Journal of Thermal Analysis and Calorimetry, Vol. 64 (2001) 629–636

THERMOANALYTICAL AND IR-SPECTRAL INVESTIGATION OF Mg(II) COMPLEXES WITH HETEROCYCLIC LIGANDS

S. C. Mojumdar[*]

Institute of Inorganic Chemistry, Slovak Academy of Sciences,
Dubravska Cesta 9, SK-842 36 Bratislava, Slovakia

Abstract

Thermogravimetry (TG), differential thermal analysis (DTA) and other analytical methods have been applied to the investigation of the thermal behaviour and structure of the complexes $Mg(pc)(na)_3 \cdot 3H_2O$ (I), $Mg(pc)(py)_2 \cdot 2H_2O$ (II), $Mg(pc)(pic)_2 \cdot 2H_2O$ (III) and $Mg(pc)(caf)_2 \cdot 4H_2O$ (IV), where *pc*=2,6-pyridinedicarboxylate, *na*=nicotinamide, *py*=pyridine, *pic*=γ-picoline and *caf*=caffeine. The thermal decomposition of these compounds is multi-stage processes. The chemical composition of the complexes, the solid intermediates and the resultant products of thermolysis have been identified by means of elemental analysis and complexometric titration. Schemes of destruction of these complexes are suggested. Heating of these compounds first resulted in a release of water molecules. In complexes I, II and IV the loss of the molecular ligands (na, py and caf) occur (on the TG curves) in one step(-2na, -2py and -2caf) and in complex III in two steps (-pic, -pic). The final product of the thermal decomposition was MgO. The thermal stability of the complexes can be ordered in the sequence: IV<I<III<II. Nicotinamide, pyridine, γ-picoline and caffeine were co-ordinated to Mg(II) through the N atom of the respective heterocyclic ring. IR data suggested a unidentate co-ordination of carboxylates to Mg(II) in complexes I–IV.

Keywords: DTA, heterocyclic ligands and Mg(II) complexes, IR-spectra, TG

Introduction

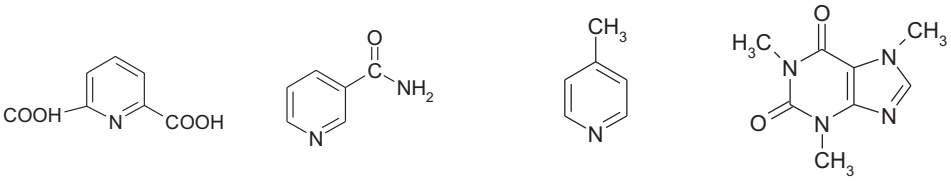
It is well documented that heterocyclic compounds play a significant role in many biological systems [1]. Especially N-donor ligand systems are components of several vitamins and drugs [2]. It is not surprising, therefore, that many authors have investigated heterocyclic compounds and also examined them as ligands in co-ordination compounds of several central atoms [3–16]. In order to enhance understanding of drug-metal ion interactions, we have studied the thermal properties of Mg(II) complexes with 2,6-pyridinedicarboxylic acid (pch) and na, py, pic or ron, which are known to be important components of biological systems.

* E-mail : uachmoju@savba.sk

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

The reveal of the relationship between the structure and thermolysis of metal carboxylate complexes, the study of the influence of metal and ligand nature on the process of thermal decomposition are of a certain interest. The stoichiometry of thermal decomposition can also be influenced by the changes of experimental conditions and origin and preparation history [17, 18]. This work is a continuation of previously reported studies [19–30]. Little data on thermal decomposition and spectral analyses of Mg(II) complexes with pch and na, py, pic or caf are available. Therefore, this paper describes the preparation of complexes I–IV formed by the nicotinamide, pyridine, γ-picoline and caffeine with Mg(II) and pch (Scheme 1), along with thermal analyses and IR spectral investigation of prepared complexes.



pch na pc caf

Scheme 1

Experimental

Preparation of the complexes

The complex I was prepared by dissolving (0.005 mole) Mg(pc)·4H_2O in 100 ml ethanol followed by the gradual addition of (0.015 mole) nicotinamide. The solution was left to stand at room temperature. The fine microcrystals thus precipitated were filtered off, washed with diethyl ether and were finally dried at room temperature.

The complexes II, III and IV were prepared by dissolving (0.005 mole) Mg(pc)·4H_2O in 100 ml ethanol followed by the gradual addition of (0.01 mole) pyridine, γ-picoline and caffeine, respectively. The solutions were left to stand at room temperature. The fine microcrystals thus precipitated were filtered off, washed with diethyl ether and were finally dried at room temperature.

Measurements

IR spectra in the region 4000–200 cm^{-1} were recorded by means of a Philips analytical PU9800 FTIR spectrometer by using Nujol mulls. Thermal decomposition of the complexes were carried out by using Paulik–Paulik–Erdey Derivatograph (Type OD 102, MOM Budapest). Measurements were carried out between room temperature and 1000°C in an atmosphere of air at a heating of 10°C min^{-1}.

Results and discussion

Chemical analysis of the complexes

The contents of C, N and H were determined by elemental analysis and the contents of magnesium were determined by complexometric titration. The results are in good agreement with theoretical expectations (variation <1%).

Thermal behaviour of the complexes

The complexes I–IV are thermally relatively stable. Thermal decomposition of the compounds is the multi-stage process. The subsequent detachment of the ligands was observed. The final product in each case was MgO.

The TG and DTA curves for the decomposition of $Mg(pc)(na)_3 \cdot 3H_2O$ (I) are shown in Fig. 1. The TG curve indicates that it is thermally stable up to 120°C. Afterwards, the TG curve shows two mass loss steps. The first step between 120 and 255°C is accompanied by 5.90% mass loss and the second step between 225 and 383°C is accompanied by 3.00% mass loss. Both steps are attributed to the dehydration process. The third step took place between 383 and 620°C and is accompanied by 59.80% mass loss. It is attributed, however, to the decomposition of the anhydrous complex to Mg(pc). The fourth step took place between 620 and 690°C and is accompanied by 24.72% mass loss. It is attributed, however, to the decomposition of Mg(pc) to MgO as the final solid product. The thermal reaction of complex I can be represented as:

$$Mg(pc)(na)_3 \cdot 3H_2O \xrightarrow{120-255°C} Mg(pc)(na)_3 \cdot H_2O \xrightarrow{255-383°C} OMg(pc)(na)_3$$
$$Mg(pc)(na)_3 \xrightarrow{383-620°C} Mg(pc) \xrightarrow{620-690°C} MgO$$

The DTA curve for complex I (Fig. 1) shows three endothermic peaks at 140, 267 and 456°C ascribed to the loss of $2H_2O$, H_2O and 3na, respectively, and a broad

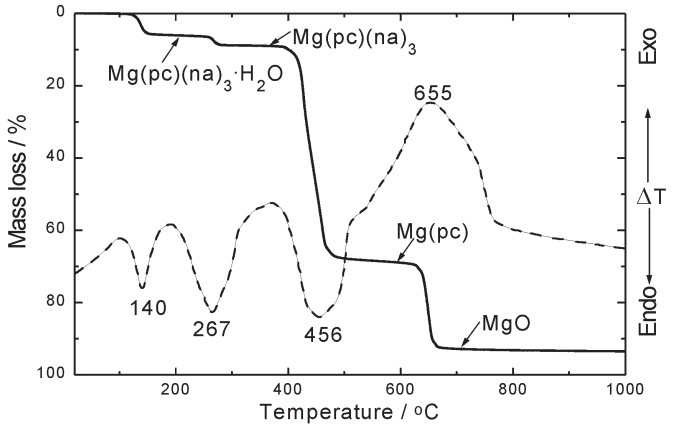


Fig. 1 TG and DTA curves of $Mg(pc)(na)_3 \cdot 3H_2O$

exothermic peak maximised at 655°C ascribed to the decomposition reaction of 2,6-pyridinedicarboxylate with the formation of MgO.

The TG and DTA curves for the decomposition of $Mg(pc)(py)_2 \cdot 2H_2O$ (II) are shown in Fig. 2. The TG curve indicates that it is thermally stable up to 170°C. Afterwards, the TG curve shows three mass loss steps. The first step between 170 and 335°C is accompanied by 9.30% mass loss, it is attributed to the dehydration process. The second step took place between 335 and 640°C and is accompanied by 41.00% mass loss. It is attributed, however, to the decomposition of the anhydrous complex to Mg(pc). The third step took place between 640 and 770°C and is accompanied by 39.16% mass loss. It is attributed, however, to the decomposition of Mg(pc) to MgO as the final solid product. The thermal reaction of complex II can be represented as:

$$Mg(pc)(py)_2 \cdot 2H_2O \xrightarrow{170-335\,^\circ C} Mg(pc)(py)_2 \xrightarrow{335-640\,^\circ C} Mg(pc) \xrightarrow{640-790\,^\circ C} MgO$$

The DTA curve for complex II (Fig. 2) shows two endothermic peaks at 215 and 395°C ascribed to the loss of $2H_2O$ and 2py, respectively and a broad exothermic peak maximised at 725°C ascribed to decomposition reaction of 2,6-pyridinedicarboxylate with the formation of MgO.

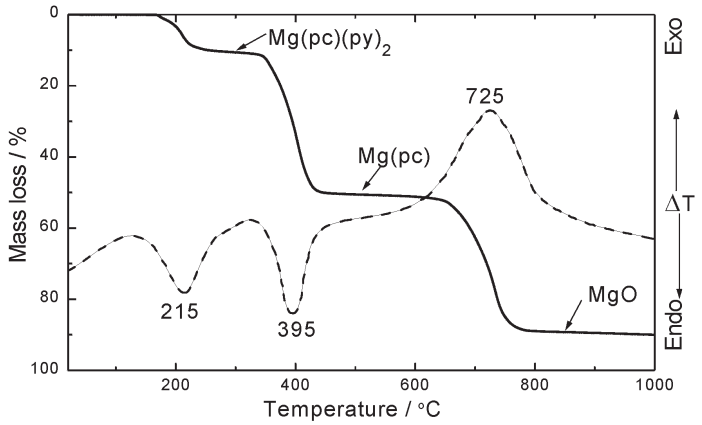


Fig. 2 TG and DTA curves of $Mg(pc)(py)_2 \cdot 2H_2O$

The TG and DTA curves for the decomposition of $Mg(pc)(pic)_2 \cdot 2H_2O$ (III) are shown in Fig. 3. The TG curve indicates that it is thermally stable up to 130°C. Afterwards, the TG curve shows four mass loss steps. The first step between 130 and 210°C is accompanied by 8.70% mass loss, it is attributed to the dehydration process. The second step between 210 and 440°C is accompanied by 22.50% mass loss and the third step between 440 and 605°C is also accompanied by 22.50% mass loss. Both steps are attributed, however, to the decomposition of the anhydrous complex to Mg(pc). The fourth step took place between 605 and 750°C and is accompanied by 36.50% mass loss. It is attributed, however, to the decomposition of Mg(pc) to MgO as the final solid product. The thermal reaction of complex III can be represented as:

$$Mg(pc)(pic)_2{\cdot}2H_2O \xrightarrow{130-210\,^\circ C} Mg(pc)(pic)_2 \xrightarrow{210-440\,^\circ C} Mg(pc)(pic)$$
$$Mg(pc)(pic) \xrightarrow{440-605\,^\circ C} Mg(pc) \xrightarrow{605-750\,^\circ C} MgO$$

The DTA curve for complex III (Fig. 3) shows three endothermic peaks at 145, 255 and 490°C ascribed to the loss of $2H_2O$, pic and pic, respectively, and a broad exothermic peak maximised at 698°C ascribed to the decomposition reaction of 2,6-pyridinedicarboxylate with the formation of MgO.

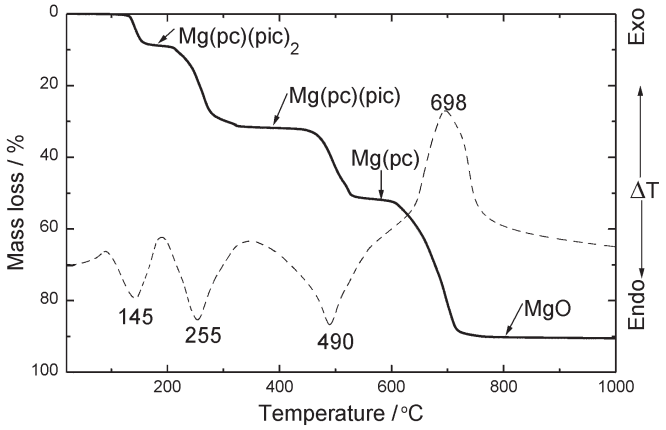


Fig. 3 TG and DTA curves of $Mg(pc)(pic)_2{\cdot}2H_2O$

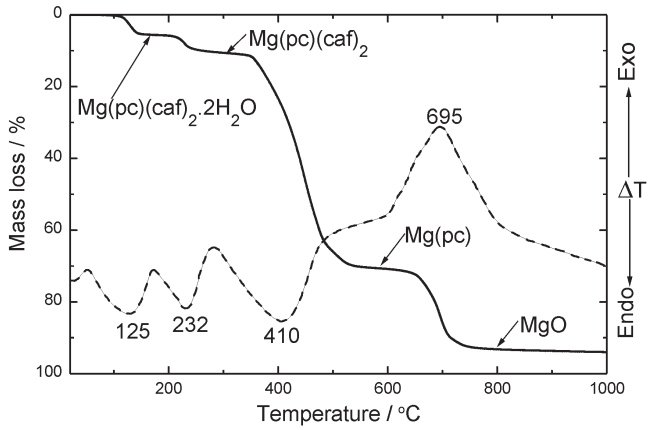


Fig. 4 TG and DTA curves of $Mg(pc)(caf)_2{\cdot}4H_2O$

The TG and DTA curves for the decomposition of $Mg(pc)_2(caf)_2{\cdot}4H_2O$ (IV) are shown in Fig. 4. The TG curve indicates that it is thermally stable up to 112°C. Afterwards, the TG curve shows four mass loss steps. The first step between 112 and 210°C is accompanied by 5.50% mass loss and the second step between 210 and 352°C is accompanied by 5.50% mass loss. Both steps are attributed to the dehydra-

tion process. The third step took place between 352 and 645°C and is accompanied by 59.60% mass loss. It is attributed, however, to the decomposition of the anhydrous complex to Mg(pc). The fourth step took place between 645 and 765°C and is accompanied by 23.17% mass loss. It is attributed, however, to the decomposition of Mg(pc) to MgO as the final solid product. The thermal reaction of complex IV can be represented as:

$$Mg(pc)(caf)_2{\cdot}4H_2O \xrightarrow{112-210\,^\circ C} Mg(pc)(caf)_2{\cdot}2H_2O \xrightarrow{210-352^\circ C} Mg(pc)(caf)_2$$
$$Mg(pc)(caf)_2 \xrightarrow{352-645^\circ C} Mg(pc) \xrightarrow{645-765^\circ C} MgO$$

The DTA curve for complex IV (Fig. 4) shows three endothermic peaks at 125, 232 and 410°C ascribed to the loss of $2H_2O$, $2H_2O$ and 2caf, respectively, and a broad exothermic peak maximised at 695°C ascribed to the decomposition reaction of 2,6-pyridinedicarboxylate with the formation of MgO.

IR spectroscopy

The most important infrared spectral data of compounds I–IV are reported in Table 1. The IR spectra of compounds I–IV showed broad absorption bands in the range 3385–3250 cm^{-1}. These frequencies correspond to the antisymmetric and symmetric OH stretching [31–33]. These bands clearly confirm the presence of water in these compounds. Carboxylate ions can co-ordinate to metal ions in a number of ways such as unidentate, bidentate (chelating) or bridging. The analysis of COO^- group bands allowed for the determination of the parameter $\Delta_{COO}=\nu COO^-(as)-COO^-(s)$. The magnitude of Δ_{COO} has been used by Nakamoto as a criteria of the way by which

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

Assignments	I	II	III	IV
ν(CN)	1605	1607	1608	1606
γ(CCC)	678, 610	682, 612	680, 613	674, 611
Mg–N	218, 226, 242	216, 229, 238	217, 235, 240	216, 229, 242
νCOO^-(as)	1699	1695	1690	1698
νCOO^-(s)	1424	1412	1408	1405
Δ_{COO}	275	283	282	293
ν(C–C)	975	971	972	974
$\nu(C-H)_{ac}$	2843, 915	2846, 917	2848, 920	2845, 921
$\nu(C-H)_{ring}$	862	861	864	863
ν(OH)	3385	3250, 3318	3328	3345
δ(HOH)	1611	1612	1613	1615
Others(650–1000 cm^{-1})	725, 754, 765 776, 812, 920	727, 752, 795 845, 940	725, 765, 823 856, 885, 942	730, 765, 812 820, 845, 931
ν(Mg–O)	250, 372, 380	253, 275, 315	313, 375	312, 390
$\pi(CO_2)$	538	539	541	540

as=antisymmetric and s=symmetric

carboxylate bind to metal ions. From the IR spectra, the calculated values of Δ_{COO} were in the range 293–275 cm^{-1}. These values together with the three bands (COO^- deformation) between 920–720 cm^{-1} and the strong band [$\pi(CO_2)$] at range 538–541 cm^{-1} appeared in the IR spectra of complexes I–IV are in good agreement with the literature data for unidentately bonded acetate structures [34]. The stretching vibration of the C=N in the pyridine ring appeared at 1590 cm^{-1} [35]. Upon complex formation the peak shifts to higher frequencies [36]. The shifts in the range 1608–1605 cm^{-1} confirm the bond formation of the metal with the nitrogen atom of the respective heterocyclic ring in complexes I–IV [35]. The absorption bands which occur in the range 242–216 cm^{-1} ν(Mg–N) also confirm the co-ordination of nicotinamide, pyridine, γ-picoline and caffeine through the nitrogen atom of the respective heterocyclic ring to Mg ion in complexes I–IV.

Conclusions

All complexes I–IV are hydrated and showed reasonable stability in air. They were soluble in water, ethanol, methanol and dimethylsulfoxide. The decomposition of these compounds were initiated by elimination of water. The loss of the molecular ligands occurs (on the TG curves) in one step in complexes I, II and IV (-3na, -2py and -2caf) and in two steps in complex III (-pic, -pic). The decomposition of 2,6-pyridinedicarboxylate occurs (on the TG curves) in one step in complexes I–IV. The thermal stability of the complexes can be ordered in the sequence: IV<I<III<II. The results revealed that MgO was left as residue at the end of the thermal degradation experiments for complexes I–IV. By means of spectral analyses the structure of the compounds have been studied. Infrared data suggested that carboxylate ions is unidentately co-ordinated to Mg(II) in complexes I–IV. Nicotinamide, pyridine, γ-picoline and caffeine were co-ordinated to Mg(II) through the nitrogen atom of the respective heterocyclic ring in complexes I–IV. The preliminary study has shown that the complexes do have a biological activity.

* * *

The authors wish to thank the Ministry of Education of the Slovak Republic for financial support.

References

1 D. Hudecová, I. Ondrejkovicová, V. Vancová and M. Melník, Chem. Papers, 52 (1998) 123.
2 E. Jóna, A. Sirota, P. Šimon and M. Kubranová, Thermochim. Acta, 258 (1995) 161.
3 R. N. Patel and K. B. Pandeya, Synth. React. Inorg. Met.-Org. Chem., 28 (1998) 23.
4 E. Jóna and M. Jamnický, J. Thermal Anal., 27 (1983) 359.
5 J. S. Skoršepa, K. Györyová and M. Melník, J. Thermal Anal., 44 (1995) 169.
6 L. Bapat, G. N. Natu, M. Bhide and J. Kher, J. Thermal Anal., 48 (1997) 819.
7 J. Radwanska-Doczekalska, D. Czakis-Sulikowska and M. Markiewicz, J. Thermal Anal., 48 (1997) 865.
8 M. Enamullah and W. Linert, J. Coord. Chem., 35 (1995) 325.

9 G. D'Ascenzo, U. B. Ceipidor, E. Cardarelli and A. D. Magri, Thermochim. Acta, 13 (1975) 449.
10 R. N. Patel and K. B. Pandeya, J. Inorg. Biochem., 72 (1998) 109.
11 M. Melník, L. Macášková and J. Mroziński, Polyhedron, 7 (1988) 1745.
12 M. Melník, I. Potočnak, L. Macášková and D. Mikloš, Polyhedron, 15 (1996) 2159.
13 M. Melník, M. Koman and T. Glowiak, Polyhedron, 17 (1998) 1767.
14 E. Jóna, M. Kubranová, P. Šimon and J. Mroziński, J. Thermal Anal., 46 (1996) 1325.
15 K. Györyová, V. Balek and V. Zeleňak, Thermochim. Acta, 234 (1994) 221.
16 V. Balek, K. Györyová and J. Simon, J. Thermal Anal., 46 (1996) 573.
17 T. Šramko, G. Liptay and E. Jóna, J. Thermal Anal., 12 (1977) 217.
18 Y. Masuda, Thermochim. Acta, 39 (1980) 235.
19 S. C. Mojumdar, M. Melník and E. Jóna, J. Anal. Appl. Pyrolysis, 46 (1998) 147.
20 S. C. Mojumdar, M. Valko and M. Melník, Chem. Papers, 52 (1998) 650.
21 S. C. Mojumdar, M. Melník and E. Jóna, J. Therm. Anal. Cal., 56 (1999) 533.
22 S. C. Mojumdar, M. Melník and M. Valko, Polish J. Chem., 73 (1999) 457.
23 S. C. Mojumdar, M. Melník and E. Jóna, J. Anal. Appl. Pyrolysis, 48 (1999) 111.
24 S. C. Mojumdar, M. Melník and E. Jóna, Polish J. Chem., 73 (1999) 293.
25 S. C. Mojumdar, M. Melník and E. Jóna, J. Therm. Anal. Cal., 56 (1999) 541.
26 S. C. Mojumdar, M. Melník, E. Jóna and D. Hudecová, Chem. Papers, 53 (1999) 265.
27 S. C. Mojumdar, M. Melník and E. Jóna, J. Anal. Appl. Pyrolysis, 53 (2000) 149.
28 S. C. Mojumdar, E. Jóna and M. Melník, J. Therm. Anal. Cal., 60 (2000) 571.
29 S. C. Mojumdar, M. Melník and E. Jóna, Thermochim. Acta, 352 (2000) 129.
30 S. C. Mojumdar, M. Melník and E. Jóna, J. Therm. Anal. Cal., 61 (2000) 915.
31 G. Deveto, G. Ponticelli and C. Preti, J. Inorg. Nucl. Chem., 37 (1975) 1635.
32 M. Melník, Coord. Chem. Rev., 36 (1981) 1.
33 M. Melník, Coord. Chem. Rev., 42 (1982) 259.
34 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Co-ordination Compounds, (4th ed.), J. Wiley, New York 1986, p. 232.
35 D. Aslanian, A. Lautic, Ch. Mantai and M. Baltanski, J. Chim. Phys., 72 (1957) 1052.
36 Y. Kidani, M. Noji and H. Koike, Bull. Chem. Soc. Jpn., 48 (1975) 239.