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Thermal analysis and thermokinetics studies on homobinuclear Cu^{II}, Co^{II}, Ni^{II} and Cd^{II} complexes with 4-amino -3,5-di(2-Pyridyl)1,2,4-triazole

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ABSTRACT

A series of Cu(II), Co(II), Ni(II)and Cd(II) complexes with 4-amino -1,2,4-triazole-3,5-di(2-Pyridyl)(abpt) have been prepared. The structure of the complexes was determined by means of element analysis, molar conductance, infrared and electronic spectra and thermal studies. The thermal decomposition study of the prepared complexes was monitored by TG, DTG and DTA analysis in dynamic atmosphere of nitrogen. TG, DTG and DTA studies confirmed the chemical formulations of these complexes. The kinetic parameters were determined from the thermal decomposition data using the graphical methods of Coats-Redfern and Horwitz- Metzger. Thermodynamic parameters were calculated using standard relations. The values of the activation energy increases by the increase of the step number, this may be attributed to the structural rigidity of the ligands. The decomposition stability order of the complexes depends on the metal used.

KEYWORDS

Synthesis;
Metal complexes;
4-amino -1,2,4-triazole-3,5-di(2-Pyridyl);
Thermal and spectroscopic studies.

1. INTRODUCTION

The use of 1,2,4-triazole, moiety as apart of ligand systems has gained considerable attention recent years[1], this mainly because of the fact that Triazole derivatives occur in several drug substances among which is the phsychopharmocological active class of benzodiazepine annelated triazoles[2]. The four nitrogen atoms of these molecules offer many modes of donation and chelation thereby making them attractive ligands.The coordination chemistry of the ligand 4-amino3.4-bis-(pyridine-2-yl)-1,2,4-triazole (abpt)was initiated by Reedijk and coworkers they reported[3-8] a variety of mononuclear and/or dinuclear complexes of transition metals with interesting spectroscopic and X-ray crystallographic studies and established a preferred chelating behavior involving the nitrogens of triazole and pyridyl group. The ligand strength is the right region to give spin crossover compounds with iron (II) salts.

The 1,2,4-triazole prepared by Dallacker[9] system is also of magnetochemical interest because it is able to act as bridge between metal centers thus mediating exchange coupling, In addition it represents a hybrid of pyrazole and imidazole with regard to the arrangement of its three hetero atoms thus promising a rich and versatile coordination chemistry. In this contribution the synthesis, purification and characterization of Cu(II), Ni(II), Co(II) and Cd(II) complexes. The complexes obtained were characterized by elemental analysis, IR, UV-Visible spectral and thermal analysis. The kinetic and thermodynamic parameters were determined from the thermal decomposition data using the graphical methods of coats-Redfern and Horowitz- Metzger. The ligand has the following structure:

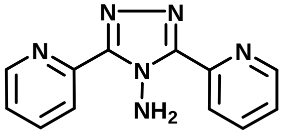


Figure 1 : Structure representation of the Ligand

2. EXPERIMENTAL

2.1. Materials

All chemicals in the preparative work were of A.R. or equivalent analytical grade, they include the following $CuCl_2.2H_2O$, $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CdCl_2.2.5H_2O$ and the title ligand (abpt).

2.2. Complex preparation

The complexes of the Ni(II) and Co(II) have been previously prepared[3] as well as Cu(II) complex[10].

For the Cd(II) complex, to a solution of 2mmol metal salt ($CdCl_2.2.5H_2O$) in hot methanol, a solution of 1mmol (abpt) in 25 hot methanol was added, the complex formed during stirring after 3-4hrs.

2.3. Physical measurements

Elemental analysis of the solid complexes were prepared in elementar system of Gmbh Vario El. Electronic spectra of the solid complexes were run on PerkinElmer Us/VIS Spectrophotometer Lambda 40 using 1-cm matched silica cells. IR-Spectra were obtained in KBr discs using 470 shimadzu infrared spectrophotometer (4000-400cm^{-1}). Conductivity measurements were carried out using CDM216 Meter lab conductivity meter in DMF solution at 10^{-3}M concentrations at room temperature.

RESULTS AND DISCUSSION

The analytical and physical data for the complexes are resumed in **TABLE 1**. The results agree with the formulas displayed in TABLE 1 for the complexes. Colour, analytical results and molar conductivity values for the prepared complexes are given in TABLE 1. The ligand used in this study is flexi dentate where it can act as neutral tetra dentate ligand. The results of the elemental analysis are consistent with 2:1or 2:2 metal ion to ligand complexes having the formula $[M_2(abpt)Cl_4]xH_2O$ and $[Ni_2(adpt)_2(H_2O)_4]Cl_4.2H_2O$, where M=Cu(II) or Co(II) or Cd(II) x =2-3. The measured molar conductance values of the complexes are in the range nonelectrolyte. On the other hand the measured molar conductance value of the Ni(II) complexes present in the range 1:4 electrolytes.

Electronic spectra

The υ_{max} and ε_{max} values of the absorption bands recoded for DMF solutions of various synthesized complexes are recorded in (TABLE 1). The bands in the range 23-35 .0 kK are assigned to $L\pi^* \leftarrow Md\pi$ metal to ligand charge transfer (MLCT) transition. The d-d transition with υ_{max} at 16.8 kK that appeared in the Ni

TABLE 1 : Physical, Elemental Analysis, IR, Electronic spectral bands and Molar Conductivity Data in MeOH of the complexes

complex	Calc(Found) %			color	Λ_m Ohm^{-1} cm^{-1} mol^{-1}	υ(kK) (ε mol^{-1} cm^2)	Assignment	υ(N-H) [cm^{-1}]	υ (C-N) [cm^{-1}]	υ (C=C) [cm^{-1}]
	C	H	N							
$[Cu_2(abpt)Cl_4]. 2H_2O$ $Cu_2Cl_4C_{12}H_{14}N_6O$ Mwt= 561.19	29.67 (29.15)	3.097 (2.59)	16.60 (16.47)	green	59.5	23.9(859.7) 11.35(236.8)	LMCT d-d	3300 1590	1350	1570
$[Co_2(abpt)Cl_4]. 3H_2O$ $Co_2Cl_4C_{12}H_{16}N_6O_3$ Mwt= 551.97	30.96 (30.21)	5.424 (5.313)	17.49 (17.22)	blue	54.8	21.69 (163.3) 14.88 (612.2)	LMCT d-d	3400 1600	1350	-
$[Ni_2(abpt)_2(H_2O)_4]. Cl_4 2H_2O$ $Ni_2Cl_4C_{24}H_{31}N_{12}O_6$ Mwt= 834.77	34.92 (34.16)	4.779 (3.820)	19.87 (19.92)	light blue	65.2	35.58(124) 16.8(116)	LMCT d-d	3250 1600	1360	-
$[Cd_2(abpt)Cl_4].3H_2O$ $Cd_2Cl_4C_{12}H_{16}N_6O_3$ Mwt= 658.92	23.4 (23.14)	2.263 (2.155)	12.79 (12.75)		37.3	21,60(168.0) 36.00(2000.0)	LMCT LMCT	3300 1600	1360	1570

(II) complex is assignable to the transition $^4A_{2g} \rightarrow ^4T_{1g}$ of the octahedral structure[14].

The d-d electronic transition of the Cu(II) and Co(II) complexes were observed as an asymmetric band with υ_{max} at 11.3 and 14.88 kK respectively, which is indicative of a tetrahedral stereochemical configuration around the Cu(II) and Co(II) ions. These are assignable to $^3T_1 \rightarrow ^3T_1(p)$ and $^3T_1 \rightarrow ^1E_1$ transitions respectively[15].

Infrared spectra

Assignments of the most prominent IR bands provide supportive structural evidence for the coordination mode in the complexes TABLE 1. The IR spectra of the free ligand and Complexes exhibit various bands in the 200-4000cm^{-1} region most relevant infrared peaks for the ligand and complexes are in TABLE 1. The observed shift of the ligand bands in the corresponding complexes was taken as evidence for the coordination of the ligand to the metal ions

The NH_2 stretching vibration at 3300cm^{-1} for the (abpt) ligand moiety is found to be at the same position in the spectra of the complexes. This indicates that this group is not coordinated to the metal ion[14]. The pyridine rings show intensive vibration bands near 1580cm^{-1} upon pyridine coordination to the metal these bands is high shifted[16]. The IR data show that this is the case for both pyridine rings of the ligands in the Ni(II) complexes as conclude from the 2:2 compositions this means that both pyridine nitrogens together with two of the triazole nitrogens are coordinated to the Nickel. In case of the Co(II), Cu(II), Cd(II) complexes there are two IR bands in the 16590-1600cm^{-1} range This means that in these 1:2M complexes each tiazole ligand uses one pyridine nitrogen and probably one tiazole nitrogen for chelate binding as was confirmed by structure determination[17]. The spectra of the free ligand has strong band, the characteristic band appearing in the 1340cm^{-1} region is assigned to the vibration of the υ(C=N) This band acquires an appreciable shift towards higher frequency in the IR spectra of the complexes strucure. The complexes showed abroad band around 3400cm^{-1} which is due to complexes υ_{OH} water molecules present in the complex. Based on the forgoing discussion the proposed structure of the complexes can be formulated as follows:

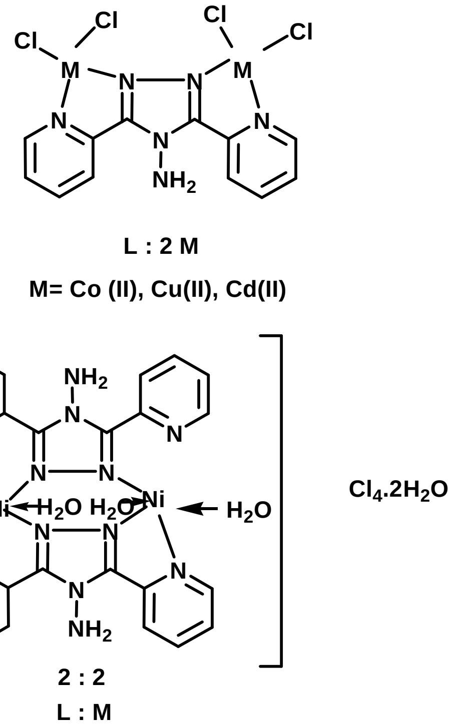


Figure 2 : Structure representation of the metal complexes

Thermal measurements

Thermogravimetric analysis of the various complexes was carried out using a shimadzu DTG 60HZ thermal analyzer, at heating rate 10°C min^{-1}in dynamic nitrogen atmosphere. The measured curves obtained during TGA scanning were analyzed to give the percentage mass loss as a function of temperature. The different decomposition data using coats-Redfern and Horwitz-Metzger methods[11-12].

Coats-Redfern equation

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

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

where α is the fraction of material decomposed, n is the order of the decomposition reaction and M=E*/R and B=ZR/ΦE*; E*, R, Z and Φ are the activation energy, molar gas constant, pre-exponential factor (Collision factor) and heating rate respectively.

Howitz-Metzger equation

$$\mathrm{Ln}\left[1-(1-\alpha)^{1-n}\right] \ \frac{\ln ZRTs^2}{OE^*}-\frac{E^*}{RTs}+\frac{E^*\theta}{RTs^2} \ \text{for } n\neq 1 \qquad (3)$$

$$\ln\left[-\ln(1-\alpha)\right] = \frac{E^*\theta}{RTs^2} \quad \text{for } n=1 \qquad (4)$$

where θ = T-Ts, Ts is the temperature at the DTG peak.

The correlation coefficient r, was computed using the least squares method for different values of n by plotting the left hand side of equation .1 and .2 against 1/T and θ for equations .3, and 4. Linear relationships were obtained for different values of n ranging from 0 to 2. The value of n which gave the best fit (r ˜ 1) was chosen as the order parameter for the decomposition stage of interest. From the intercept and linear slope of such stage, the kinetic parameters E*and Z were calculated.

Thermodynamic parameters entropy (ΔS*), enthalpy (ΔH*) and free energy (ΔG*) of activation were calculated using the following standard relations[13].

$$\Delta s^* = \left[\ln \frac{Ln\ Zh}{KTs}\right] \qquad (5)$$

$$\Delta H^* = \Delta E^* + \Delta\ nRT \qquad (6)$$

$$\Delta G^* = \Delta E^* + Ts\ \Delta\ S^* \qquad (7)$$

Where h, plank's constant ; K, Boltzman Constant ; R, Molar gas constant ; Ts, Temperature at the DTG Peak.

Thermal decomposition studies

The thermal analysis of the complexes in nitrogen atmosphere show 6-7 decomposition steps TABLE 2, the kinetic and thermodynamic parameters are in TABLE 3.

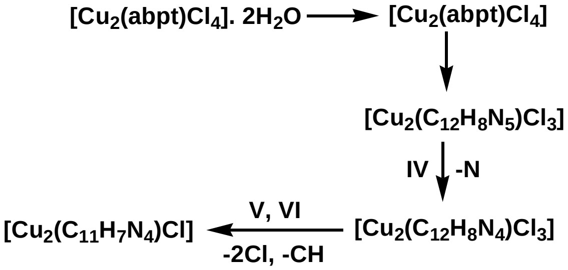
TABLE 2 : TGA data for the metal complexes

Complex no.	Temp. range°C	Step no.	Weight loss %	Loss of moiety	process
			Calc(found)		
	18.72-194.73	I, II	6.64 (96.339)	$2H_2O$	Dehydration
	195.79-266.85	III	9.55 (9.192)	NH_2+Cl	Decomposition
$[Cu_2(abpt)Cl_4]$. $2H_2O$	267.67-328, .11	IV	2.58 (1.189	N	Decomposition
	329.34-373.8	V	6.54 (7.765)	Cl	Decomposition
	374.67-524.9	VI	8.94 (10.22)	Cl, CH	Decomposition
	19.59-225.18		9.73 (11.64)	$3H_2O$	Dehydration
	226.00-340.44	I, II, III	12.78 (11.33)	2Cl	Decomposition
$[Co_2(abpt)Cl_4]$. $3H_2O$	341.66-447.52	IV	2.88 (4.041)	NH_2	Decomposition
	448.75-499.43	V	6.395 (4.675)	Cl	Decomposition
		VI			Decomposition
	28.14-117.0	I, II	12.93 (11.89)	$6H_2O$	Dehydration
	118.22-293.13	III	4.24 (4.961)	Cl	Decomposition
$[Ni_2(abpt)_2(H_2O)_4]$. Cl_4 $2H_2O$	293.94-355.74	IV	10.409 (9.843)	2Cl+NH_2	Decomposition
	356.95-443.8	V	6.165 (6.063)	Cl+NH_2	Decomposition
	444.61-498.34	VI	9.580 (8.819)	N_2+C_4H_4	Decomposition
	19.82-211.48	I, II, III	8.206 (8.172)	3H2O	Dehydration
	212.7-248.59	IV	2.429 (3.1331)	NH2	Decomposition
$[Cd_2(abpt)_2\ Cl_4]$. $3H_2O$	249.81-336.26	V	10.77 (9.175)	2Cl	Decomposition
	337.48-423.93	VI	2.192 (2.519)	N	Decomposition
	426.38-562.58	VII	40.25 (32.849)	C_{12} H_8 N3+2Cl	Decomposition

Thermal analysis of [$Cu_2(abpt)Cl_4$].$2H_2O$

The TGA of the complex Cu(II) gave six steps (Figure 3). The first step (T=18.72-66.73°C, E*= 24.808 K_J/mol) is assignable to the removal of the one water molecule. The second step (T=67.54- 194.73 °C), E*=101.95 K_J/mol) is assignable to the removal of the second water molecule. The third step (T = 195.79-266.85°C, E*=116.9535 K_J/mol) is assignable to the removal of the dissociation of the abpt ligand with the removal of NH_2 moiety and chlorine atom. The fourth step (T= 267.67-328.11 °C, E*= 158.86 K_J/mol) is assignable to the removal of nitrogen atom. The fifth step (T= 329.34 -373.86°C, E*= 162.762 K_J/mol) is assignable to the removal of chlorine atom. Step six (T=

374.67 – 524.9°C, E*= 134.192 K_J/mol) is assignable to the removal of chlorine atom and CH moiety.



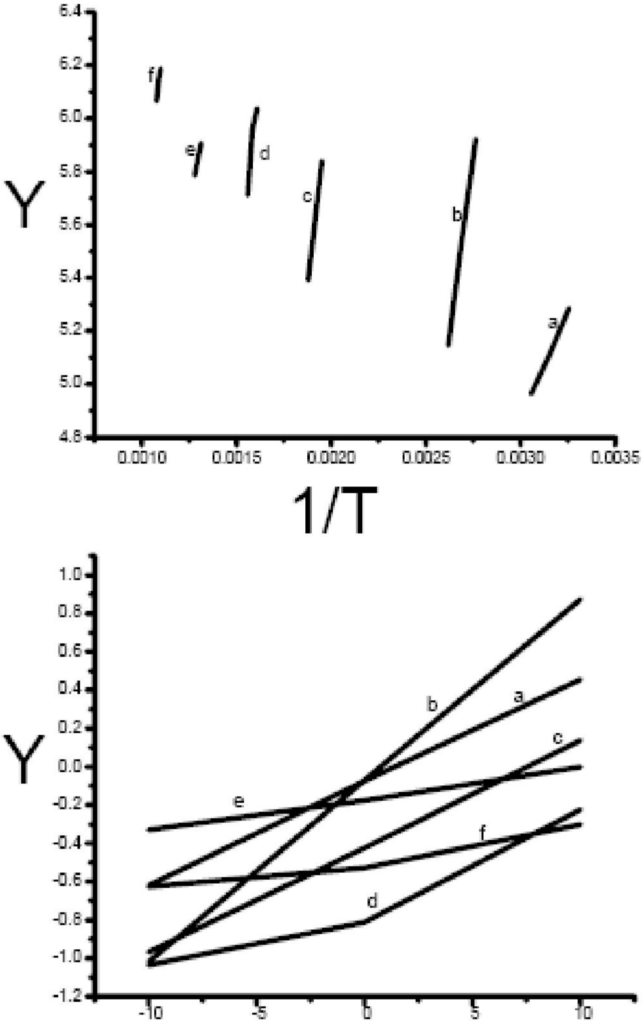
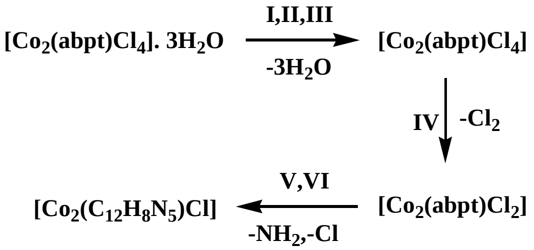


Figure 3 : Coats- Redfern and Horwitz –metzger plots of Copper complex
For different steps of decomposition
a: first step, b: second step, c: third step, d: fourth step, e: fifth step, f: sixth step

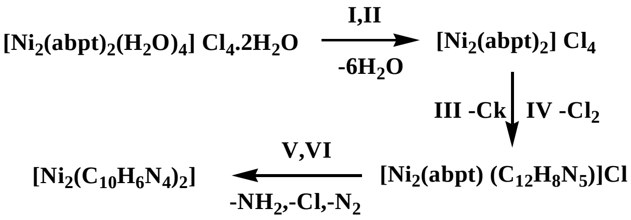
Thermal analysis of [Co_2(abpt)Cl_4]. $3H_2O$

The Cobalt complex TGA displays six decomposition steps. The first step (T=19.59-68.23°C, E*=30.358 K_J/mol), the second step (T=69.64-162.64°C, E*=40.607 K_J/mol), the third step ((T=163.64-225.18°C, E*=112.959 K_J/mol).The first three steps are assignable to removal of three water molecules. The fourth step (T=226.00 -340.44°C, E*=102.08 K_J/mol) is assignable to removal of two chlorine atoms. The fifth step (T=341.66-447.52°C, E*=199.49 K_J/mol) is assignable to removal of NH_2 moiety. The sixth step (T= 448.75-199.43°C, E*=579.185 K_J/mol) is assignable to removal of two chlorine



Thermal analysis of [Ni_2(abpt)$_2$(H_2O)$_4$]Cl_4. $2H_2O$

The Nickel complex TGA displays six decomposition steps. The first step (T=28.14-57.22°C, E*=64.26 K_J/mol), the second step (T=58.43-117.02°C, E*=103.691K_J/mol). The first two steps are assignable to the removal of six water molecules. The third step ((T=118,22-293013°C, E*=118.01 K_J/mol) is assignable to removal of one chlorine atom. The fourth step (T=293.94 -355.74°C, E*=194.4312 K_J/mol) is assignable to removal of two chlorine atoms and NH_2 moiety. The fifth step (T=356.95-443.8°C, E*=186.743 K_J/mol) is assignable to removal of NH_2 moiety. The sixth step (T= 444.75-498.34°C, E*=308.259 K_J/mol) is assignable to removal of two nitrogen atoms and four CH moiety



Thermal analysis of [Cd_2(abpt)Cl_4]$3H_2O$

The Cadmium complex TGA displays eight decomposition steps. The first step (T=19.82-77.32°C, E*=56.45 K_J/mol), the second step (T=78.54-107.9°C,

$E^*=78.086K_J$/mol).The third step ((T=109.12-211.48°C, $E^*=118.96\ K_J$/mol). The first three steps are assignable to removal of the three water molecules. The fourth step (T=212.7 -248.59°C, $E^*=214.23\ K_J$/mol) is assignable to removal of two NH_2 moiety. The fifth step (T=249.81- 336.26°C, $E^*= 222.73\ K_J$/mol) is assignable to removal of two chlorine atoms. The sixth step (T= 337.48- 423.93°C, $E^*=48.37\ K_J$/mol) is assignable to removal of one nitrogen atom. The seventh step (T= 426.38- 562.58°C, $E^*= 247.82\ K_J$/mol) is assignable to presence of $2/3Cd_3N_2$ as residue. Step eight (T= 564.62- 751.79°C, $E^*= 249.8716\ K_J$/mol) is assignable to the removal of the nitrogen and some cadmium metal since it melts at 325 °C.

Studying the TGA and DTA curves for the complexes indicates that there is a series of thermal changes on their DTA curves associate the weight loss in the TGA curves. This study leads to the following conclusions:

(1) The presence of more than one exothermic peak in the DTA curves of the complexes reveals that the pyrolysis occurs in several steps[18].

(2) The difference in the shape of the DTA curves of the complexes with respect to each other may attribute to the structural features of the ligand or the strength of the chelation between the metal ion and the ligand. This also led to the variety in the thermal behavior of the complexes[19].

(3) On heating the complexes containing water molecules from room temperature, the loss in weight indicated by TGA curves is accompanied in some cases by endothermic peaks in the DTA curves. This weight loss may correspond to the evolution of water molecules[19].

(4) The thermal behavior of the complexes displays an observable difference with respect to each other. This difference indicates that thermal behavior of these complexes depends mainly on the type of the metal ion rather than the ligand.

(5) Most complexes having DTA curves characterized by the presence of main sharp and strong exothermic peaks in their ends. These peaks are associated with a weight loss on the TGA curves corresponding to the decomposition of the stable intermediate compounds in to the corresponding final residue.

Thermodynamic parameters

The entropy (ΔS^*), enthalpy (ΔH^*) and free energy (ΔG^*) of activation were calculated for the complexes using standard equation[13] and the values are in TABLE 3. The obtained data could be discussed as follows:

(1) The entropy were found to be negative, which indicates a more ordered activated state that may be possible through the chemisorptions of the decomposition products[20-22].

(2) The high values of the free energy of activation (ΔG^*) for most of the steps in the decomposition reactions of the complexes mean that the decomposition reactions are slower than that of the normal ones[13].

(3) The values of the free energy of activation (ΔG^*) of a given complexes, generally increase significantly for the subsequent decomposition stages. This is due to increasing the values of $T\Delta S^*$ significantly from one step to another which overrides the values of ΔH^*[13].

(4) There is much closeness in the enthalpy (ΔH^*) values obtained by coats-Redfern equation and Howitz-Metzger equation, indicating that the thermal degradation of these complexes follow the standard methods.

Kinetic parameters and thermal behaviour

(i) The thermal decomposition of the complexes is not simple and the processes generally involve overlapping steps which together with the great diversity of possible intermediate products precludes exhaustive interpretations. Although by successful prediction and interpretation of thermal decomposition patterns for many complexes.

(ii) The procedure for the thermal decomposition A(s) ? B(s)+C(g) which can be studied kinetically.

(iii) All the complexes having a uniform decomposition pattern.

(iv) in all complexes dehydration being the first steps, whenever they containing the water molecules, loss of the side chain of the ligand being the second step and the loss of the ligand fragments are the third or the later steps with the ultimate products.

(v) In most cases the values of the kinetic parameters

TABLE 3 : Kinetic and thermodynamic parameteres for the thermal decomposition of metal complexes ΔE, ΔH and ΔG in KJ/mol^{-1} Z in S^{-1}, Δs in KJ/mol^{-1}K^{-}

Complex no.	step	order	Coats.Redfern			Thermodynamic parametrs			Horwitz-Metzge			Thermodynamic parametrs		
			R	E	Z	Δs	ΔH	ΔG	r	E	Z	Δs	ΔH	Δ G
[Cu_2(abpt)Cl_4]. $2H_2O$	1st	0.33	0.9999	32.23	519.63	-193,44	34.86	96.22	0.9987	35.96	3.933x 10^{3}	176.61	38.59	96.61
	2nd	1.0	0.9999	101.95	1642.12	-185.19	105.04	173.84	1.0	108.21	2.209x10^{3}	-182.74	111.301	179.23
	3rd	0.33	0.9998	116.953	1910.741	-186.76	121.29	214.84	1.0	124.64	1.612x10^{10}	-54.166	128.62	157.25
	4th	0.0	0.9599	122.95	2000.03	-187.96	128.2	246.92	0.9679	133.72	3.48x10^{8}	-87.63	138.97	194.321
	5th	0.0	0.9974	71.28	1150.73	-194.22	77.69	227.54	0.9994	80.79	5.804x10^{2}	-199.91	87.20	241.443
	6th	0.0	0.9657	96.65	1558.93	-193.13	104.27	281.44	0.9750	112.83\	3.78x10^{3}	-185.77	120.45	290.87
[Co_2(abpt)Cl_4]. $3H_2O$	1st	0.33	0.9872	27.78	448.09	-194.63	30.405	91.87	0.9931	33.024	9.266x10^{2}	-188.59	35.64	95.124
	2nd	0.5	1.0	40.60	654.175	-193.67	44.05	123.57	0.9999	47.492	4.891x10^{3}	-177.03	50.90	123.63
	3rd	1.0	0.9992	140.13	2310.07	-184.20	143.98	229.48	0.9988	147.97	4.186x10^{14}	31.327	151.82	137.289
	4th	0.0	0.9999	86.401	1400.62	-189.52	90.83	192.00	1.0	95.74	5.961x10^{6}	-120.43	100.17	164.45
	5th	0.33	0.9999	185.75	3055.09	-184.27	191.17	311.413	1.0	197.33	2.904x10^{13}	6.31	202.7	198.63
	6th	2.0	0.9935	875.81	14308.5	172.901	882.94	1010.60	0.9928	809.614	6.397x10^{61}	930.78	815.75	128.52
	7th	1.0	1.0	196.52	3168.85	-187.27	204.174	376.5	1.0	210.07	39.14x10^{8}	-70.64	217.72	282.75
[Ni_2(abpt)$_2$(H_2O)$_4$]. Cl_4 $2H_2O$	1st	2.0	0.9828	103.83	1109.54	-193.68	106.06	165.31	0.9807	108.95	8.296x10^{15}	59.18	111.632	29.54
	2nd	0.0	0.9949	79.65	1300.76	186.88	82.64	144.85	0.9964	85.53	1.33x10^{10}	-52.64	88.52	107.453
	3rd	2.0	0.9373	148.88	2398.418	-183.07	152.37	229.416	0.9376	155.646	3.588x10^{17}	88.29	159.144	121.99
	4th	0.0	0.9835	177,16	2916.26	-184.39	182.14	292.66	0.9475	206.35	4.588x10^{15}	48.98	211.33	181.97
	5th	2.0	0.9994	465.20	7591.11	-177.75	468.78	481.26	0.9985	479.22	2.82x10^{34}	407.5	485.05	198.99
	6th	1.0	0.9857	360.73	5835.48	-180.35	366.86	499.88	0.9815	384.06	1.419x10^{25}	229.07	390.192	221.23
	7th	0.66	0.4314	14.97	35.4	-109.54	22.41	120.516	0.9997	102.226	1.432x10^{3}	-193.64	109.67	283.08
	8th	0.0	0.9897	179.47	2912.64	-188.68	187.79	376.82	0.9919	195.22	3.64x10^{7}	-110.24	203.54	313.99
[Cd_2(abpt) Cl_4]. $3H_2O$	1st	0.33	0.9993	54.41	883,74	188.913	57.011	116.11	0.9999	59.859	3.15x10^{7}	-101.76	62.46	94.29
	2nd	2.0	0.998	202.32	3276,69	-179.37	205.38	271,42	0.9972	209.32	5.5x10^{28}	303.59	212.38	100.611
	3rd	0.5	0.9858	118.96	1960.24	-184.27	122.26	195.47	0.9891	126.173	1.259x10^{14}	22.63	129.47	120.48
	4th	0.33	0.9999	191.92	3101.06	-182.44	196.111	288.08	0.9997	198.975	3.617x10^{18}	106.00	203.166	149.72
	5th	1.0	0.9998	273.83	44.29.74	-180.59	278.62	382.81	0.9999	283.44	1.24x10^{24}	210.84	288.23	166.600
	6th	2.0	0.9918	80.849	1309.815	-191.79	86.27	211.503	0.9628	74.806	2317.90	-187.01	80.23	202.335
	7th	0.5	0.9999	247.82	400.78	184.121	254.214	400.80	0.9999	265.4	2.19x10^{15}	40.59	272.01	239.704
	8th	2.0	0.9677	297.98	4810.49	183.904	305.73	477.181	0.9695	312.19	5.71x10^{14}	28.124	319.94	293.72

obtained from Horwitz-Metzger equation are higher than the values obtained from Coats-Redfern equation.This is due to the inherent error involved in the approximation method employed in the derivation of the Horwitz- Metzger equation.

(vi) In general, there is a direct relation between E* and Z for the obtained complexes. The relatively low values of Z indicate the slow nature of the pyrolysis reaction.

(vii) In most cases the values of the activation energy for the second stage of decomposition were found to be higher than that of the first stage, which indicates that the decomposition rate of the second stage is lower than the first. This may be attributed to the structure rigidity of the remaining complex[21,23,24].

(viii) The order (n) of the decomposition reaction does not provide any meaningful information about the decomposition mechanisms of the complexes[25].

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