

Thermal Decomposition and IR Spectra of Mg(II) Compounds with Caffeine

^aS. C. MOJUMDAR, ^bM. MELNÍK, and ^cE. JÓNA

^a*Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-842 36 Bratislava
e-mail: uachmoju@savba.sk*

^b*Department of Inorganic Chemistry, Faculty of Chemical Technology,
Slovak University of Technology, SK-812 37 Bratislava*

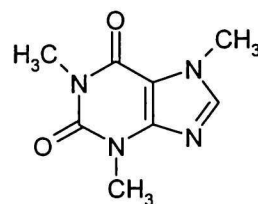
^c*Department of Chemistry, University of Trenčín, SK-020 32 Púchov*

Received 28 September 1998

Thermogravimetry (TG), differential thermal analysis (DTA), and other analytical methods have been applied to the investigation of the thermal behaviour and structure of the compounds $\text{Mg}(\text{ac})_2(\text{caf})_2 \cdot 3\text{H}_2\text{O}$ (*I*), $\text{Mg}(\text{Clac})_2(\text{caf}) \cdot 2\text{H}_2\text{O}$ (*II*), $\text{Mg}(\text{Cl}_2\text{ac})_2(\text{caf}) \cdot \text{H}_2\text{O}$ (*III*) and $\text{Mg}(\text{Cl}_3\text{ac})_2(\text{caf})_2 \cdot 5\text{H}_2\text{O}$ (*IV*) ($\text{ac} = \text{CH}_3\text{COO}^-$, $\text{Clac} = \text{ClCH}_2\text{COO}^-$, $\text{Cl}_2\text{ac} = \text{Cl}_2\text{CHCOO}^-$, $\text{Cl}_3\text{ac} = \text{Cl}_3\text{CCOO}^-$, and $\text{caf} = \text{caffeine}$). Thermal decomposition of these compounds is a multi-stage process. The compositions of the complexes and the solid state intermediate and resultant products of thermolysis have been identified by means of elemental analysis and complexometric titration. The possible scheme of destruction of the complexes is suggested. Heating of the compounds first results in a release of water molecules. In complexes *I*, *II*, and *III* the loss of the volatile ligand (caf) occurs (on the TG curves) in one step (-2caf or $-\text{caf}$) and in complex *IV* in two steps ($-\text{caf}$, $-\text{caf}$). The final product of the thermal decomposition was MgO . The thermal stability of the complexes increases in the sequence: *I*, *IV*, *II*, *III*. Caffeine was coordinated to $\text{Mg}(\text{II})$ through the N(9) atom of its heterocyclic ring. IR data suggest a unidentate coordination of carboxylates to magnesium in complexes *I*–*IV*.

It is well-documented that heterocyclic compounds play a significant role in many biological systems, especially *N*-donor ligand systems being a component of several vitamins and drugs [1, 2]. It is not surprising, therefore, that many authors have investigated heterocyclic compounds and also examined them as ligands in coordination compounds of several central atoms [3–13]. In order to enhance understanding of drug–metal ion interactions, we have been studying the thermal properties of magnesium(II) complexes with caffeine, which is known as an important component of biological systems.

The revelation 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. This work is a continuation of previously reported studies [14–19] on the thermal and spectral properties of magnesium(II) complexes with pyridine and substituted pyridines. This paper describes the preparation of complexes formed by the acetate, mono-, di-, and trichloroacetates with caffeine, along with thermal analyses and IR spectral investigation of prepared complexes.



Caffeine

EXPERIMENTAL

The complexes were prepared by treating caffeine (0.01 mol, complexes *I*, *IV* and 0.005 mol, complexes *II*, *III*) with appropriate magnesium(II) acetate or halogenoacetate (0.005 mol) in hot ethanol solution. The solution was left to stand at room temperature. The fine microcrystals that precipitated were filtered off, washed with cold ethanol and dried at room temperature.

The infrared spectra were obtained on Philips analytical PU9800 FTIR spectrometer by using Nujol mulls in the $\tilde{\nu}$ range 200–4000 cm^{-1} . The thermal decomposition was carried out on Paulik–Paulik–Erdey Derivatograph (Type OD 102, MOM Budapest) in air atmosphere by using a platinum crucible with

Table 1. Analytical Data of the Complexes I–IV

Complexes	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$			
	C	H	N	Mg
I	41.05	5.47	19.16	4.16
	41.09	5.36	19.23	4.15
II	32.62	4.08	12.68	5.51
	32.97	4.23	12.44	5.50
III	29.25	2.84	11.37	4.94
	29.20	2.90	11.25	4.95
IV	29.00	3.63	13.53	2.94
	29.10	3.75	13.52	2.95

a sample mass of 100 mg in the temperature range 20–1000 °C. The rate of temperature increase of 10 °C min⁻¹ was chosen for all measurements.

Elemental analyses (C, H, N) were carried out by means of an Erba 1106 analyzer and the content of Mg was established by complexometric titration. The analytical data of the compounds I–IV reported in Table 1 show a good agreement between the experimental and calculated data.

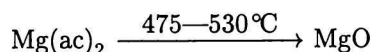
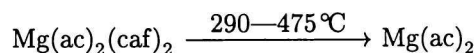
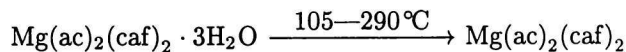
RESULTS AND DISCUSSION

The thermal decomposition data of the compounds I–IV are collected in Table 2. 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 was MgO.

Table 2. Thermal Decomposition Data of the Complexes I–IV

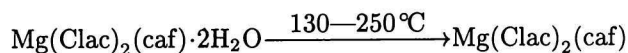
Complex	DTA		TG		
	θ_{max}	Process	Δm_r	Released component	Residue
	°C		% found (calc.)		
Mg(ac) ₂ (caf) ₂ · 3H ₂ O	160	endo	9.25 (9.24)	3H ₂ O	
	370	endo	66.40 (66.42)	2caf	
	500	exo	Decomposition		MgO
Mg(Clac) ₂ (caf) · 2H ₂ O	180	endo	8.20 (8.15)	2H ₂ O	
	300	endo	44.00 (43.99)	2caf	
	650	exo	Decomposition		MgO
Mg(Cl ₂ ac) ₂ (caf) · H ₂ O	165	endo	3.60 (3.66)	H ₂ O	
	330	endo	39.40 (39.40)	caf	
	530	exo	Decomposition		MgO
Mg(Cl ₃ ac) ₂ (caf) ₂ · 5H ₂ O	120	endo	4.40 (4.35)	2H ₂ O	
	175	endo	6.50 (6.53)	3H ₂ O	
	250	exo	23.50 (23.46)	caf	
	410	endo	23.50 (23.46)	caf	
	700	exo	Decomposition		MgO

The TG and DTA curves for Mg(ac)₂(caf)₂ · 3H₂O are shown in Fig. 1. The TG curve for that complex indicates that it is stable at temperature up to 105 °C, when there begins the slow decomposition to MgO, as to the final product formed at 530 °C. The TG curve shows two bendings at 290 °C and 475 °C. They correspond to the presence of two intermediate decomposition products: Mg(ac)₂(caf)₂ and Mg(ac)₂. The most probable thermal decomposition scheme is



The DTA curve for the complex (Fig. 1) presents two endothermic peaks at 160 °C and 370 °C corresponding to the loss of 3H₂O and 2caf, respectively, and a broad exothermic maximum with the centre about 500 °C corresponding to decomposition reactions of 2ac with simultaneous formation of MgO.

The TG and DTA curves for Mg(Clac)₂(caf) · 2H₂O are shown in Fig. 2. The TG curve for that complex indicates that it is stable at temperature up to 130 °C, when there begins the slow decomposition to MgO, as to the final product formed at 715 °C. The TG curve shows two bendings at 250 °C and 500 °C. They correspond to the presence of two intermediate decomposition products: Mg(Clac)₂(caf) and Mg(Clac)₂. The most probable thermal decomposition scheme is



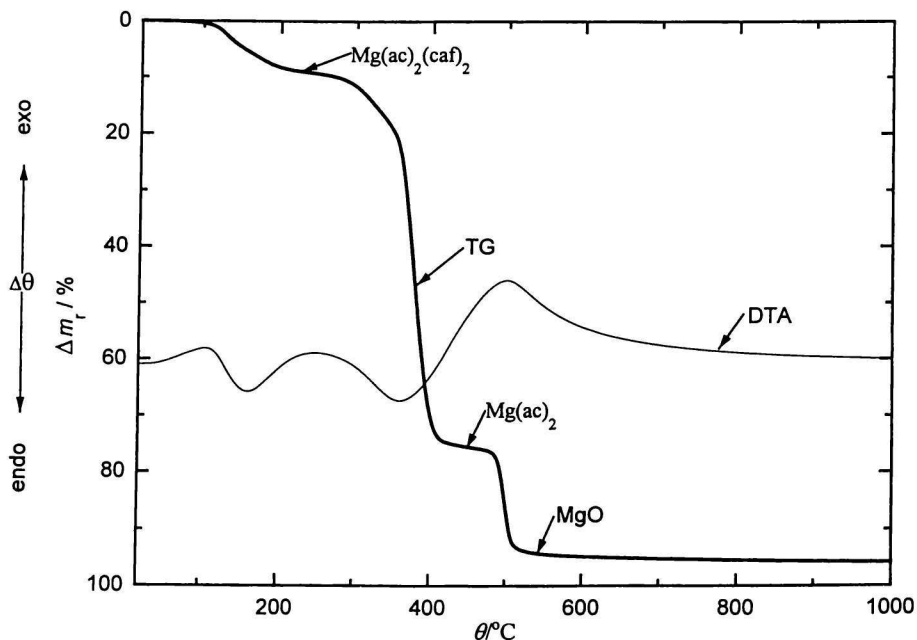


Fig. 1. TG and DTA curves of $\text{Mg}(\text{ac})_2(\text{caf})_2 \cdot 3\text{H}_2\text{O}$.

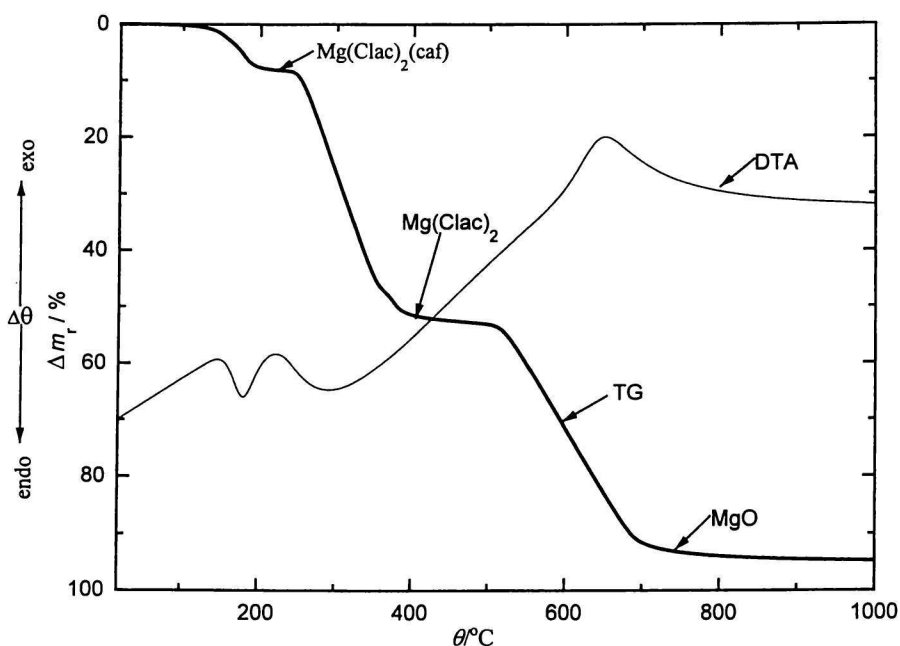
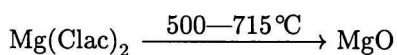
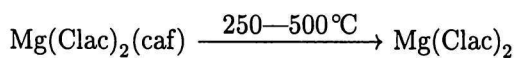


Fig. 2. TG and DTA curves of $\text{Mg}(\text{Clac})_2(\text{caf}) \cdot 2\text{H}_2\text{O}$.



The DTA curve for the complex (Fig. 2) presents two endothermic peaks at 180°C and 300°C corresponding to the loss of 2H₂O and caf, respectively, and a broad exothermic maximum with the centre

about 650°C corresponding to decomposition reaction of 2Clac with simultaneous formation of MgO.

The TG and DTA curves for $\text{Mg}(\text{Cl}_2\text{ac})_2(\text{caf}) \cdot \text{H}_2\text{O}$ are shown in Fig. 3. The TG curve for that complex indicates that it is stable at temperature up to 160°C, when there begins the decomposition to MgO, as to the final product formed at 650°C. The TG curve shows two bendings at 270°C and 440°C. They correspond to the presence of two intermediate decomposi-

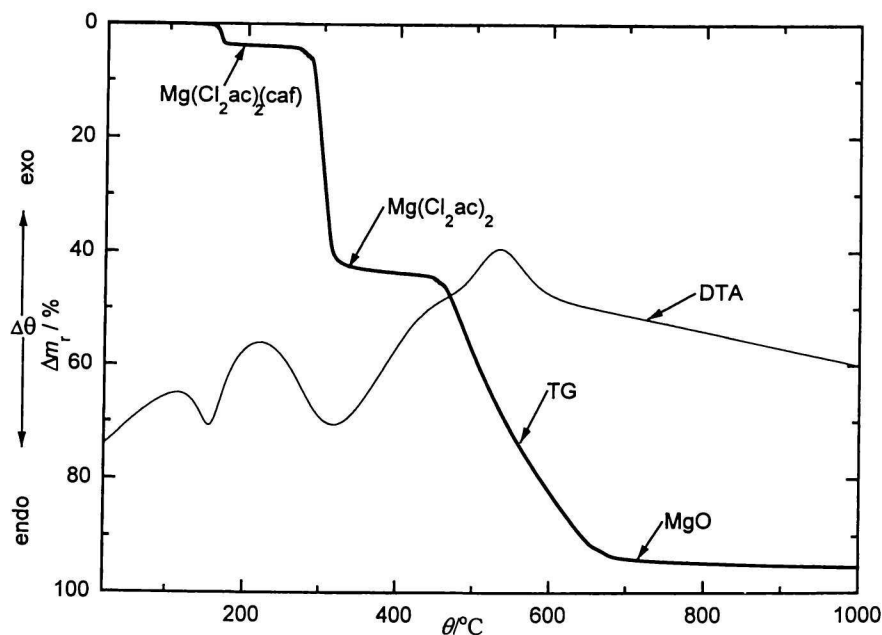
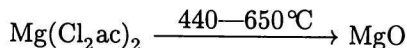
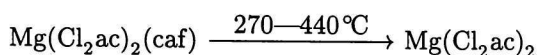
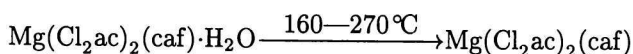


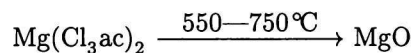
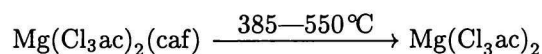
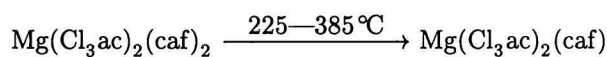
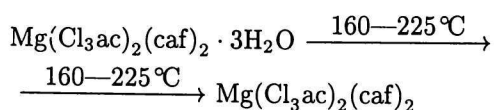
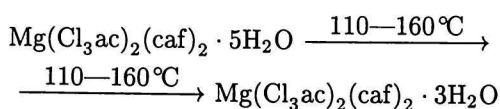
Fig. 3. TG and DTA curves of $\text{Mg}(\text{Cl}_2\text{ac})_2(\text{caf}) \cdot \text{H}_2\text{O}$.

tion products: $\text{Mg}(\text{Cl}_2\text{ac})_2(\text{caf})$ and $\text{Mg}(\text{Cl}_2\text{ac})_2$. The most probable thermal decomposition scheme is



The DTA curve for the complex (Fig. 3) presents two endothermic peaks at 165°C and 330°C corresponding to the loss of H_2O and caf, respectively, and an exothermic maximum at 540°C corresponding to decomposition reaction of $2\text{Cl}_2\text{ac}$ with simultaneous formation of MgO.

The TG and DTA curves for $\text{Mg}(\text{Cl}_3\text{ac})_2(\text{caf})_2 \cdot 5\text{H}_2\text{O}$ are shown in Fig. 4. The TG curve for that complex indicates that it is stable at temperature up to 110°C, when there begins the decomposition to MgO, as to the final product formed at 750°C. The TG curve shows four bendings at 160°C, 225°C, 385°C, and 550°C. They correspond to the presence of four intermediate decomposition products: $\text{Mg}(\text{Cl}_3\text{ac})_2(\text{caf})_2 \cdot 3\text{H}_2\text{O}$, $\text{Mg}(\text{Cl}_3\text{ac})_2(\text{caf})_2$, $\text{Mg}(\text{Cl}_3\text{ac})_2(\text{caf})$, and $\text{Mg}(\text{Cl}_3\text{ac})_2$. The most probable thermal decomposition scheme is



The DTA curve for the complex (Fig. 4) presents two endothermic peaks at 120°C and 175°C corresponding to the loss of $2\text{H}_2\text{O}$ and $3\text{H}_2\text{O}$, respectively, and an exothermic maximum with the centre about 250°C corresponding to decomposition reaction of caf. Further endothermic and exothermic peaks occur at 410°C and 700°C corresponding to the loss of remaining caf and $2\text{Cl}_3\text{ac}$, respectively, with simultaneous formation of MgO.

According to the anion ligands, the thermal stability of the complexes is increased as follows: *I*(ac), *IV*(Cl_3ac), *II*(Clac), *III*(Cl_2ac). Heating of the compounds first results in a release of water molecules in one step in complexes *I*–*III* and in two steps in complex *IV*. Caffeine was eliminated in complexes *I*–*III* in one step and in complex *IV* in two steps (- caf, caf). The results of thermal decomposition of the complexes were compared with literature results of metal(II) complexes with carboxylates and halogenocarboxylates [20–23]. The stoichiometry of thermal decomposition can also be influenced by the changes of experimental conditions [24–26].

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*–*IV* are reported in Table 3. The absorption bands

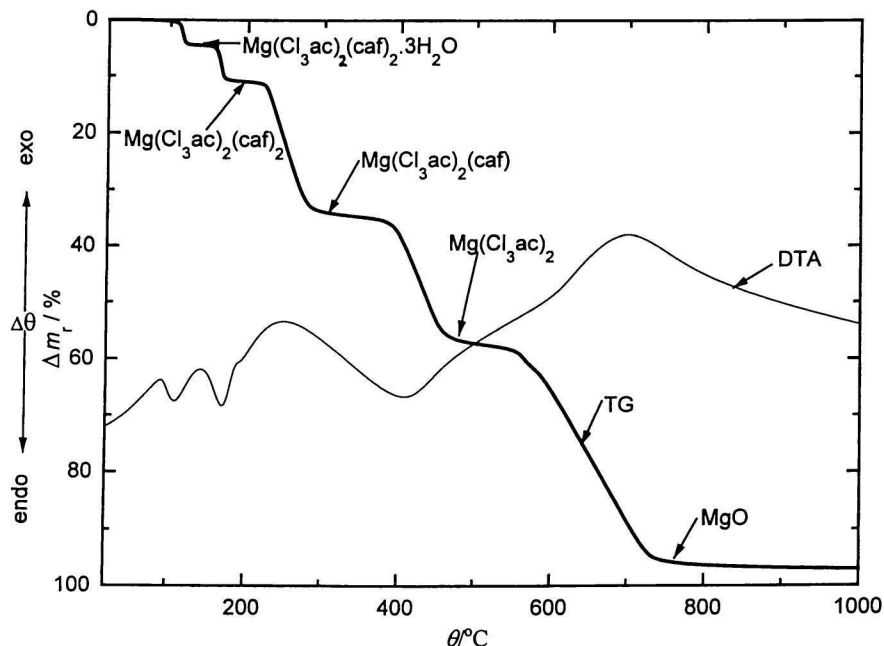

 Fig. 4. TG and DTA curves of $\text{Mg}(\text{Cl}_3\text{ac})_2(\text{caf})_2 \cdot 5\text{H}_2\text{O}$.

 Table 3. Infrared Spectral Data ($\tilde{\nu} = 200\text{--}4000\text{ cm}^{-1}$) of Complexes I–IV

Assignment	$\tilde{\nu}_i$				
	Caffeine	I	II	III	IV
$\nu(\text{CO})$	1659	1662	1644	1669	1663
$\nu(\text{CN})$	1599	1597	1598	1596	1595
$\gamma(\text{CCC})$	644	667	698	671	682
	611	610	610	612	613
Mg—N	206, 214, 229	214, 227, 237	206, 237, 242	206, 228, 237	
$\nu_{\text{as}}(\text{COO}^-)$		1698	1701	1706	1713
$\nu_{\text{s}}(\text{COO}^-)$		1463	1408	1417	1410
Δ_{COO}		235	293	289	303
$\nu(\text{C—C})$	974	972	974	973	976
$\nu(\text{C—H})_{\text{ac}}$		2847, 926	2845, 909	2847, 920	2849, 932
$\nu(\text{C—H})_{\text{ring}}$	862	860	864	863	861
$\nu(\text{OH})$		3335	3239, 3366	3308	3380
$\delta(\text{HOH})$		1655	1643	1637	1651
$\rho(\text{H}_2\text{O})$		744, 758, 760	747, 760, 783	704, 769, 823	742, 760, 804
		788, 800, 925	864, 951	854, 891, 943	833, 841, 941
$\nu(\text{Mg—O})$		258, 370, 391	254, 277, 308	313, 390	320, 393

as = asymmetric, s = symmetric.

$\nu(\text{OH})$ and $\delta(\text{HOH})$ which occur in the $\tilde{\nu}$ range 3239–3380 cm^{-1} and 1637–1655 cm^{-1} , respectively, confirm the presence of water of crystallization. The absorption bands which occur in the $\tilde{\nu}$ range 600–1000 cm^{-1} (rocking and wagging stretching) and 258–393 cm^{-1} $\nu(\text{Mg—O})$ confirm the presence of water as coordinated in the complexes [27]. The presence of water as water of crystallization and as coordinated water in the compounds is further supported by the thermal decomposition data. Carboxylate ions can coordinate to metal ions in a number of ways such as uniden-

tate, bidentate (chelating) or bridging and there is an evidence of that fact in the IR spectrum. The analysis of COO^- group bands frequencies allowed on determination of parameter $\Delta_{\text{COO}} = \tilde{\nu}(\nu_{\text{as}}(\text{COO}^-)) - \tilde{\nu}(\nu_{\text{s}}(\text{COO}^-))$. The magnitude of Δ_{COO} has been used by Nakamoto [28] as a criterion of the way of carboxylate binding with metal ions. Calculated from the examined spectra values of Δ_{COO} are in the $\tilde{\nu}$ range 235–303 cm^{-1} . These values and three bands (COO deformation) at 720–920 cm^{-1} of complexes I–IV are in good accord with the literature data for

unidentately bonded acetates structures [29]. The absorption bands which occur in the $\bar{\nu}$ range 206—242 cm^{-1} ($\nu(\text{Mg—N})$) confirm the coordination of caffeine to Mg ion through the N(9) atom of its heterocyclic ring [30]. The crystal structure of metal(II) complexes with caffeine also proved that the caffeine coordinates to metal ions through the N(9) atom of its heterocyclic ring [31].

Without X-ray analysis, no definite structure can be described for the different components. However, the spectroscopic and analytical data available enable to predict the structures which are supported also by the thermal decomposition studies.

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

REFERENCES

- Jóna, E., Kubranová, M., Šimon, P., and Mroziński, J., *J. Therm. Anal.* 46, 1325 (1996).
- Jóna, E., Sirota, A., Šimon, P., and Kubranová, M., *Thermochim. Acta* 258, 161 (1995).
- Jóna, E., Sirota, A., Šimon, P., Horvath, I., and Kubranová, M., *Progress in Coordination and Organometallic Chemistry, Proc. Int. Conf. Smolenice, Slovakia*. P. 297. Slovak University of Technology Press, Bratislava, 1997.
- Papánková, B., Mašlejová, A., and Šimon, P., *TERMANAL '97, Proc. Int. Conf. Belušké Slatiny, Slovakia*. P. 48. CHTF-STU Press, Bratislava, 1997.
- Skoršepa, J. S., Györyová, K., and Melník, M., *J. Therm. Anal.* 44, 169 (1995).
- Györyová, K. and Nour El-Dien, F. A., *TERMANAL '97, Proc. Int. Conf. Belušké Slatiny, Slovakia*. P. 62. CHTF-STU Press, Bratislava, 1997.
- Jóna, E., Hvastijová, M., and Kohut, J., *J. Therm. Anal.* 41, 161 (1994).
- Melník, M., Sirota, A., Ondrejčovičová, I., Jóna, E., and Hudcová, D., *Progress in Coordination and Organometallic Chemistry, Proc. Int. Conf. Smolenice, Slovakia*. P. 215. Slovak University of Technology Press, Bratislava, 1997.
- Langfelderová, H., Macášková, L., Melník, M., and Gažo, J., *Z. Anorg. Chem.* 445, 233 (1978).
- D'ascenzo, G., Ceipidor, U. B., Cardarelli, E., and Magri, A. D., *Thermochim. Acta* 13, 449 (1975).
- Melník, M., Macášková, L., and Mroziński, J., *Polyhedron* 7, 1745 (1988).
- Melník, M., Potočňak, I., Macášková, L., and Mikloš, D., *Polyhedron* 15, 2159 (1996).
- Jóna, E. and Jamnický, M., *J. Therm. Anal.* 27, 359 (1983).
- Mojumdar, S. C., Jóna, E., and Melník, M., *TERMANAL '97, Proc. Int. Conf. Belušké Slatiny, Slovakia*. P. 58. CHTF-STU Press, Bratislava, 1997.
- Mojumdar, S. C., Melník, M., and Jóna, E., *NOVTECH '97, Proc. Int. Conf. Žilina, Slovakia*. P. 67. Juraj Matušik Press, Žilina, 1997.
- Mojumdar, S. C., Melník, M., Jóna, E., and Enamullah, M., *J. Bangladesh Acad. Sci.*, in press.
- Mojumdar, S. C., Melník, M., and Jóna, E., *J. Anal. Appl. Pyrolysis* 48, 111 (1999).
- Mojumdar, S. C., Melník, M., and Valko, M., *Pol. J. Chem.* 73, 457 (1999).
- Mojumdar, S. C., Valko, M., and Melník, M., *Chem. Papers* 52, 650 (1998).
- Allan, J. R. and Gavin, J. *J. Therm. Anal.* 18, 263 (1980).
- Mroziński, J. and Heyduk, E., *Thermochim. Acta* 93, 85 (1985).
- Melník, M., Mroziński, J., and Holloway, C. E., *J. Coord. Chem.* 29, 209 (1993).
- D'ascenzo, G., Ceipidor, U. B., and Angelis, G. D., *Thermochim. Acta* 58, 175 (1972).
- Šramko, T., Liptay, G., and Jóna, E., *J. Therm. Anal.* 12, 217 (1977).
- Masuda, Y., *Thermochim. Acta* 39, 235 (1980).
- Jóna, E., Šramko, T., and Gažo, J., *J. Therm. Anal.* 16, 213 (1979).
- Deveto, G., Ponticelli, G., and Preti, C., *J. Inorg. Nucl. Chem.* 37, 1635 (1975).
- Nakamoto, K., *Infrared Spectra of Inorganic and Coordination Compounds*. 2nd Edition, p. 80. Wiley—Interscience, New York, 1970.
- Stoilova, D., Nikolov, G., and Balarev, K., *Izv. Akad. Nauk SSSR, Ser. Khim.* 9, 371 (1976).
- Ondrejčovičová, I., Drobuliaková, D., and Melník, M., *Current Trends in Coordination Chemistry, Proc. Int. Conf. Smolenice, Slovakia*. P. 447. Slovak University of Technology Press, Bratislava, 1995.
- Melník, M., Koman, M., and Glowiak, T., *Polyhedron* 17, 1767 (1998).