Polish J. Chem., **75**, 957–964 (2001)

Copper(II) Pyridine-2,6-dicarboxylates. Coordination and Distortion Isomers of [Cu(pydca)(H_2O)$_2$]

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(Received July 7th, 2000; revised manuscript March 12th, 2001)

Copper(II) pyridine-2,6-dicarboxylate dihydrate and its ronicol (ron), nicotinamide (nia) and caffeine (caf) complexes were prepared and their spectral, magnetic as well as their bio-activites were studied. X-ray analysis of [Cu(pydca)(H_2O)$_2$] (pydca = pyridine-2,6-dicarboxylate) shows, that the complex exists in two isomeric forms: monoclinic and triclinic and it is an example of the coordination isomerism. Triclinic forms also exists in two isomeric forms, differing mostly by degree of distortion and being an example of the distortion isomerism. On the basis of spectral and magnetic properties for Cu(pydca)L (L = ron, nia or caf) a square-pyramidal coordination of the copper(II) ion can be proposed. Highest bio-activity shows [Cu(pydca)(H_2O)$_2$].

Key words: crystal structure, monomers, magnetic properties, antimicrobial effects, EPR, electronic spectra, synthesis

Although a great number of copper(II) carboxylates have been investigated [1–3] only a few are recorded for pyridine-2,6-dicarboxylates. [Cu(pydca)(H_2O)$_2$], (pydca = pyridine-2,6-dicarboxylate), exists in two isomeric forms, monoclinic and triclinic.

X-ray analyses of monoclinic [Cu(pydca)(H_2O)$_2$] was carried out [4] and showed, that in the polymeric chain each copper(II) atom has tetragonal bipyramidal geometry. X-ray analyses of triclinic [Cu(pydca)(H_2O)$_2$] showed [5] that the copper(II) atom is pentacoordinated with a square pyramidal configuration. X-ray analysis of three examples of the composition [Cu(pydca)(mim)(H_2O)]·n solvent; mim = 1-, 2- or 5-methylimidazole showed [6] that the complexes are monomeric and isostructural. Copper(II) atoms are five-coordinated and the coordination sphere indicates a square-pyramidal geometry. X-ray analysis of [Cu(pydca)(4-dmapy)], (4-dmapy = 4-dimethylaminopyridine), showed [7] that the copper(II) atom is in a square-planar environment (CuO_2N_2). Structural analysis of [Cu(pydca)(1-mim)(H_2O)$_{0.5}$], 1-mim

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= 1-methylimidazole, showed [7] that there are square-pyramidal [Cu(pydca)(1-mim)(H_2O)] and square planar [Cu(pydca)(1-mim)] units.

In this study we report the synthesis, spectral and magnetic properties, antibacterial and antifungal activities of [Cu(pydca)(H_2O)$_2$] and [Cu(pydca)L] (L = 3-pyridylcarbinol (ronicol), nicotinamide or caffeine).The [Cu(pydca)(H_2O)$_2$] was studied also by X-ray.

EXPERIMENTAL

Preparation of the complexes: A disodium pyridine-2,6-dicarboxylate solution was prepared from an aqueous solution of NaOH (0.02 mol) by addition of pyridine-2,6-dicarboxylic acid (0.01 mol), following by boiling. The partially evaporated solution was filtered hot and the filtrate placed in a refrigerator. White disodium pyridine-2,6-dicarboxylate, which slowly precipitated, was isolated and dried at room temperature. The copper(II) pyridine-2,6-dicarboxylate dihydrate was prepared by reaction of a solution of disodium pyridine-2,6-dicarboxylate (0.01 mol, pH adjusted to 4.5–5.0 using the free acid) with an aqueous solution of copper(II) sulfate in equimolar ratio. The solution was boiled, filtered and left to crystallize in a refrigerator. The blue product, that precipitated, was washed with cold water and dried at room temperature. Crystals of [Cu(pydca)(H_2O)$_2$], suitable for structural determination, were obtained by recrystallizing the crude product from water.

The copper(II) pyridine-2,6-dicarboxylates of composition [Cu(pydca)L] (L = ron, nia or caf) were prepared by treating L with [Cu(pydca)(H_2O)$_2$] in an equimolar ratio in hot metanol. The resulting solutions were filtered and the filtrate left to stand at room temperature, allowing fine blue microcrystals to precipitate and dried at room temperature. The compounds are stable in air at ambient temperature. Elemental analyses of the copper(II) pyridine-2,6-dicarboxylate confirmed the composition indicated.

Spectroscopic studies: IR spectra in the region 400–3600 cm^{-1} were measured with a Nicolet FTIR Magna-IR 750 spectrometer, and electronic spectra in the region 10000–28000 cm^{-1} were measured with a Perkin-Elmer 450 spectrophotometer. In both cases, Nujol suspension techniques were used. The EPR spectra of powdered samples were obtained using a Bruker SRD 200D (X-band) at room temperature. The data are summarized in Table 1.

Magnetic studies: Magnetic susceptibility was measured by the Faraday method between 77.4–293 K, using a sensitive Sartorius M-25D electrobalance. Susceptometer was equipped with Oxford Instruments CF-1200 continuous – flow cryostat and an electromagnet operating at 0.5 T. The calibrant employed was HgCo(NCS)$_4$ [8], for which the magnetic susceptibility was taken as 16.44×10^{-6} cm^3 g^{-1}. The correction for diamagnetism of the constituent atoms was calculated using Pascal's constants [9]. The value $N\alpha = 60\times10^{-6}$ cm^3 mol^{-1} was used for the temperature independent paramagnetism of the copper(II) ion. The effective magnetic moment was calculated from the equation, $\mu_{eff} = 2.83\ (\chi_M \times T)^{1/2}$ (B.M.).

Structure determination: Data collection and cell refinement of the Cu(pydca)(H_2O)$_2$ were carried out using SYNTEX P2_1 diffractometer software [10]. Intensity data were connected for Lorentz and polarization factors. The structure was solved by the heavy atom method with SHELXS86 [11], and subsequent Fourier synthesis using SHELXL93 [12], anisotropic thermal parameters were refined for all non-hydrogen atoms. Geometrical analysis was performed using SHELXL93 [12]. The structure was drawn using ORTEP [13]. The final parameters after refinement are summarized in Table 3. Independent atomic coordinates and equivalent isotropic thermal parameters are given in Tables 4. Supplementary material including hydrogen atomic coordinates ($\times10^4$), anisotropic displacement parameters for non-hydrogen atoms (Å$\times10^3$) have been deposit at the Cambridge Crystallographic Data Centre. Structure of Cu(pydca)(H_2O)$_2$ has CCDC number 139881. Observed and calculated structural factors are available on request from authors.

Bio-test: The antibacterial activity of the newly prepared copper(II) pyridine-2,6-dicarboxylates was evaluated by a microdilution method [14] using G^+ bacterial strains *Staphylococcus aureus* CCM3824 and G^- bacterial strains *Escherichia coli* CCM5172. The effects of these compounds on the yeast *Candida parapsilosis* (isolated from human patrient) were determined [15]. The culture of bacteria and yeasts were incubated under vigorous shaking. The efficiency of prepared deviates on filamentous fungi *Rhizopus oryzae*, (obtained from the Collection of Microorganisms, Slovak Technical University), *Botrytis cinerea* CCMF-16, *Altelnaria alternate* CCMF-128, *Mycrosporum gypseum* (isolated from human patient), was tested by macrodilution technique on solidified broth medium during static culturing [15]. Chromatographically pure compounds were dissolved in dimethylsulfoxide, their final composition never exceeded 1.0 mol% in either control on treated samples. Concentration of complexes under study, range from 1.25 to 10.0 mmol l^{-1} for filamentous fungi, 1.25–5.0 mmol l^{-1} for yeasts and 5.0 mmol l^{-1} for bacteria, was used.

The antimicrobial activity was characterized by the IC_{50} values (concentration of a derivative which in comparison to the control inhibits the growth of microorganisms to 50%) and MIC values (minimal inhibitory concentration of a derivative which inhibits microbial growth by 100%). The IC_{50} and MIC values were read from toxicity curves. MIC experiments on subculture dished were used to assess the minimal microbial concentration (MMC). Subcultures were prepared separately in Petri dishes containing competent agar medium and incubated at 30°C for 48 h (bacteria, yeasts) and at 25°C for 96 h (filamentous fungi). The MMC value was taken as the lowest concentration, which showed no visible growth of microbial colonies in the subculture dishes.

RESULTS AND DISCUSSION

The IR spectrum of $[Cu(pydca)(H_2O)_2]$ shows strong absorption bands at 3185 cm^{-1} and 3300 cm^{-1}. These frequencies correspond to the asymmetric and symmetric OH stretches and confirm the presence of water in the complex. These stretches were absent in the spectra of all the other compounds. The IR spectrum of disodium pyridine-2,6-dicarboxylate showed carboxylate stretching frequencies, $\nu_{as}(COO^-)$ at 1638 cm^{-1} and $\nu_s(COO^-)$ at 1433 cm^{-1}. Each compound showed carboxylates stretching frequencies $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ and the data are given in Table 1. Upon complexation, the ν_{as} shifted to the higher and ν_s to the lower frequency, compared to values for the free carboxylate ion taken as sodium salts. This indicates an unidentate coordination of carboxylate group to copper ion [16]. Unidentate coordination removes the equivalence of the two oxygen atoms. This should increase $\nu_{as}(COO^-)$, decrease $\nu_s(COO^-)$ and increase the separation (Δ) between the $\nu(COO^-)$ frequencies, relative to values for the free carboxylate ion. Δ value > 200 cm^{-1} indicate a highly unsymmetric unidentate coordination [17]. The stretching vibration of the C=N of the heterocyclic ring appears at around 1578 cm^{-1}, and on complexation a shift to higher frequencies is observed. In the present examples this shift (to about 1600 cm^{-1}, Table 1) may suggest bond formation by the metal atom to the heterocyclic ring nitrogen atom, thereby increasing the dipol contribution of $C=N^+$ in the heterocyclic ring [18].

The solid state electronic spectra of compounds (Table 1) showed a broad asymmetrical band with a shoulder at lower wavelengths. The solid state electronic spectrum of the $[Cu(pydca)(H_2O)_2]$ exhibits a broad ligand field band with a maximum at 12600 cm^{-1} and a shoulder at 11300 cm^{-1}. Similar spectra were observed for [Cu(pydca)L], but both the broad ligand field band as well as shoulder are blue shifted. EPR spectrum of $[Cu(pydca)(H_2O)_2]$ is a pseudorhombic with three g-values (Table 1). Remaining three compounds show an axial type of spectra with $g_{\|} > g_{\perp}$. All electron paramagnetic resonance spectra are typical for S = 1/2 and indicative of the $d_{x^2-y^2}$, ground state.

Table 1. Spectral data of [Cu(pydca)L].

L	Infrared spectra (cm^{-1})			Electronic spectra (cm^{-1})		EPR		
	ν_{as}(COO)	ν_s(COO)	ν(CN)*			$g_\perp$	$g_{\|\|}$	g_{av}
H_2O	1688 s 1665 s	1435 m	1590 m	12600	11300 sh	a		2.16
ron	1690 s 1655 m	1430 m	1600 m	13400	12000 sh	2.05	2.25	2.12
nia	1700 m 1670 s	1410 m	1605 m	13600	12300 sh	2.06	2.26	2.13
caf	1660 s	1425 m	1600 m	13200	12100 sh	2.07	2.24	2.12

a; g_1 =2.05, g_2 = 2.14, g_3 = 2.30
*stretching vibration ν(C=N) of the heterocyclic ring.

Magnetic susceptibility measurements of polycrystalline samples of the compounds between 77 and 300 K obey the Curie-Weiss law, where the Curie constant C = $Ng^2\beta^2S(S+1)/3k$ with S = 1/2 as follows $\chi_M^{corr} = C/(T-\theta)$. The best values of the Curie (C) and Weiss (θ) constants are given in Table 2. All copper(II) compounds possess a negative Weiss constant, suggesting a very weak antiferromagnetic interaction, occurring in the crystal lattices between molecules of the compounds.

Table 2. Magnetic data of [Cu(pydca)L][a].

L	μ_{eff} (B.M.) at 300 K	Curie Constant C (cm^3 K mol^{-1})	Weiss constant θ (K)	Diamagnetic corr. ×10^6 (cm^3 mol^{-1})
H_2O	1.75	0.616	–9.9	–95.5
ron	2.01	0.647	–8.9	–143
nia	2.00	0.663	–3.3	–141
caf	1.99	0.603	–1.8	–150

[a] in the temperature range 77–300 K.

On the basis of the spectral and magnetic data, a square-pyramidal geometry is deduced for [Cu(pydca)L] and it is suggested that the $d_{x^2-y^2}$ level is the lowest. The $[Cu(pydca)(H_2O)_2]$ was also studied by X-ray method. The crystallographic data show that the complex crystallizes in the triclinic system, with the space group P-1 (Table 3).

Table 3. Crystal data and structure refinement for [Cu(pydca)(H_2O)$_2$].

Empirical formula	$C_7H_7CuNO_6$
Formula weight	264.68
Temperature	293(2) K
Wavelength	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 4.7060(10) (Å)
	b = 8.956(2) (Å)
	c = 10.311(2) (Å)
	α = 81.31(3) (°)
	β = 85.72(3) (°)
	γ = 83.34(3) (°)
Volume	426.0(2) (Å^3)
Z	2
Density (calculated)	2.064 (Mg/m^3)
Absorption coefficient	2.573 (mm^{-1})
F(000)	266
Crystal size	0.4 × 0.3 × 0.25 (mm)
θ range for data collection	2.31 to 32.58 (°)
Index ranges	$0 \le h \le 6$, $-13 \le k \le 13$, $-15 \le l \le 15$
Reflection collected	2880
Independent reflection	2563 (R_{int} = 0.0150)
Absorption correction	No
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2507/0/164
Goodness-of-fit on F^2	1.064
Final R indices $[I > 2\sigma(I)]$	R = 0.0375, wR2 = 0.0925
R indices (all data)	R = 0.0540, wR2 = 0.1239
Largest diff. peak and hole	0.985 and –1.428 (e Å^{-3})

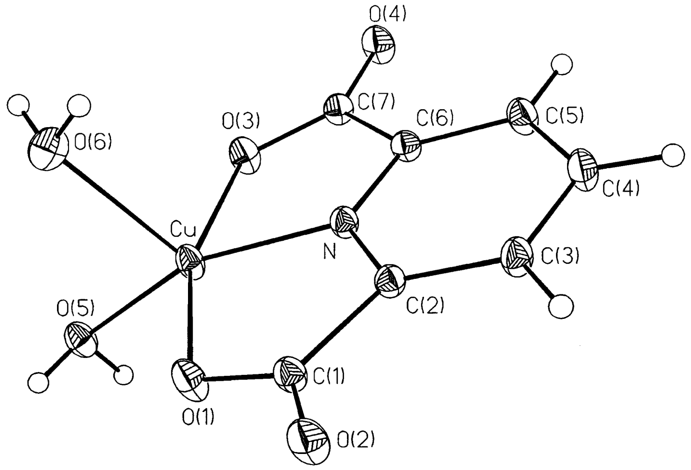

Figure 1. ORTEP drawing of Cu(pydca)(H_2O)$_2$.

The structure and the numbering scheme of the compound are shown in Fig.1. The coordination geometry around central copper(II) atom is square-pyramidal (4+1). Three of the square-planar coordination sites are occupied by the tridentate pyridine-2,6-dicarboxylate anion, a carboxylate O(1) and O(3) atoms and a N atom. The fourth site of the square plane is occupied by an O(5) atom of a water molecule at a distance of 1.966(2) Å. The fifth coordinated atom, an O(6) atom of a second water molecule at a distance of 2.155(2) Å, lies at the apex of the pyramid. The coordination bond distances and angles around the Cu(II) atom are given in Table 4. The displacement of copper(II) atom from its coordination plane is 0.253(1) Å towards the apical water molecule.

Table 4. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [Å × 10^3] for [Cu(pydca)(H_2O)$_2$]. U(eg) is defined as one third of the trace of the orthogonalized *Uij* tensor.

	x	y	z	U(eq)
Cu	2097(1)	4296(1)	2832(1)	23(1)
O(4)	–1145(4)	2260(2)	178(2)	34(1)
C(7)	77(4)	2676(2)	1046(2)	23(1)
O(1)	5005(3)	3878(2)	4204(2)	31(1)
O(2)	8595(4)	2189(2)	4932(2)	33(1)
O(3)	–496(3)	3949(2)	1477(2)	28(1)
C(6)	2432(4)	1626(2)	1728(2)	21(1)
C(5)	3359(4)	140(2)	1567(2)	26(1)
C(1)	6512(4)	2594(2)	4256(2)	23(1)
C(2)	5617(4)	1568(2)	3364(2)	20(1)
N	3584(3)	2277(2)	2599(2)	20(1)
C(4)	5493(5)	–630(2)	2354(2)	30(1)
C(3)	6666(4)	79(2)	3263(2)	26(1)
O(5)	–424(3)	5927(2)	3539(2)	27(1)
O(6)	4519(4)	5898(2)	1571(2)	32(1)

The geometrical effect of five-membered ring formation on the copper coordination polyhedron can be shown by the fact that the intra-ring bond angles O(1)–Cu–N and O(3)–Cu–N (80.15(7)° and 80.70(7)°) are both much less than the inter-ring bond angles O(1)–Cu–O(5) and O(3)–Cu–O(5) 99.29(7)° and 96.91(7)°, respectively. Two five-membered rings with a Cu–N bond in common are formed by coordinating to the Cu(II) atom. The dihedral angle between the [N–C(2)–C(1)]–[N–C(6)–C(3)] is 2.83°.

As was mentioned in the introduction, monoclinic [Cu(pydca)(H_2O)$_2$] [4] forms a polymeric chains running parallel to [001]. The pyridine-2,6-dicarboxylate acts as a tridentate ligand and coordinates to copper(II) atom through the nitrogen atom, and two carboxylate oxygen atoms in a main coordination plane, which is completed by the water molecule (Cu–O(5), 1.940(4) Å). The coordination is completed to square-pyramidal by two longer distances (Cu–O(6), 2.396 Å; Cu–O(3), 2.423 Å). The O(3) is in a bridging position. In the triclinic form [5] the base of the pyramid around the copper(II) atom is formed by the tridentate pyridine-2,6-dicarboxylate anion and one water molecule. The second water molecule is in the apical position. Selected bond distances and bond angles for all three [Cu(pydca)(H_2O)$_2$] are given in Table 5. The [Cu(pydca)(H_2O)$_2$] exists in two isomeric forms, a monoclinic and triclinic, which are examples of the coordination number isomerism [19]. Triclinic form also exists in two isomeric forms, differ mostly by degree of distortion and is an example of the distortion isomerism [3].

Table 5. Selected Cu–L bond distances [Å] and L–Cu–L bond angles [°] in [Cu(pydca)(H_2O)$_2$]; (symmetry codes: (i) x, 0.5 – y, 0.5 + z).

	Monoclinic[a] (polymeric) Å	Triclinic[b] P1 (monomeric) Å	Triclinic P-1 (this work) (monomeric) Å
Cu–N	1.898(4)	1.917(8)	1.905(2)
Cu–O(1)	2.037(3)	1.995(9)	2.006(2)
Cu–O(3)	2.050(4)	1.994(9)	2.002(2)
Cu–O(5)	1.940(4)	1.989(8)	1.966(2)
Cu–O(6)	2.396(4)	2.154(8)	2.155(2)
Cu–O(3)$^{\mathrm{i}}$	2.423(4)		
N–Cu–O(1)	80.3(1)	80.5(4)	80.15(7)
N–Cu–O(3)	80.5(1)	80.3(4)	80.70(7)
O(1)–Cu–O(5)	95.6(1)	97.6(3)	99.29(7)
O(3)–Cu–O(6)	103.6(1)	98.6(3)	96.91(7)
Chromophore	CuO_5N	CuO_4N	CuO_4N
Cu-out of plane		0.2563(16)	0.253(1)

[a]Ref. [4]; [b]Ref. [5].

The results of preliminary screening are presented in Table 6, showing that the tested compounds differ in their antimicrobial and filamentous fungi activities. The highest inhibition activity against *S. aureus* as well as Filamentous fungi shows [Cu(pydca)(H_2O)$_2$]. This proves clearly that in [Cu(pydca)(H_2O)$_2$] exists a cooperative effect between the copper(II) and pyridine-2,6-dicarboxylate. On the other hand, the additional N-donor ligand, as nicotinamide or ronicol, made a somewhat weaker the cooperative effect, which influences the respective inhibitions. The experimental facts indicate, that the free ligands, as well as their copper(II) compounds, exhibit almost the same inhibition action againts yeasts (Table 6).

Table 6. Antimicrobial activity of pydcaH$_2$, ron, nia and their copper(II) complexes (IC$_{50}$ and MIC m mol^{-1}).

Compound	Bacteria				Yeasts			
	S. aureus		*E. coli*		*C. albicans*		*C. parapsilosis*	
	IC$_{50}$	MIC	IC$_{50}$	MIC	IC$_{50}$	MIC	IC$_{50}$	MIC
pydcaH$_2$	>5	>5	>5	>5	>5	>5	>5	>5
[Cu(pydca)(H$_2$O)]	>5	>5	>5	>5	>5	>5	>5	>5
[Cu(pydca)(ron)]	>5	>5	>5	>5	>5	>5	>5	>5
[Cu(pydca)(nia)]	>5	>5	>5	>5	>5	>5	>5	>5
ron	>5	>5	>5	>5	>5	>5	>5	>5
nia	>5	>5	>5	>5	>5	>5	>5	>5

Compound	Filamentous Fungi							
	R. oryzae		*A. alternate*		*B. cinerea*		*M. gypseum*	
	IC$_{50}$	MIC	IC$_{50}$	MIC	IC$_{50}$	MIC	IC$_{50}$	MIC
pydcaH$_2$	3.6	5s	6.3	10s	3.5	5s	< 2.5	≤ 2.5s
[Cu(pydca)(H$_2$O)]	2.7	5s	7	10s	3.5	5c	3.8	10s
[Cu(pydca)(ron)]	5.6	> 10	>10	>10	3.5	5c	5.5	>10
[Cu(pydca)(nia)]	<2.5	5s	8.7	>10	4.2	10s	6	>10
ron	>10	> 10	>10	>10	>10	>10	>10	>10
nia	>10	> 10	>10	>10	5	>10	>10	>10

s – concentration inducing a microbicidal effect
c – concentration inducing a microbistatical effect

Acknowledgment

This work was supported in part from Grant No. 3T09A03915 of the Polish State Committee for Scientific Research.

REFERENCES

1. Melnik M., *Coord. Chem. Rev.*, **36**, 42 (1981).
2. Melnik M., *Coord. Chem. Rev.*, **42**, 259 (1982).
3. Melnik M., Kabešová M, Macášková L. and Holloway C.E., *J. Coord. Chem.*, **45**, 31 (1998).
4. Biagini Cingi M., Chilsi Villa A., Guastini C. and Nardelli M., *Gazz. Chim. Ital.*, **101**, 825 (1971).
5. Sileo E.E., Rigotti G., Rivero B.E. and Blesa M.A., *J. Phys. Chem. Solids*, **58**, 1127 (1997).
6. Ang H.-G., Kwik W.-L., Hanson G.R., Crowther J.A., McPartlin M. and Choi N., *J. Chem. Soc., Dalton Trans.*, 3193 (1991).
7. Su C.-C. and Chiu S.-Y., *Polyhedron*, **15**, 2623 (1996).
8. Figgis B.N. and Nyholm R.S., *J. Chem. Soc.*, 4190 (1958).
9. König E., "Magnetic Properties of Coordination and Organometallic Transition Metal Compounds", Springer-Verlag, Berlin, (1966).
10. Pavelčík F., *Program XP2$_1$*, Comenius Univ. Pharmaceutical Fac., Bratislava, Slovakia, (1993).
11. Sheldrick G.M., *SHELXS86*, (Crystallographic Computing 3, Sheldrick G.M., Krueger C. and Goddard R.) (1985), p. 175. Oxford University Press.
12. Sheldrick G.M., *SHELXL93*, Program for Refinement of Crystal Structure. Univ. of Göttingen, Germany, (1994).
13. Johnson C.K., *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, (1965).
14. Jantová S., Hudecová D., Stankovský S., Špirková K. and Ru[etová L., *Folia Microbiol.*, **40**, 611 (1995).
15. Hudecová D., Jantová S., Melnik M. and Uher M., *Folia Microbiol.*, **41**, 473 (1996).
16. Deacon G.B. and Philips R.J., *Coord. Chem Rev.*, **33**, 227 (1980).
17. Nakamoto K., Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley-Interscience, NY, pp. 231 (1978).
18. Nakamoto K., Morimoto Y. and Martel A.E., *J. Am. Chem. Soc.*, **83**, 4528 (1961).
19. Melnik M., *Coord. Chem. Rev.*, **47**, 239 (1982).