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THERMAL STABILITY OF Ni(II) AND Cu(II) MIXED LIGAND COMPLEXES DERIVED FROM BIOLOGICALLY IMPORTANT SCHIFF BASES, AZOLES AND MORPHOLINE

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درس التحلل الحراري لعدد من الليجندات المختلطة للنيكل والنحاس الثنائيين مع قواعد شيف: أرثوهيدروكسي اسيتوفينون ايثانول أمين وسليسيليدين أرثو امينوفينول وسليسيلدين ارثو تولودين وكذلك مع بعض الأزولات والمورفولين. ويكون تسخين المركبات مصحوبا في البداية بإنطلاق الأزولات أو المورفولين يليه تكسير ليجندات قواعد شيف. ودرست كيناتيكية التحليل الحراري كما حسبت بعض الثوابت الكينتيكية والثيرموديناميكية.

Thermogravimetry (TG) and differential thermogravimetry (DTG) have been applied to the investigation of the thermal behavior of six mixed ligand complexes of Ni(II) and Cu(II) comprising the Schiff bases: o-hydroxyacetophenoneethanolimine (OHAE), N-salicylidene-o-iminophenol (SOP) and N-salicylidene-o-toluidine (SOT) as well as morpholine (Morph) and certain azoles. The azoles used are: 2-amino-thiazole (2-Atz), benzothiazole (Btz), 2-methylbenzothiazole (2-Mbtz), 3-methyl-2-selenoxobenzothiazole (3-Msbtz) and thiabendazole (Tbdz). Heating the compounds first results in a release of the morpholine or the azoles. Kinetics of the decomposition reactions were studied using non-mechanistic equations.

INTRODUCTION

Schiff bases continue to occupy an important position as ligands in coordination chemistry even after almost a century. Complexes of Schiff bases with metals were found to perform a crucial role in

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biological systems[1]. Their metal complexes are noted for their antifungal and antibacterial activities, where the increase in these activities may be due to the effect of the metal ion on the normal cell process[2&3]. Furthermore, 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[4-6].

In view of the biological importance of Schiff bases and heterocyclic compounds and in view of our interest in the coordination chemistry of these ligands[7-10], the present article describes the thermal decomposition of a number of mixed ligand complexes of Ni(II) and Cu(II) with Schiff bases azoles and morpholine in order to enhance more understanding of drug-metal ion interactions.

EXPERIMENTAL

All solvents and reagents used in this work were of analytical grades. The mixed ligand complexes were prepared according to reported literature procedures[10]. The thermal studies were carried out in nitrogen flow (20 ml/min) on a Shimadzu analyzer SOH, heating rate being adjusted to 10°C/min.

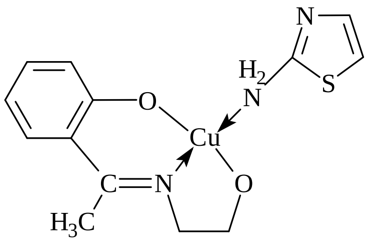
RESULTS AND DISCUSSION

The structure of the complexes as reproduced from reference 10 are depicted in Fig. 1. The thermal decomposition data of the compounds are collected in Tables 1 and 2. The complexes are thermally relatively stable and thermal decompositions of the compounds are multistage processes. Subsequent detachment of the ligands was observed. The complexes were subjected to a TG analysis from 50-700°C in nitrogen atmosphere.

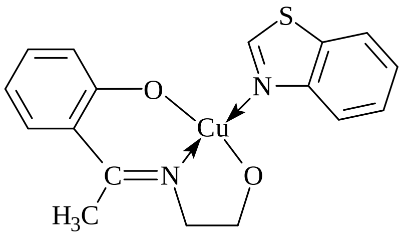
The thermoanalysis curve of [Cu(OHAE)(2-Atz)] involves five successive steps in the temperature ranges 75-150, 153-243, 250-315, 360-475 and 650-725°C. The first and second steps are connected with the expulsion of the 2-aminothiazole molecule (calc. 29.3%, found 30.0%) (eq. 1). The third step of mass loss 28.3% has an activation energy of 46.9 kJ/mol. The TG curve displays the fourth and the fifth steps as small steps with mass losses of 5.3 and 5.9%, respectively. However, the fifth step is characterized by an activation energy of 228.7% kJ/mol.

$$[\mathrm{Cu(OHAE)(2\text{-}Atz)}] \xrightarrow{75\text{-}243^\circ\mathrm{C}} [\mathrm{Cu(OHAE)}] + 2\text{-}\mathrm{Atz} \qquad (1)$$

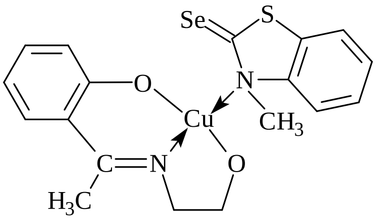
For [Cu(OHAE)(Btz)] the TG thermogram (Fig. 2) reveals four decomposition steps. The first step (40-175°C) is commensurate with



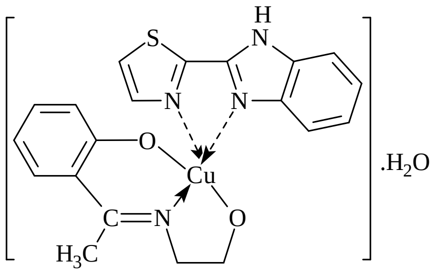
Cu((OHAE)(2-Atz)]



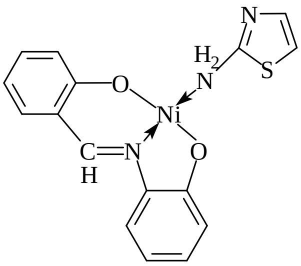
[Cu(OHAE)(Btz)]



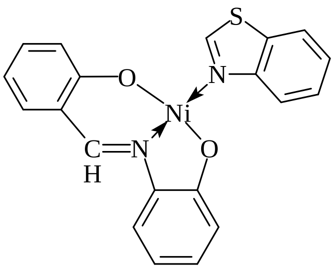
[Cu(OHAE)(3-Msbtz)]



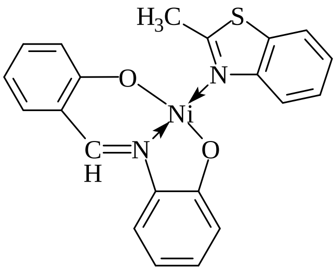
[Cu(OHAE)(Tbdz)].H_2O



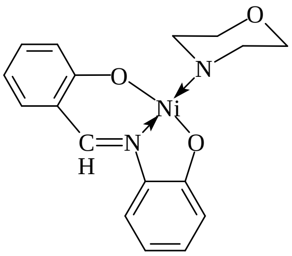
[Ni(SOP)(2-Atz)]



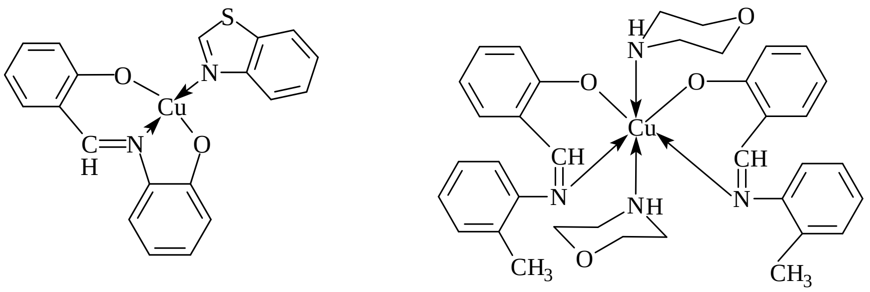
[Ni(SOP)(Btz)]



Ni(SOP)(2-Mbtz)]



[Ni(SOP)(Morph)]



[Cu(SOP)(Btz)]

$[Cu(SOT)_2(Morph)_2]$

Fig. 1: The structures of the complexes.

Table 1: Thermal decomposition data of the compounds in nitrogen flow.

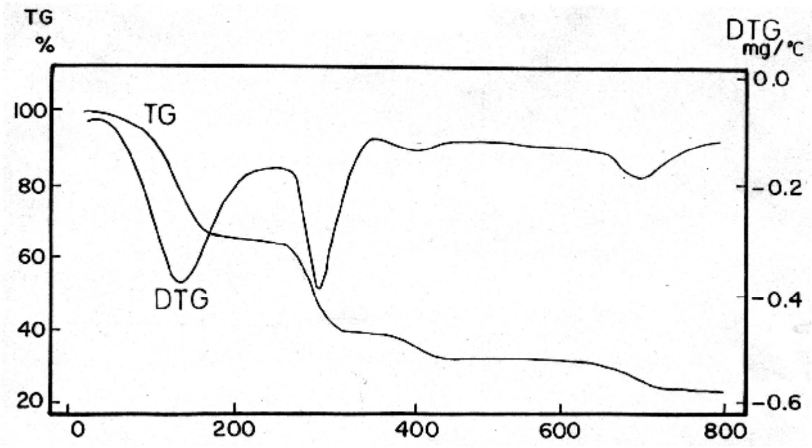
Compound	Step	TG/DTG			Mass loss (%)
		T_i /°C	T_m /°C	T_f /°C	
[Cu(OHAE)(2-Atz)]	1st	75	105	150	14.9
	2nd	153	190	243	15.1
	3rd	250	287	315	28.3
	4th	360	415	475	5.3
	5th	650	710	725	5.9
[Cu(OHAE)(Btz)]	1st	40	128	157	36.5
	2nd	264	285	307	25.3
	3rd	362	403	444	4.5
	4th	630	700	788	4.7
[Cu(OHAE)(3-Msbtz)]	1st	60	75	100	5.6
	2nd	103	140	230	43.5
	3rd	240	305	375	31.7
	4th	450	475	490	5.8
	5th	600	650	700	4.5
$[Cu(OHAE)(Tbdz)].H_2O$	1st	50	90	150	4.0
	2nd	150	210	275	43.8
	3rd	278	325	390	20.7
	4th	590	650	715	3.5

T_i = Initial temperature.
T_m = Maximum temperature.
T_f = Final temperature.

Table 2: Thermal decomposition data of the compounds in nitrogen flow (contd.).

Compound	Step	TG/DTG			Mass loss (%)
		T_i /°C	T_m /°C	T_f /°C	
[Ni(SOP)(2-Atz)]	1st	100	126	150	6.3
	2nd	150	175	300	20.7
	3rd	350	430	450	20.5
	4th	452	530	600	29.5
[Ni(SOP)(Btz)]	1st	100	178	250	33.5
	2nd	395	428	547	24.7
	3rd	480	528	540	26.3
[Ni(SOP)(2-Mbtz)]	1st	55	125	280	36.0
	2nd	355	425	460	19.3
	3rd	475	525	570	23.5
[Ni(SOP)(Morph)]	1st	75	211	320	25.0
	2nd	325	428	460	26.8
	3rd	470	531	600	25.5
[Cu(SOP)(Btz)]	1st	49	128	290	33.0
	2nd	300	364	450	57.5
[Cu(SOT)$_2$(Morph)$_2$]	1st	50	48-209	299	27.0
	2nd	325	385	453	32.5

T_i = Initial temperature.
T_m = Maximum temperature.
T_f = Final temperature.



Temperature (°C)

Fig. 2: TG-DTG curves of [Cu(OHAE)(Btz)]

the expulsion of the benzothiazole molecule (calc. 35.9%, found 36.5%) (eq. 2) with an activation energy of 48.1 kJ/mol. The second mass loss (25.3%) occurs in the temperature range 264-307°C with an activation energy of 93.9 kJ/mol. The third (4.5%) and fourth (4.7%) steps which represent the smallest steps are shown on the TG trace in the temperature ranges 362-444 and 630-788°C, respectively.

$$[Cu(OHAE)(Btz)] \xrightarrow{40\text{-}157°C} [Cu(OHAE)] + Btz \qquad (2)$$

The TG profile of [Cu(OHAE)(3-Msbtz)] exhibits five decomposition steps in the temperature ranges 60-100, 103-230, 240-375, 450-490 and 600-700°C. The first and second steps correspond to the decomposition of 3-methyl-2-selenoxobenzothiazole (calc. 48.6%, found 49.1%) (eq. 3). The calculated activation energy for the second and the third steps are 50.6 kJ/mol and 95.5 kJ/mol, respecitvely. The fourth (5.8%) and fifth (4.5%) steps are the smallest ones.

$$[Cu(OHAE)(3\text{-}Msbtz)] \xrightarrow{60\text{-}230°C} [Cu(OHAE)] + 3\text{-}Msbtz \qquad (3)$$

[Cu(OHAE)(Tbdz)].H_2O undergoes a stepwise decomposition in four decomposition stages well discernible in the TG and DTG curves in the temperature ranges 50-150, 150-275, 278-390 and 690-715°C. The mass loss at the first step points to the elimination of a water molecule (calc. 4.0%, found 4.1%). The DTG curve displays this mass loss at 90°C indicating that this water molecule can be considered as lattice water (eq. 4). The second step is commensurate with the release of the thiabendazole molecule (calc. 43.7%, found 43.8%) (eq. 5). This step is associated with an activation energy amounts to 50.9 kJ/mol. The third step (20.7%) has an activation energy of 70.5% kJ/mol. The fourth step of 3.5% mass loss is a small step. The end product corresponds to CuO (calc. 17.9%, found 19.0%).

$$[Cu(OHAE)(Tbdz)].H_2O \xrightarrow{50\text{-}150°C} [Cu(OHAE)(Tbdz)] + H_2O \qquad (4)$$

$$[Cu(OHAE)(Tbdz)] \xrightarrow{150\text{-}275°C} [Cu(OHAE)] + Tbdz \qquad (5)$$

The thermal curve of [Ni(SOP)(2-Atz)] indicates a four-stage thermal decomposition in the temperature range 100-150, 150-300, 350-450 and 452-600°C. A small step (2.1%) appears at about 95°C (DTG peak) which is ascribed to absorbed water. The first and second steps are suggested to represent decomposition of the 2-aminothiazole molecule (calc. 27.4%, found 27.0%) (eq. 6). The third step of 20.5% mass loss is characterized by an activation energy of 182.5 kJ/mol. For the fourth step (29.5%) the calculated activation energy was found to be 150.2 kJ/mol. Based on the weight loss consideration NiO was the final residue (calc. 24.5%, found 25.0%).

$$[Ni(SOP)(2\text{-}Atz)] \xrightarrow{100\text{-}300°C} [Ni(SOP)] + 2\text{-}Atz \qquad (6)$$

The TG profile of [Ni(SOP)(Btz)] exhibits three decomposition steps in the temperature ranges 100-250, 395-457 and 480-542°C. The first step accounts for the release of the benzothiazole molecule (calc. 33.3%, found 33.7%) (eq. 7) with an activation energy of 43.2 kJ/mol. The second step represents a mass loss of 24.7%, with an activation energy of 140.0 kJ/mol. The third step (26.3%) has an activation energy of 95.6 kJ/mol. The residual mass is greater than that calculated for NiO (calc. 19.4%, found 20.0%). It is possible that part of the carbon liberated from thermal decomposition of the ligands is included in the residue.

$$[Ni(SOP)(Btz)] \xrightarrow{100\text{-}250°C} [Ni(SOP)] + Btz \qquad (7)$$

The thermal curve of [Ni(SOP)(2-Mbtz)] indicates a three-stage thermal decomposition in the temperature ranges 55-280, 355-460 and 475-525°C. The first step is composed of two overlapping steps appearing separated in the DTG curve. The first step suggests decomposition of the 2-methylbenzothiazole molecule (calc. 35.6%, found 36.0%) (eq. 8). The second step 19.3% has an activation energy of 140.9 kJ/mol. The third step possesses a mass loss of 23.5% and the calculated activation energy amounts to 96.6 kJ/mol. NiO is the final product (calc. 18.9%, found 19.5%).

$$[Ni(SOP)(2\text{-}Mbtz)] \xrightarrow{55\text{-}280°C} [Ni(SOP)] + 2\text{-}Mbtz \qquad (8)$$

[Ni(SOP)(Morph)] undergoes a decomposition in three stages in the 75-320, 325-460 and 470-600°C temperature ranges. The first step is a slow step and is connected with the evolution of a morpholine molecule (calc. 24.4%, found 25.0%) (eq. 9) with an activation energy of 32.1 kJ/mol. The second step (26.8%) has an activation energy of 113.7 kJ/mol. The third mass loss (25.5%) is associated with an activation energy of 126.7 kJ/mol.

$$[Ni(SOP)(Morph)] \xrightarrow{75\text{-}320°C} [Ni(SOP)] + Morph \qquad (9)$$

The pyrolysis curve of [Cu(SOP)(Btz)] yields two steps in the temperature ranges 49-290 and 300-320°C. The first step accounts for the expulsion of the benzothiazole molecule (calc. 33.0%, found 32.3%) (eq. 10) with an activation energy of 41.0 kJ/mol. The second step is a major step

(57.5%) and possesses an activation energy of 45.6 kJ/mol.

$$[\mathrm{Cu(SOP)(Btz)}] \xrightarrow{\text{100-300°C}} [\mathrm{Cu(SOP)}] + \mathrm{Btz} \qquad (10)$$

The TG thermogram of $[\mathrm{Cu(SOT)_2(Morph)_2}]$ displays two stages in the temperature ranges 50-299 and 325-455°C. The first step seems to be composed of two overlapping steps but well separated on the DTG curve. This step may be associated with the liberation of two morpholine molecules (calc. 26.4%, found 27.0%) (eq. 11). The second step (32.5%) is a rather fast step with an activation energy of 139.7 kJ/mol.

$$[\mathrm{Cu(SOT)_2(Morph)_2}] \xrightarrow{\text{50-299°C}} [\mathrm{Cu(SOT)_2}] + 2\mathrm{Morph} \qquad (11)$$

Evaluation of the kinetic parameters

The kinetic parameters were evaluated only for clear-cut and non-overlapping stages. Kinetic studies were not attempted for decomposition stages, which occur within a very narrow temperature range because accuracy of the measurements without a sufficient number of points from the curve could not be obtained to derive meaningful results for kinetic parameters. According to Coats-Redfern[11] and Horowitz-Metzger[12] the kinetic parameters n, E and Z can be calculated by means of the following equations:

Coats-Redfern equation

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = M/T + \mathrm{B} \qquad \text{for } n \neq 1 \qquad (12)$$

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = M/T + \mathrm{B} \qquad \text{for } n = 1 \qquad (13)$$

where α is the fraction of material reacted, n is the order of the decomposition reaction and M = -E/R and B= ZR/ϕE; where E, R, Z and ϕ are the activation energy, gas constant, pre-exponential factor and heating rate, respectively.

Horowitz-Metzger equation

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{1-n}\right] = \ln\frac{ZRT_S^2}{\phi E} - \frac{\mathrm{E}}{\mathrm{RT_S}} + \frac{\mathrm{E}\theta}{\mathrm{RT_S^2}} \qquad \text{for } n \neq 1 \qquad (14)$$

$$\ln[-\ln(1-\alpha)] = \frac{\mathrm{E}\theta}{\mathrm{RT_S^2}} \qquad \text{for } n = 1 \qquad (15)$$

where θ = T – T_S, T_S is the temperature at the DTG peak.

The correlation coefficient *r* is computed using the least squares method for equations (12), (13), (14) and (15). Linear curves were drawn for different values of *n* ranging from 0 to 2. The value of *n*, which gave the best fit, was chosen as the order parameter for the decomposition stage of interest. The kinetic parameters were calculated from the plots of the left hand side of equations (12) and (13) against 1/T and against θ for equations (14) and (15).

Changes in entropy (ΔS*), enthalpy (ΔH*) and free energy (ΔG*) of activation[13] were computed using equations (16), (17) and (18).

$$\Delta S^* = 2.303\left(\log\frac{Zh}{kT_S}\right)\mathrm{R} \qquad (16)$$

$$\Delta H^* = E - RT_S \qquad (17)$$

$$\Delta G^* = \Delta H^* - T_S\Delta S^* \qquad (18)$$

where k and h are Boltzmann and Plank constants, respectively. The kinetic and thermodynamic parameters are compiled in Tables 3-8.

Conclusion remarks

(i) Non-isothermal decomposition of the complexes under study resembles the reaction

$$A_{(s)} \rightarrow B_{(s)} + C_{(g)}$$

which can be studied kinetically.

(ii) The calculated activation energies of the complexes are relatively low indicating their relative law stability. The activation energy values of the copper complexes are lower than those of the corresponding nickel complexes which can be attributed to the autocatalytic effect of copper on the thermal decomposition of the copper complexes. Catalytic activity of many compounds containing Cu(II) was reported in the literature[14&15].

(iii) In most cases the kinetic parameters observed in the Horowitz-Metzger equation are higher than that of the values from Coats-Redfern equation. This is due to the inherent error involved in the approximation method employed in the derivation of Horowitz-Metzger equation[12].

(iv) The value of ΔG* increases significantly for the subsequent decomposition stages of a given complex. This is due to increasing the values of TΔS* from one stage to another which overrides the values of ΔH*. The ΔG* increase reflects also that the rate of removal of the subsequent ligand will be lower than that of the precedent ligand[16&17]. This may be attributed to the structural rigidity of the remaining complex after the expulsion of one and more ligands, as compared with the precedent complex, which requires more energy, TΔS*, for its arrangement before undergoing any compositional change.

(v) The negative values of ΔS* for all the complexes means that the activation complex is more ordered than the reactants and

Table 3: Kinetic parameters for the thermal decomposition of [Cu(OHAE)(2-Atz)] and [Cu(OHAE)(Btz)].

Compound	Step	Coats-Redfern equation				Horowitz-Metzger equation			
		n	*r*	E	Z	n	*r*	E	Z
[Cu(OHAE)-(2-Atz)]	3rd	0.0	0.998	39.9	$7.9x10^{4}$	0.0	0.996	49.6	$5.4x10^{3}$
		0.3	0.999	46.9	$2.3x10^{4}$	0.3	0.999	57.6	$7.3x10^{3}$
		0.5	0.997	49.8	$9.9x10^{3}$	0.5	0.997	59.5	$8.7x10^{3}$
		0.6	0.996	53.7	$5.3x10^{3}$	0.6	0.995	62.6	$2.2x10^{4}$
		1.0	0.995	61.6	$1.5x10^{3}$	1.0	0.981	72.4	$7.6x10^{4}$
		0.0	0.981	91.5	$3.9x10^{6}$	2.0	0.980	103.3	$8.6x10^{6}$
	5th	0.0	0.979	158.6	$6.3x10^{5}$	0.0	0.991	170.9	$5.4x10^{4}$
		0.3	0.986	183.5	$1.8x10^{7}$	0.3	0.993	192.1	$3.8x10^{6}$
		0.5	0.989	190.6	$3.8x10^{7}$	0.5	0.997	201.2	$7.1x10^{8}$
		0.6	0.992	209.5	$4.2x10^{8}$	0.6	0.998	219.3	$2.9x10^{9}$
		1.0	0.996	228.7	$4.5x10^{10}$	1.0	0.999	237.2	$3.6x10^{11}$
		2.0	0.995	342.6	$6.8x10^{13}$	2.0	0.986	350.1	$5.4x10^{14}$
[Cu(OHAE)-(Btz)]	1st	0.0	0.971	26.6	$5.6x10^{3}$	0.0	0.973	20.4	$5.6x10^{3}$
		0.3	0.986	31.9	$1.1x10^{4}$	0.3	0.985	25.4	$8.2x10^{3}$
		0.5	0.993	35.5	$9.5x10^{4}$	0.5	0.989	29.3	$1.6x10^{4}$
		0.6	0.996	38.1	$3.9x10^{5}$	0.6	0.993	34.1	$3.1x10^{4}$
		1.0	0.999	48.1	$4.8x10^{6}$	1.0	0.998	45.2	$5.6x10^{5}$
		2.0	0.991	84.9	$2.1x10^{8}$	2.0	0.997	78.3	$4.6x10^{7}$
	2nd	0.0	0.996	73.1	$1.8x10^{4}$	0.0	0.991	85.9	$2.3x10^{3}$
		0.3	0.997	83.2	$1.6x10^{5}$	0.3	0.994	90.5	$1.2x10^{4}$
		0.5	0.998	88.3	$2.6x10^{5}$	0.5	0.996	93.6	$3.7x10^{4}$
		0.6	0.999	93.9	$1.8x10^{6}$	0.6	0.997	98.7	$6.1x10^{6}$
		1.0	0.993	104.7	$1.3x10^{7}$	1.0	0.989	110.7	$5.6x10^{7}$
		2.0	0.991	146.7	$4.6x10^{10}$	2.0	0.988	150.9	$4.8x10^{10}$

E in kJmol^{-1}, Z in s^{-1}.

Table 4: Kinetic parameters for the thermal decomposition of [Cu(OHAE)(3-Msbtz)] and [Cu(OHAE)(Tbdz)].H_2O.

Compound	Step	Coats-Redfern equation				Horowitz-Metzger equation			
		n	*r*	E	Z	n	*r*	E	Z
[Cu(OHAE)-(3-Msbtz)]	2nd	0.0	0.972	27.9	$5.5x10^{4}$	0.0	0.970	23.2	$4.6x10^{3}$
		0.3	0.986	32.8	$8.1x10^{4}$	0.3	0.975	27.3	$7.3x10^{3}$
		0.5	0.991	37.8	$3.5x10^{3}$	0.5	0.980	30.7	$2.6x10^{4}$
		0.6	0.992	41.7	$4.9x10^{4}$	0.6	0.990	35.7	$4.1x10^{4}$
		1.0	0.997	50.6	$9.1x10^{4}$	1.0	0.998	37.8	$5.6x10^{5}$
		0.0	0.992	90.7	$2.1x10^{9}$	2.0	0.991	81.9	$5.7x10^{8}$
	3rd	0.0	0.991	76.3	$2.7x10^{4}$	0.0	0.990	82.2	$3.9x10^{3}$
		0.3	0.993	87.4	$3.6x10^{5}$	0.3	0.992	87.3	$1.2x10^{4}$
		0.5	0.994	91.4	$4.6x10^{5}$	0.5	0.993	90.6	$5.7x10^{4}$
		0.6	0.995	95.5	$3.2x10^{6}$	0.6	0.996	94.3	$7.2x10^{5}$
		1.0	0.994	110.6	$2.7x10^{7}$	1.0	0.991	105.7	$7.1x10^{6}$
		2.0	0.990	150.7	$5.7x10^{11}$	2.0	0.989	145.1	$8.7x10^{10}$
[Cu(OHAE)-(Tbdz)].H_2O	2nd	0.0	0.971	27.7	$5.5x10^{4}$	0.0	0.977	19.7	$6.1x10^{3}$
		0.3	0.979	32.6	$5.8x10^{4}$	0.3	0.986	22.9	$8.1x10^{3}$
		0.5	0.992	37.5	$7.3x10^{4}$	0.5	0.988	27.6	$1.7x10^{4}$
		0.6	0.995	39.5	$8.1x10^{4}$	0.6	0.989	37.6	$3.7x10^{4}$
		1.0	0.998	50.9	$9.1x10^{4}$	1.0	0.997	42.7	$6.1x10^{5}$
		2.0	0.991	87.7	$1.3x10^{8}$	2.0	0.990	79.8	$4.8x10^{7}$
	3rd	0.0	0.999	70.5	$2.8x10^{4}$	0.0	0.999	80.8	$3.3x10^{3}$
		0.3	0.990	81.7	$2.9x10^{5}$	0.3	0.991	91.9	$2.3x10^{4}$
		0.5	0.992	89.6	$3.1x10^{5}$	0.5	0.992	95.7	$4.8x10^{4}$
		0.6	0.991	95.5	$2.8x10^{6}$	0.6	0.998	98.5	$7.1x10^{6}$
		1.0	0.993	110.7	$4.7x10^{7}$	1.0	0.989	110.6	$7.1x10^{7}$
		2.0	0.987	150.6	$5.6x10^{12}$	2.0	0.988	160.7	$5.9x10^{11}$

E in $kJmol^{-1}$, Z in s^{-1}.

Table 5: Kinetic parameters for the thermal decomposition of [Ni(SOP)(2-Atz] and [Ni(SOP)(Btz)].

Compound	Step	Coats-Redfern equation				Horowitz-Metzger equation			
		n	*r*	E	Z	n	*r*	E	Z
[Ni(SOP)-(2-Atz)]	3rd	0.0	0.983	105.1	$2.6x10^{5}$	0.0	0.991	113.0	$2.4x10^{6}$
		0.3	0.989	126.7	$1.6x10^{6}$	0.3	0.992	135.7	$1.4x10^{6}$
		0.5	0.991	135.2	$4.7x10^{6}$	0.5	0.994	145.6	$3.7x10^{7}$
		0.6	0.993	151.1	$6.1x10^{7}$	0.6	0.995	160.3	$7.8x10^{9}$
		1.0	0.999	182.5	$2.3x10^{10}$	1.0	0.997	189.4	$8.1x10^{9}$
		0.0	0.990	285.6	$5.7x10^{21}$	2.0	0.990	300.2	$9.9x10^{20}$
	4th	0.0	0.980	91.0	$2.3x10^{3}$	0.0	0.980	102.1	$4.0x10^{2}$
		0.3	0.981	107.3	$2.1x10^{4}$	0.3	0.983	118.5	$1.7x10^{3}$
		0.5	0.985	116.2	$9.2x10^{4}$	0.5	0.985	127.6	$2.5x10^{3}$
		0.6	0.988	125.7	$5.0x10^{5}$	0.6	0.988	136.5	$6.2x10^{4}$
		1.0	0.993	148.5	$9.4x10^{6}$	1.0	0.994	157.7	$2.9x10^{5}$
		2.0	0.998	150.2	$4.6x10^{8}$	2.0	0.999	161.1	$2.1x10^{7}$
[Ni(SOP)-(Btz)]	1st	0.0	0.998	31.6	$6.2x10^{4}$	0.0	0.997	40.9	$8.3x10^{3}$
		0.3	0.997	34.3	$2.7x10^{4}$	0.3	0.998	43.8	$9.1x10^{3}$
		0.5	0.996	36.4	$1.4x10^{4}$	0.5	0.996	48.9	$5.7x10^{4}$
		0.6	0.994	38.5	$9.7x10^{3}$	0.6	0.995	50.7	$7.1x10^{4}$
		1.0	0.999	43.2	$6.8x10^{3}$	1.0	0.999	55.6	$8.1x10^{4}$
		2.0	0.993	57.2	$2.9x10^{4}$	2.0	0.990	63.3	$3.1x10^{5}$
	2nd	0.0	0.966	75.9	$4.8x10^{3}$	0.0	0.974	91.0	$8.9x10^{3}$
		0.3	0.972	84.8	$2.7x10^{3}$	0.3	0.978	101.9	$7.3x10^{3}$
		0.5	0.974	89.4	$7.1x10^{3}$	0.5	0.980	106.6	$1.5x10^{4}$
		0.6	0.977	94.3	$1.9x10^{4}$	0.6	0.981	111.7	$3.7x10^{4}$
		1.0	0.981	105.1	$5.3x10^{4}$	1.0	0.984	115.8	$5.3x10^{4}$
		2.0	0.990	140.0	$8.9x10^{5}$	2.0	0.991	153.7	$2.1x10^{5}$
	3rd	0.0	0.996	95.6	$3.8x10^{3}$	0.0	0.997	78.9	$5.1x10^{2}$
		0.3	0.991	115.7	$1.1x10^{5}$	0.3	0.989	106.7	$5.2x10^{4}$
		0.5	0.990	128.2	$8.1x10^{5}$	0.5	0.975	118.7	$6.1x10^{4}$
		0.6	0.989	140.3	$5.6x10^{6}$	0.6	0.979	131.5	$7.1x10^{5}$
		1.0	0.986	168.0	$2.6x10^{8}$	1.0	0.978	157.8	$7.3x10^{7}$
		2.0	0.985	226.1	$6.8x10^{15}$	2.0	0.976	255.9	$8.1x10^{14}$

E in kJmol^{-1}, Z in s^{-1}.

Table 6: Kinetic parameters for the thermal decomposition of [Ni(SOP)(2-Mbtz] and [Ni(SOP)(Morph)].

Compound	Step	Coats-Redfern equation				Horowitz-Metzger equation			
		n	*r*	E	Z	n	*r*	E	Z
[Ni(SOP)-(2-Mbtz)]	2nd	0.0	0.985	73.7	$4.8\text{x}10^{3}$	0.0	0.971	91.5	$5.6\text{x}10^{3}$
		0.3	0.987	82.3	$2.7\text{x}10^{3}$	0.3	0.978	100.6	$8.2\text{x}10^{4}$
		0.5	0.988	89.2	$6.9\text{x}10^{3}$	0.5	0.980	105.2	$2.6\text{x}10^{4}$
		0.6	0.990	90.4	$1.7\text{x}10^{4}$	0.6	0.981	113.3	$3.2\text{x}10^{4}$
		1.0	0.992	103.2	$6.1\text{x}10^{4}$	1.0	0.985	116.4	$5.6\text{x}10^{4}$
		0.0	0.997	140.9	$9.1\text{x}10^{5}$	2.0	0.991	150.1	$4.6\text{x}10^{5}$
	3rd	0.0	0.996	96.9	$3.8\text{x}10^{3}$	0.0	0.997	80.9	$6.1\text{x}10^{2}$
		0.3	0.991	116.5	$9.1\text{x}10^{4}$	0.3	0.989	110.7	$5.6\text{x}10^{3}$
		0.5	0.986	130.8	$8.1\text{x}10^{5}$	0.5	0.985	119.5	$7.2\text{x}10^{4}$
		0.6	0.97	142.5	$5.6\text{x}10^{6}$	0.6	0.981	135.6	$8.5\text{x}10^{5}$
		1.0	0.977	170.3	$3.1\text{x}10^{7}$	1.0	0.984	160.8	$8.4\text{x}10^{7}$
		2.0	0.978	270.4	$3.1\text{x}10^{14}$	2.0	0.987	260.4	$8.9\text{x}10^{13}$
[Ni(SOP)-(Morph)]	1st	0.0	0.979	16.9	$7.1\text{x}10^{2}$	0.0	0.980	25.9	$2.1\text{x}10^{3}$
		0.3	0.986	18.9	$7.3\text{x}10^{3}$	0.3	0.982	27.7	$9.2\text{x}10^{3}$
		0.5	0.990	19.5	$1.5\text{x}10^{4}$	0.5	0.985	28.9	$1.6\text{x}10^{4}$
		0.6	0.993	20.6	$1.1\text{x}10^{5}$	0.6	0.987	30.7	$8.1\text{x}10^{4}$
		1.0	0.997	23.8	$9.1\text{x}10^{5}$	1.0	0.992	33.6	$7.6\text{x}10^{5}$
		2.0	0.998	32.1	$5.2\text{x}10^{6}$	2.0	0.999	43.7	$6.6\text{x}10^{6}$
	2nd	0.0	0.982	79.3	$2.8\text{x}10^{3}$	0.0	0.981	95.7	$6.3\text{x}10^{2}$
		0.3	0.987	89.3	$7.6\text{x}10^{3}$	0.3	0.985	97.7	$6.2\text{x}10^{3}$
		0.5	0.989	95.7	$2.6\text{x}10^{4}$	0.5	0.987	112.3	$3.7\text{x}10^{4}$
		0.6	0.992	101.2	$6.8\text{x}10^{4}$	0.6	0.988	118.5	$4.1\text{x}10^{4}$
		1.0	0.994	113.7	$3.3\text{x}10^{5}$	1.0	0.991	122.7	$1.6\text{x}10^{5}$
		2.0	0.990	158.9	$3.6\text{x}10^{9}$	2.0	0.989	167.9	$1.8\text{x}10^{8}$
	3rd	0.0	0.978	84.7	$2.3\text{x}10^{3}$	0.0	0.980	96.7	$6.6\text{x}10^{2}$
		0.3	0.982	96.5	$5.4\text{x}10^{3}$	0.3	0.985	107.8	$7.7\text{x}10^{3}$
		0.5	0.986	103.3	$2.3\text{x}10^{4}$	0.5	0.989	114.9	$3.2\text{x}10^{3}$
		0.6	0.989	109.4	$3.1\text{x}10^{4}$	0.6	0.991	120.1	$5.6\text{x}10^{4}$
		1.0	0.996	126.7	$5.7\text{x}10^{5}$	1.0	0.995	136.3	$7.1\text{x}10^{4}$
		2.0	0.995	182.1	$6.8\text{x}10^{9}$	2.0	0.993	192.4	$7.1\text{x}10^{9}$

E in kJmol^{-1}, Z in s^{-1}.

Table 7: Kinetic parameters for the thermal decomposition of [Cu(SOP)(Btz)] and [Cu(SOT)$_2$(Morph)$_2$].

Compound	Step	Coats-Redfern equation				Horowitz-Metzger equation			
		n	*r*	E	Z	n	*r*	E	Z
[Cu(SOP)-(Btz)]	1st	0.0	0.983	22.9	$2.6x10^3$	0.0	0.986	30.7	$5.3x10^3$
		0.3	0.988	25.7	$1.1x10^4$	0.3	0.988	32.5	$8.2x10^4$
		0.5	0.990	26.6	$9.5x10^4$	0.5	0.990	35.6	$5.6x10^5$
		0.6	0.991	27.5	$6.9x10^4$	0.6	0.992	37.8	$3.1x10^5$
		1.0	0.995	41.0	$3.9x10^4$	1.0	0.999	39.7	$8.7x10^5$
		0.0	0.991	75.8	$2.1x10^5$	2.0	0.998	49.8	$4.6x10^6$
	2nd	0.0	0.975	25.9	$1.8x10^3$	0.0	0.980	20.9	$4.3x10^3$
		0.3	0.978	29.5	$9.6x10^3$	0.3	0.983	27.5	$2.2x10^3$
		0.5	0.981	35.6	$5.6x10^4$	0.5	0.985	33.7	$6.7x10^3$
		0.6	0.985	39.8	$8.8x10^4$	0.6	0.987	36.5	$6.3x10^4$
		1.0	0.990	43.7	$1.1x10^3$	1.0	0.995	40.7	$9.7x10^4$
		2.0	0.983	65.5	$3.6x10^5$	2.0	0.991	61.5	$4.5x10^6$
[Cu(SOT)$_2$-(Morph)$_2$]	3rd	0.0	0.989	94.7	$3.3x10^4$	0.0	0.990	105.6	$4.7x10^3$
		0.3	0.990	106.1	$5.4x10^5$	0.3	0.992	118.7	$6.6x10^4$
		0.5	0.993	114.6	$2.3x10^6$	0.5	0.993	126.3	$3.2x10^5$
		0.6	0.996	121.6	$9.1x10^6$	0.6	0.995	133.5	$6.6x10^6$
		1.0	0.998	139.7	$1.4x10^8$	1.0	0.997	144.3	$5.1x10^7$
		2.0	0.997	203.8	$6.8x10^{10}$	2.0	0.991	218.2	$7.2x10^9$

E in kJmol^{-1}, Z in s^{-1}

Table 8: Thermodynamic parameters for decomposition of the complexes.

Compound	Step	Coats-Redfern equation			Horowitz-Metzger equation		
		ΔS* $JK^{-1}mol^{-1}$	ΔH* $kJmol^{-1}$	ΔG* $kJmol^{-1}$	ΔS* $JK^{-1}mol^{-1}$	ΔH* $kJmol^{-1}$	ΔG* $kJmol^{-1}$
[Cu(OHAE)-(2-Atz)]	3rd	-166.5	42.3	135.5	-176.0	53.0	151.5
	5th	-50.7	220.6	270.4	-33.4	229.1	261.8
[Cu(OHAE)-(Btz)]	1st	-119.3	44.8	92.6	-137.3	41.9	96.9
	2nd	-131.1	88.0	171.5	-121.3	93.4	170.7
	4th	-125.1	184.0	302.5	-140.4	173.1	306.2
[Cu(OHAE)-(3-Msbtz)]	2nd	-152.6	47.2	110.2	-137.4	34.4	91.1
	3rd	-125.8	90.8	163.4	-138.2	89.5	169.4
[Cu(OHAE)-(Tbdz)].H_2O	2nd	-153.9	46.9	121.2	-138.1	38.7	105.4
	3rd	-165.3	65.6	163.6	-183.3	75.9	185.8
[Ni(SOP)-(2-Atz)]	3rd	-53.6	176.7	214.4	-62.3	183.6	227.4
	4th	-87.2	143.6	213.6	-112.6	154.1	244.9
[Ni(SOP)-(Btz)]	1st	-174.8	39.5	118.3	-155.4	51.9	122.0
	2nd	-138.0	134.2	230.9	-149.7	147.9	252.8
	3rd	-184.4	89.0	236.7	-201.1	72.3	233.4
[Ni(SOP)-(2-Mbtz)]	2nd	-137.8	135.1	231.3	-141.0	144.3	242.7
	3rd	-184.5	90.3	237.5	-199.7	74.3	233.5
[Ni(SOP)-(Morph)]	1st	-120.2	28.1	86.2	-99.8	39.7	88.0
	2nd	-145.5	107.9	209.9	-170.9	116.9	236.7
	3rd	-151.6	120.0	241.9	-160.2	129.6	258.4
[Cu(SOP)-(Btz)]	1st	-159.3	37.7	101.6	-133.6	30.4	90.0
	2nd	-192.5	38.4	161.0	-160.1	27.6	129.6
[Cu(SOT)$_2$-(Morph)$_2$]	2nd	-95.5	134.3	197.1	-103.8	138.9	207.2

that the reactions are slow. The more ordered nature may be due to polarization of bonds in the activation state, which might happen through charge transfer electronic transitions[9].

REFERENCES

1- C. P. Raptopoulou, A. N. Papadopoulou, D. A. Malamatari, E. Loannidis, G. Molsidis, A. Terzis and D. P. Kessissoglou, Inorg. Chim. Acta, 272, 283 (1998).

2- T. Snamt and S. Umezari, Bull. Chem. Soc. Jpn., 29, 975 (1956).

3- N. Dharmaj, P. Viswanathamurthi and K. Natarajan, Transition Met. Chem., 26, 105 (2001).

4- S. C. Mojumdar, M. Melnik and E. Jona, Thermochim. Acta, 352, 157 (2000) and references therein.

5- L. S. Goodman and A. Gilman, "The Pharmacological Basis of Therapeutics", 5th Ed., Macmillan, New York (1975).

6- R. Lackhan and B. Ternai, Adv. Heterocy. Chem., 17, 99 (1974).

7- A. A. M. Aly, M. S. El-Meligy, A. S. A. Zidan and M. El-Shabasy, Synth. React. Inorg. Met.-Org. Chem., 17, 257 (1987).

8- A. A. M. Aly, M. S. El-Meligy, A. S. Zidan and M. El-Shabasy, An. Quim., 86, 19 (1990).

9- A. H. Osman, A. A. M. Aly, M. Abd El-Mottaleb and G. A. H. Gouda, Bull. Korean Chem. Soc., 25, 45 (2004).

10- A. A. M. Aly, A. H. Osman, M. Abd El-Mottaleb and G. A. H. Gouda, Bull. Pharm. Sci., Assiut University, 29, 137 (2006).

11- A. W. Coats and J. P. Redfern, Nature, 20, 68 (1964).

12- H. Horowitz and G. Metzger, Anal. Chem., 35, 1464 (1963).

13- S. Glasston, "Textbook of Physical Chemistry", 2nd Ed., Macmillan, 1974, p. 1103.

14- A. M. El-Awad, J. Therm. Anal. Cal., 61, 197 (2000).

15- A. Imura, Y. Inoue and I. Yasumori, Bull. Chem. Soc. Jpn., 56, 2203 (1983).

16- P. B. Maravalli and T. R. Goudar, Thermochim. Acta, 325, 35 (1999).

17- K. K. M. Yusuff and R. Sreekala, Thermochim. Acta, 159, 357 (1990).