



Thermal studies on cobalt(II), nickel(II) and copper(II) ternary complexes of *N*-(2-acetamido) iminodiacetic acid and imidazoles

E.M. Abdalla^a, A.A. Said^{b,*}

^a Chemistry Department, Faculty of Science, Minia University, Minia, Egypt

^b Chemistry Department, Faculty of Science, Assiut University, Assiut, Egypt

Received 26 June 2002; received in revised form 24 February 2003; accepted 1 April 2003

Abstract

The thermal decomposition of Co(II), Ni(II) and Cu(II) complexes has been studied using thermogravimetry (TG) and differential TG (DTG). The complexes have been characterized by IR spectroscopy. The results reveal that the decomposition of these complexes is accompanied by the formation of metal acetate as an intermediate fragments. On the basis of the applicability of a non-isothermal kinetic equations, it was demonstrated that the stability of the complexes follows the order Co(II) > Cu(II) > Ni(II). These stably correspond to the strength of chelation between the metal ions and the primary and secondary ligands. A possible mechanism of the thermal decomposition of the complexes is suggested.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Thermal decomposition; *N*-(2-acetamido) iminodiacetic acid; Imidazoles; Metal complexes

1. Introduction

In an increasing number of areas of technology and hence, industry, progress is recognized as being directly related to understanding the factors influencing the reactivity of solids and how they react and interact in specific environments. However, the study of organometallic compounds in the solid state by qualitative and quantitative thermochemical methods has received considerable attention. The majority of compounds, including complexes, suffer physical and chemical changes when subjected to heat energy. The interest of the thermal analysis study of organometallic compounds aims to relate composition, structure

and material processing with those properties suitable for various technological application. However, mixed ligand complexes containing imidazole moiety are considered important in the context of understanding the amount of metal ion complexation in the biological systems [1]. For this purpose, extensive studies were carried out on such mixed ligand complexes [2–5]. On the other hand, little data have been published on the thermal analysis of cobalt, nickel and copper ternary complexes of *N*-(2-acetamido) iminodiacetic acid and imidazoles. Therefore, the present work was devoted to describe the thermal decomposition of Co(II), Ni(II) and Cu(II) ternary complexes of *N*-(2-acetamido) iminodiacetic acid and imidazoles. In addition, possibly to understand the effects of these metal ions on the complexes stability during their thermolysis.

* Corresponding author.

E-mail address: a.a.said@acc.aun.edu.eg (A.A. Said).

2. Experimental

The mixed ligand complexes under investigation were synthesized by the procedures previously described [6].

2.1. Thermal analysis

Thermal analysis was performed using computerized a Dupont Thermal Analyzer 2000 Apparatus (USA). Thermogravimetry (TG) and differential TG (DTG) curves were recorded up to 700 °C at a heating rate 10 °C min⁻¹ in an atmosphere of air (30 ml min⁻¹). The kinetic data from TG and DTG curves were evaluated using non-isothermal methods [7–12]. Many authors have employed different computational methods among which Freeman–Carroll [7], Coats–Redfern [8], Horowitz–Matzger [9], Dolyla [10], and modified Zsako [11] and Satava–Skvara [12] methods are well known and have been tested by several researchers [13–17].

2.2. Infrared (IR) spectroscopy

IR spectra of the solid complexes and their calcination products were recorded in the range 4000–400 cm⁻¹ on a Shimadzu IR-470 spectro photometer using KBr disc technique.

3. Results and discussion

3.1. Characterization of complexes

The analytical data with some physical properties of the obtained ternary complexes are published previously [6]. The data obtained revealed coordination of the divalent anions of the primary acid ligand, *N*-(2-acetamido) iminodiacetic acid (ADA)²⁻ and the neutral molecules of the secondary base ligands, imidazoles, to the divalent transition metal ion. A general molecular formula M(ADA)(B)(H₂O)_n was suggested for the different prepared complexes, where B is the secondary ligand imidazole. The formation of these ternary complexes can be represented by the following chemical equation:



These complexes were found insoluble in most common organic solvents.

The IR spectra of the complexes of Co(II), Ni(II) and Cu(II) were measured and represented in Fig. 1. It shows that, these complexes containing the secondary ligand 1,2-dimethyl imidazole display a characteristic band in the range 3400–3370 cm⁻¹ which can be attributed to the antisymmetric and symmetric OH stretching vibrations of the hydrate water molecules present in these complexes. The distinct bands that appear in the range 3370–3160 cm⁻¹ in the spectra of all complexes can be attributed to the stretching vibration of the NH₂ group of the primary acid ligand ADA²⁻ and to the secondary ligand NH stretching vibration in imidazoles, respectively. Therefore, the latter assignment may suggest that the molecules of the secondary ligands imidazoles coordinate to the central ion in their neutral form. The distinct band occurring in the range 1675–1650 cm⁻¹ in the spectra of complexes can be attributed to the C=O group of ADA²⁻ moiety. The characteristic band appearing in the 1640–1575 cm⁻¹ region in all the complexes is typical of coordinated carboxylate stretching [18]. This assignment is based on the fact that the unionized and uncoordinated COO stretching band occurs at 1750–1700 cm⁻¹, whereas the coordinated COO stretching band [18] appears at 1640–1575 cm⁻¹. Thus, the absence of any band in the range 1750–1700 cm⁻¹ in all complexes spectra is consistent with the conclusion that the divalent anions of the primary acid ligand ADA²⁻ are coordinated to the central metal ion, i.e. the two carboxylate groups of this ligand are involved in coordination, the band assigned in the 1430–1380 cm⁻¹ region is probably ascribed to the symmetric stretching vibration of the coordinated carboxylate [18]. However, the band appearing in the 1600–1575 cm⁻¹ region is most likely attributed to the stretching vibration of the γ (CN) belonging to the secondary imidazole ligands [19]. The spectra also display a band in the 1170–1140 cm⁻¹ region which is corresponded to CH₂ stretching vibration [12].

3.2. Thermal analysis

3.2.1. Cobalt(II) complexes

Thermal decomposition of cobalt complexes is represented in Fig. 2, while Table 1 presents the kinetic data of the main decomposition stages. The TG and

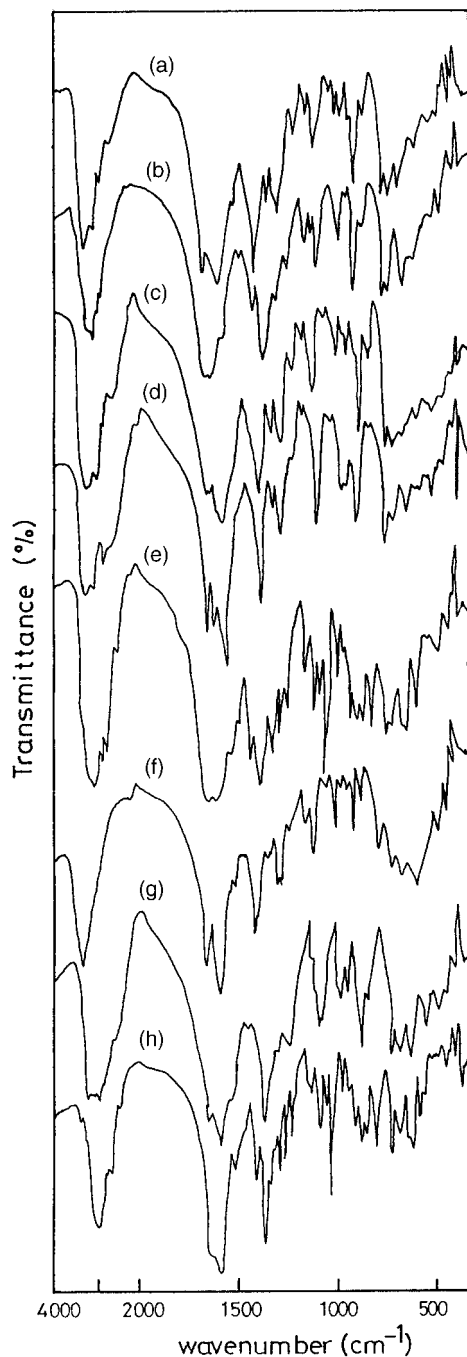


Fig. 1. IR spectra of complexes: (a) Cu(ADA)-1,2-dimethyl; (b) Cu(ADA)-2-methyl; (c) Ni(ADA)-1,2-dimethyl; (d) Ni(ADA)-2-methyl; (e) Ni(ADA); (f) Co(ADA)-1,2-dimethyl; (g) Co(ADA)-2-methyl, and (h) Co(ADA)-imidazoles.

DTG curves exhibit a series of thermal changes during elevation temperature. From Fig. 2 and Table 1, some trends and conclusions may arrive at:

- (i) The weight loss observed on TG curves on heating the complexes from room temperature up to 250 °C associated with one or two peaks on the DTG curves. This weight loss corresponds to the physically adsorbed and the crystalline water molecules.
- (ii) The weight loss extended between 270 and 350 °C accompanied with broad peaks on the DTG curves may be attained to the decomposition of the complexes into an intermediate fragments.
- (iii) The main sharp and strong peaks observed on the DTG curves with maxima at 388, 414 and 377 °C and losses in weight accompanying these stages are 40.5, 40.2 and 40.03% for Co(II)-ADA, Co(II)-ADA-2-methyl and Co(II)-ADA-1,2-dimethyl imidazoles, respectively, correspond to the decomposition of the intermediate fragments formed in the second stages into final products.
- (iv) According to the maximum decomposition temperature and the value of the activation energy of the main stage cited in Table 1, the thermal stabilities of Co(II) complexes are in the following sequence: Co(II)-ADA-2-methyl > Co(II) ADA > Co(II)-ADA-1,2-dimethyl imidazoles.
- (v) There appears to be a big difference between the thermal behavior of the complexes in the temperature less than 350 °C. This behavior may depend upon the strength of the chelation as a result of the effect of the substitution.

3.2.2. Nickel(II) complexes

The TG and DTG curves of Ni(II) complexes are shown in Fig. 3 and the data of the thermal decomposition of the main decomposition stages are cited in Table 1. From Fig. 3 and Table 1, some trends and conclusions can be summarized as follows:

- (i) The decomposition of Ni(II)-ADA-imidazole proceeds in three stages. The weight loss on heating up to 250 °C which accompanying with a small peak on the DTG curve maximized at

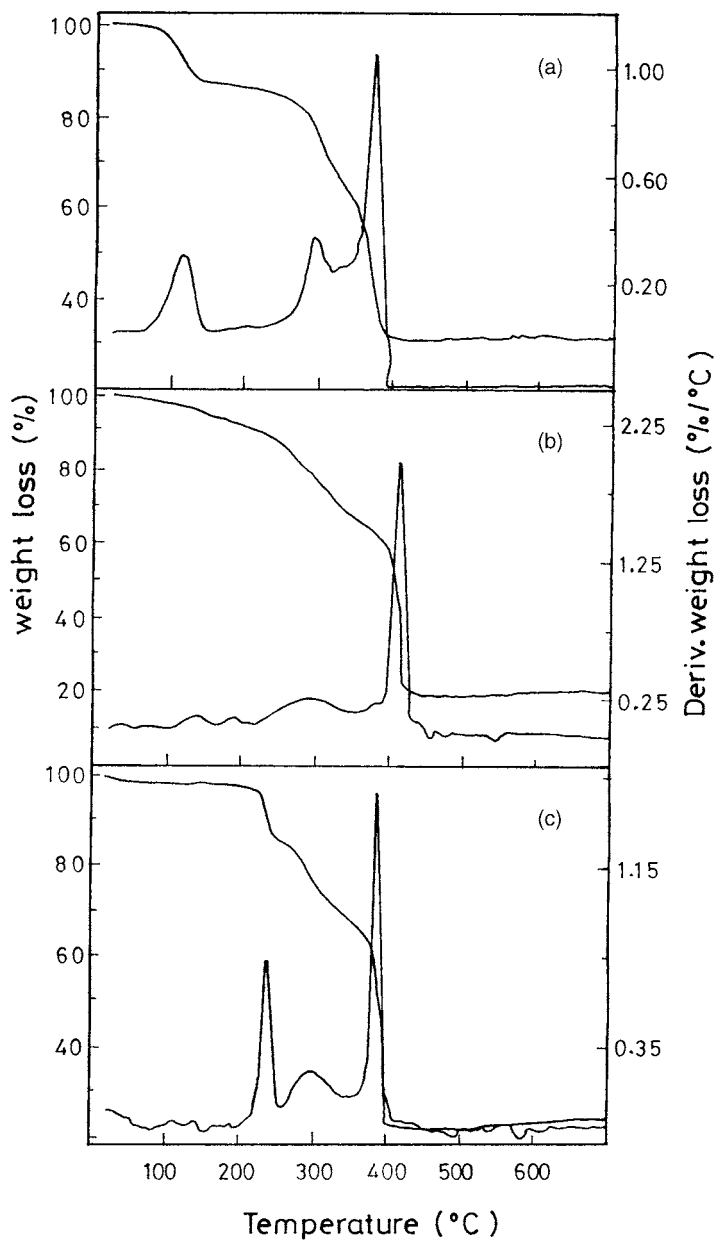


Fig. 2. TG and DTG curves of: (a) Co(ADA)-1,2-dimethyl; (b) Co(ADA)-2-methyl; and (c) Co(ADA)-imidazole complexes.

175 °C corresponds to the evolution of crystalline water molecules.

- (ii) The weight loss observed in the range 270–330 °C which associated with sharp and strong peak on the DTG curve maximized at 314 °C may,

correspond to the ignition and degradation of secondary organic ligand.

- (iii) On heating above 330 °C, the weight loses which accompanying with a sharp and strong main decomposition stage maximized at 371 °C may

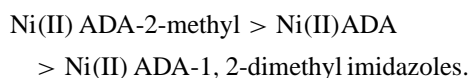
Table 1

Kinetic parameters for non-isothermal decomposition of the main stages of Co(II), Ni(II) and Cu(II) complexes

Complex	Decomposition temperature range (°C)	T_{\max} (°C)	Weight loss		E_a (kJ mol ⁻¹)	A (min ⁻¹)	S (J mol ⁻¹ K)	G (kJ mol ⁻¹ K)	H (kJ mol ⁻¹)	Order
			Found	Calculated						
CoC ₉ H ₁₂ N ₄ O ₅ ·5H ₂ O	350–400	387	40.46	43.70	753.2	1.3E+54	750.0	-5.02E+5	741.10	2
CoC ₁₀ H ₁₄ N ₄ O ₅ ·5H ₂ O	400–430	412	40.20	42.20	825.6	4.1E+56	798.0	-5.50E+5	814.10	2
CoC ₁₁ H ₂₀ N ₄ O ₅ ·5H ₂ O	330–420	373	40.03	40.50	516.0	1.8E+34	178.9	-1.15E+5	505.10	2
NiC ₉ H ₁₂ N ₄ O ₅ ·3H ₂ O	330–390	371, 377	40.81	43.66	360.0	4.3E+16	33.1	-2.13E+4	351.90	1
NiC ₁₀ H ₁₄ N ₄ O ₅ ·5H ₂ O	400–440	425, 426	40.80	42.10	301.7	2.3E+18	65.4	-4.55E+4	290.20	1
NiC ₁₁ H ₂₀ N ₄ O ₅ ·5H ₂ O	340–380	364, 374	41.10	40.60	223.9	2.4E+13	23.0	-1.31E+5	213.20	1
CuC ₁₀ H ₁₄ N ₄ O ₅ ·5H ₂ O	380–430	408, 413	40.40	41.86	669.1	2.7E+46	603.0	-4.13E+5	657.70	1
CuC ₁₁ H ₂₀ N ₄ O ₅ ·5H ₂ O	340–390	365, 370	40.50	40.48	586	3.1 E+32	566.6	-3.64E+5	576.10	2

correspond to the decomposition of the intermediate formed in the second step into final products.

- (iv) The substitution of Ni(II)-ADA-imidazole with 2-methyl or 1,2-dimethyl, curves (b and a), shows a big difference between the thermal behavior of Ni(II)-ADA-imidazole, curve (c), and these complexes below 350 °C. This behavior may depend upon the strength of the chelation between metal ions and the primary and secondary ligands.
- (v) The losses in weight accompanying the main decomposition stages are 40.8 and 41.1% for Ni(II)-ADA-2-methyl and Ni(II)-1,2-dimethyl imidazoles, respectively, corresponding to the decomposition of the intermediate fragments [19].
- (vi) It is of interest to observe here that the main decomposition stage splits into two maxima. This means that the decomposition of the intermediate associated with the formation of another intermediate which quickly decomposes to final products.
- (vii) Comparing the E_a values (Table 1) accompanying the main decomposition stages indicates that the stabilities of Ni(II) complexes are in the following order:



3.2.3. Copper(II) complexes

Thermal decomposition of Cu(II) complexes is represented in Fig. 4 and the thermal data of the main decomposition stages are cited in Table 1. From the table and looking the set of curves, some trends and conclusions may be drawn:

- (i) The TG and DTG curves undergo a series of thermal changes with a weight loss. These curves show that the decomposition proceeds in three steps.
- (ii) The small weight loss observed on the TG curve of Cu(II)-ADA-2-methyl imidazole correspond to the physically adsorbed water. The weight loss accompanying a sharp and strong peak observed on the DTG curve maximized at 242 °C may correspond to the evolution of strongly bonded water molecules. On the other hand, the weight loss observed on TG curve for Cu(II)-ADA-1,2-dimethyl imidazole on heating up to 250 °C shows three broad peaks on the DTG curves. This behavior may be explained on the basis that the removal of water molecules proceeds in different ways.
- (iii) The weight loss observed above 250 °C and extended between 250–380 and 250–350 °C for Cu(II)-ADA-2-methyl and Cu(II)-ADA-1,2-dimethyl imidazoles, respectively, which associated with broad peaks on the DTG curves

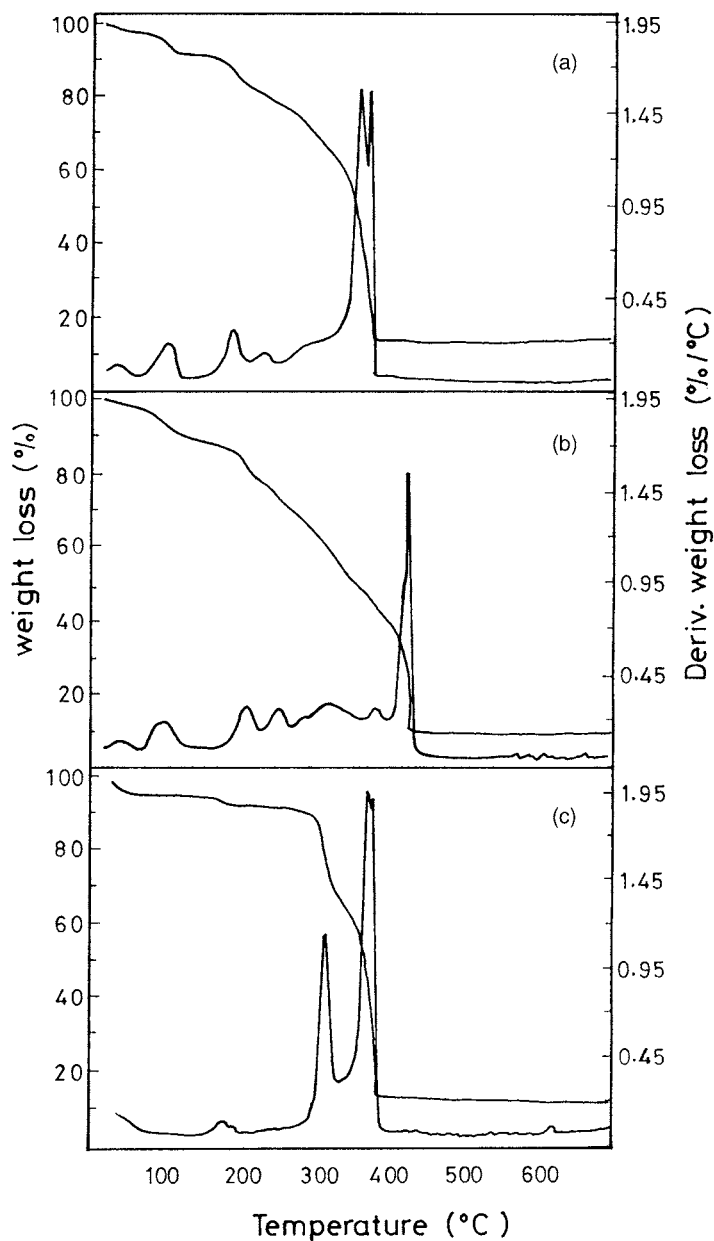


Fig. 3. TG and DTG curves of: (a) Ni(ADA)-1,2-dimethyl; (b) Ni(ADA)-2-methyl; and (c) Ni(ADA)-imidazole complexes.

may be attributed to ignition and degradation of the second ligand along the rupture of the bonds.

- (iv) The sharp and strong main peak observed above 350 °C for the two complexes is associated with

40.4 and 40.5% for Cu(II)-ADA-2-methyl and 1,2-dimethyl imidazoles, respectively, corresponding to the decomposition of the intermediate fragments formed in the second stages into final products.

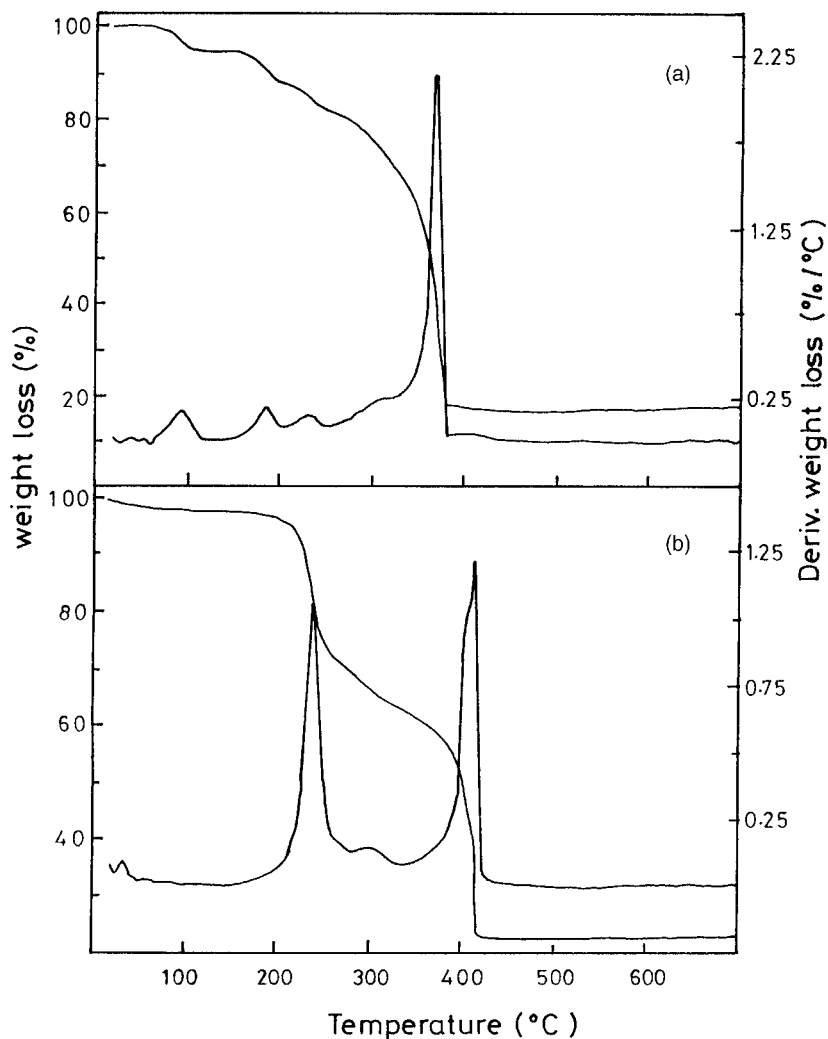


Fig. 4. TG and DTG curves of: (a) Cu(ADA)-1,2-dimethyl; and (b) Cu(ADA)-2-methyl imidazole complexes.

- (v) According to the maximum decomposition temperature and the values of activation energies of the main stages cited in Table 1, the thermal stabilities of Cu(II) complexes are

Cu(II)-ADA-2-methyl > Cu(II)-ADA-1,2-dimethyl imidazoles. This order of stability is in accordance with that obtained with Co(II) and Ni(II) complexes.

However, from the above results it is possible to suggest that the water of crystallization molecules are bonded in different ways; physically adsorbed water

dehydrated on heating up to 100 °C, whereas the coordination water is strongly bonded with a metal ion lost on heating up to 250 °C. The decomposition and degradation of the secondary ligand is accompanied by one or two decomposition stages via the formation of intermediate fragments. The complexes decompose during heating above 330 °C into final product via the decomposition of the intermediate containing primary ligand.

It is interesting to observe from the thermal decomposition of the main stages for all complexes under investigation that their behavior reflects some similar-

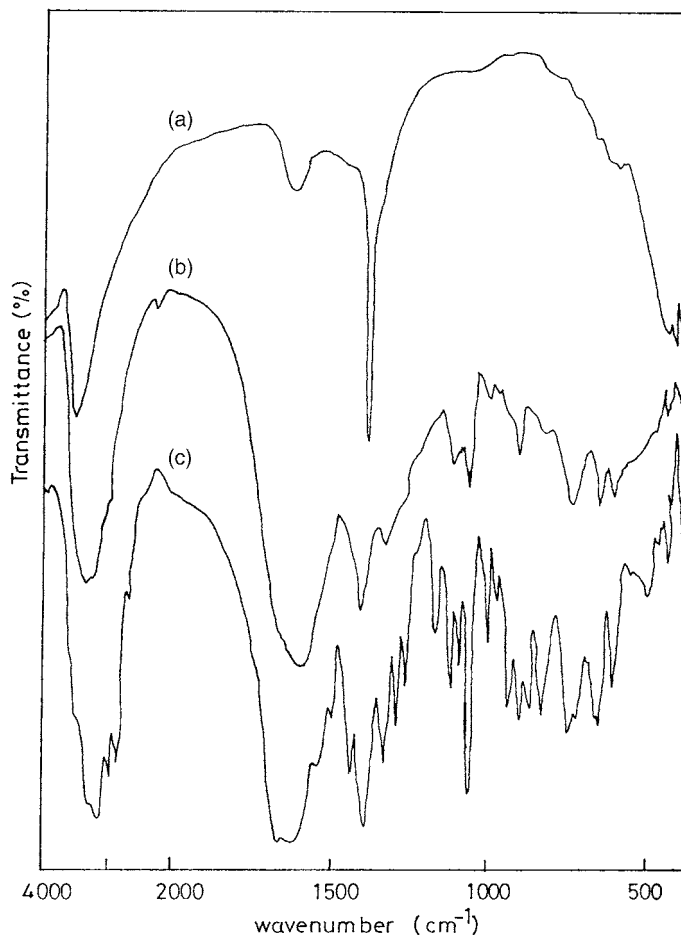
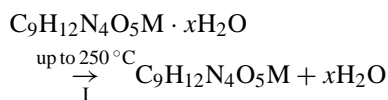
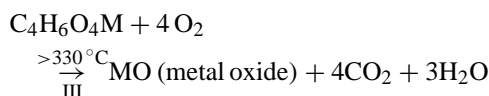
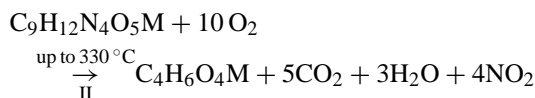


Fig. 5. IR spectra of Ni(ADA)-1,2-dimethyl imidazole complex calcined at 330 °C (a) and 300 °C (b); original sample (c).

ities in their thermolysis as well as their stabilities. This may support that the thermal decomposition of all complexes proceed with similar intermediate fragments. The weight loss associated with this stage as indicated in Table 1 was found to be in good agreement with the calculated weight loss for the decomposition of the metal acetates [20] (as intermediate compounds) (see Table 1). In support of the above results, the IR spectra of Ni(II)-ADA-1,2-dimethyl imidazole (as an example) calcined at 300 and 330 °C for 2 h were recorded and represented in Fig. 5. A comparison between the IR spectra of the original and calcined sample at 300 °C indicates a sharp reduction and/or disappearance of the bands correspond to the

secondary ligand. This leads to the conclusion that the decomposition process above 250 °C starts with the secondary ligand. Moreover, the sharp band assigned at 1380 cm^{-1} together with the broad band at 1630 cm^{-1} for the sample calcined at 330 °C (curve a), may be corresponded to the formation of nickel acetate as an intermediate compound [12–21]. Consequently, the decomposition of metal complexes under investigation proceeds in three stages according to the following suggested mechanism:





It is worth-noting from the DTG curves of the main decomposition stage above 330°C shows overlap, a rapid peak or arrest associated with weight loss on the TG curves. Thus, the stage II of the above mechanism may be accompanying with the formation of metal carbonates [16–22] which quickly decompose into metal oxide, according to the following equations:



In addition, the magnitude of activation energy measured for solid phase decomposition reaction has been often ascribed to the energy barrier in the limiting step, e.g. bond rupture, electron or proton transfer or enthalpy of dissociation. The comparison of E_a values of the main stages of all complexes takes the following order:

Co(II) complexes > Cu(II) complexes
> Ni(II) complexes

4. Conclusions

These investigations have shown that Co(II), Ni(II) and Cu(II) complexes are stable compounds. Their stabilities correspond to the strength of the chelation between the metal ions and primary and secondary ligands. The thermal decomposition processes of these compounds proceed via formation of stable metal

acetates. The formation of metal acetates is proved by the weight loss accompanying these stages and the IR spectroscopy.

References

- [1] H. Sigel, E. Fischer, *Prifs*, J. Am. Chem. Soc. 99 (1977) 4489.
- [2] D.D. Perrin, Dempsey, *Buffers for pH and Metal Ion Control*, Champan & Hall, London, 1974.
- [3] R. Nakon, C.R. Krishnamoorthy, S. Townshend, J. Cryson, *Inorg. Chem. Acta* 124 (1988) 15.
- [4] M.R. Mohamoud, H.A. Azab, H. Mansour, A.H. Mohamed, *Chem. Scripta* 29 (1989) 247.
- [5] L. Antolini, L.P. Pattaglia, A. Corradi, G. Marcotrigiano, L. Menaue, G.C. Pellacani, KM. Saladini, *Inorg. Chem.* 21 (1982) 1391.
- [6] E. Abdalla, O.M. El-Rawadi, S.A. Ibrahim, *Bull. Polish Acad. Sci.* 45 (1997) 391.
- [7] E.S. Freeman, B. Carroll, *J. Chem.* 62 (1958) 394.
- [8] A.W. Coats, J.P. Redfern, *Nature* 201 (1964) 68.
- [9] H.H. Horowitz, G. Metzger, *Anal. Chem.* 35 (1963) 1464.
- [10] C.D. Dolya, *J. Appl. Polym. Sci.* 15 (1961) 285.
- [11] J. Zsako, *J. Phys. Chem.* 72 (1968) 2406.
- [12] V. Satava, F. Skvara, *J. Am. Ceram. Soc.* 52 (1969) 591.
- [13] E. Garcia Catro, M.A. Arranz, P. Leton, *Thermochim. Acta* 170 (1990) 7.
- [14] A.A. Said, I.M. Kenawy, *J. Therm. Anal.* 36 (1990) 1257.
- [15] M.M. Abd El-Wahab, *Thermochim. Acta* 256 (1995) 271.
- [16] EL-H.M. Diefalla, A.A. El-Bellihi, S.N. Basahel, M. Abdel-Wahab, Z.A. Omran, *Thermochim. Acta* 230 (1993) 143.
- [17] M.A. Moustafa, Z.A. Omran, W.A.A. Bayoumy, M.A. Mousa, *J. Therm. Anal. Calorim.* 63 (2001) 609.
- [18] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed., Wiley, New York, 1978.
- [19] M. Mohan, K. Kumar, M. Kumar, N.K. Jha, *Inorg. Chem. Acta* 136 (1987) 65.
- [20] W. Brzyska, A. Krol, M.M. Milanova, *Thermochim. Acta* 16 (1990) 95.
- [21] A.A. Said, R.M. Hassan, *Polym. Degrad. Stabil.* 39 (1993) 393.
- [22] G.A. Haseein, B.A.A. Balboul, G.A.H. Mekhemer, *J. Anal. Appl. Pyrol.* 56 (2000) 263.