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# Thermal stability and kinetic studies of new dinuclear copper(II) complexes with octaazamacrocyclic and multidonor bidentate ligands

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## Abstract

The thermal properties of four copper(II) complexes with  $N,N',N'',N'''$ -tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc) and several bidentate ligands N,S (thiosemicarbazide and thiourea) or N,O donors (semicarbazide and urea), of the general formula  $[\text{Cu}_2(\text{X})\text{tpmc}](\text{ClO}_4)_4$ , have been investigated by thermogravimetry (TG) and differential scanning calorimetry (DSC). The thermal stability order can be recognized for the examined complexes, depending on coordinated bidentate bridging N,S or N,O ligand. Kinetic data demonstrated first-order thermal decomposition. A plausible mechanism has been proposed which explains the major products of the degradation. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Copper(II) complexes; Dinuclear complexes; Thermal analysis; Kinetic studies

## 1. Introduction

Multidonor ligands containing nitrogen and sulfur/oxygen as potential donor atoms and their versatile chelating ability with transition metals in the complexes, have attracted considerable interest in biological systems due to their pharmacological properties [1,2], complexing ability towards some toxic metals and major influences of their specific molecular structure on corrosion inhibition [3–5] have not been fully explored. On the other hand, in view of macrocyclic ligand,  $N,N',N'',N'''$ -tetrakis(2-pyridylmethyl)-1,4,8,11-tetraazacyclotetradecane (tpmc) is especially

suitable to achieve, in the *boat* coordination mode [6–9], stable dinuclear metal(II) complexes with an additional bidentate ligand which forms a bridge between the two metal atoms.

This paper is the extension of the study on the synthesis of four copper(II) complexes with octaazamacrocyclic ligand tpmc and chelating ligands, i.e. thiosemicarbazide (tsc), semicarbazide (sc), thiourea (tu) or urea (u), respectively (Fig. 1), which showed microbiological activity against some bacteria [10]. The enhanced activity compared to the ligands indicates that the coordinated copper atoms have an influence on the antibacterial effects [10]. The metal ions are thus firmly held in the cavities of tpmc, such that the biological function of each is impaired by, e.g. competing demetallation reactions. Binding an active center to the labile fifth coordination site of the Cu(II) instead of the N,S or N,O ligands provides now

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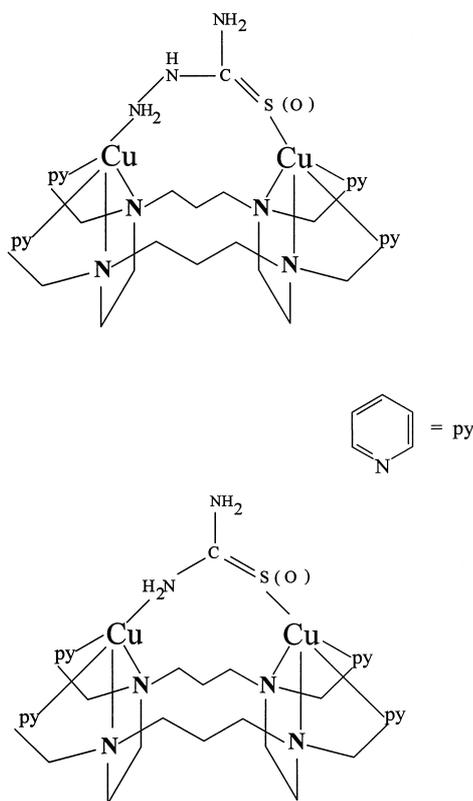


Fig. 1. Suggested structure of the complex cation  $[\text{Cu}_2(\text{X})\text{tpmc}]^{4+}$  ( $\text{X} = \text{tsc}, \text{sc}, \text{tu}$  or  $\text{u}$ ).

“cooperative” binding between them when such conditions prevail. The behavior of these solid compounds when heated can suggest hypotheses concerning the reaction mechanism and how labile is Cu/N,S or N,O bond as well. Some molecular properties of the complexes can also be derived [11,12]. However, the thermal analyses of these types of complexes have been poorly described.

In order to further our present knowledge and to gain new informations for future applicable research about potentially biologically important molecules, we are to test their thermal properties. The objective of the present work was investigation of the thermal decomposition reactions of the  $[\text{Cu}_2(\text{X})\text{tpmc}](\text{ClO}_4)_2$  complexes as well as kinetic parameters of the accompanying processes derived from their thermogravimetry (TG) and differential scanning calorimetry (DSC) curves.

## 2. Experimental

### 2.1. Material preparation

The complexes  $[\text{Cu}_2(\text{X})\text{tpmc}](\text{ClO}_4)_4$  (**2**)–(**5**) were obtained by mixing the starting complex  $[\text{Cu}_2\text{tpmc}](\text{ClO}_4)_4$  (**1**), which was prepared by the procedure described in literature [13] and ligand tsc, sc, tu or u in molar ratio 1:1, in acetonitrile [10].

### 2.2. Methods

Thermogravimetric curves (TG and DSC) were recorded on a DuPont 1090 thermal analyzer in a nitrogen atmosphere up to  $550^\circ\text{C}$  at a heating rate of  $20^\circ\text{C min}^{-1}$ . The masses of the samples used in TG and DSC measurements were in the range 3.43–7.32 mg. Mass spectra were recorded on a double focusing reverse geometry Finnigan-MAT 8230 mass spectrometer at a resolution of 1000 using a combined EI–CI source at  $200^\circ\text{C}$ , as described earlier [14].

## 3. Results and discussion

### 3.1. Thermal stability of the complexes

In Table 1, the pertinent thermal decomposition data are collected. The TG–DSC curves of the thermal decomposition of the primary complex (**1**) of the complex (**2**) as well as of the octaazamacrocyclic ligand tpmc are shown in Fig. 2.

Comparison of the TG and DSC curves leads to the conclusion that the diagrams contain very complicated thermal effects. The results point out that all the complexes (**2**)–(**5**), like the starting complex (**1**) (Fig. 2a and b), in nitrogen atmosphere are stable up to about  $235^\circ\text{C}$ . The absence of any thermal change before this temperature indicates that the samples restructuring do not take place before the degradation processes started. Only one well defined but not simple exothermic peak of all the complexes appears in the  $235$ – $286^\circ\text{C}$  range. The presence of some less well-defined peaks suggested that consecutive reactions take place with overlapped reaction steps too. The shape of DSC curves with very sharp peak reflects very fast decomposition processes, which can be

Table 1  
Thermal parameters for the complexes (1)–(5)

Complex	$T_i$ (°C) <sup>a</sup>	$T_p$ (°C) <sup>b</sup>	$\Delta H_r$ (kJ/g)	$\Delta m$ (%)	Residue	Found/calculated values for residue mass (g/mol (%))	
<b>1</b>	[Cu <sub>2</sub> tpmc](ClO <sub>4</sub> ) <sub>4</sub>	275.8	286.0	−7.37	91.02	CuCl	97.86 (8.98)/99.00 (9.08)
<b>2</b>	[Cu <sub>2</sub> (tsc)tpmc](ClO <sub>4</sub> ) <sub>4</sub>	235.1	244.2	−4.11	83.69	2CuS	192.6 (16.31)/191.2 (16.19)
<b>3</b>	[Cu <sub>2</sub> (sc)tpmc](ClO <sub>4</sub> ) <sub>4</sub>	269.2	275.3	−3.36	85.02	2CuO	174.6 (14.98)/159.1 (13.65)
<b>4</b>	[Cu <sub>2</sub> (tu)tpmc](ClO <sub>4</sub> ) <sub>4</sub>	250.7	256.5	−4.41	85.54	Cu <sub>2</sub> S	168.6 (14.45)/159.2 (13.65)
<b>5</b>	[Cu <sub>2</sub> (u)tpmc](ClO <sub>4</sub> ) <sub>4</sub>	257.5	272.5	−5.82	87.28	Cu <sub>2</sub> O	146.2 (12.72)/143.1 (12.45)

<sup>a</sup>  $T_i$ : initial temperature.

<sup>b</sup>  $T_p$ : peak temperature.

related to volatilization upon simple decomposition by heating.

The decomposition of the free macrocycle tpmc (Fig. 2c) showed an endothermic reaction (absent in the complexes) giving a temperature peak at 163.1°C. In spite of this, the (1)–(5) complexes degradation started above 235°C, with a total weight loss,  $\Delta m$  (83–91%) of the each individual complex (Table 1), demonstrating their high thermal stability and purity. The complexes on heating undergo thermal decomposition followed by the reduction process of the Cu(II) → Cu(I) (for (1), (4) and (5)) due to the electron transfer mechanism and probably the oxidation of the ligands. The intermediate products may undergo chemical reaction(s) as a consequence of the secondary processes of the thermal degradation with numerous products in a gaseous phase. The total exoenthalpy change ( $\Delta H_r < 0$ ) for these reactions is very high, composed of the sum of the different effects in the processes of the complex thermal decomposition.

In complex compounds as it is known [15], thermal stability is often affected by the tendency of the external ion to enter the coordination sphere. In addition, the perchlorate ions as strong oxidizing agents, there is no tendency to enter but spontaneous explosive autocatalytic reactions are expected. Thus, the additional ligands leave the coordination sphere as their oxidation affected by the presence of the perchlorate ions occurs first. It is supported by the two fragments in mass spectra of the tetracations [Cu<sub>2</sub>(X)tpmc]<sup>4+</sup> appearing at  $m/z$  196, 191, 192, 188 for (2)–(5), respectively, and of the basic [Cu<sub>2</sub>tpmc]<sup>4+</sup> cation at  $m/z$  173.

The thermal stability is largely dependent on the nature of the bidentate ligands. For a particular complex, the initial temperature of decomposition and the

total weight loss at the end of reaction are different (Table 1). The most thermally stable is the starting complex (1), in comparison with the compounds (2)–(5), where the more rigid and folded *boat* conformation of the tpmc is presented when the bidentate ligand bridges the two copper ions. The influence of different donor atoms presented besides nitrogen, as sulfur (in tsc and tu) or oxygen (in sc and u) is reflected too. The relatively lower thermal stability for (2) and (4) in relation to (3) and (5) could be ascribed to the higher polarizability of the sulfur than that of the oxygen atom [16]. The absence of peaks containing the additional ligand moiety in mass spectra is characteristic, indicating that the chelating N,S or N,O ligands are, as expected, weaker coordinating agents than the macrocyclic tpmc ligand. This behavior reflects the fact that stepwise removal of a cyclic ligand from the coordination sphere of a metal tends to be more difficult than for open-chain chelate ligands [17]. Indeed, the coordinated cyclic ligand may require major, unfavorable rearrangement, such as folding, within the coordination sphere before dissociation can occur.

Finally, a formation of copper sulfides and oxides as the end products according to the calculated masses from TG curves and the found weights are evident, i.e. copper(I) chloride (1), copper(II) sulfide (2), copper(II) oxide (3), copper(I) sulfide (4) and copper(I) oxide (5).

### 3.2. The rate data

The kinetics of the thermal decomposition of the complexes (1)–(5) at a constant heating rate have been interpreted according to the modified method proposed by Borchardt and Danniels [18]. Thus, for the first-order reaction the rate constant  $k$  is presented

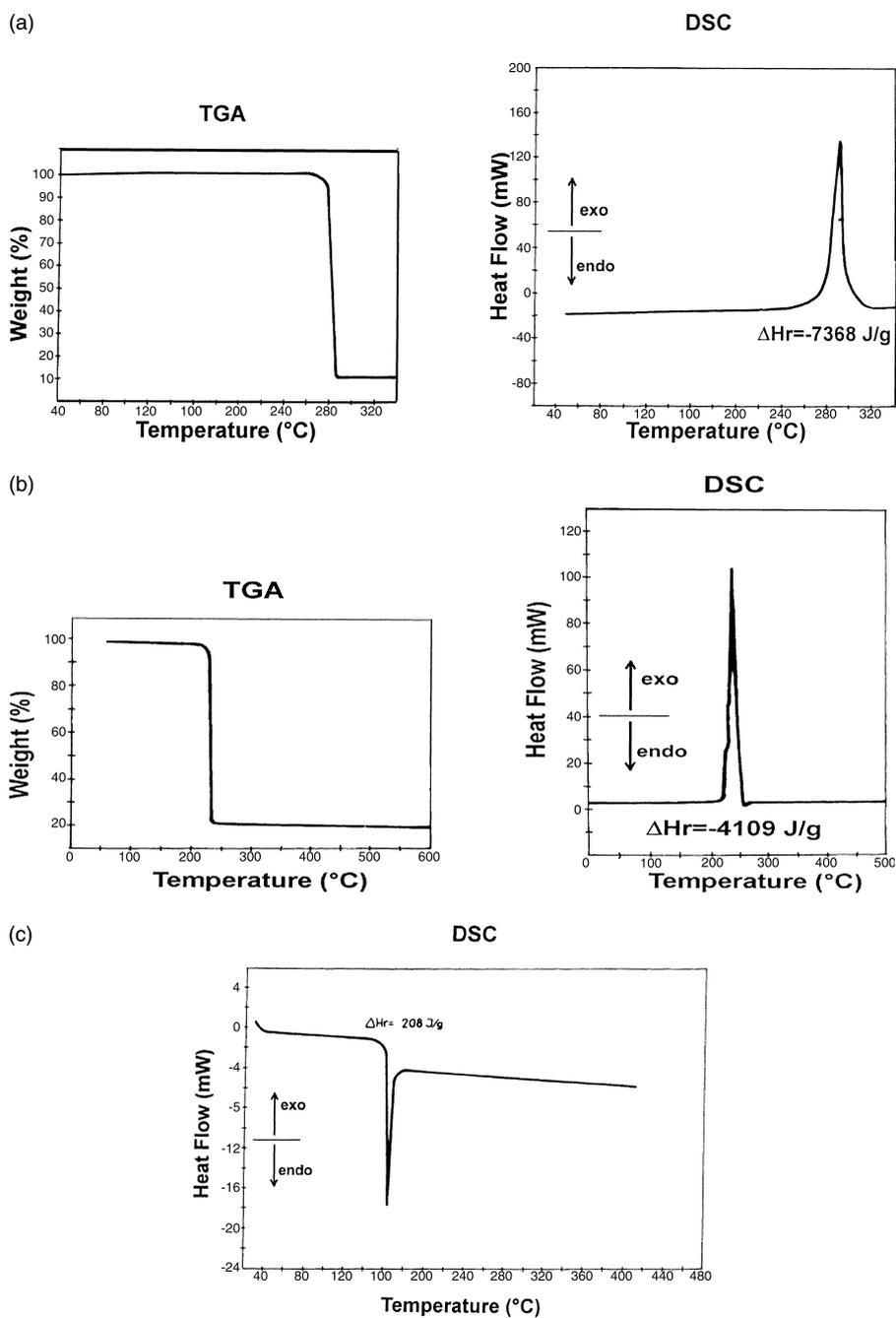


Fig. 2. DSC and TG curves of the starting complex (1) (a) of the complex (2) (b) and of the macrocyclic ligand tpmc (c) (in nitrogen) at a heating rate of  $20^\circ\text{C min}^{-1}$ .

by the equation:  $k = \Delta Y/A - a$ , where  $A$  stands for the area comprised between the DSC curve and the base line,  $a$  the fraction of this area corresponding to  $t = t_i$  and  $\Delta Y = dH/dt$  is measured and plotted directly as a function of time. The kinetic parameters, appearing in Arrhenius-like kinetic law of reaction  $k = Z \exp(-E_a/RT)$ , can be evaluated and used to provide a valid description of the thermal behavior. The plot of  $\log k$  vs.  $1/T$  allows one to obtain the activation energy  $E_a$  directly from the slope of the straight line. The apparent reaction order  $n$ , being based upon asymmetry of DSC peaks, proposed by Kissinger [19], can be obtained from the equation  $n = 1.26 S^{1/2}$ , where  $S$  is the peak shape factor. The results obtained for kinetic parameters by Borchardt–Danniels and Kissinger methods from DSC curves of the (1)–(5) complexes are listed in Table 2.

In order to check these results, a clear confirmation can be gained from the Arrhenius plots applying different methods, i.e. Maycock [20], Živković–Dobovišek [21] and Rogers–Morris [22] methods (from the DSC curves), and Newkirk [23], Freeman–Carroll [24] and Coats–Redfern [25] methods (from the TG curves). A series of parallel straight lines with correlation coefficients ranging between 0.9986 and 0.9998 results. From the Arrhenius plots, constant values of the activation energy are obtained that agree with the values listed in Table 3.

It can be seen from kinetic results that all processes of the thermal degradation are very fast and not simple, so for less than 1 min a rapid loss mass occurred (83–91%) producing many gaseous products as be seen in mass spectra [10]. Primarily due to the complexity of this rapid process of degradation, our main interest lay in the determination of the empirical rate for the over-all decomposition, as the observed

first-order rate constant does not directly measure a degradation process [11]. The observed pre-exponential factor  $Z$  is slightly higher to the maximum value expected for unimolecular decomposition [26]. The following order of activation energy can be recognized for the examined complexes, depending on the additional ligands:  $sc > u > tsc > tu$ . Very small differences of activation energy values are in agreement with the simple order of reaction in spite of the fact that the decomposition of the complexes is not a straightforward process. It most probably interferes with structural rearrangements due to the macrocyclic and chelate effects and the different binding power of the bridging ligands [11]. Half-life times also show that influence of presented oxygen besides nitrogen as a donor atoms (in additional ligands  $sc$  and  $u$ ) reflects in a faster reaction of decomposition in relation to sulfur–nitrogen donor ligands ( $tsc$  and  $tu$ ). Half-life times are, however, a satisfactory way of comparing the stabilities of series of compounds [11,12]. The thermal decomposition of the starting complex was much faster than the corresponding reaction for derived complexes (2)–(5), as expected, taking into account the already observed different conformation of the macrocycle  $tpmc$  in these compounds. In general, deriving of such parameters can help very much in the study of different effects in a series of similar thermal decomposition reactions [11,27].

The activation parameters relating to the rate constant  $k$  were calculated in the usual way [28] (Table 4). The less dissociation will occur for the cyclic ligand due to its macrocyclic effect [29] along with the fact that nitrogen atoms are less polarizable than the sulfur and oxygen ones [16]. The inequality in enthalpic contribution appears to reflect a variance in structural transformations needed to break old and form new

Table 2

Rate constant and related kinetic parameters of the over-all decomposition for the (1)–(5) complexes obtained from DSC curves by Borchardt–Danniels and Kissinger's methods [18,19]<sup>a</sup>

Complex	$k \times 10^3$ (s <sup>-1</sup> )	$T$ (K)	$Z$ (s <sup>-1</sup> )	$E_a$ (kJ/mol)	$n$	$t_{1/2}$ (s)
1	15.0	559.0	$1.2 \times 10^{21}$	245	1.10	46.2
2	3.0	517.2	$9.1 \times 10^{15}$	183	1.13	231.0
3	6.1	548.3	$1.2 \times 10^{18}$	213	1.03	113.6
4	5.0	529.5	$3.0 \times 10^{14}$	170	0.99	138.6
5	7.2	545.5	$4.2 \times 10^{16}$	196	1.10	96.3

<sup>a</sup> Parameters:  $T$ , temperature at maximum rate;  $Z$ , the pre-exponential factor;  $E_a$ , the activation energy;  $n$ , the reaction order;  $t_{1/2}$ , the half-life times; the correlation coefficients for the linear regression are 0.999 for all cases.

Table 3  
The activation energy of the decomposition for the (1)–(5) complexes obtained from a few different methods

Method	Equation	Experimental technique	$E_a$ (kJ/mol)				
			1	2	3	4	5
Borchardt–Danniels [18]	$\ln k = \ln \frac{\Delta m W}{A - a} = f\left(\frac{1}{T}\right)$	DSC	245	183	213	170	196
Maycock [20]	$\frac{\ln a - \ln b}{(1/T_a) - (1/T_b)} = -\frac{E}{R}$	DSC	245	185	215	172	194
Živković–Dobovišek [21]	$\log\left(\frac{1}{t} \ln \frac{S}{S - S_t}\right) = f\left(\frac{1}{T}\right)$	DSC	255	193	223	181	208
Rogers–Moriss [22]	$\log d_j = f\left(\frac{1}{T_j}\right)$	DSC	246	182	216	173	193
Newkirk [23]	$\ln k = f\left(\frac{1}{T}\right)$	TG	243	180	219	168	192
Freeman–Carroll [24]	$\frac{\Delta \log(dx/dt)}{\Delta \log(1 - \alpha)} = f\left(\frac{\Delta(1/T)}{\Delta \log(1 - \alpha)}\right)$	TG	243	187	221	175	199
Coats–Redfern [25]	$\log\left(-\frac{\log(1 - \alpha)}{T^2}\right) = f\left(\frac{1}{T}\right)$	TG	205	158	189	154	178

chemical bonds in the transition state, depending on the nature of the bridging chelating ligands and thus producing the corresponding difference in the nature of bonds between metal ions and the respective ligands involved. It should be noted that the positive value of the entropy term exhibiting the change in the order of the system is indeed expected for the degradation processes especially as a consequence of gaseous products obtained.

### 3.3. Reaction mechanism

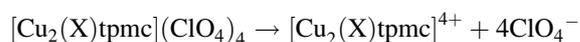
The variety and character of the products, the high pre-exponential factor and the high activation energy associated with the empirical first-order rate constant all point to a complex mechanism for the

Table 4  
Activation parameters relating to the rate constant  $k$  of the complexes (1)–(5)

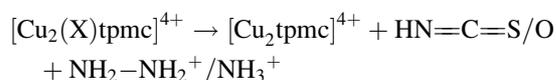
Complex	$\Delta H$ (kJ/mol)	$\Delta S$ (J/K mol)	$\Delta G$ (kJ/mol)
1	240	145	159
2	179	48	154
3	208	88	160
4	166	19	155
5	192	60	159

decomposition. Concerning possible mechanism of thermal degradation of the complexes (1)–(5) it could distinguish a few exothermic reactions of decomposition, which involve degradation of the complexes in the solid state with corresponding loss in weight and formation of final product copper sulfides and oxides. A mechanism can be written which leads to first-order kinetics and also explains the general features of the decomposition, although considerably more data need to be gathered to place any high degree of confidence in this mechanism.

Generally, thermal decomposition taking into account mass spectra [10] as well, can be summarized by the following reactions:



where  $m/z$  values are 196, 191, 192, 188 for (2)–(5), respectively.



where  $m/z$  values are 173, 32, and 17 for (1)–(5), (2) and (3), and (4) and (5), respectively.

Besides general features of the fragmentation, possible redox reactions of the intermediate products in

gaseous phase can be explained as well are



On these circumstances, in the very high temperature runs  $\text{Cu}(\text{OH})_2$  could be formed which could be decomposed to  $\text{CuO}$ , but in atmosphere where  $\text{H}_2\text{S}$  is presented, metal sulfide as residue are expected, as well. The last peaks in mass spectra [10] at 99 (for the starting complex) and at 96, 79, 160, 143 for (2)–(5), respectively, undoubtedly correspond to different  $\text{Cu}(\text{I})$  and  $\text{Cu}(\text{II})$  species proposed in the thermal analysis as the end products.

#### 4. Conclusions

The thermal behavior for the complexes (2)–(5) is largely dependent on the nature of the additional ligands. In contrast, for the basic complex  $[\text{Cu}_2\text{tpmc}](\text{ClO}_4)_4$  all thermal parameters consists with its higher stability. For a particular complex, the initial temperature of decomposition and the total weight loss as well as the end products are different. The effect of the various multidonor atoms is reflected on the rate constant and related kinetic and activation parameters, observed for the examined complexes in the order with  $\text{sc} > \text{u} > \text{tsc} > \text{tu}$  bidentate ligands. For all the complexes, the over-all decomposition is first order in reactant. The activation energy of the reaction decomposition for the (1)–(5) complexes obtained from a few different methods are in good agreement with calculated values. The half-life times show that faster reactions of decomposition occurred in the complexes with additional ligand with oxygen ( $\text{sc}$  and  $\text{u}$ ) than that with sulfur ( $\text{tsc}$  and  $\text{tu}$ ) atom besides common nitrogens. In terms of the mechanism, a plausible pathway that entails generally decomposition with some regard to the nature of the intermediates and reaction products is proposed.

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#### References

- [1] G. Maffii, E. Testa, R. Ettore II Farmaco (Eds.), *Scientifica* 13 (1958) 187.
- [2] R.D. Grasseti, J.F. Murray Jr., M.E. Brokke, A.D. Gutman, *J. Med. Chem.* 13 (1970) 273.
- [3] B. Ita, U.J. Ekpe, U.J. Ibok, *J. Appl. Chem. Agric. Res.* 1 (1994) 12.
- [4] U.J. Ekpe, U.J. Ibok, B.I. Ita, O.E. Offiong, E.E. Ebenso, *Mater. Chem. Phys.* 40 (1995) 87.
- [5] B.I. Ita, O.E. Offiong, *Mater. Chem. Phys.* 48 (1997) 164.
- [6] G. Vučković, D. Opsenica, S.P. Sovilj, D. Poleti, M. Avramov-Ivić, *J. Coord. Chem.* 42 (1997) 241.
- [7] Z.M. Miodragović, G. Vučković, S.P. Sovilj, D.D. Manojlović, M.J. Malinar, *J. Serb. Chem. Soc.* 63 (1998) 781.
- [8] G. Vučković, D. Opsenica, S.P. Sovilj, D. Poleti, *J. Coord. Chem.* 47 (1999) 331.
- [9] S.P. Sovilj, G. Vučković, K. Babić-Samardžija, N. Matsumoto, V.M. Jovanović, J. Mrozinski, *Synth. React. Inorg. Met.-org. Chem.* 29 (1999) 785.
- [10] S.P. Sovilj, G. Vučković, V.M. Leovac, D.M. Minić, *Pol. J. Chem.* 74 (2000) 945.
- [11] S.P. Sovilj, K. Babić-Samardžija, D.M. Minić, *Mater. Sci. Forum* 352 (2000) 271.
- [12] U.B. Cejpider, R. Bucci, A.D. Magri, *Thermochim. Acta* 161 (1990) 37.
- [13] E. Asato, H. Toftlund, S. Kida, M. Mikuriya, K. Murray, *Inorg. Chim. Acta* 165 (1989) 207.
- [14] S.P. Sovilj, K. Babić-Samardžija, *Synth. React. Inorg. Met.-org. Chem.* 29 (1999) 1655.
- [15] R.C. Mackenzie, *Differential Thermal Analysis*, Academic Press, London, 1970 (Chapter 12).
- [16] M.J.M. Campbell, *Coord. Chem. Rev.* 15 (1975) 299 and references cited therein.
- [17] M. Kodama, E. Kimura, *J. Chem. Soc., Dalton Trans.* (1976) 2341.
- [18] H.J. Borchardt, F. Daniels, *J. Am. Chem. Soc.* 79 (1957) 41.
- [19] H.E. Kissinger, *J. Res. Nat. Bur. Stand.* 57 (1956) 217.
- [20] J.M. Maycock, *Thermochim. Acta* 1 (1970) 389.
- [21] Ž.D. Živković, B. Dobovišek, *Thermochim. Acta* 32 (1979) 285.
- [22] R.N. Rogers, E.D. Morris, *Anal. Chem. Soc.* 38 (1966) 412.
- [23] A.E. Newkirk, *Analyt. Chem.* 32 (1960) 1558.
- [24] E.S. Freeman, B. Carroll, *J. Phys. Chem.* 62 (1958) 394.
- [25] A.W. Coats, J.P. Redfern, *Nature* 201 (1964) 68.
- [26] P. Jewsbury, *J. Phys. Solid State Phys.* 10 (1977) 671.
- [27] S.S. Kandil, M.M. Abou Sekkina, *Thermochim. Acta* 188 (1991) 43.
- [28] A.A. Frost, R.G. Pearson, *Kinetics and Mechanism*, Wiley, New York, 1961.
- [29] F.P. Hinz, D.W. Margerum, *Inorg. Chem.* 13 (1974) 2941.