

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

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Received 29 October 1998

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  $\text{Mg}(\text{SCN})_2(\text{mpc})_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Mg}(\text{SCN})_2(\text{caf})_2 \cdot 7\text{H}_2\text{O}$ . The highest antimicrobial effects were manifested by the compound  $\text{Mg}(\text{pc}) \cdot \text{H}_2\text{O}$  (pc = pyridine-2,6-dicarboxylate), especially against filamentous fungi *R. oryzae* and dermatophytic fungi *Microsporum gypseum* ( $\text{IC}_{50} = 320 \mu\text{g cm}^{-3}$  and  $537 \mu\text{g cm}^{-3}$ , respectively). Antimicrobial effect of the compounds is decreased in the sequence: *Microsporum gypseum*, *Botrytis cinerea*, *Rhizopus oryzae*, *Fusarium nivale*, and *Alternaria alternata*.

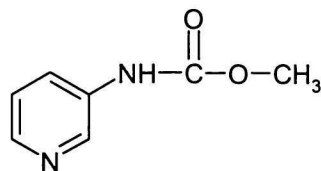
It is well known that many metal cations play an active role in a great number of various biological processes [1]. An antimicrobial effect was observed for Mg(II) azidokojate [2]. It is also well known that heterocyclic compounds play a significant role in many biological systems. Especially six-membered 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.

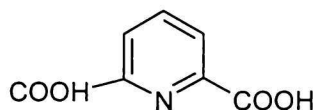
## EXPERIMENTAL

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  $\text{cm}^{-1}$ .

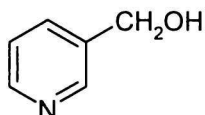
The effect on *Rhizopus oryzae*, *Botrytis cinerea*, and phytopathogenic fungi *Alternaria alternata* and *Fusarium nivale* (obtained from the Collection of Microorganisms of the Department of Biochemistry and Microbiology, Faculty of Chemical Technology, Slovak University of Technology) and dermatophytic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



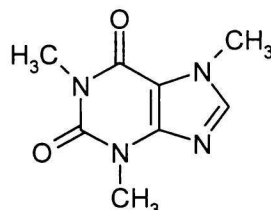
mpc



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  $0.005 \text{ cm}^3$  of the spore suspension (density  $10^5 \text{ cm}^{-3}$ ). Duplicate sets of agar plates were incubated at  $25^\circ \text{C}$  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  $1000 \mu\text{g cm}^{-3}$ . The antifungal effect was characterized by  $\text{IC}_{50}$  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  $\text{IC}_{50}$  values were read from toxicity curves.

MIC experiments on subculture dishes were used to assess the minimal microbicidal concentration (MMC) and minimal microbistatistical (MMS) concentration values. Subcultures were prepared separately into Petri dishes containing competent agar medium for fungal strains and incubated at  $25^\circ \text{C}$  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

$\text{Mg}(\text{ac})_2(\text{mpc})_3 \cdot 3\text{H}_2\text{O}$  (I),  $\text{Mg}(\text{Clac})_2(\text{mpc})_2 \cdot 3\text{H}_2\text{O}$  (II),  $\text{Mg}(\text{Cl}_3\text{ac})_2(\text{mpc})_2 \cdot 3\text{H}_2\text{O}$  (III),  $\text{Mg}(\text{SCN})_2(\text{mpc})_2 \cdot 3\text{H}_2\text{O}$  (IV), where  $\text{ac} = \text{CH}_3\text{COO}^-$ ,  $\text{Clac} =$

$\text{ClCH}_2\text{COO}^-$ ,  $\text{Cl}_3\text{ac} = \text{Cl}_3\text{CCOO}^-$  were prepared by dissolving mpc (0.01 mol) in  $100 \text{ cm}^3$  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  $\text{Mg}(\text{pc}) \cdot \text{H}_2\text{O}$  (V) and  $\text{Mg}(\text{pc}) \cdot 4\text{H}_2\text{O}$  (VI) were prepared by dissolving  $\text{Mg}(\text{OH})_2$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (0.01 mol), respectively in  $100 \text{ cm}^3$  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.

$\text{Mg}(\text{Clac})_2(\text{ron})_2 \cdot 3\text{H}_2\text{O}$  (VII),  $\text{Mg}(\text{Cl}_2\text{ac})_2(\text{ron})_2 \cdot 3\text{H}_2\text{O}$  (VIII),  $\text{Mg}(\text{Cl}_3\text{ac})_2(\text{ron})_2 \cdot 3\text{H}_2\text{O}$  (IX), and  $\text{Mg}(\text{SCN})_2(\text{ron})_2 \cdot 3\text{H}_2\text{O}$  (X),  $\text{Cl}_2\text{ac} = \text{Cl}_2\text{CHCOO}^-$ , were prepared by treating 3-(hydroxymethyl)pyridine (0.01 mol) with appropriate halogenoacetato- and thiocyanato-Mg(II) complexes (0.005 mol), respectively in  $100 \text{ cm}^3$  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.

$\text{Mg}(\text{ac})_2(\text{caf})_2 \cdot 3\text{H}_2\text{O}$  (XI),  $\text{Mg}(\text{Clac})_2(\text{caf}) \cdot 2\text{H}_2\text{O}$  (XII),  $\text{Mg}(\text{Cl}_3\text{ac})_2(\text{caf})_2 \cdot 5\text{H}_2\text{O}$  (XIII), and  $\text{Mg}(\text{SCN})_2(\text{caf})_2 \cdot 7\text{H}_2\text{O}$  (XIV) were prepared by treating caffeine with appropriate acetato-, halogenoacetato- or thiocyanato-Mg(II) complexes, respectively in  $200 \text{ cm}^3$  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*

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

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

Assignment	mpc	caf	<i>I</i>	<i>II</i>	<i>III</i>	<i>V</i>	<i>XI</i>	<i>XII</i>	<i>XIII</i>
$\nu(\text{CO})$	1686	1659	1657	1686	1686		1662	1644	1663
$\nu(\text{CN})$	1586	1599	1601	1602	1603	1598	1607	1608	1605
$\gamma(\text{CCC})$	669, 639	644	677, 640	639, 621	680, 637	648	667, 610	698, 610	682, 613
$\nu_{\text{as}}(\text{COO}^-)$			1728	1728	1723	1698	1698	1701	1713
$\nu_{\text{s}}(\text{COO}^-)$			1420	1429	1416	1410	1463	1408	1410
$\Delta_{\text{COO}}$			308	299	307	288	235	293	303
$\nu(\text{C—C})$	932	974	926	933	918	995	972	974	976
$\nu(\text{C—H})_{\text{ac}}$			2849	2959	2853	2849	2847	2845	2849
$\nu(\text{OH})$			3614	3528	3308	3420	3335	3366	3380
$\delta(\text{HOH})$			1620	1616	1638	1603	1655	1643	1651
Others			769, 804,	770, 802,	723, 736,	702, 723,	744, 758,	747, 760,	742, 760,
(650—1000 $\text{cm}^{-1}$ )			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
$\pi(\text{CO}_2)$			544	544	533	537	538	542	543

as = antisymmetric, s = symmetric.

**Table 3.** Infrared Spectral Data ( $\bar{\nu}/\text{cm}^{-1}$  200–4000)

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

as = antisymmetric, s = symmetric.

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

Compound	1		2		3		4		5	
	{IC <sub>50</sub> }	{MIC}	{IC <sub>50</sub> }	{MIC}	{IC <sub>50</sub> }	{MIC}	{IC <sub>50</sub> }	{MIC}	{IC <sub>50</sub> }	{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 <sup>s</sup>	600	700 <sup>s</sup>	615	800 <sup>c</sup>	537	1000 <sup>c</sup>
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 <sup>s</sup>
XII	in		in		>1000		x		400	>1000
XIII	>1000		>1000		>1000		x		120	1000 <sup>s</sup>
XIV	>1000		>1000		1000	>1000	x		115	1000 <sup>s</sup>
ron	in		in		>1000		x		>1000	
caf	>1000		>1000		660	>1000	x		90	500 <sup>s</sup>
mpc	>1000		>1000		630	1000 <sup>c</sup>	1000	>1000	750	1000 <sup>s</sup>
pc	580	>1000	200	1000 <sup>s</sup>	600	700 <sup>c</sup>	735	800 <sup>c</sup>	560	1000 <sup>c</sup>

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  $\mu\text{g cm}^{-3}$ , x = not tested, c – microbicidal effect, s – microbistatistical effect.

sorption bands which occur in the range 3277–3614  $\text{cm}^{-1}$  (symmetric and antisymmetric OH stretching) and 1607–1651  $\text{cm}^{-1}$   $\delta(\text{HOH}$  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  $\text{COO}^-$  group bands frequencies allowed the determination of parameter  $\Delta_{\text{COO}} = \bar{\nu}(\nu_{\text{as}}(\text{COO}^-)) - \bar{\nu}(\nu_{\text{s}}(\text{COO}^-))$ . The magnitude of  $\Delta_{\text{COO}}$  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  $\Delta_{\text{COO}}$  are in the  $\bar{\nu}$  range 235–338  $\text{cm}^{-1}$ . These values and three bands ( $\text{COO}^-$  deformation) at 720–920  $\text{cm}^{-1}$  and a strong band ( $\pi(\text{CO})_2$ ) near 540  $\text{cm}^{-1}$  [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  $\text{cm}^{-1}$ , respectively. Upon complex formation

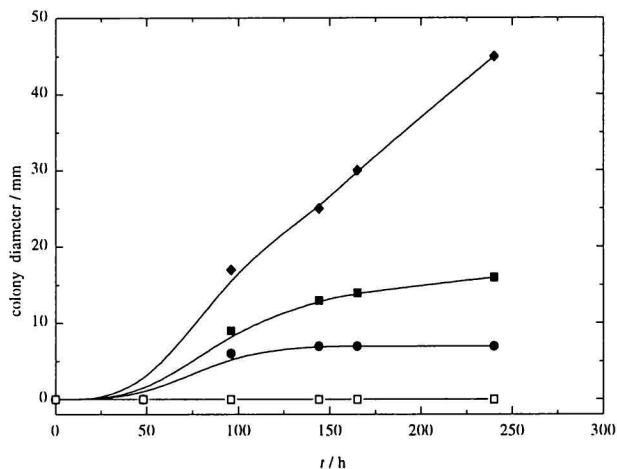


Fig. 1. Colony growth inhibition of *Microsporum gypseum* by compound XIII. Final concentration numerical values of compound  $\rho/(\mu\text{g cm}^{-3})$ :  $\square$  1000,  $\bullet$  500,  $\blacksquare$  250,  $\blacklozenge$  0.

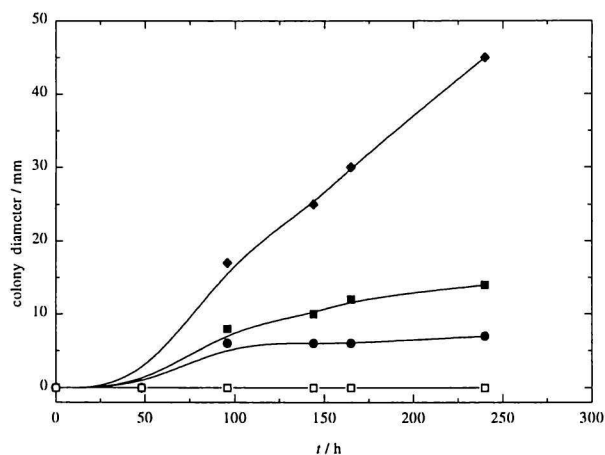


Fig. 2. Colony growth inhibition of *Microsporum gypseum* by compound XIV. Final concentration numerical values of compound  $\rho/(\mu\text{g cm}^{-3})$ :  $\square$  1000,  $\bullet$  500,  $\blacksquare$  250,  $\blacklozenge$  0.

the peak shifts to higher frequencies [33]. The shifts (to about  $1605\text{ cm}^{-1}$ ) 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 ( $\text{M}-\text{NCS}-\text{M}'$ ). 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  $2039-2143\text{ cm}^{-1}$  (CN stretching) and  $806-827\text{ cm}^{-1}$  (CS stretching for *N*-bonded and  $\delta(\text{NCS})$  stretching near  $480\text{ cm}^{-1}$  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 prod-

ucts 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  $\text{IC}_{50}$  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* ( $\text{IC}_{50}/(\mu\text{g cm}^{-3}) = 320, 537, 600, \text{ and } 615$ , respectively). The MIC values of that compound against *R. oryzae* and *B. cinerea* were  $1000\text{ }\mu\text{g cm}^{-3}$  and  $700\text{ }\mu\text{g cm}^{-3}$ , respectively. Microbicidal effect of that compound at  $1000\text{ }\mu\text{g cm}^{-3}$  was also observed on *B. cinerea*. The MIC values of that compound against *F. nivale* and *M. gypseum* were  $800\text{ }\mu\text{g cm}^{-3}$  and  $1000\text{ }\mu\text{g cm}^{-3}$ , 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* ( $\text{IC}_{50}/(\mu\text{g cm}^{-3}) = 200, 560, 580, 600, \text{ and } 700$ , respectively). The MIC/ $(\mu\text{g cm}^{-3})$  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 microbistatistical 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,  $I = \text{VI}$ ,  $\text{II} = \text{III} = \text{IV} = \text{VII} = \text{VIII} = \text{IX} = \text{X} = \text{ron}$ . 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 ( $\text{IC}_{50} > 1000\text{ }\mu\text{g cm}^{-3}$ ).

*Acknowledgements.* This study was supported by the Grant Agency of the Slovak Ministry of Education (Registr. No. 95/5195/199, 95/909, and 1/4203/97).

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