Journal of Thermal Analysis and Calorimetry, Vol. 81 (2005) 205–210

A STUDY ON SYNTHESIS AND THERMAL, SPECTRAL AND BIOLOGICAL PROPERTIES OF CARBOXYLATO-Mg(II) AND CARBOXYLATO-Cu(II) COMPLEXES WITH BIOACTIVE LIGANDS

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Synthesis, elemental (CHN), spectral (FTIR), thermogravimetry (TG), differential thermal analysis (DTA) and complexometric titration have been applied to the investigation of the thermal behavior and structure of the complexes: $Mg(ac)_2(mpc)_3\cdot 3H_2O$(**I**), $Mg(Clac)_2(mpc)_2.3H_2O$(**II**), $Mg(Cl_2ac)_2(mpc)_2.3H_2O$(**III**), $Mg(Cl_3ac)_2(mpc)_2.3H_2O$(**IV**) and $[Cu(ac)_2(mpc)]_2\cdot 3H_2O$(**V**) (*ac*=$CH_3COO^-$, Clac=$ClCH_2COO$, $Cl_2ac=Cl_2CHCOO^-$, $Cl_3ac=Cl_3CCOO^-$ and *mpc*=methyl-3-pyridyl carbamate). Thermal decomposition of these complexes is a multi-stage processes. 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 decomposition of the complexes is suggested. Heating the complexes first resulted in a release of water molecules. The TG results show that the loss of the volatile ligand (mpc) occurs in one step for complexes **II**, **IV** and **V**, and in two steps for complexes **I** and **III**. The final solid product of thermal decomposition was MgO or CuO. The thermal stability of the complexes can be ordered in the sequence: **I**=**II**<**IV**<**III**<**V**. Mpc was coordinated to Mg(II) or Cu(II) through the nitrogen atom of its heterocyclic ring. IR data suggest to a unidentate coordination of carboxylates to magnesium or copper *n* complexes **I**–**V**. The preliminary studies have shown that the complexes do have antimicrobial activities against bacteria, yeasts and/or fungi. The highest antimicrobial activities were manifested by the complex **V**.

Keywords: *DTA, elemental analysis, IR and antimicrobial activities, Mg(II) and Cu(II) complexes, TG*

Introduction

The ability of metal cations and organic ligands is very well known to play an active role in a great number of biological processes. The activity of metallic ions and heterocyclic complexes has been examined from various points of view [1–11]. Therefore, it is not surprising that many authors have investigated heterocyclic complexes and also examined them as ligands in coordination complexes of several central atoms [12–30]. In order to enhance the understanding of drug-metal ion interactions, we have been studying the thermal properties of Mg(II) and Cu(II) complexes with methyl-3-pyridyl carbamate (Fig. 1), which is known as an important component of biological systems.

To reveal the relationship between the structure and thermolysis of metal carboxylate complexes with heterocyclic ligands, the study of the influence of metal and ligand nature on the process of thermal decomposition are of a great interest. This work is a continuation of our previously reported studies [31–45] on the thermal, spectral and biological properties of Mg(II), Cu(II), Co(II) and Fe(III) complexes with pyridine and substituted pyridines. This paper describes the preparation of Mg(II) and Cu(II) complexes, formed with the acetates and as well as methyl-3-pyridyl carbamate, along with the investigation on their thermal and spectral properties as well as their antimicrobial activities.

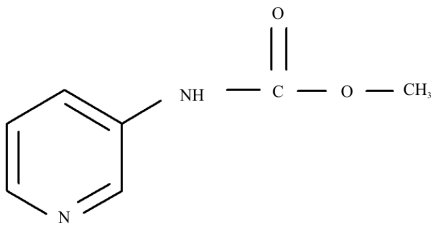

Fig. 1 Structure of methyl-3-pyridyl carbamate

Experimental

Preparation of the complexes

The complexes **I**–**V** were prepared by treating methyl-3-pyridylcarbamate (1.52 g, 0.01 mole) with

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1388–6150/$20.00

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appropriate quantity of Mg(II) or Cu(II) acetate or halogenoacetate (0.005 mole) in hot methanol solution. The solution was left to stand at room temperature. The precipitated fine micro-crystals were filtered off, washed with cold methanol and dried at room temperature.

Measurements

The infrared spectra were obtained using a Philips analytical PU9800 FTIR spectrometer with Nujol mulls in the range 200–4000 cm^{-1}, while the thermal decomposition studies were carried out on a Paulik–Paulik–Erdey Derivatograph (Type OD 102, MOM Budapest) in static air atmosphere by using a platinum crucible with a sample massof 100 mg in the range 20-1000°C. A heating rate of 10 K min^{-1} was chosen for all measurements.

The antimicrobial activity of the Mg(II) and Cu(II) complexes under investigation was evaluated by using Gram-positive bacteria (*Bacillus subtilis*), Gram-negetive bacteria (*Escherichia coli*), yeast (*Candida albicans*), filamentous fungi (*Rhizopus oryzae*, *Aspergillus flavus*, *Botrytis cinerea*, *Alternaria alternata*, and *Fusarium nivale*), and dermatophytic strains (*Microsporum gypseum* and *Trichophyton terrestre*).

To test the antimicrobial activity on bacteria and yeasts, 100 cm^3 of appropriate liquid medium (bacteria - Mueller—Hinton, yeasts - Sabouraud-glucose) was inoculated with 1 cm^3 of growing overnight culture and distributed in 5 cm^3 aliquots into L-shaped tubes (adapted for direct measurements of absorbance) with 0.05 cm^3 of solution of the tested complexes in dimethyl sulfoxide (DMSO). The cultures of bacteria and yeasts were then incubated under vigorous shaking at 30°C. Absorbances of duplicate sets of tubes were measured at λ=650 nm at intervals.

The effects on filamentous fungi were tested during static culturing. Therefore 0.06 cm^3 of the tested complexes in DMSO was added to Petri dishes (diameter 60 mm) immediately before pouring 6 cm^3 of malt extract agar (filamentous fungi) or Sabouraud-glucose agar (dermatophytes) to obtain desired concentrations of inhibitors. The solidified plates were then inoculated in the centre with 0.005 cm^3 of the spore suspension (spore density 10^5 cm^{-3}) of the filamentous fungi from 21 days old strains in 0.1 vol. % aqueous Tween 80. Duplicate sets of agar plates were incubated at 25°C and the diameters of growing colonies were measured at intervals (96, 144, 196, 360 and 384 h for *M. gypseum* and *T. terrestre*; 72, 96, 120, 144 and 168 h for *A. flavus*, *B. cinerea*, *A. alternata* and *F. nivale*; and 24 and 48 h for *R. oryzae*).

Chromatographically purified complexes were dissolved in DMSO. Its final concentration never exceeded 1 vol. % in both control and treated samples. This concentration of DMSO did not affect the growth of tested microorganisms. The complexes under investigation were tested at concentrations ranging from 100 to 1000 μg cm^{-3}. The antimicrobial effect was characterized by IC_{50} values (concentration of a compound compared 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} and MIC values could be read from the toxicity curves.

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

Results and discussion

Analysis of complexes

The content of N, C and H was determined by elemental analysis, and the contents of Mg(II) and Cu(II) were determined by complexometric titration. The analytical data of the complexes **I**–**V** reported in Table 1 are in a good agreement with the theoretical values.

Thermal behavior of the complexes

The thermal decomposition data of the complexes **I**–**V** are collected in Table 2. The thermal decomposition of the complexes is a multi-stage process. The subsequent detachment of the ligands was observed. The final product was MgO or CuO, which was identified by X-ray diffraction analysis. The TG and DTA curves for complexes **I**–**V** are shown in the Figs 2–6.

The most probable thermal decomposition scheme for complex **I** may be:

$$Mg(ac)_2(mpc)_3\cdot 3H_2O \xrightarrow{95-200^\circ C} Mg(ac)_2(mpc)_3+3H_2O$$

$$Mg(ac)_2(mpc)_3 \xrightarrow{200-290^\circ C} Mg(ac)_2(mpc)+2mpc$$

$$Mg(ac)_2(mpc) \xrightarrow{290-520^\circ C} Mg(ac)_2+mpc$$

$$Mg(ac)_2 \xrightarrow{520-650^\circ C} MgO + \text{Decomposition products}$$

The most probable thermal decomposition scheme for complex II may be:

$$Mg(Clac)_2(mpc)_2\cdot 3H_2O \xrightarrow{95-210^\circ C} Mg(Clac)_2(mpc)_2+3H_2O$$

Table 1 Analytical data of complexes

Complexes	Experimental %				Theoretical %			
	C	H	N	*M**	C	H	N	*M**
I	45.71	5.64	13.00	3.71	45.96	5.52	12.87	3.72
II	37.49	4.49	9.50	4.25	37.92	5.56	9.83	4.27
III	33.85	3.62	8.64	3.80	33.83	3.75	8.77	3.81
IV	30.49	3.10	7.71	3.47	30.54	3.11	7.92	3.45
V	34.40	4.90	8.01	18.24	34.43	4.88	8.03	18.22

* *M* = Mg(II) or Cu(II)

Table 2 Thermal decomposition data

Complexes	DTA results		TG results		
	T_{peaks}/°C	T_{range}/°C	Mass loss/ % Found (calc.)	Loss of	Composition of the residue
I	160 endo	95–200	8.27 (8.25)	$3H_2O$	
	250 endo	200–290	54.89 (54.90)	2mpc	
	350 exo	290–520	78.20 (78.20)	mpc	
	630 exo	520–700	96.28 (96.30)	2ac	MgO
II	150 endo	95–170	9.48 (9.50)	$3H_2O$	
	240 endo	170–350	62.90 (62.90)	2mpc	
	720 exo	350–800	95.72 (95.70)	2Clac	MgO
III	150 endo	130–170	8.46 (8.50)	$3H_2O$	
	210 exo	170–320	32.28 (32.30)	mpc	
	375 exo	320–480	56.12 (56.10)	mpc	
	650 exo	570–800	96.19 (96.20)	$2Cl_2ac$	MgO
IV	190 endo	105–205	7.63 (7.60)	$3H_2O$	
	250 exo	205–290	50.65 (50.70)	2mpc	
	690 exo	290–760	96.55 (96.50)	$2Cl_3ac$	MgO
V	150 endo	130–260	7.80 (7.75)	$3H_2O$	
	285 endo	260–320	48.00 (47.92)	2mpc	
	595 exo	320–650	77.10 (77.19)	2ac	CuO

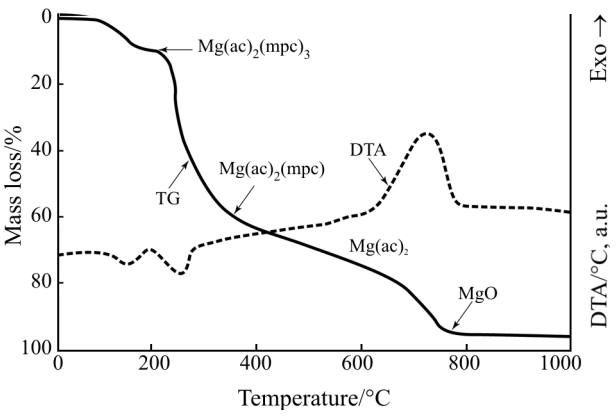

Fig. 2 TG and DTA curves of $Mg(ac)_2(mpc)_3 \cdot 3H_2O$(**I**). Sample mass: 100 mg, heating rate: 10 K min^{-1}, atmosphere: static air

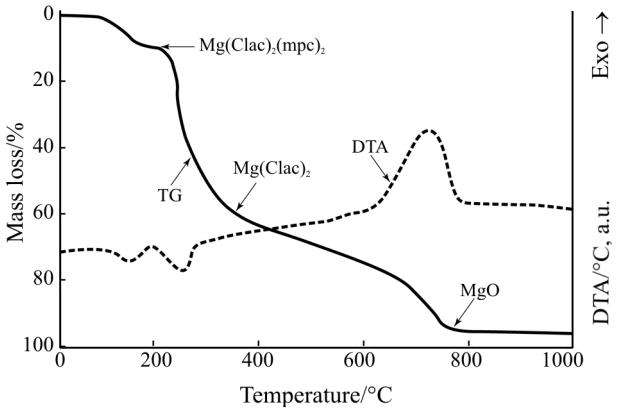

Fig. 3 TG and DTA curves of $Mg(Clac)_2(mpc)_2 \cdot 3H_2O$(**II**). Sample mass 100 mg, heating rate: 10 K min^{-1}, atmosphere: static air

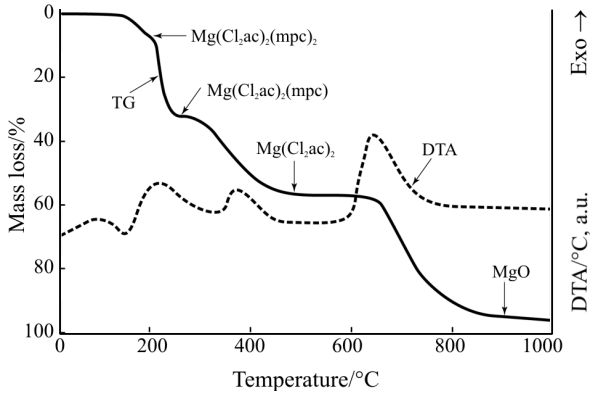

Fig. 4 TG and DTA curves of $Mg(Cl_2ac)_2(mpc)_2{\cdot}3H_2O$(III). Sample mass 100 mg, heating rate: 10 K min^{-1}, atmosphere: static air

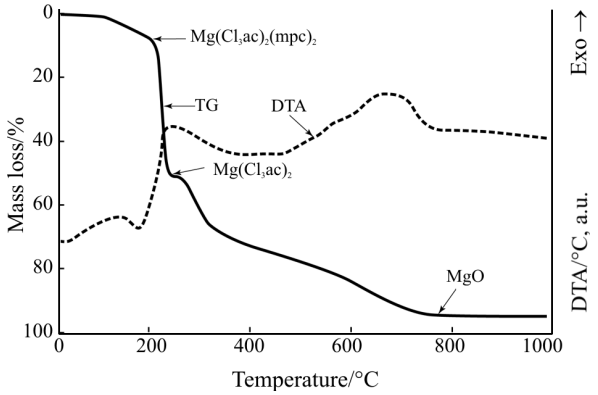

Fig. 5 TG and DTA curves of $Mg(Cl_3ac)_2(mpc)_2{\cdot}3H_2O$(IV). Sample mass 100 mg, heating rate: 10 K min^{-1}, atmosphere: static air

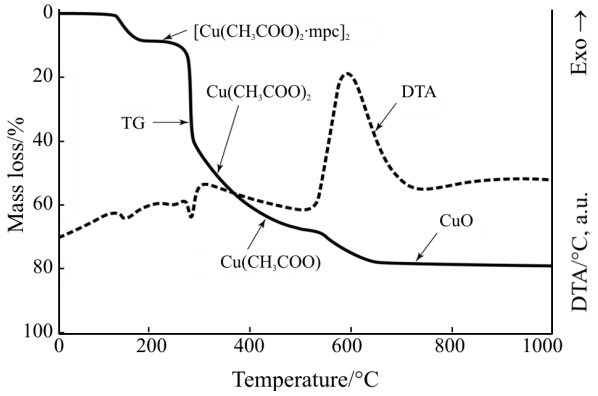

Fig. 6 TG and DTA curves of $[Cu(CH_3COO)_2.mpc]_2{\cdot}3H_2O$. Sample mass 100 mg, heating rate: 10 K min^{-1}, atmosphere: static air

$$Mg(Clac)_2(mpc)_2 \xrightarrow{210-350^\circ C} Mg(Clac)_2+2mpc$$

$$Mg(Clac)_2 \xrightarrow{350-780^\circ C} MgO+\text{Decomposition products}$$

The most probable thermal decomposition scheme for complex **III** may be:

$$Mg(Cl_2ac)_2(mpc)_2{\cdot}3H_2O \xrightarrow{130-205^\circ C} Mg(Cl_2ac)_2(mpc)_2+3H_2O$$

$$Mg(Cl_2ac)_2(mpc)_2 \xrightarrow{205-290^\circ C} Mg(Cl_2ac)_2(mpc)+mpc$$

$$Mg(Cl_2ac)_2(mpc) \xrightarrow{290-620^\circ C} Mg(Cl_2ac)_2+mpc$$

$$Mg(Cl_2ac)_2 \xrightarrow{620-620^\circ C} MgO+\text{Decomposition products}$$

The most probable thermal decomposition scheme for complex **IV** may be:

$$Mg(Cl_3ac)_2(mpc)_2{\cdot}3H_2O \xrightarrow{105-205^\circ C} Mg(Cl_3ac)_2(mpc)_2+3H_2O$$

$$Mg(Cl_3ac)_2(mpc)_2 \xrightarrow{205-290^\circ C} Mg(Cl_3ac)_2+2mpc$$

$$Mg(Cl_3ac)_2 \xrightarrow{290-760^\circ C} MgO+\text{Decomposition products}$$

The most probable thermal decomposition scheme for complex **V** may be:

$$[Cu(ac)_2mpc]_2{\cdot}3H_2O \xrightarrow{130-260^\circ C} Cu[ac)_2.mpc]_2+3H_2O$$

$$[Cu(ac)_2mpc]_2 \xrightarrow{260-320^\circ C} 2Cu(ac)_2+2mpc$$

$$Cu(ac)_2 \xrightarrow{320-650^\circ C} CuO+\text{Decomposition products}$$

IR-spectra

The modes of the coordinated ligands in the complexes have been investigated by means of infrared absorption spectra. The most important infrared frequencies attributed to the vibrations of the complexes **I**–**V** are reported in Table 3. The absorption bands ν(OH) and δ(HOH), which occur in the range 3308–3416 and 1616–1638 cm^{-1}, respectively, confirm the presence of water of crystallization. The absorption bands, which occur in the range 600–1000 cm^{-1} (Rocking and Wagging stretching) and 237–393 cm^{-1} ν(M–O) confirm the presence of water as coordinated in the complexes [46]. The presence of water as water of crystallization and as coordinated water in the complexes is further borne out by the thermal decomposition data. Carboxylate ions can coordinate to metal ions in a number of ways, such as unidentate, bidentate (chelating) or bridging, and they are observable in the IR spectra. The analysis of COO^- group bands frequencies allowed the determination of $\Delta_{COO}=\nu COO^-(as)-COO^-(s)$. The magnitude of Δ_{COO} has been used by Nakamoto [47] as a criterion for the way of carboxylate binding with metal ions. The Δ_{COO} values calculated are in the range 249–308 cm^{-1}. These Δ_{COO} values, the three bands of COO deformation at 720–920 cm^{-1}, and the strong band of $[\pi(CO_2)]$ near 540 cm^{-1} of complexes **I**–**V** agree with the literature data for unidentately bonded acetates structures [48]. The absorption bands, which occurred in the range 200–254 cm^{-1} for ν(M–N), confirm the coordination of methyl-3-pyridyl carbamate to Mg(II) and Cu(II) ions through the nitrogen atom of its heterocyclic ring.

Table 3 Infrared spectral data (4000–200 cm^{-1}) of complexes **I**–**V**

Assignment	mpc	**I**	**II**	**III**	**IV**	**V**
ν(NH)	3441, 3185	3196	3441, 3187	3185	3235, 3123	3185, 3441
ν(CO)	1686	1657	1686	1691	1686	1648
	1618	1620	1617	1617	1637	1617
ν(ring)	1586	1598	1597	1595	1596	1590
	1561	1562	1562	1567	1568	1561
δ(Py)	619, 407	611	621, 407	605, 418	615, 414	642, 632
$\nu(C–H)_{ring}$	803	804	802	804	816	819
γ(CCC)	669	677	639	671	680	682
	639	640	621		637	629
M–N		252	206, 214	206, 252	254	208, 212
$\nu COO^{-}(as)$		1728	1728	1736	1723	1736
$\nu COO^{-}(s)$		1420	1429	1487	1416	1435
Δ_{COO}		308	299	249	307	301
ν(C–C)	932	926	933	943	918	919
ν(CH)	2851	2849	2959	2847	2853	2917
ν(OH)		3614	3528	3308	3308	3482
δ(HOH)		1620	1616	1617	1638	1626
$\rho(H_2O_)$		769, 804, 889	770, 802, 860	704, 769, 823	723, 736, 773	723, 767
ν(M–O)		906, 926, 945	899, 833, 949	854, 891, 943	839, 902, 939	891, 918
$\pi(CO_2)$		279, 331, 376	248, 304, 331	237, 313, 393	291, 335, 391	260, 355
		544	544	532	523	525

as=Antisymmetric, *s*=Symmetric and *M*=Mg(II) or Cu(II)

Table 4 Antimicrobial activity of Mg(II) and Cu(II) complexes, characterized by the numerical values of IC_{50}/(μg cm^{-3})

Complexes	1	2	3	4	5	6	7
I	> 1000	1000[a]	1000[a]	>1000	1000[a]	900[a]	1000
II	In	In	In	In	>1000	500[b]	1000
III	>1000	>1000	1000	>1000	1000[a]	930[a]	900
IV	>1000	>1000	In	>1000	>1000	940[a]	950
V	200[c]	500[d]	600[e]	500[e]	250[f]	300[f]	360

1 – *R.* oryzae, 2 – *B. cinerea*, 3 – *F. nivale*, 4 – *A. alternata*, 5 – *M. gypseum*, 6 – *T. terrestre*, 7 – *C. albicans*, *In*=inactive
[a]MIC, MMC > 1000 μg cm^{-3}; [b]MIC, MMC=700 μg cm^{-3}; [c]MIC, MMS=900 μg cm^{-3}; [d]MIC, MMS=700 μg cm^{-3}; [e]MIC, MMC=700 μg cm^{-3}; [f]MIC, MMC=600 μg cm^{-3}

Antimicrobial activities

The antimicrobial activities of the tested complexes are presented in Table 4. All Mg(II) complexes (**I**–**IV**) were inactive against bacteria. However the Cu(II) complex (**V**) exhibited antibacterial activities against Gram-positive bacteria *Bacillus subtilis* IC_{50} of 400 μg cm^{-3} and Gram-negative bacteria *Escherichia coli* IC_{50} of 450 μg cm^{-3}. The highest antimicrobial activity was manifested by the complex **V** (Table 4).

Conclusions

All complexes **I**–**V** are hydrated and show reasonable stability in air below 95°C. The decompositions of these complexes were initiated by an elimination of water. The results reveal that MgO or CuO remained as a residue at the end of the thermal degradation of complexes **I**–**V**. The stoichiometry of thermal decomposition can also be influenced by the differences in experimental conditions, origin, and preparation history [49, 50]. Spectroscopic and analytical data together with the thermo-analytical methods available

enabled us to predict the structures of these complexes. The copper complex, **V** exhibited higher antimicrobial activities compared to the magnesium complexes **I**–**IV**.

Acknowledgements

The authors wish to thank the National Research Council Canada for financial support.

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DOI: 10.1007/s10973-005-6998-8