Thermochimica Acta 507–508 (2010) 66–70

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermal studies of acetylacetonato aniline acetohydrazone and complexes with divalent ions of Mn, Co, Ni and Cu

Tahani I. Kashar*

Chemistry Department, Faculty of Science, Menoufia University, Egypt

ARTICLE INFO

Article history:
Received 10 March 2010
Received in revised form 17 April 2010
Accepted 5 May 2010
Available online 12 May 2010

Keywords:
Activation energy
Metal complexes
Thermal analysis

ABSTRACT

The thermal studies of acetylacetonato aniline acetohydrazone and its divalent metal ions Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} complexes were studied and discussed in terms of its molecular structure and type of metal ions. TG curves display mostly three steps of thermal decomposition. The first step is due to dehydration followed by the elimination of the anions from the complexes. The anhydrous free anion complexes undergo further decomposition forming metal oxides as final products. The activation energies E_a were evaluated and discussed in accordance with the structure of the complexes, which was assured, by elemental analyses and IR spectra.

1. Introduction

Schiff bases and related metal ions complexes, with interesting ligational features, have experienced long standing applications in biological, pharmacological, catalytic, analytical and various other fields [1–5]. Many authors investigated coordination compounds due to their chemical, biological, environmental, ion-exchange and catalytic importance [6–10]. DTA and TG were used to study the modes of thermal decomposition of some divalent cobalt, nickel and copper complexes of Schiff bases [11,12]. The studies also included the determination of thermo-kinetic parameters [13]. The stoichiometry of thermal decomposition and the relationship between thermal parameters of the complexes were studied by some authors [14]. In this work we aim to study the thermal analysis (DTA and TG) as well as the kinetic parameters of decomposition of some complexes prepared from acetylacetonato aniline acetohydrazone Schiff base.

2. Experimental

A mixture of equimolar amount of aniline, ethyl chloro acetate and sodium acetate trihydrate in absolute ethanol was refluxed for 3 h. The reaction mixture was cooled and poured onto ice-water. The so obtained solid was isolated and crystallized from ethanol to give ethyl anilino acetate. A mixture of equimolar amounts of ethyl anilino acetate and hydrazine hydrate was magnetically stirred. The so obtained white solid was isolated, dired dissolved in ethanol and then treated with acetylacetone. The reaction mixture was refluxed for 4 h. The solid formed was filtered off, washed several times with EtOH and dired under vacuum. All the complexes were prepared by mixing Mn(II), Co(II), Ni(II), Cu(II) salts and the ligand (AAAH) in (1:1) metal:ligand stoichiometries. The mixtures were stirred for 3 h. The products precipitated were removed by filtration washed several times with ethanol and dired in vacuo over P_2O_5. The differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out on a Shimadzu DT-50 and TG-50 thermal analyzers within the temperature range of 20–800 °C at a heating rate of 10 °C/min using highly purified nitrogen gas, free of any other gases, in the surrounding atmosphere with a flow rate 30 ml/min [15].

3. Results and discussion

The analytical data of the ligand and its complexes with physical properties are summarized in Table 1.

3.1. IR spectra

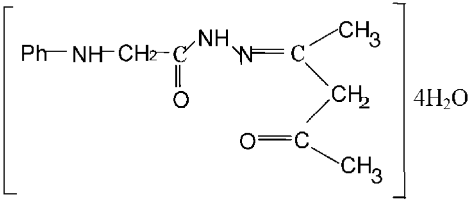
The characteristic bands in the IR spectra of the ligand and its metal complexes are listed in Table 2. The presence of water molecule in the ligand and complexes are confirmed by the presence of broad bands at 3422–3345 cm^{-1} due to νOH of water molecules associated with the complex and the two weak bands around 840 and 720 cm^{-1} which can be assigned to H_2O rocking and wagging modes of vibrations [16]. In the spectra of the complexes the bands due to νC=O (amide I) and νC=O (β-diketone) are shifted

---

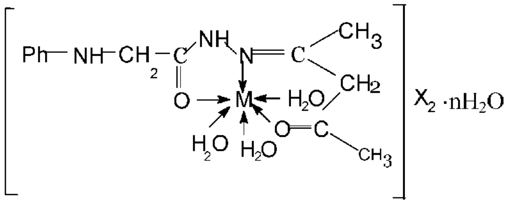
* Tel.: +20 968276998.
E-mail address: tahanikashar@yahoo.com.

0040-6031/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2010.05.002

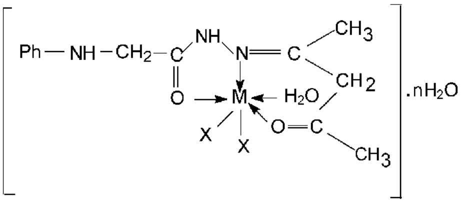
to higher frequency confirming the coordination of the metals to both carbonyl groups [17]. The shift of νC=N and νN–N to lower frequency and the shift of δNH to higher frequency confirming the coordination of azomethine nitrogen to the metal ions [18]. This result is in accordance with the expectation that N-coordination to a metal ion having filled π-orbital should result in a shift towards the lower energy region in the νC=N [19]. The presence of coordinated monodentate acetate ions in the copper acetate complex is confirmed by the existence of two bands at 1470 and 1326 cm^{-1} assigned to υ asymmetric and υ symmetric acetate. The difference between the two frequencies is higher than 110 cm^{-1}. These values confirm the presence of monodentate acetate anion [18,20,21] in the metal complex. A support of this is the presence of νC=O of the free acetate at 1741 cm^{-1}. The presence of νNO3 in the spectrum of copper nitrate complex is assigned by the presence of two bands at 1390 and 1280 cm^{-1} [22]. On the basis of the above results the complexes are formed via bonding to both carbonyl groups and azomethine nitrogen indicating that the ligand acts as dibasic tridentate toward the metal ions. The ligand and its complexes under investigation were found to have the following structures:



The ligand (AAAH)



M= Ni	n= 4	X= Cl
M= Co	n= 3	X= Cl
M= Cu	n= 1	X= Cl
M= Cu	n= 1	X= NO_3



M= Mn	n= 4	X= Cl
M= Cu	n= 1	X= Ac

3.2. *TG and DTA study*

The results of DTA thermal analysis of the prepared ligand AAAH (Table 3) show three endothermic peaks at 75, 120 and 180 °C corresponding to the weight losses of 21.1% due to removal of four molecules of water. The decomposition steps at 230–280 and 400–460 °C with weight losses of 30.3% and 27.9% due to melting with decomposition and loss of aniline molecule and nitrogen as NO_2 followed by further decomposition

The results of the thermogravimetric analysis of the metal ions complexes under study (Table 3 and Fig. 1) show that the divalent metal ions complexes lost their hydration water below 100 °C and loss the coordination water molecules near 230 °C. This finds support from the disappearance of the bands due to various modes of vibration of water molecules (ν_{H_2O} at 3400 cm^{-1}, in plane deformation δ_{H_2O} at 1350 cm^{-1} and out of plane deformation γ_{H_2O} at 975 cm^{-1}) in the spectra of copper acetate complex heated at 200 °C for 3 h in a drying oven as shown in Fig. 2. The IR spectra of 280 °C-heated copper acetate complex show the disappearance of two acetate group frequencies situated at 1470 and 1326 cm^{-1} assigned to asymmetric and symmetric monodentate acetate respectively [18,20,21]. On the other hand, the IR spectra of 280 °C-heated copper nitrate complex show the disappearance the bands due to both various modes of vibration of water molecules and nitrate group ν_{NO_3} at 1390 and 1280 cm^{-1} [22]. The TGA of the prepared complexes display decomposition of the organic ligand in two strongly interacting steps within the range from 290 to 650 °C. The first one is the loss of aniline molecules followed by further decomposition and formation of the metal oxides. The metal contents were calculated from the mass of the solid residue and were found to be in good agreement with the results of the elemental analysis within satisfactory experimental errors.

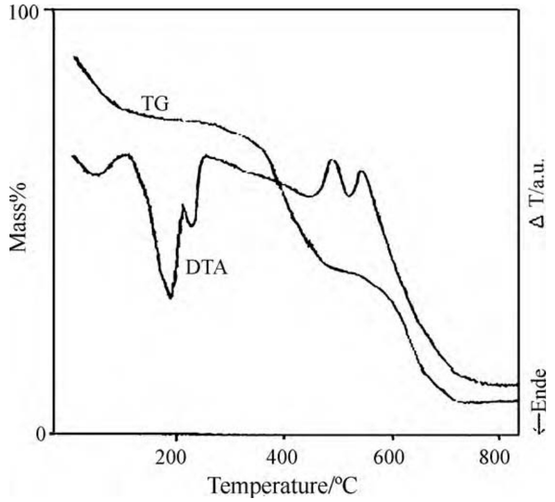


Fig. 1. DTA and TGA curves of copper acetate complex.

Accordingly, the reactions representing the three thermal decompositions of the metal ion complexes can be represented as

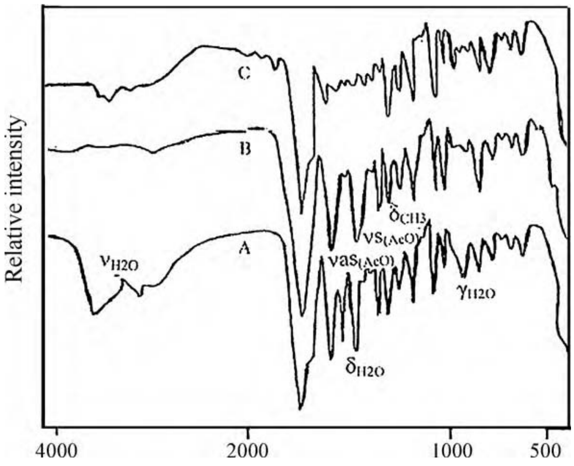


Fig. 2. IR spectra of copper acetate complex: (A) original complex; (B) after heating to 200 °C; and (C) after heating to 280 °C.

Table 1
Analytical data of acetylacetonato aniline acetohydrazone (AAAH) and its divalent metal complexes.

Compound formula (M.wt)	Colour	M.P. (d.p.) (°C)	Calc. (found) (%)			
			C	H	N	Cl
AAAH($H_2L{\cdot}4H_2O$)	Yellow	235	48.9	7.8	13.2	–
			(48.95)	(7.12)	(12.95)	–
[Mn(H_2L)$Cl_2{\cdot}H_2O$]$\cdot4H_2O$	Pale brown	>300	33.8	5.8	9.1	15.36
			(34.13)	(6.01)	(9.0)	(15.01)
[Co(H_2L)$\cdot3H_2O$]$Cl_2{\cdot}3H_2O$	Deep yellow	>300	32.17	5.98	8.66	14.64
			(32.07)	(6.14)	(8.31)	(14.91)
[Ni(H_2L)$\cdot3H_2O$]$Cl_2{\cdot}4H_2O$	Yellowish green	>300	24.7	4.9	10.89	14.1
			(24.74)	(4.59)	(11.1)	(13.92)
[Cu(H_2L)$\cdot3H_2O$]$Cl_2{\cdot}H_2O$	Brown	>300	34.4	5.5	9.3	15.7
			(34.5)	(5.12)	(9.7)	(15.49)
[Cu(H_2L)$\cdot Ac_2{\cdot}H_2O$]$\cdot H_2O$	Deep green	(290)	43.9	5.8	9.0	–
			(44.0)	(5.11)	(8.81)	–
[Cu(H_2L)$\cdot3H_2O$]$(NO_3)_2{\cdot}H_2O$	Brown	>300	30.7	4.9	13.8	–
			(30.51)	(4.7)	(14.01)	–

follows:

$$[M(H_2L)X_2 \cdot nH_2O]nH_2O \xrightarrow[70-220\,^{\circ}C]{-nH_2O} [M(H_2L)X_2]$$

$$[M(H_2L)X_2] \xrightarrow[230-360\,^{\circ}C]{-2X} M(H_2L)$$

$$M(H_2L) \xrightarrow[270-650\,^{\circ}C]{\text{further decomposition}} MO$$

On the basis of the above results one can conclude the following:

(a) Lattice and coordinated water molecules are removed from the prepared complexes upto 240 °C.
(b) The anions (acetate, chlorides and nitrate) are removed within the range of 230–350 °C.
(c) The prepared complexes undergo further decomposition and formation of metal oxides within the range of 380–750 °C.

The order, n and the energy of activation E^* of the decomposition steps were determined using the Coats–Redfern equation [23,24] in the form:

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = \frac{M}{T} + B \quad \text{for}\, n \neq 1 \tag{1}$$

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \frac{M}{T} + B \quad \text{for}\ \ n = 1 \tag{2}$$

where $M = -E^*/R$ and $B = \ln AR/\Phi E^*$; E^*, R = gas constant, A = pre-exponential factor and Φ is the heating rate (10 °C min^{-1}).

The correlation factor, r, is computed using the least squares method for Eqs. (1) and (2). The curves were plotted for values of n ranging from 0 to 1. The values of n, which gave the best linear plot was chosen as the order parameter for the decomposition stage of interest and the heat of activation was calculated from its slope.

The other activation kinetic parameters (ΔH^*, ΔS^*, ΔG^*) were computed using the standard equations [12]

$$\Delta H^* = E^* - RT,$$

$$\Delta S^* = R\left[\ln\left(\frac{Ah}{KT}\right)\right] \quad \text{and}$$

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

where K is Boltzmann constant and h is the Plank's constant. The necessary values of the temperature were taken from the middle of the step and then converted to Kelvin.

The order and the kinetic parameters of the ligand and its complexes are listed in Table 4 from which it is clear that:

(a) The negative values of ΔS^* for the dehydration step indicate that the complex is more activated than the reactant and/or the thermal decomposition reaction is slower than normal [25]. This can be explained on the premise that the degradation step involves simultaneous processes. The first one is the volatilization of the water molecules from the solid complex with positive entropy (ΔS^*) followed by the formation of a more ordered anhydrous complex with negative entropy ($-\Delta S^*$) value. The determined value is the resultant of the two processes [26]. The second step is the loss of the anion molecules with negative entropy change (ΔS^*). The third step corresponding to the decomposition of the ligand also has a negative entropy change.
(b) There are no obvious trends in the values of E^* or the activation enthalpy ΔH^*. However, the values of ΔG^* increase for subsequent decomposition stages of a given complex with increasing the order of the decomposition stage which means that the rate of decomposition for the second stage is slower than for the first one [27]. Actually, the values of ΔG^* of the complexes increase from first step to second step and then decreased to the third step indicating that the rate of decomposition of the

Table 2
Important IR bands of acetylacetonato aniline acetohydrazone (AAAH) and its divalent metal complexes.

Complex	ν((	νNH	νC=O (amide I)	νC=O (β-diketone)	νC=N	νN–N	νM–O
AAAH($H_2L{\cdot}4H_2O$)	3422 (br)	3290 (w)	1662 (s)	1641 (s)	1603 (m)	1155 (m)	–
[Mn(H_2L)$Cl_2{\cdot}H_2O$]$\cdot4H_2O$	3390 (br)	3210 (w)	1649 (m)	1622 (s)	1589 (s)	1178 (m)	514 (m)
[Co(H_2L)$\cdot3H_2O$]$Cl_2{\cdot}3H_2O$	3386 (br)	3235 (w)	1603 (s)	1602 (m)	1594 (m)	1179 (m)	515 (m)
[Ni(H_2L)$\cdot3H_2O$]$Cl_2{\cdot}4H_2O$	3392 (br)	3243 (w)	1649 (s)	1612 (s)	1579 (s)	1165 (m)	524 (m)
[Cu(H_2L)$\cdot3H_2O$]$Cl_2{\cdot}H_2O$	3348 (br)	3227 (w)	1624 (s)	1619 (m)	1587 (s)	1161 (m)	498 (m)
[Cu(H_2L)$\cdot Ac_2{\cdot}H_2O$]$\cdot H_2O$	3379 (br)	3251 (w)	1648 (m)	1621 (s)	1591 (s)	1166 (m)	502 (m)
[Cu(H_2L)$\cdot3H_2O$]$(NO_3)_2{\cdot}H_2O$	3345 (br)	3217 (w)	1632 (m)	1602 (m)	1582 (w)	1178 (m)	517 (m)

s: sharp peak; m: medium; w: weak; br: broad.

Table 3
Thermal analysis data of acetylacetonato aniline acetohydrazone (AAAH) and its divalent metal complexes.

Complex	DTA Peaks			TGA Peaks				Assignment
	Wt. of sample mg	Temp.	Peak	Wt. of sample (mg)	Temp.	Wt. calcd.	Loss% found	
AAAH($H_2L{\cdot}4H_2O$)	2.42	75, 120, 180	Endo	5.54	50–220	22.5	21.1	Loss of four water molecules and rearrangement
		270	Endo		250–400	28.8	30.3	Loss of one aniline
		450	Exo		400–600	28.8	27.9	Due to loss of nitrogen as NO_2 and further decomposition.
$[Mn(H_2L)Cl_2{\cdot}H_2O]{\cdot}4H_2O$	2.98	70, 180	Endo	8.01	50–200	19.5	20.1	Loss of four lattice and one coordinate water molecules
		330, 380, 470	Exo		250–560	35.3	33.9	Loss of one aniline and two HCl molecules
		590	Exo		570–800	26.4	26.4	Further decomposition and formation of MnO_2 as stable form
$[Co(H_2L){\cdot}3H_2O]Cl_2{\cdot}3H_2O$	3.2	70, 150, 200	Endo	2.53	70–200	22.4	21.7	Loss of three lattice and three coordinate water molecules
		280, 330	Exo		240–450	34.2	35.5	Loss of two HCl and one aniline molecules
		430, 590	Exo		550–800	29.1	30.2	Further decomposition and formation of CoO as stable form
$[Ni(H_2L){\cdot}3H_2O]Cl_2{\cdot}4H_2O$	4.31	80, 140	Exo	3.15	50–150	14.3	12.9	Loss of four lattice water molecules
		180, 330	Exo		160–350	25.2	27	Loss of the coordinate water and two HCl molecules
		420, 550	Endo		400–760	45.6	44.3	Loss of one aniline molecule followed by further decomposition and formation of NiO as stable form
$[Cu(H_2L){\cdot}3H_2O]Cl_2{\cdot}H_2O$	1.37	80, 180, 220	Endo	2.07	50–260	15.9	16.2	Loss of one lattice and three coordinate water molecules
		280	Exo		300–510	36.4	36.5	Loss two HCl and one aniline molecules
		450, 570	Exo		520–800	30.2	28.9	Further decomposition and formation of CuO as stable form
$[Cu(H_2L){\cdot}Ac_2{\cdot}H_2O]{\cdot}H_2O$	1.92	70, 190, 230	Endo	3.23	50–270	7.8	8.2	Loss of one lattice and one coordinate water molecules
		300, 385	Exo		280–480	45.2	44.9	Loss two acetate and one aniline molecules
		600	Exo		500–800	29.9	28.3	Further decomposition and formation of CuO as stable form
$[Cu(H_2L){\cdot}3H_2O](NO_3)_2{\cdot}H_2O$	2.48	70	Endo	2.41	50–220	14.2	14.9	Loss of one lattice and three coordinate water molecules
		220, 275, 360	Exo		250–400	42.6	41.8	Loss two nitrate and one aniline molecules
		460	Exo		410–800	27.6	26.8	Further decomposition and formation of CuO as stable form

Table 4
Kinetic parameters of decomposition of acetylacetonato aniline acetohydrazone (AAAH) and its divalent metal complexes.

Complex	Step	*n*	*r*	*T* (K)	Coats–Redfern equation			
					E^* (kJ mol^{-1})	ΔH^* (kJ mol^{-1})	ΔS^* (kJ mol^{-1} K^{-1})	ΔG^* (kJ mol^{-1})
AAAH($H_2L{\cdot}4H_2O$)	1st	0.5	0.9769	418	0.103146	−3.45191	−0.17448	69.48131
	2nd	0.33	0.9961	670	18773.43	−5.52925	−0.06991	41.3115
$[Mn(H_2L)Cl_2{\cdot}H_2O]{\cdot}4H_2O$	1st	1	0.994	387	52.56761	−3.21476	−0.12332	44.50991
	2nd	0.66	0.9871	639	0.04492	−5.27925	−0.17786	108.3747
	3rd	1	0.9958	963	660.5979	−7.99516	−0.09471	83.2115
$[Co(H_2L){\cdot}3H_2O]Cl_2{\cdot}3H_2O$	1st	0.66	0.9829	400	24.71155	−3.32267	−0.12932	48.40439
	2nd	0.66	0.9862	630	0.055325	−5.20904	−0.17625	105.8277
	3rd	1	0.991	868	0.350384	−7.20651	−0.15825	130.152
$[Ni(H_2L){\cdot}3H_2O]Cl_2{\cdot}4H_2O$	1st	1	0.9562	407	97.22802	−3.38034	−0.11779	44.5604
	2nd	0.66	0.9965	649	0.06369	−5.36061	−0.17483	108.1052
	3rd	0.66	0.9942	881	2.287629	−7.25186	−0.14253	118.319
$[Cu(H_2L){\cdot}3H_2O]Cl_2{\cdot}H_2O$	1st	0.66	0.9856	484	30880.2	−3.95001	−0.06848	29.19349
	2nd	1	0.981	601	325.55	−4.99011	−0.10451	57.8199
	3rd	0.66	0.9651	880	0.008083	−7.27859	−0.18946	159.442
$[Cu(H_2L){\cdot}Ac_2{\cdot}H_2O]{\cdot}H_2O$	1st	1	0.9907	477	355.6942	−3.95988	−0.10569	46.45593
	2nd	1	0.9451	594	883.056	−4.92949	−0.09631	52.28115
	3rd	0.5	0.9901	840	0.097953	−6.93396	−0.16911	135.119
$[Cu(H_2L){\cdot}3H_2O](NO_3)_2{\cdot}H_2O$	1st	1	0.992	408	642.213	−3.38516	−0.10208	38.26429
	2nd	0.66	0.988	620	0.044483	−5.1219	−0.17819	105.3585
	3rd	0.33	0.9908	879	0.000405	−7.29716	−0.21434	181.1085

third stage is higher than that of the first and second ones. This indicate that in the first step, the free part of the chelated ligand may be subject to partial decomposition then in the other step the remainder part is degraded and finally form the representative metal oxide. This can be attributed to the structural rigidity of the chelating ligands, which requires more energy for its rearrangement to get the correct order compared with the activated complex [12].

(c) The activation energy E^* values calculated by Coats–Redfern method are shown to follow the order Cu(II) > Mn(II) > Ni(II) > Co(II) which is not perfectly in agreement with the electropositive character of the metal ions. The activation energies increase with increasing the ionic radius, thus confirming that the stability of the complexes of the ligand increases in the same direction of increasing ionic radius. This discrepancy in the trend can be explained by the presence of the free benzene ring of the aniline part of the complexes which may cause an induced strong electron delocalization over the whole complex molecule. This high induced electron delocalization is a major contribution and affects the stability of the complex. As the ionic radius of the metal ion increases, the delocalization along the azomethine group increases and the stability of the complex increases in the same direction.

From the data of thermal analysis curves and the calculated kinetic parameters of the decomposition of the prepared complexes show that the thermal stability of the metal complexes depends essentially on the nature of both the central metal ions and the ligand.

4. Conclusion

The foregoing results and discussion indicate that the thermal degradation of the metal complexes under study proceeds in three steps. The first one is the dehydration of the complexes followed by the elimination of different anions. The anhydrous anion-free complex undergoes decomposition to the metal oxide (MO) through the loss of aniline molecules followed by further decomposition. The energy of activation of the thermal decomposition as determined from the rate of reaction depends on the nature of the metal ions being in the order Cu(II) > Mn(II) > Ni(II) > Co(II).

References

[1] Y. Zhao, Chromatographia 51 (2000) 231.
[2] H. Tsukube, S. Shinoda, Chem. Rev. 102 (2002) 2389.
[3] Z.H. Chohan, H. Pervez, A. Rauf, K.M. Khan, C.T. Supuran, J. Enzym. Inhib. Med. Chem. 19 (2004) 417.
[4] K.V. Gudasi, R.V. Shenoy, R.S. Vadavi, M.S. Patil, S.A. Patil, Indian J. Chem. 44A (2005) 2247.
[5] T. Premkumar, S. Govindarajan, World J. Microbiol. Biotech. 22 (2006) 1105.
[6] S.C. Mojumdar, L. Martiska, D. Valigura, M. Melnik, J. Therm. Anal. Calorim. 81 (2005) 243.
[7] D. Czakis-Sulikowska, A. Czylkowska, A. Malinowska, J. Therm. Anal. Calorim. 67 (2002) 667.
[8] E. Jóna, M. Kubranova, P. Imon, J. Mrozinski, J. Therm. Anal. Calorim. 46 (1996) 1325.
[9] S.C. Mojumdar, G. Madhurambal, M.T. Saleh, J. Therm. Anal. Calorim. 81 (2005) 205.
[10] R.K. Verma, L. Verma, A. Bhushan, B.P. Verma, J. Therm. Anal. Calorim. 90 (2007) 725.
[11] R.M. Issa, S.M. Abu-El-Wafa, F.A. El-Sayed, Thermochim. Acta 126 (1988) 235.
[12] S.S. Kandil, F.I. Abdel-Hay, R.M. Issa, J. Therm. Anal. Calorim. 63 (2001) 173.
[13] N.A. El-Wakiel, J. Therm. Anal. Calorim. 77 (2004) 839.
[14] E. Jona, A. Maslejova, M. Kubranuva, P.J. Siumon, J. Therm. Anal. Calorim. 46 (1996) 129.
[15] L. Meites, Polarographic Techniques, 1st ed., Interscience Publishers Inc., NY, 1955.
[16] P.R. Shukla, V.K. Singh, A.M. Jaiswal, J. Indian Chem. Soc. 60 (1983) 321.
[17] S. Ghosh, A. Maiti, Indian J. Chem. 28A (1989) 980.
[18] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd ed., John Wiley, 1978.
[19] R.J. Butcher, J. Josinski, G.M. Mockler, E. Sinn, J. Chem. Soc. (1976) 1099.
[20] G.B. Deacon, R.J. Phillips, Coord. Chem. Rev. 33 (1980) 227.
[21] R. Srinivasan, I. Sougandi, K. Velavan, R. Venkatestan, V. Babu, P.S. Rao, Polyhedron 23 (2004) 1115.
[22] A.B.P. Lever, E. Mantovani, B.S. Ramaswamy, Can. J. Chem. 49 (1971) 1957.
[23] A.W. Coats, J.P. Redfern, Nature 201 (1964) 68.
[24] A.S.A. Zidan, A.I. El-Sayed, M.S. El-Meleigy, A.A. Aly, O.F. Mohammed, J. Therm. Anal. Calorim. 62 (2000) 665.
[25] A.A. Frost, R.G. Pearson, Kinetic and Mechanism, Wiley, New York, 1961.
[26] R.M. Issa, A.M. Khedr, A. Tawfik, Synth. React. Inorg. Met.-Org. Chem. 34 (2004) 1187.
[27] M. Greisher, J. Lewis, R.C. Slade, J. Chem. Soc. A (1964) 1442.