ELSEVIER

Thermochimica Acta 348 (2000) 139–146

thermochimica acta

www.elsevier.com/locate/tca

Thermal studies of transition metal complexes of acetylsalicylhydroxamic acid

V.T. Yılmaz*, F. Yılmaz

Department of Chemistry, Faculty of Arts and Sciences,
Ondokuz Mayıs University, 55119 Kurupelit, Samsun, Turkey

Received 8 July 1999; received in revised form 9 December 1999; accepted 16 December 1999

Abstract

Thermal decompositions of acetylsalicylhydroxamic acid and of the Co(II), Ni(II), Cu(II) and Zn(II) complexes has been investigated by TG, DTG and DTA. The complexes decompose to yield very stable solid intermediates at about 195°C which are characterized by IR spectroscopy, elemental analysis and magnetic moment measurements. Thermal decomposition results in the formation of the metal oxides as residues. Kinetic parameters for the dehydration and decomposition stages are also derived. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Metal acetylsalicyhydroxamates; Thermal analysis; Kinetic analysis

1. Introduction

Monohydroxamic acids have the general formula of RCON(R′)OH and form complexes with metal ions via coordination through the oxygen atoms [1–11]. These complexes are also known to act as antibiotics, tumour inhibitors and drugs [12–14]. Hydroxamic acids are also biochemically important ligands. The active sites of some biological enzymes include the hydroxamic acids [15]. They are involved in biological processes such as microbial iron transport [15], inhibition of the nickel-dependent urease enzymes [16] and the zinc-dependent matrix metalloproteinases [17].

Most of the work was carried out for identification of structure and chelating properties of hydroxamic acids in solution and solid states, however, there are only a few papers describing the thermal behaviour and stability of hydroxamic acid derivatives and their complexes in the solid state [18–23]. Capitan and Capitan-Vallvey et al. studied thermal decomposition of some metal complexes of salicylhydroxamic acid and 5,5′-methylendisalicylhydroxamic acid [18,19]. Salinas et al. [20,21] reported thermal behaviour of mandelohydroxamic acid and iminobenzohydroxamic acid derivatives. Thermal decomposition mechanisms of the iron(III) complex of 2-indolehydroxamic acid [22] and organotin salicylhydroxamates [23] appeared recently.

In a previous work [24], we reported the synthesis of acetylsalicylhydroxamic acid (AcSHA) and its transition metal complexes. In this paper, the thermal behaviour of acetylsalicylhydroxamic acid complexes of Co(II), Ni(II), Cu(II) and Zn(II) in the solid state is reported.

---

* Corresponding author. Fax: +90-362-457-6081.
E-mail address: vtyilmaz@samsun.omu.edu.tr (V.T. Yılmaz)

PII: S0040-6031(00)00347-6

Table 1
Thermoanalytical data (TG, DTG, DTA) for AcSHA and its metal complexes

Compound	Decomposition temperature (°C)	Stage	Temperature range (°C)	DTG_{max} (°C)	Removed group	Mass loss (%)		Total mass loss (%)		Solid decomposition product	Colour
						Found	Calcd.	Found	Calcd.		
AcSHA: $C_9H_9NO_4$	146[a]										White
		1	150–195	180(−)	$CH_3CONHOH$	38.43	38.46			$C_7H_4O_2$[b]	
		2	195–250	229(+)	$C_7H_4O_2$	61.22	61.54	99.65	100.00	–	
[Co(AcSHA)(OH)]: $C_9H_9NO_5Co$	169										Pink
		1	115–172	162(−)	CH_3COH	16.62	16.30			$[Co(C_7H_5NO_4)]$	Dark- blue
		2, 3, 4	218–625	265 (+), 302(+), 533(+)	$C_7H_5NO_3$	56.36	55.95	72.98	72.25	CoO	Black
$[Ni(AcSHA)_2]\cdot H_2O$: $C_{18}H_{18}N_2O_9Ni$	179										Pale-blue
		1	32–82	46(+)	H_2O	3.61	3.87			$[Ni(C_9\ H_8NO_4)_2]$	Pale-blue
		2	151–195	179(−)	$C_9H_9NO_4$	41.59	41.96			$[Ni(C_9H_7NO_4)]$	Dark- green
		3, 4	285–600	370(+), 540(+)	$C_9H_7NO_3$	38.26	38.09	83.46	83.92	NiO	Grey
[Cu(AcSHA)(OH)]: $C_9H_9NO_5Cu$	287										Green
		1	200–280	270(−)		35.27					
		2	280–365	322(−)		33.52		69.62	71.04	CuO	Brown
$[Zn(AcSHA)(OH)]\cdot H_2O$: $C_9H_9NO_5Zn$	186										White
		1	84–123	109(+)	H_2O	6.33	6.11			$[Zn(C_9\ H_7NO_4)]$	White
		2	160–192	186(−)	CH_3COH	14.47	14.94			$[Zn(C_7H_5NO_4)]$	Brown
		3	217–742	272(+)	$C_7H_5NO_3$	51.16	51.29	71.86	72.35	ZnO	White

[a] Melting point.

[b] In the liquid state.

2. Experimental

2.1. Preparation of complexes

AcSHA ($C_9H_9NO_4$) and corresponding metal complexes were prepared by the method reported earlier [24]. Upon complexation, AcSHA loses its acidic proton and therefore, the corresponding metal complexes may also be regarded as salts of hydroxamic acid.

2.2. Instrumentation

The simultaneous TG, DTG and DTA curves were obtained using a Rigaku TG8110 thermal analyser combined with TAS100 thermogravimetric analyser. The measurements were made in dynamic nitrogen atmosphere at a heating rate of 10 K min^{-1}. Approximately 10 mg samples were contained in a platinum crucible using calcinated α-alumina as reference material.

Identification of the solid intermediates formed at 195°C after 30 min heating in an oven were studied by IR spectroscopy, elemental analyses and magnetic moment measurements. IR spectra were obtained with a Mattson FTIR spectrometer in the 4000–250 cm^{-1} range, using KBr pellets. Room temperature magnetic susceptibility measurements were carried out using a Sherwood Scientific MXI model Gouy balance. C, H and N analyses were carried out at TÜBİTAK Marmara Research Centre (Gebze).

2.3. Kinetic analysis

Dehydration and decomposition stages were chosen for a detailed kinetic study. The kinetic parameters such as energy of activation (E_a) and order of reaction (n) were evaluated by employing Freeman–Carroll method [25] with Jeres modification [26].

3. Results and discussion

The thermoanalytical data for AcSHA and the corresponding metal complexes are sumarized in Table 1. Kinetic data associated with dehydration and decomposition are given in Table 2.

3.1. Thermal decompositions

3.1.1. AcSHA

The ligand melts at 146°C and begins to decompose above 150°C and takes place in two consecutive steps (Fig. 1). In the first step, mass loss calculations indicate the exothermic release of acetylhydroxamic acid ($CH_3CONHOH$) (experimental 38.43%, calculated 38.46%). Degradation of the organic residue occurs in the second step in the temperature range 195–230°C.

3.1.2. [Co(AcSHA)(OH)]

A careful examination of the thermal decomposition curves of this complex (Fig. 2) reveals that decomposition proceeds via four steps. The complex is stable up to 115°C and undergoes a violent exothermic decomposition in the temperature range 115–172°C. Mass loss calculations (experimental 16.62%, calculated 16.30%) and IR spectra of the solid intermediate formed at 195°C suggest the loss of acetaldehyde (CH_3CHO). A colour change from pink

Table 2
Kinetic data for metal hydroxamates

Reaction	E_a (kJmol^{-1})	n	r^a
$[Co(C_9H_8NO_4)(OH)]_{(s)} \xrightarrow[-CH_3COH]{115-172\ ^{\circ}C} [Co(C_7H_5NO_4)]_{(s)}$	20.6	0	0.99
$[Ni(C_9H_8NO_4)_2]\cdot H_2O_{(s)} \xrightarrow[-H_2O]{32-82\ ^{\circ}C} [Ni(C_9H_8NO_4)_2]_{(s)}$	16.4	1	0.99
$[Ni(C_9H_8NO_4)_2]_{(s)} \xrightarrow[-C_9H_9NO_4]{151-195\ ^{\circ}C} [Ni(C_9H_7NO_4)]_{(s)}$	19.9	0	0.99
$[Zn(C_9H_8NO_4)(OH)]H_2O_{(s)} \xrightarrow[-H_2O]{84-123\ ^{\circ}C} [Zn(C_9H_8NO_4)(OH)]_{(s)}$	18.6	1	0.99
$[Zn(C_9H_8NO_4)(OH)]_{(s)} \xrightarrow[-CH_3COH]{160-192\ ^{\circ}C} [Zn(C_7H_5NO_4)]_{(s)}$	21.0	0	0.98

[a] Correlation coefficient of the linear plot.

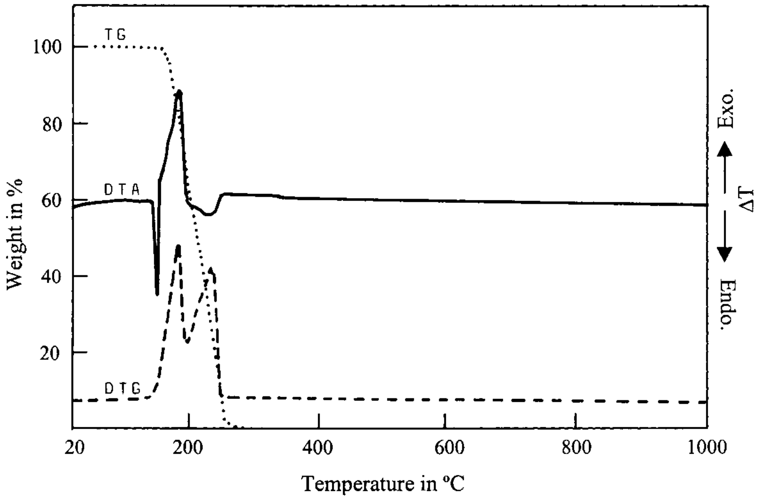


Fig. 1. Thermal analysis curves of AcSHA.

to deep blue was also observed during decomposition. The order of the decomposition reaction was zero and the E_a value was calculated as 20.6 kJ mol^{-1}. The intermediate formed is stable up to 220°C and decomposes in three steps to give CoO as the end product at 625°C.

3.1.3. [Ni(AcSHA)$_2$]·H$_2$O

This complex decomposes in four stages (Fig. 3). The first stage corresponds to dehydration in the temperature range 32–82°C. Thermal dehydration is first order with an energy of activation of 16.4 kJ mol^{-1}. In the second stage, the anhydrous complex undergoes a strong exothermic decomposition between 150 and 195°C to produce a stable solid moiety. A large mass loss (41.59%) was observed in this decomposition stage with a sharp colour change from pale-blue to dark blue. This conforms to the loss of an AcSHA molecule, thereby leading to formation of [Ni($C_9H_7NO_4$)] with an E_a value of 19.9 kJ mol^{-1}.

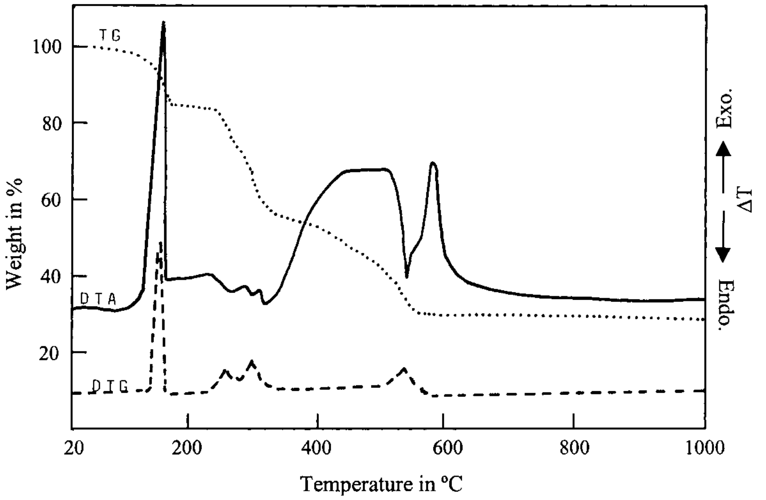


Fig. 2. Thermal analysis curves of [Co(AcSHA)(OH)].

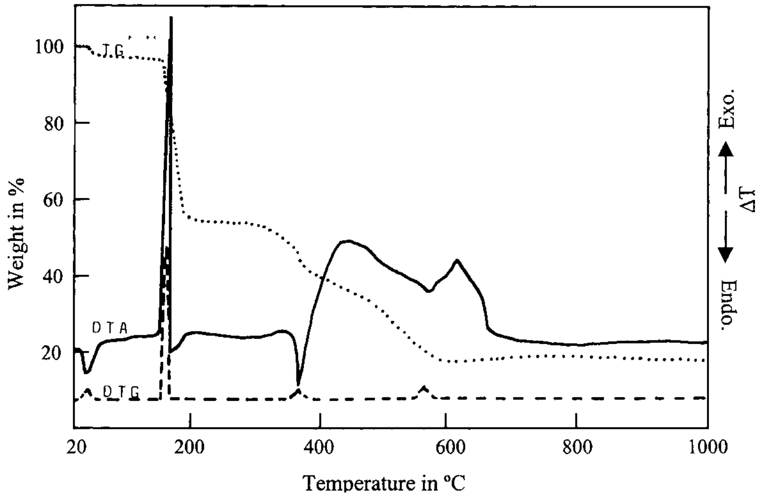


Fig. 3. Thermal analysis curves of $[Ni(AcSHA)_2]\cdot H_2O$.

The third and fourth stages correspond to the decomposition of the intermediate to yield NiO as the final decomposition product.

3.1.4. [Cu(AcSHA)(OH)]

The thermal mode of decomposition of the complex is shown in Fig. 4 and indicates that it is thermally stable up to 200°C. The thermal decomposition appears to take place in two exothermic stages at 270 and 322°C, respectively. These two decomposition processes follow a continuous mass loss with a break at 280°C and therefore, no intermediate of definite stoichiometry could be isolated. The final decomposition product was estimated as CuO.

3.1.5. [Zn(AcSHA)(OH)]·H₂O

Thermal dehydration of the complex apparently occurs in a single step (Fig. 5). The E_a and n values were found to be 18.6 kJ mol^{-1} and 1, respectively. The mass loss of 14.47% in the temperature range

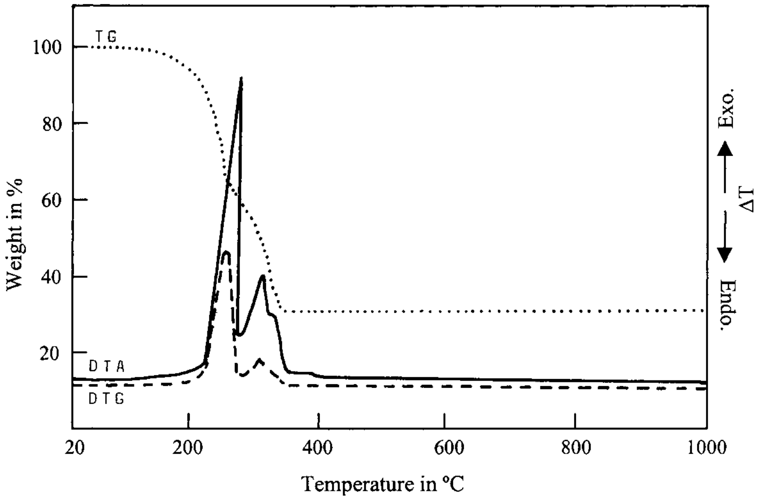


Fig. 4. Thermal analysis curves of [Cu(AcSHA)(OH)].

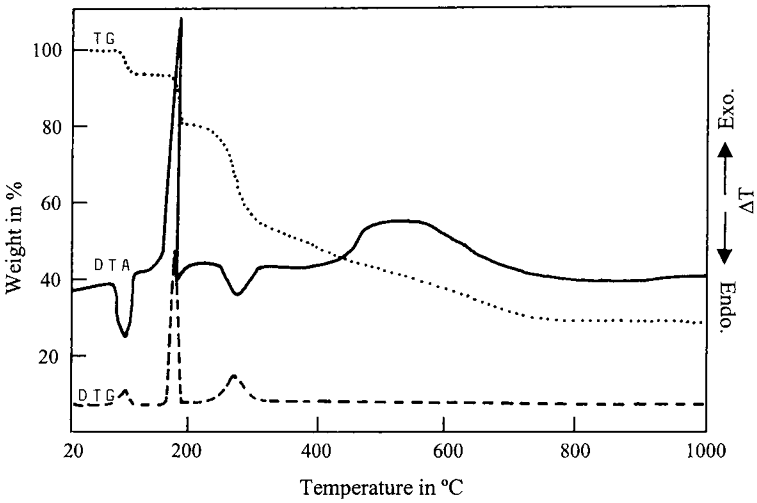


Fig. 5. Thermal analysis curves of [Zn(AcSHA)(OH)]·H_2O.

160–192°C accounts for the exothermic elimination of CH_3CHO and formation of a stable solid intermediate. The decomposition process is of zero order with an E_a value of 21 kJ mol^{-1}. The major decomposition is observed in the temperature range 217–712°C with a mass loss of 51.16% to yield ZnO.

The order of dehydration of the complexes was found to be 1 while the order of decomposition was zero. The energies of activation of dehydration were somewhat lower than those of decomposition.

3.2. Identification of solid intermediates

From the TG curves of the metal complexes, it is observed that after the violent exothermic decomposition, all complexes except the Cu(II) complex exhibit a plateau between 190 and 210°C. Mass loss calculations for the Co(II) and Zn(II) complexes correspond to the elimination of CH_3CHO (Table 1). This is also supported by the qualitative analysis of the gas CH_3CHO, which gives an acid reaction towards wet litmus paper. The Ni(II) complex exhibits different thermal behaviour. In the temperature range 150–195°C, a large mass loss (41.59%) occurs which is attributed to the release of a molecule of AcSHA.

The elemental analyses of the solid intermediates formed at 195°C are given in Table 3 and the most prominent IR frequencies are listed in Table 4. Most absorption bands are strongly affected by heating at 195°C. The solid intermediates formed by heating of the Co(II) and Zn(II) complexes did not contain the characteristic ν(NH) mode in the region 3200–3350 cm^{-1} and acetyl carbonyl ν(C=O) at about 1685 cm^{-1}, but still exhibit a broad band at about 3500 cm^{-1}, which is due to ν(OH). A new sharp absorption band centered around 1660 cm^{-1} is assigned to the N-hydroxylactam mode of ν(C=O) [18,19]. However, the Ni(II) complex exhibits

Table 3
Analytical data for the solid intermediates formed at 195°C

Complex	F.W. (g/mol)	C (%)		H (%)		N (%)		μ_s in B.M.		Colour
		Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	
[Co($C_7H_5NO_4$)]	226.0	38.06	37.20	2.70	2.23	5.25	6.19	3.93	3.87	Dark blue
[Ni($C_9H_7NO_4$)]	251.9	42.10	42.91	2.99	2.78	5.77	5.56	2.94	2.83	Dark green
[Zn($C_7H_5NO_4$)]	232.5	37.04	36.16	2.96	2.16	5.42	6.02	Dia.	Dia.	Brown

Table 4
Important IR bands of metal hydroxamates and the solid intermediates formed at 195°C[a]

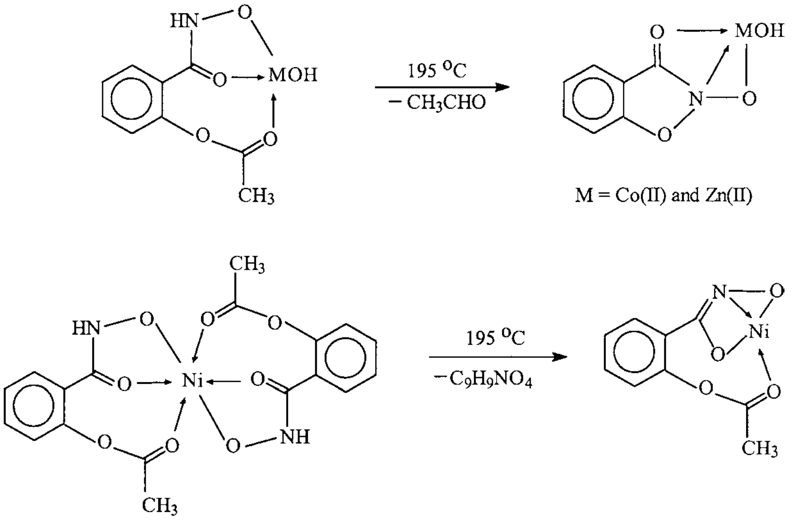
Compounds	ν(OH)	ν(NH)	ν(C=O) (acetyl)	ν(C=O) (hydroxylactam)	ν(C=N)	ν(C–N)	ν(M–O)
[Co(AcSHA)(OH)]	3542s	3235w	1687s	–	–	1324m	427w
195°C sinter [Co($C_7H_5NO_4$)]	3414m	–	–	1658s	–	1327m	437w
[Ni(AcSHA)$_2$]·H_2O	3450s,b	3076w	1674s	–	–	1351sh	409w
195°C sinter [Ni($C_9H_7NO_4$)]	–	–	1761s	–	1646s	–	441w
[Zn(AcSHA)(OH)]·H_2O	3462s,b	3286sh	1685s	–	–	1314m	445w
195°C sinter [Zn($C_7H_5NO_4$)]	3418m	–	–	1664s	–	1333m	435w

[a] s, strong; m, medium; sh, shoulder; b, broad; w, weak.

ν(C=O) of acetyl carbonyl which shifted from 1674 to 1761 cm^{-1} due to changes in the structure. A new band appears at 1646 cm^{-1}, corresponding the stretching mode of the C=N group [27]. The absorption bands around 1540 cm^{-1} disappeared and some bands below 1000 cm^{-1} also disappeared or weakened.

These observations suggest an intramolecular interaction which leads to formation of the N-hydroxylactam structure for the Co(II) and Zn(II) complexes and stabilization of the enol form of AcSHA in the Ni(II) complex in the solid state [6]. The formation of the N-hydroxylactam moiety is also reported as the decomposition intermediates of metal complexes of hydroxamic acid derivatives [18,19]. The elemental analyses (Table 3) of the solid intermediates are in good agreement with the tentative formula and the magnetic moment values of the intermediates and clearly indicate that the heated complexes have tetrahedral coordination geometry and high-spin electronic configurations. All intermediates decompose to produce the respective metal oxides as the final decomposition product. This also indicates the presence of reasonably ionic metal–oxygen bonds in the complexes.

Based on the thermal and spectroscopic data, the following decomposition reactions may be proposed for the metal complexes of AcSHA.



Acknowledgements

This work was supported by the Research Fund of Ondokuz Mayıs University.

References

[1] A.S. Bhaduri, P. Ray, Anal. Chem. 154 (1957) 103.
[2] F. Baroneelli, G. Grossi, J. Inorg. Nucl. Chem. 25 (1965) 1085.
[3] K. Bhatt, Y.K. Agrawal, Synth. Inorg. Met.-Org. Chem. 2 (1972) 175.
[4] T.P. Sharma, Y.K. Agrawal, J. Inorg. Nucl. Chem. 37 (1975) 1830.
[5] T. Maehr, Pure Appl. Chem. 28 (1971) 603.
[6] B. Chatterjee, Coord. Chem. Rev. 26 (1978) 281.
[7] E.M. Khary, M.M. Shoukry, M.M. Khalil, M.M.A. Mohamed, Transition Met. Chem. 21 (1996) 176.
[8] J.N. Nwabueze, Transition Met. Chem. 21 (1996) 258.
[9] J.N. Nwabueze, Transition Met. Chem. 22 (1997) 123.
[10] D.A. Brown, D. McKeith, W.K. Glass, Inorg. Chim. Acta 35 (1979) 5.
[11] E.C. O'Brien, S. LeRoy, J. Levaillain, D.J. Fitzgerald, K.B. Nolan, Inorg. Chim. Acta 266 (1997) 117.
[12] B.G. Malstrom, Biochemical Functions of Iron Deficiency, Academic Press, New York, 1970.
[13] J.B. Nielands, Microbial Iron Metabolism, Academic Press, New York, 1974.
[14] T. Emery, in: H. Sigel (Ed.), Metal Ions in Biological Systems, Vol. 7, Marcel Dekkar, New York, 1978.
[15] H. Kehl (Ed.), Chemistry and Biology of Hydroxamic Acids, Karger, New York, 1992.
[16] S. Odake, K. Nakahashi, T. Morikawa, S. Takebe, K. Kobashi, Chem. Pharm. Bull. 40 (1992) 2764.
[17] F. Grams, M. Crimmin, L. Hinnes, P. Huxley, M. Pieper, H. Tschesche, W. Bode, Biochemistry 34 (1995) 14012.
[18] L.F. CapitanVallvey, D. Gazquez, F. Salinas, Thermochim. Acta 56 (1982) 15.
[19] F. Capitan, D. Gazquez, A.F. Cueto, F. Capitan-Vallvey, Thermochim. Acta 75 (1984) 313.
[20] F. Salinas, I.J. Perez-Alvarez, J.L. Martinez-Vidal, A.R. Fernandez-Alba, Thermochim. Acta 127 (1988) 285.
[21] F. Salinas, M.C. Mahedero, I. Duran-Meras, Thermochim. Acta 143 (1989) 85.
[22] V. Lopez-Arza, P. Valiente, M. Jimenez-Arrabal, A. Sanchez, Thermochim. Acta 232 (1994) 243.
[23] N. Sharma, S.S. Bhatt, V. Sharma, S.C. Chaudhry, J. Thermal Anal. 53 (1998) 241.
[24] V.T. Yılmaz, F. Yılmaz, Transition Met. Chem. 24 (1999) 726.
[25] E.S. Freeman, B. Carroll, J. Phys. Chem. 62 (1958) 394.
[26] A. Jeres, J. Thermal Anal. 26 (1983) 315.
[27] K. Nakamoto, Infrared and Raman spectra of Inorganic and Coordination Compounds, Wiley, New York, 1978.