—Ni—N(3)	89.4(9)
N(1)—Ni—N(4)	90.2(10)	N(1)—Ni—N(5)	95.2(10)
N(1)—Ni—N(6)	172.6(10)	N(2)—Ni—N(3)	168.5(9)
N(2)—Ni—N(4)	94.6(10)	N(2)—Ni—N(5)	94.9(8)
N(2)—Ni—N(6)	96.9(8)	N(3)—Ni—N(4)	80.1(10)
N(3)—Ni—N(5)	91.5(9)	N(3)—Ni—N(6)	93.8(8)
N(4)—Ni—N(5)	169.8(10)	N(4)—Ni—N(6)	96.9(8)
N(5)—Ni—N(6)	78.1(9)		

collected by filtration, washed with ethanol or acetone and finally dried *in vacuo*.

Some special conditions used in preparing complexes are described in the following text (*O*-methylpyridine-2-carboximidate is denoted as ligand L).

It should be noted that, unlike previously described procedures[7,8] for preparing complexes **V**, **VI**, **XII** and **XVII**, no other catalysts (such as sodium methoxide, sodium hydroxide or various amines) need to be added to reaction solutions. Moreover, when methanolic solutions of some metal(II) halides containing a considerable excess of pyridine-2-carbonitrile were heated under reflux for various times from several hours to a few days, we isolated, in addition to *O*-methylpyridine-2-carboximidate itself and its complexes, a solid mixture of various addition products. The study of the composition and the structure of these products is in progress.[16]

Copper(II) complexes

$[CuBr_2L_1]$ (**I**) *and* $[CuBrL_2]Br \cdot 2H_2O$ (**III**). The complexes were prepared by Methods A-2 and A-4 using anhydrous $CuBr_2$ as a starting salt. Dark green complex **I** started to crystallize from the reaction solution after about 1 h; pale blue complex **III** was separated after several days from the filtrate having been left after the isolation of complex **I**.

$[CuBrL_2]Br$ (**II**). Light blue powder was prepared by heating solid complex **III** at 105°C (Method C).

$[CuCl_2L_1]$ (**IV**) *and* $[CuCl_2L_2]$ (**V**). Both complexes were obtained as crystals by Method A-2. Copper(II) chloride dihydrate was used as a starting metal(II) salt in preparing blue–green complex **IV**; anhydrous copper(II) chloride was used for the synthesis of light blue complex **V**.

$[CuCl_2L_2] \cdot 2H_2O$ (**VI**). Pale blue powder of complex **VI** was obtained by Method B-4 using $CuCl_2 \cdot 2H_2O$. After cooling the final solution to room temperature, a light green solid of an unknown structure immediately precipitated in a small amount. Addition of acetone (1 : 1) to the filtrate left caused the deposition of complex **VI**.

Cobalt(II) complexes

For the synthesis of all complexes, anhydrous cobalt(II) salts were used. The pure complexes **VII**, **XI** and **XIII** were obtained only in small quantities.

$[CoBr_2L_1] \cdot 0.5(CH_3)_2CO$ (**VII**). The green complex was obtained by Method A-1. The reaction mixture was concentrated as much as possible in a desiccator over $CaCl_2$ and then treated with acetone. The deposited solid was dried *in vacuo* at room temperature.

$[CoBr_2L_2]$ (**VIII**). The yellow powder was obtained by thermal decomposition of the solid complex **IX** at 120°C (Method C).

$[CoBr_2L_2] \cdot 2H_2O$ (**IX**). The orange crystals were prepared by Methods A-2 and B-2. Deposition of the complex, however, starts already during refluxing of the reaction solution (Method B-2).

$[CoL_3]Br_2 \cdot 2H_2O$ (**X**). The reddish orange crystals were obtained in a high yield by method A-4. The solid complex was isolated by addition of acetone to the final solution and slow evaporation of the solvents at room temperature.

$[CoCl_2L_1] \cdot H_2O$ (**XI**). The blue-green crystals were prepared by Method A-1.

$[CoCl_2L_2]$ (**XII**). To achieve a pure product as orange crystals, Method B-4 appears to be the only suitable one for the preparation of complex **XII**.

$[Co(NCS)_2L_1] \cdot CHCl_3$ (**XIII**). The blue–green complex was obtained by modified Method A-1. The mixture of deposited solids was washed with acetone and the blue filtrate left was then concentrated in a desiccator over $CaCl_2$. Complex **XIII** was precipitated by addition of chloroform and dried *in vacuo* at room temperature.

$[Co(NCS)_2L_2]$ (**XIV**). The pure complex was obtained by Method B-4. The formation of the orange solid was observed after several minutes of refluxing the reaction solution.

Nickel(II) complexes

The preparation of several bis- and tris-(*O*-methylpyridine-2-carboximidate)nickel(II) complexes have been reported in our previous paper.[9] The present paper describes the preparation of perchlorate complexes **XVI** and **XVII** as well as a new bromo complex **XV**.

$[NiL_3]Br_2 \cdot 4H_2O$ (**XV**). The pink crystals, suitable for X-ray structural analysis, were obtained using anhydrous $NiBr_2$ by modified Method B-4. The reaction solution was heated under reflux for 1 h and then was slowly evaporated to reduce volume to about 10 cm^3 at room temperature. Finally, 20 cm^3 of acetone was added. Well-shaped monocrystals of complex **XV** were obtained when this methanol–acetone mixture was placed in an open dish for several days at about 0°C. If this mixture was left to crystallize at room temperature, a powder-like compound with a composition close to $[NiL_3]Br_2 \cdot 2H_2O$ was obtained.[9]

$[Ni(ClO_4)L_2]ClO_4 \cdot 2H_2O$ (**XVI**) *and* $[NiL_3](ClO_4)_2$ (**XVII**). Crystals of light blue complex **XVI** and pink complex **XVII** were prepared by following modified Methods B-2 and B-4, respectively. Owing to the composition of the starting nickel(II) salt, 20 cm^3 of 2,2-dimethoxypropane were added to a methanolic solution (30 cm^3) of $Ni(ClO_4)_2 \cdot 6H_2O$ and the resulting mixture was heated under reflux for 1 h. A methanolic solution (20 cm^3) of pyridine-2-carbonitrile was then added and the reaction solution was further heated under reflux for 8 h. After cooling to room temperature, acetone (1 : 1) was added to the final solution and crystals started to deposit after several days.

RESULTS AND DISCUSSION

While a mixture of pyridine-2-carbonitrile and methanol remains unchanged for long periods, the presence of metal(II) salts yields complexes containing *O*-methylpyridine-2-carboximidate as a ligand. The formulation of the new ligand as an imino ether has formerly been supported by the preparation of some nickel(II) complexes directly from *O*-methylpyridine-2-carboximidate,[9] which have spectral and magnetic properties identical with those prepared from pyridine-2-carbonitrile. Moreover, we have also succeeded in obtaining high yields of this addition product from reaction mixtures containing some nickel(II) salts and a considerable excess of the starting pyridine-2-carbonitrile.[9]

Stereochemistry of solid complexes

All of these complexes contain *N,N*-coordinated *O*-methylpyridine-2-carboximidate ligands (see IR spectra). In agreement with this finding and based on the values of magnetic moments, molar conductivities and electronic spectral data, the composition and the stereochemistry were assigned to the complexes under investigation (Table 4).

Copper(II) complexes. Molar conductivity values in nitrobenzene and acetonitrile show that all chloro complexes, as well as bromo complex **I**, are non-electrolytes.[17] All halide anions are coordinated to the central atom copper(II). However, the molar conductivities of complexes **II** and **III** in acetonitrile and, in part, in nitrobenzene are typical for those of 1 : 1 electrolytes, i.e. one bromide anion is coordinated to the central atom copper(II), the other acts as a counter-ion.

The electronic spectra of complexes **I** and **IV** are consistent with a planar structure, but those of complexes **V** and **VI** are typical for a tetragonally distorted octahedral copper(II) complex.[7,18] Unlike the assignment of Barnard,[7] however, we formulate complex **VI** as $[CuCl_2L_2] \cdot 2H_2O$. Bromo complexes **II** and **III** exhibit a broad asymmetrical band with a maximum at about 15,700 cm^{-1} and shoulders on its low-energy side in the electronic spectra which is typical for five coordinate copper(II) complexes with almost a square-pyramidal structure.[18] The suggested compositions of these complexes, namely $[CuBrL_2]Br$ for complex **II** and $[CuBrL_2]Br \cdot 2H_2O$ for complex **III**, are also in a good agreement with their molar conductivity values obtained in acetonitrile.

Cobalt(II) complexes. The composition and stereochemistry of complexes **VII**, **XI** and **XIII** were tentatively assigned on the basis of their electronic and IR spectra. Spectral properties of complex **XI** are, however, identical with those of $[CoCl_2L_1] \cdot H_2O$ prepared by a different method.[7] The similarity of the electronic spectra complexes **VII** and **XIII** to the spectrum of complex **XI** supports subsequently their formulation as $[CoBr_2L_1] \cdot 0.5 (CH_3)_2CO$ and $[Co(NCS)_2L_1] \cdot CHCl_3$ with a pseudo-tetrahedral chromophore structure.

The electronic spectra of the other cobalt(II) complexes are clearly consistent with an octahedral or a tetragonally distorted octahedral structure.[18] Similarly, the values of magnetic moments for these complexes are within the region usually found for

Table 4. Magnetic moments, electronic spectral data, molar conductivities and stereochemistry of solid complexes

No.	Complex[a]	μ_{eff} (BM)	Maxima of absorption band[b] (cm^{-1})			$\Lambda_M^{c,d}$	Λ_M^e (Ω^{-1} cm^2 mol^{-1})	Stereo-chemistry[g]
I	$[CuBr_2L_1]$	1.94		14,500 12,500sh		85^c	2^e	S
II	$[CuBrL_2]Br$	1.94		15,700 11,800sh 10,600sh		153^c	13^e	P
III	$[CuBrL_2]Br \cdot 2H \cdot 2H_2O$	1.93		15,700 11,800sh 10,700sh		155^c	16^e	P
IV	$[CuCl_2L_1]$	1.84		14,000br		25^c	0^e	S
V	$[CuCl_2L_2]$	1.87		15,300br		72^c	6^e	O
VI	$[CuCl_2L_2] \cdot 2H_2O$	1.86		15,500br		70^c	8^e	O
VIII	$[CoBr_2L_2]$	4.75	9,800	19,100 20,000		190^c	8^e	O
IX	$[CoBr_2L_2] \cdot 2H_2O$	4.93	9,800br	18,900 19,900		185^c	12^e	O
X	$[CoL_3]Br_2 \cdot 2H_2O$	4.91	10,400	19,900 18,400sh		296^c	$-^f$	O
XII	$[CoCl_2L_2]$	4.71	10,200 7,000sh	19,200 20,500		40^c	2^e	O
XIV	$[Co(NCS)_2L_2]$	4.73	10,200	21,000br		118^c	14^e	O
XV	$[NiL_3]Br_2 \cdot 4H_2O$	3.07	11,800br	18,600		173^d	$-^f$	O
XVI	$[Ni(ClO_4)L_2]ClO_4 \cdot 2H_2O$	3.39	9,500 8,800sh	12,600 13,100sh	17,100br	205^d	30^e	P
XVII	$[NiL_3](ClO_4)_2$	3.15	11,700br	18,500		192^d	67^e	O

[a] *O*-methylpyridine-2-carboximidate is denoted by L.
[b] sh, shoulder; br, broad.
[c] In acetonitrile.
[d] In dimethylformamide.
[e] In nitrobenzene.
[f] Not dissolved.
[g] S, square-planar; P, square-pyramidal; O, octahedral.

distorted octahedral cobalt(II) complexes.[11] Complex **X** is insoluble in nitrobenzene, but it behaves as a 1 : 2 electrolyte in acetonitrile and dimethylformamide. The molar conductivities of complex **XII** in all of the solvents are typical for those of non-electrolytes.[17] It should be noted, however, that complexes **VIII**, **IX** and **XIV** usually changed colour when dissolved in organic solvents used for conductivity measurements. While their molar conductivities in nitrobenzene are nearly consistent with those of non-electrolytes, the conductivities in acetonitrile and dimethylformamide indicate that a reaction with the solvents occurs. This behaviour of cobalt(II) complexes is very often observed[7,11] and it is due to a change in the environment of the cobalt(II) atom from octahedral (in the solid state) to tetrahedral (in the solution) not containing coordinated anions.

Nickel(II) complexes. Both electronic spectra and magnetic moment values of complexes **XV** and **XVII** are consistent with the octahedral environment of the central nickel(II) atoms.[11] Their molar conductivities in dimethylformamide as well as in nitrobenzene for complex **XVII** suggest that both compounds are 1 : 2 electrolytes with non-coordinated anions. Complex **XV** is insoluble in nitrobenzene and both complexes change colour when dissolved in acetonitrile.

Complex **XVI** has unusual spectral and magnetic properties which may be attributed to the nickel(II) complex with a nearly square-pyramidal structure.[11] The molar conductivity in nitrobenzene is typical for those of 1 : 1 electrolytes.[17] Unfortunately, complex **XVI** changed its colour when dissolved in acetonitrile or dimethylformamide. In agreement with the above results, we formulate complex **XVI** as $[Ni(ClO_4)L_2]ClO_4 \cdot 2H_2O$, i.e. as the five-coordinate nickel(II) complex which contains only one coordinated perchlorate group. The IR spectral data further support this conclusion (see below).

Crystal structure of complex **XV**

The X-ray crystal structure of complex **XV** has been determined. The crystals were well shaped but unstable under the experimental conditions. Their partial decomposition, probably, results in a rather high factor *R*.

The crystal structure of this complex consists of [Ni(*O*-methylpyridine-2-carboximidate)$_3$]$^{2+}$ cations, Br$^-$ counter-anions and H_2O molecules. All atoms are in general positions. As shown in Fig. 1, the nickel atom in the complex cation is nearly octahedrally surrounded by three N(pyridine) atoms and by three N(imino ether group) donor atoms in the facial configuration. Thus the *O*-methylpyridine-2-carboximidate molecules are *N,N*-coordinated as bidentate chelate ligands. In general the distances between the nickel and the nitrogen(pyridine ring) atoms are significantly longer than those of the nickel and the nitrogen(imino ether group) atoms as given in Table 3.

IR spectra

The structure of the organic ligand in the complexes was determined mainly on the basis of IR data. The spectra of the solid complexes no longer exhibit the most characteristic band assigned to the stretching vibration $\nu(C{\equiv}N)$ of the nitrile group in free pyridine-2-carbonitrile (at 2235 cm^{-1}). At the same time, however, several new, often very intense, characteristic bands appear. Now the crystal and molecular structure of complex **XV** fully confirms the formation of the new organic ligand, i.e. the

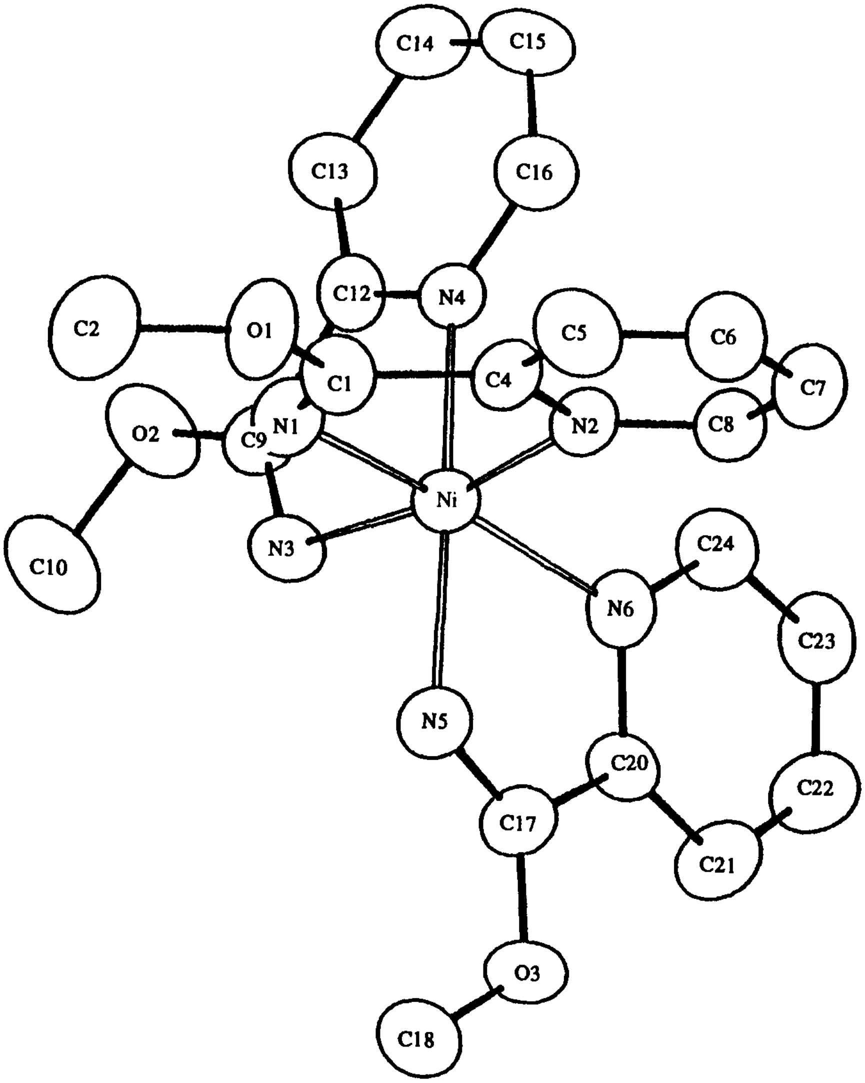

Fig. 1. Structure of [Ni-(*O*-methylpyridine-2-carboximidate)$_3$]$^{2+}$ cation in complex **XV**.

conversion of the nitrile to the imino ether. The IR spectra of the other complexes, when compared with that of complex **XV**, provide evidence that all the complexes studied contain coordinated *O*-methylpyridine-2-carboximidate molecules as the only organic ligands.

A few IR data of *O*-alkylpyridine-2-carboximidate have been published,[7,8] but neither a systematic investigation nor a sufficient assignment of the characteristic bands have previously been performed. However, other similar imino ethers such as *O*-methylacetimidate[19] and *O*-methylbenzimidate[20] have been investigated in more detail. Some maxima of the characteristic absorption bands of the imino ether group for *O*-methylpyridine-2-carboximidate itself are given in Table 5. An assignment of these bands stems mainly from the interpretation of IR spectral data for *O*-methylacetimidate. Unfortunately, in the region 1650–800 cm^{-1} many vibrational modes are of a mixed character so they cannot be attributed with any certainty to definite group vibrations. Moreover, many modes in this region do not fall into such narrowly defined wavenumber ranges. Unlike the assignment of Prichard and Orville-Thomas,[19] but in agreement with that of Hadži and Prevoršek,[20] the band at 1368 cm^{-1} is, therefore, attributed to ν(=C—O—) stretching mixed, in part, with δ(NH) of the imino ether group. *O*-methylpyridine-2-carboximidate also shows a strong band at 1187 cm^{-1}

Table 5. Characteristic IR bands (in cm^{-1}) of imino ether group for *O*-methylpyridine-2-carboximidate (L) and its solid complexes[a]

No.	Compound	ν(NH)	ν(C=N)	ν(=C—O—) + δ(NH)	$\delta_w(OCH_3)$	ν_a(COC)	ν_S(COC)	ν(MN)
	L	3,280s	1,650s	1,368s	1,187s	1,085s	961s	
I	$[CuBr_2L_1]$	3,293m	1,644s	1,392m	1,223s 1,200m	1,156m,br	953s	320s[b] 297m[b]
II	$[CuBrL_2]Br$	3,256m,br	1,647s	1,401s	1,219s,br	1,152s	961m	316m
III	$[CuBrL_2]Br \cdot 2H_2O$	3,212m,br	1,645s	1,400m	1,217s,br	1,152s	959s	314s
IV	$[CuCl_2L_1]$	3,376s 3,343m	1,659s	1,380s	1,210m 1,179m	1,134s	955s	322s[b] 286s[b]
V	$[CuCl_2L_2]$	3,140m,br	1,643s	1,393s	1,215s 1,195m	1,147s	950s	310s
VI	$[CuCl_2L_2] \cdot 2H_2O$	3,200s,br	1,650s	1,407s	1,226s	1,147s	957s	311s
VII	$[CoBr_2L_1] \cdot 0.5(CH_3)_2CO$	3,231m	1,645s	1,402m	1,235m 1202m	1,145m 1,134m	959s	286m
VIII	$[CoBr_2L_2]$	3,235s	1,647s	1,383s	1,202s	1,146s 1,134s	959m	287m
IX	$[CoBr_2L_2] \cdot 2H_2O$	3,233s	1,645s	1,379s	1,202s	1,144s 1,134s	959m	287m
X	$[CoL_3]Br_2 \cdot 2H_2O$	3,229m 3,166m	1,645s	1,377s	1,200s	1,136s	959m	280m
XI	$[CoCl_2L_1] \cdot H_2O$	3,247s	1,646s	1,399s	1,213m 1,202m	1,156s	970m 959m	289s
XII	$[CoCl_2L_2]$	3,205s	1,647s	1,381s	1,200s	1,140s 1,130s	959m	284s
XIII	$[Co(NCS)_2L_1] \cdot CHCl_3$	3,250m,br 3,170m,br	1,642s,br	1,402s	1,229s 1,202m	1,163m	953s	311s,br[b]
XIV	$[Co(NCS)_2L_2]$	3,281m	1,651s	1,385s	1,196s	1,134s	961s	280s
XV	$[NiL_3]Br_2 \cdot 4H_2O$	3,160m,br	1,651s	1,377s	1,208s 1,190s	1,140s	963m	284m
XVI	$[Ni(ClO_4)L_2]ClO_4 \cdot 2H_2O$	3,337s	1,657s	1,402s	1,217s	1,154s	978m 965m	299m,br
XVII	$[NiL_3](ClO_4)_2$	3,308s	1,653s	1,385s	1,210s 1,192m	1,144s	963m	286s

[a] s, strong; m, medium; br, broad; sh, shoulder; ν, stretching; δ, in-plane deformation; δ_W, wagging mode; M—N, metal nitrogen (imino ether group).

[b] Mixed bands or some of the observed bands also belong to another vibrational mode.

which is attributed[19] to the wagging of the O—CH_3 group. This characteristic vibration band of alkoxy groups, however, arises also from the C—O stretching vibration or may be due to the skeletal vibrations.[21] Moreover, *O*-methylpyridine-2-carboximidate exhibits two additional strong bands clearly belongingto ν_a(COC) and ν_s(COC) vibrations. We observed thus at least four bands in the region 1400–950 cm^{-1} which can unambiguously be linked to C—O—C and/or C—O vibrations. *O*-methylpyridine-2-carboximidate also exhibits several bands belonging to typical vibrations of the 2-pyridinyl ring.[21]

The most significant spectral changes following a coordination of *O*-methylpyridine-2-carboximidate molecules (Table 5) were observed as shifts of the bands at 1085 cm^{-1} and 1368 cm^{-1} due to ν_a(COC) and mixed [ν(=C—O—) + δ(NH)] vibrations, respectively, to higher wavenumbers. The band attributed to the ν(C=N) vibration 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 a supply of electrons from the C—O—C moiety. The fragment N=C—O—C of the imino ether group is more delocalized in complexes and the bond 'order' of the =C—O— group is raised. All data are also consistent with the conclusion that the 2-pyridinyl ring in *O*-methylpyridine-2-carboimidate is in all complexes simultaneously coordinated through the nitrogen atom.[22] Thus both the knowledge of the crystal of complex **XV** and IR spectral data confirm *N*,*N*-coordination of *O*-methylpyridine-2-carboximidate molecules in all solid complexes.

Thiocyanate complexes **XIII** and **XIV** show a very strong and broad (partly split) band in the region 2090–2070 cm^{-1}. The position of this band due to ν(C=N) indicates the presence of monodentate NCS groups which are coordinated through the nitrogen atom.[22]

The coordination mode of the perchlorate groups in solid complexes **XVI** and **XVII** was established mainly on the basis of their IR spectra. While complex **XVII** exhibits only ionic perchlorate groups (a very broad band with maximum at about 1080 cm^{-1}), the presence of at least one unidentate coordinated group of ClO_4^- in complex **XVI** is confirmed by observation of the broad band with two strong maxima at 1103 cm^{-1} and 1057 cm^{-1} belonging to $\nu_3(ClO_4)$ vibrations.[22] Further support for this conclusion was made on the analysis of the bands belonging to the vibrations of the perchlorate groups in the regions 1000–900 cm^{-1} [$\nu_1(ClO_4)$] and 500–400 cm^{-1} [$\nu_2(ClO_4)$] by analogy with other studies.[7,22]

Composition and stereochemistry of solid complexes

All solid complexes prepared by the reaction of pyridine-2-carbonitrile with methanol in the presence of metal(II) salts under study are listed in Table 6. According to their composition, the complexes can be classified into four different groups: $[MX_2L_1]$, $[MXL_2]X$, $[MX_2L_2]$ and $[ML_3]X_2$. Solvent molecules, present in some of the complexes, are always found outside the primary coordination sphere. *O*-Methylpyridine-2-carboximidate molecules which are formed by the above reaction act as *N*,*N*-coordinated ligand L only. The complexes exhibit a square-planar, a tetrahedral, a square-pyramidal or an octahedral configuration of donor atoms.

The composition and stereochemistry of the complexes are the result of several factors such as reaction conditions (temperature, reaction time, metal to nitrile molar ratio) and the nature of the metal(II) salts. Nearly all modes of synthesis (Methods A-1, A-2, ..., C) were used in attempts to prepare the complexes, but the solids with the composition given in Table 6 were only isolated. The most satisfactory results in preparing the complexes described in this paper were obtained by those listed in Table 1. While the use of copper(II) salts leads to the isolation of complexes containing both one and two molecules of *O*-methylpyridine-2-carboximidate, the nickel(II) salts form complexes with two or three molecules of ligand L. Cobalt(II) complexes contain one, two or three molecules of ligand L.

The stereochemistry of these complexes is in good agreement with that for copper(II), cobalt(II) and nickel(II) complexes usually prepared from reaction mixtures containing similar ligands.[11,12] The nickel(II) complexes are predominantly of an octahedral structure, the cobalt(II) complexes are of an octahedral or tetrahedral structure and, finally, the copper(II) complexes exhibit an octahedral, a square-pyramidal or a square-planar structure.

These results are very important for the possible use of the metal(II) salts under study as acid catalysts in reactions, such as the alcoholysis of nitriles to form imino ethers. The latter compounds are useful intermediates for the preparation of important acids,[2,5] esters,[5,23] amidines,[23] triazines,[24] oxazolines[25,26] or polymers,[19] but the slow initial reaction rate of the nitrile with alcohol without the presence of metal salts reduces the usefulness of these reactions. Therefore, catalysis of this step by metal complexes or by other means is of interest and commercial importance.[27]

In general four-coordinate square-planar or five-coordinate square-pyramidal metal complexes are

Table 6. Composition of solid complexes[a] prepared by the methanolysis of pyridine-2-carbonitrile in the presence of some metal(II) salts

M	X							
	Br		Cl		NCS		ClO_4	
Cu(II)	$[CuBr_2L_1]$	**I**[b]	$[CuCl_2L_1]$	**IV**[d]				
	$[CuBrL_2Br$	**II**	$[CuCl_2L_2]$	**V**[d]			$[Cu(ClO_4)_2L_2]$	
	$[CuBrL_2]Br \cdot 2H_2O$	**III**	$[CuCl_2L_2] \cdot 2H_2O$	**VI**[d]				—[d]
Co(II)	$[CoBr_2L_1] \cdot 0.5(CH_3)_2CO$	**VII**	$[CoCl_2L_1] \cdot H_2O$	**XI**[d]	$[Co(NCS)_2L_1] \cdot CHCl_3$	**XIII**		
	$[CoBr_2L_2]$	**VIII**	$[CoCl_2L_2]$	**XII**$_d$	$[Co(NCS)_2L_2]$	**XIV**		
	$[CoBr_2L_2] \cdot 2H_2O$	**IX**						
	$[CoL_3]Br_2 \cdot 2H_2O$	**X**					$[CoL_3](ClO_4)_2$	—[d]
Ni(II)	$[NiBr_2L_2]$	—[c]	$[NiCl_2L_2]$	—[c]	$[Ni(NCS)_2L_2]$	—[c]		
	$[NiBr_2L_2] \cdot H_2O$	—[d]					$[Ni(ClO_4)L_2]ClO_4 \cdot 2H_2O$	**XVI**
	$[NiL_3]Br_2 \cdot 2H_2O$	—[c]	$[Nil_3]Cl_2 \cdot 2H_2O$	—[c]	$[NiL_3](NCS)_2$	—[c]	$[NiL_3](ClO_4)_2$	**XVII**[d]
	$[NiL_3]Br_2 \cdot 4H_2O$	**XV**						

[a] *O*-methylpyridine-2-carboximidate is denoted by L.

[b] Preparation and properties of numbered compounds are described in the present paper.

[c] See ref. 9.

[d] Prepared by a similar route in refs 7 and 8.

good catalysts for similar reactions.[28,29] Our results presented here also show that some copper(II) halides forming the four- and five-coordinate complexes, can be useful as new catalysts in the preparation of both imino ethers and other organic compounds.

Supplementary material available—Atomic coordinates, thermal parameters and complete bond lengths and angles for complex **XV** have been deposited with the Editor as supplementary data. Atomic coordinates have also been deposited with the Cambridge Crystallographic Data Centre.

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