Characterization of Some New Mg(II) Complexes with Heterocyclic *N*-Donor Ligands and their Antimicrobial Effects

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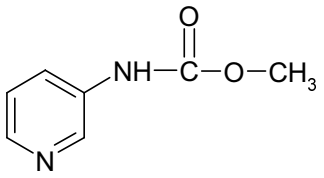
Synthesis, analytical data, IR spectra, as well as antimicrobial activities of 14 Mg(II) compounds are presented. Antimicrobial activities of 4 free ligands were also tested. By means of IR spectral analysis the stereochemistry around Mg(II) atom in the complexes had been studied. Methyl (3-pyridyl)carbamate (mpc), 3-(hydroxymethyl)pyridine (ron), and caffeine (caf) were coordinated to Mg(II) through the nitrogen atom of the respective heterocyclic ring. IR data suggest a unidentate coordination of carboxylate ions to Mg(II). The antimicrobial effects have been tested on various strains of filamentous fungi. A significant morphological change of *Botrytis cinerea* was observed with the compounds $Mg(SCN)_2(mpc)_2 \cdot 3H_2O$ and $Mg(SCN)_2(caf)_2 \cdot 7H_2O$. The highest antimicrobial effects were manifested by the compound $Mg(pc) \cdot H_2O$ (pc = pyridine-2,6-dicarboxylate), especially against filamentous fungi *R. oryzae* and dermatophytic fungi *Microsporum gypseum* (IC_{50} = 320 μg cm^{-3} and 537 μg cm^{-3}, respectively). Antimicrobial effect of the compounds is decreased in the sequence: *Microsporum gypseum*, *Botrytis cinerea*, *Rhizopus oryzae*, *Fusarium nivale*, and *Alternaria alternata*.

It is well known that many metal cations play an active role in a great number of various biological processes [1]. An antimicrobial effect was observed for Mg(II) azidokojate [2]. It is also well known that heterocyclic compounds play a significant role in many biological systems. Especially six-membered ring system is a component of several vitamins and drugs [3]. Therefore, it is not surprising that many authors have investigated heterocyclic compounds as ligands in coordination complexes of several central atoms and also examined their antimicrobial activities [4—18]. From our point of view it was challenging to study the interactions between metal ions and heterocyclic nitrogen compounds that occur in living systems and are used as medicaments. This work is a continuation of our previously reported studies [19—30]. There had been studied the antimicrobial activities of some Cu(II), Ni(II), and Fe(III) compounds [1]. But the reported data on antimicrobial activities and IR spectra of Mg(II) compounds are too rare. The present work was aimed at the study of IR spectra and antifungal efficiency of Mg(II) compounds with the bioactive ligands: methyl (3-pyridyl)carbamate, pyridine-2,6-dicarboxylic acid (pch), 3-(hydroxymethyl)pyridine, and caffeine.

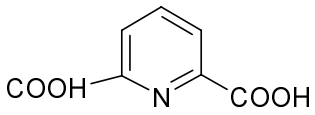
EXPERIMENTAL

Elemental analyses (C, H, N) were carried out by means of an Erba 1106 analyzer. The IR spectra were obtained on Philips analytical PU9800 FTIR spectrometer by using Nujol mulls in the range 200—4000 cm^{-1}.

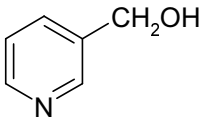
The effect on *Rhizopus oryzae*, *Botrytis cinerea*, and phytopathogenic fungi *Alternaria alternata* and *Fusarium nivale* (obtained from the Collection of Microorganisms of the Department of Biochemistry and Microbiology, Faculty of Chemical Technology, Slovak University of Technology) and dermatophytic strains *Microsporum gypseum* (isolated from patients) was tested during static culturing. 0.1 cm^3 of the tested compound in dimethyl sulfoxide (DMSO) was added to Petri dishes immediately before pouring 10 cm^3 of malt extract agar (phytopathogenic fungi and *R.*



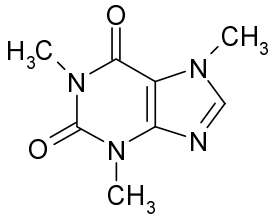
mpc



pch



ron



caf

oryzae) or Sabouraud glucose agar (*M. gypseum*) to obtain desired concentrations of inhibitors. The solidified plates were then inoculated in the centre with 0.005 cm^3 of the spore suspension (density 10^5 cm^{-3}). Duplicate sets of agar plates were incubated at 25 °C and the diameters of growing colonies were measured at intervals.

Chromatographically pure compounds were dissolved in DMSO. Their final content never exceeded 1 vol. % either with the control or the treated samples. The final content of DMSO being was not inhibitory to the cultures of tested microorganisms. The compounds under investigation were tested at concentrations ranging from 100 to 1000 μg cm^{-3}. The antifungal effect was characterized by IC_{50} values (concentration of a compound which in comparison to the control inhibits microbial growth by 50 %) and MIC values (minimal inhibitory concentration of a compound which inhibits microbial growth by 100 %). The IC_{50} values were read from toxicity curves.

MIC experiments on subculture dishes were used to assess the minimal microbicidal concentration (MMC) and minimal microbistatical (MMS) concentration values. Subcultures were prepared separately into Petri dishes containing competent agar medium for fungal strains and incubated at 25 °C for 96 h. The MMC and MMS values were taken as the lowest concentration which showed no visible (MMC) or visible (MMS) growth of microbial colonies in the subculture dishes.

Complexes *I*—*XIV*

$Mg(ac)_2(mpc)_3 \cdot 3H_2O$ (*I*), $Mg(Clac)_2(mpc)_2 \cdot 3H_2O$ (*II*), $Mg(Cl_3ac)_2(mpc)_2 \cdot 3H_2O$ (*III*), $Mg(SCN)_2(mpc)_2 \cdot 3H_2O$ (*IV*), where ac = CH_3COO^-, Clac = $ClCH_2COO^-$, Cl_3ac = Cl_3CCOO^- were prepared by dissolving mpc (0.01 mol) in 100 cm^3 of methanol and by gradually adding methanol solution of appropriate acetato-, halogenoacetato- or thiocyanato-Mg(II) compounds in the mole ratio 4:1. The solutions were reduced in volume at room temperature and left to crystallize. The complexes formed were filtered off, washed with ether and dried at room temperature.

Compounds $Mg(pc) \cdot H_2O$ (*V*) and $Mg(pc) \cdot 4H_2O$ (*VI*) were prepared by dissolving $Mg(OH)_2$ and $MgCl_2 \cdot 6H_2O$ (0.01 mol), respectively in 100 cm^3 of methanol and by gradually adding pyridine-2,6-dicarboxylic acid (0.01 mol). The solutions were reduced in volume at room temperature and left to crystallize. The complexes which formed, were filtered off, washed with ether and dried at room temperature.

$Mg(Clac)_2(ron)_2 \cdot 3H_2O$ (*VII*), $Mg(Cl_2ac)_2(ron)_2 \cdot 3H_2O$ (*VIII*), $Mg(Cl_3ac)_2(ron)_2 \cdot 3H_2O$ (*IX*), and $Mg(SCN)_2(ron)_2 \cdot 3H_2O$ (*X*), Cl_2ac = Cl_2CHCOO^-, were prepared by treating 3-(hydroxymethyl)pyridine (0.01 mol) with appropriate halogenoacetato- and thiocyanato-Mg(II) complexes (0.005 mol), respectively in 100 cm^3 of hot ethanol solution. The solutions were left to stand at room temperature. The fine microcrystals that precipitated were filtered off, washed with cold ethanol and dried at room temperature.

$Mg(ac)_2(caf)_2 \cdot 3H_2O$ (*XI*), $Mg(Clac)_2(caf) \cdot 2H_2O$ (*XII*), $Mg(Cl_3ac)_2(caf)_2 \cdot 5H_2O$ (*XIII*), and $Mg(SCN)_2(caf)_2 \cdot 7H_2O$ (*XIV*) were prepared by treating caffeine with appropriate acetato-, halogenoacetato- or thiocyanato-Mg(II) complexes, respectively in 200 cm^3 of hot ethanol solution in the mole ratio 2:1. The solutions were left to stand at room temperature. The fine microcrystals that precipitated were filtered off, washed with cold ethanol and dried at room temperature.

RESULTS AND DISCUSSION

The new Mg(II) complexes reported in this paper are soluble in water, ethanol, methanol, acetone, and DMSO. The content of carbon, hydrogen, and nitrogen was determined by elemental analysis and the content of magnesium was established by complexometric titration. The analyses confirm (Table 1) the theoretical composition of the complexes *I*—*XIV* (variation $< 1\%$).

The modes of the coordinated ligands in the complexes have been investigated by means of infrared absorption spectra. The most important infrared spectral data are reported in Tables 2 and 3. The ab-

Table 1. Analytical Data of the Complexes *I*—*XIV*

	w_i(calc.)/% w_i(found)/%			
Complex	C	H	N	Mg
I	45.96	5.52	19.16	3.72
	45.71	5.64	19.23	3.71
II	37.92	4.56	12.68	4.27
	37.49	4.49	12.44	4.25
III	30.54	3.11	11.37	3.45
	30.49	3.10	11.25	3.47
IV	38.50	4.41	16.84	4.87
	38.40	4.38	16.79	4.85
V	40.13	2.39	6.69	11.61
	40.06	2.36	6.71	11.60
VI	31.90	4.18	5.31	9.23
	31.60	4.28	5.25	9.23
VII	39.73	4.96	5.79	5.03
	39.75	4.93	5.75	5.05
VIII	34.77	3.98	5.07	4.40
	34.70	4.08	5.12	4.42
IX	30.91	3.22	4.51	3.91
	30.89	3.20	4.42	3.90
X	40.75	4.85	13.58	5.89
	40.70	4.86	13.59	5.85
XI	41.05	5.47	11.37	4.16
	41.09	5.36	11.25	4.15
XII	32.62	4.08	12.68	5.51
	32.97	4.13	12.44	5.50
XIII	29.00	3.63	13.53	2.94
	29.10	3.65	13.52	2.95
XIV	32.99	5.19	21.38	3.71
	33.13	5.20	21.39	3.70

Table 2. Infrared Spectral Data ($\tilde{\nu}$/cm^{-1} 200—4000)

Assignment	mpc	caf	*I*	*II*	*III*	*V*	*XI*	*XII*	*XIII*
ν(CO)	1686	1659	1657	1686	1686		1662	1644	1663
ν(CN)	1586	1599	1601	1602	1603	1598	1607	1608	1605
γ(CCC)	669, 639	644	677, 640	639, 621	680, 637	648	667, 610	698, 610	682, 613
ν_{as}(COO$^-$)			1728	1728	1723	1698	1698	1701	1713
ν_{s}(COO$^-$)			1420	1429	1416	1410	1463	1408	1410
Δ_{COO}			308	299	307	288	235	293	303
ν(C—C)	932	974	926	933	918	995	972	974	976
ν(C—H)$_{ac}$			2849	2959	2853	2849	2847	2845	2849
ν(OH)			3614	3528	3308	3420	3335	3366	3380
δ(HOH)			1620	1616	1638	1603	1655	1643	1651
Others			769, 804,	770, 802,	723, 736,	702, 723,	744, 758,	747, 760,	742, 760,
(650—1000 cm^{-1})			889, 906	860, 833	773, 839	752, 783	760, 788	783, 864	804, 833
			926, 945	899, 949	902, 939	854, 918	800, 925	951	841, 941
$\pi(CO_2)$			544	544	533	537	538	542	543

as = antisymmetric, s = symmetric.

Table 3. Infrared Spectral Data ($\tilde{\nu}$/cm^{-1} 200—4000)

Assignment	ron	*IV*	*X*	*XIV*	*VI*	*VII*	*VIII*	*IX*
ν(CN)$_{\mathrm{ring}}$	1597	1601	1609	1608	1598	1608	1609	1608
γ(CCC)	640	631	650	644	648	619	637	646
ν(C—C)	953				997	955	952	949
ν_{as}(COO$^-$)					1703	1684	1732	1665
ν_{s}(COO$^-$)					1414	1346	1462	1366
Δ_{COO}					289	338	270	299
ν(CN)		2103	2116	2143				
		2056	2068	2039				
ν(CS)		810	810	806				
δ(NCS)		476	473	476				
ν(OH)		3374	3333	3343	3389	3277	3366	3380
δ(HOH)		1611	1607	1613	1639	1637	1631	1607
Others		775, 862,	650, 789,	686, 738,	696, 709,	610, 694,	610, 772,	613, 677,
(600—1000 cm^{-1})		911, 936,	823, 939,	748, 764,	720, 750,	770, 816,	812, 895,	802, 831,
		955, 982	987	855, 930	852, 920	893, 984	937	938
π(CO$_2$)					537	536	540	539

as = antisymmetric, s = symmetric.

Table 4. Antimicrobial Activity (IC$_{50}$/(μg cm^{-3}) and MIC/(μg cm^{-3})) of Mg(II) Compounds

Compound	1		2		3		4		5	
	{IC$_{50}$}	{MIC}	{IC$_{50}$}	{MIC}	{IC$_{50}$}	{MIC}	{IC$_{50}$}	{MIC}	{IC$_{50}$}	{MIC}
I	>1000		>1000		1000	>1000	>1000		1000	>1000
II	in		in		in		in		>1000	
III	>1000		>1000		>1000		in		>1000	
IV	in		>1000		1000	>1000	>1000		>1000	
V	1000	>1000	320	1000^s	600	700^s	615	800^c	537	1000^c
VI	>1000		>1000		in		>1000		1000	>1000
VII	in		in		in		x		>1000	
VIII	in		in		in		x		>1000	
IX	in		in		in		x		>1000	
X	in		in		in		x		>1000	
XI	>1000		>1000		>1000		x		230	1000^s
XII	in		in		>1000		x		400	>1000
XIII	>1000		>1000		>1000		x		120	1000^s
XIV	>1000		>1000		1000	>1000	x		115	1000^s
ron	in		in		>1000		x		>1000	
caf	>1000		>1000		660	>1000	x		90	500^s
mpc	>1000		>1000		630	1000^c	1000	>1000	750	1000^s
pc	580	>1000	200	1000^s	600	700^c	735	800^c	560	1000^c

1 – *A. alternata*, 2 – *R. oryzae*, 3 – *B. cinerea*, 4 – *F. nivale*, 5 – *M. gypseum*.
in = no inhibition of growth of microorganisms in concentration 1000 μg cm^{-3}, x = not tested, *c* – microbicidal effect, *s* – microbistatical effect.

sorption bands which occur in the range 3277—3614 cm^{-1} (symmetric and antisymmetric OH stretching) and 1607—1651 cm^{-1} δ(HOH bending) confirm the presence of water of crystallization [31]. Carboxylate ions can coordinate to metal ions in a number of ways such as unidentate, bidentate (chelating) or bridging and there is an evidence of that fact in the IR spectrum. The analysis of COO$^-$ group bands frequencies allowed the determination of parameter $\Delta_{\mathrm{COO}} = \tilde{\nu}(\nu_{\mathrm{as}}(\mathrm{COO}^-)) - \tilde{\nu}(\nu_{\mathrm{s}}(\mathrm{COO}^-))$. The magnitude of Δ_{COO} has been used by *Nakamoto* [32] as a criterion of the way of carboxylate binding with metal ions. Calculated from the examined spectra the values of Δ_{COO} are in the $\tilde{\nu}$ range 235—338 cm^{-1}. These values and three bands (COO$^-$ deformation) at 720—920 cm^{-1} and a strong band (π(CO)$_2$) near 540 cm^{-1} [32] of carboxylato-Mg(II) complexes are in good accord with the literature data for unidentately bonded carboxylate structures.

The stretching vibration of the C=N in the pyridine ring of mpc, caf, and ron appeared at 1586, 1599, and 1597 cm^{-1}, respectively. Upon complex formation

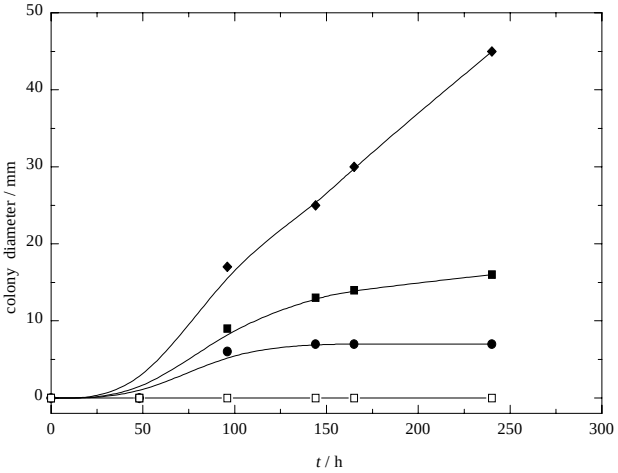


Fig. 1. Colony growth inhibition of *Microsporum gypseum* by compound *XIII*. Final concentration numerical values of compound $\rho/(\mu g\ cm^{-3})$: □ 1000, ● 500, ■ 250, ♦ 0.

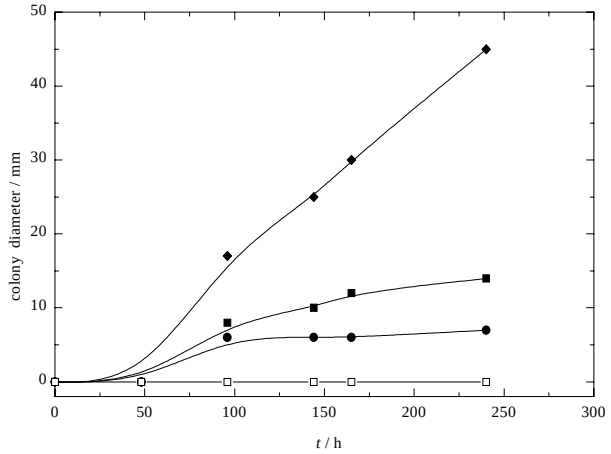


Fig. 2. Colony growth inhibition of *Microsporum gypseum* by compound *XIV*. Final concentration numerical values of compound $\rho/(\mu g\ cm^{-3})$: □ 1000, ● 500, ■ 250, ♦ 0.

the peak shifts to higher frequencies [33]. The shifts (to about 1605 cm^{-1}) in complexes may suggest the bond formation of the metal with the nitrogen of respective pyridine ring [34].

The SCN group may coordinate to a metal through the nitrogen or the sulfur or both (M—NCS—M′). Several empirical criteria have been developed to determine the bonding type of the NCS group in metal complexes [32]. The absorption bands which occur in the range 2039—2143 cm^{-1} (CN stretching) and 806—827 cm^{-1} (CS stretching for *N*-bonded and δ(NCS) stretching near 480 cm^{-1} for *N*-bonded) confirm the coordination of the SCN group to Mg(II) through nitrogen in complexes *IV*, *X*, and *XIV*.

Thermal decomposition of these compounds is the multistage process. The composition of the complexes and the solid state intermediate and resultant products of thermolysis had been identified by means of elemental analysis and complexometric titration. The possible scheme of destruction of the complexes are suggested in [28, 30, 35, 36]. Heating the compounds first results in a release of water molecules. The final product of the thermal decomposition was MgO.

Antimicrobial activity of the 14 Mg(II) compounds and 4 free ligands was investigated against 5 different fungal strains. Antimicrobial activity of the compounds characterized by the IC_{50} and MIC is summarized in Table 4. The compounds *IV* and *XIV* induced morphological changes in growing hyphae of *B. cinerea* at concentration which partially inhibited growth. The highest antimicrobial activity was manifested by the compound *V* and pyridine-2,6-dicarboxylic acid. The most sensitive fungi to the compound *V* were *R. oryzae*, *M. gypseum, B. cinerea*, and *F. nivale* ($IC_{50}/(\mu g\ cm^{-3})$ = 320, 537, 600, and 615, respectively). The MIC values of that compound against *R. oryzae* and *B. cinerea* were 1000 $\mu g\ cm^{-3}$ and 700 $\mu g\ cm^{-3}$, respectively. Microbicidal effect of that compound at 1000 $\mu g\ cm^{-3}$ was also observed on *B. cinerea*. The MIC values of that compound against *F. nivale* and *M. gypseum* were 800 $\mu g\ cm^{-3}$ and 1000 $\mu g\ cm^{-3}$, respectively and the effect was microbicidal. The most sensitive fungi to the ligand pyridine-2,6-dicarboxylic acid were *R. oryzae*, *M. gypseum*, *A. alternata*, *B. cinerea,* and *F. nivale* ($IC_{50}/(\mu g\ cm^{-3})$ = 200, 560, 580, 600, and 700, respectively). The MIC/($\mu g\ cm^{-3}$) values of that compound against *B. cinerea*, *F. nivale*, *R. oryzae,* and *M. gypseum* were 700, 800, 1000, and 1000, respectively. Microbicidal effect on *B. cinerea*, *F. nivale,* and *M. gypseum* and microbistatical effect on *R. oryzae* of that compound were observed. On the whole, *M. gypseum* was the most sensitive fungi to the tested compounds. The efficiency of the tested compounds on *M. gypseum* is lowered in the sequence: caffeine, *XIV*, *XIII*, *XI*, *XII*, *V*, pch, mpc, *I* = *VI*, *II* = *III* = *IV* = *VII* = *VIII* = *IX* = *X* = ron. Figs. 1 and 2 illustrate the growth inhibition of *M. gypseum* by the compounds *XIII* and *XIV*. Sensibility of fungi to the tested compounds is decreased in the sequence: *Microsporum gypseum*, *Botrytis cinerea*, *Rhizopus oryzae*, *Fusarium nivale,* and *Alternaria alternata*. Upon complex formation, antimicrobial efficiency of ron almost did not change but of caf and mpc decreased. The highest differences were observed in the case of pch. Upon complex formation its antimicrobial efficiency was increased against *F. nivale* and *M. gypseum*, not changed against *B. cinerea* (compound *V*) and decreased in other cases. The antimicrobial activity of simple Mg salts was also tested. Simple Mg salts were inactive on tested microorganisms ($IC_{50} > 1000\ \mu g\ cm^{-3}$).

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