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Full Paper

Synthesis, spectroscopic and thermal studies on nano-sized complexes of Co(II),Ni(II),Cu(II)and Cd(II) ions with the bioactive mercaptotriazoles and N,N'-donor secondary ligands

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Abstract

Mixed ligand complexes of Co(II), Ni(II), Cu(II) and Cd(II)} with 4-(2-pyridylmethylenamino)-3-mercapto-5-benzayl-1,2,4-triazole (L_1), 4-(3-pyridylmethylenamino)-3-mercapto-5-benzayl-1,2,4-triazole (L_2), 4-(4-pyridylmethylenamino)-3-mercapto-5-benzayl-1,2,4-triazole (L_3),bipyridyl (bipy) and 1,10-phenanthroline (phen) were prepared. They have general formula $[M(L)(bipy)Cl_2].nH_2O$ and $[M(L)(phen)Cl_2].nH_2O$, where M=Co(II); Ni(II); Cu(II) or Cd(II). The complexes have been characterized by elemental analysis, spectroscopic measurements (FT-IR, UV-Vis.),transmission electron microscopy (TEM), as well as molar conductance, magnetic measurements and thermal studies. The complexes are hexacoordinated and the structure, thus assumed to have an octahedral geometry. The prepared materials show the existence of nano-particles with spherical shape. The TEM image shows that the particle diameter is 35.2 - 32.8 nm with a mean particle size of 34 nm. The thermal decomposition study of the prepared complexes was monitored by TG, DTG and DTA analysis in a dynamic nitrogen atmosphere. TG, DTG and DTA studies confirmed the chemical formulations of these complexes. The relative thermal stability of the chelates is evaluated. The final decomposition products were found to be the corresponding metal sulfides. The thermodynamic activation parameters such as $\Delta S^{\#}$, $\Delta H^{\#}$ and $\Delta G^{\#}$ were calculated from the TG curves.

Keywords: mixed ligands complexes, nanoparticles, thermodynamic parameters.

1. Introduction

α,ά-Bipyridyl (bipy), 1,10-phenanthroline (phen) and their substituted derivatives, both in the metal-free state and as ligands coordinated to transition metals, disturb the functioning of a wide variety of biological systems. When the metal-free N, N-chelating bases are found to be bioactive it is usually assumed that the sequestering of trace metals is involved, and that the resulting metal complexes are the actual active species. Copper and some of its complexes have been shown to induce apoptosis of murine leukemia cell lines [1]. The casiopeinas are a group of Cu(II) mixed-ligand antineoplastic agents which contain 1,10-phenanthroline or α,ά-bipyridyl and other bidentate ligands. These compounds exhibit cytotoxicity, genotoxicity and antitumor effects, but their mode of action is presently unknown [2]. A number of reports have appeared in the literature highlighting the use of transition metal complexes as both antibacterial and antifungal agents [3]. The *in vitro* antibacterial action of 1,10-phenanthroline has been demonstrated in several species of bacteria. Phenanthroline metal complexes can be bacteriostatic and bacteriocidal toward many gram-positive bacteria they are relatively ineffective against gram-negative organisms.1,10-phenanthroline has been extensively used as a ligand in both analytical and preparative coordination chemistry [4]. As an important building block, the 1,10-phenanthroline unit plays a very important role in the development of the supramolecular chemistry [5–7]. Furthermore, considering the unique combination of chemical stabilities, redox properties, luminescence emission and excited state lifetime, derivatives of 1,10-phenanthroline are also used for the preparation of polypyridyl metal complexes, particularly Ru(II) complexes [8].Those of 1,10-phenanthroline have shown the most encouraging results, probably because of their ability to intercalate between the intercalation between the bases of DNA [9,10] the literature review reveals that the molecular mechanism of copper (II) phenanthroline and copper (II) bipyridyl complex is very minimum. In the present study, we report the synthesis mixed ligand of Cu(II), Ni(II), Co(II) and Cd(II) metal complexes by using α,ά-bipyridyl and 1,10-phenanthroline in the presence of 4-substituted-amino-3-mercapto-5-benzayl-1,2,4-triazoles. The structures of the mixed ligands complexes were characterized by elemental and thermal analyses, FT-IR, and electronic spectra, transmission electron microscopy (TEM), as well as conductivity and magnetic susceptibility measurements at room temperature. The degradation kinetics have been studied by Coats-Redfern and Horowitz-Metzger methods. Thermodynamic parameters (ΔS, ΔH *and* ΔG) have been evaluated using the standard equations.

2. Experimental

2.1. Materials and Measurements

All chemicals used in the preoperative work were of analytical grade, they include the following:1,10-phenanthroline (phen), α,ά-bipyridyl (bipy),carbon disulphide, potassium hydroxide, absolute ethanol, dimethylformamide (DMF), phenylacetic acid, pyridine-2-carboxyaldehyde, pyridine-3-carboxyaldehyde and pyridine-4-carboxyaldehyde, $CuCl_2\cdot 2H_2O$, $NiCl_2\cdot 6H_2O$, $CoCl_2\cdot 6H_2O$ and $CdCl_2\cdot 2.5H_2O$. They were used without further purification.

2.2. Synthesis of the 4-Substituted-amino-3-Mercapto-5-Benzayl-1,2,4-Triazoles

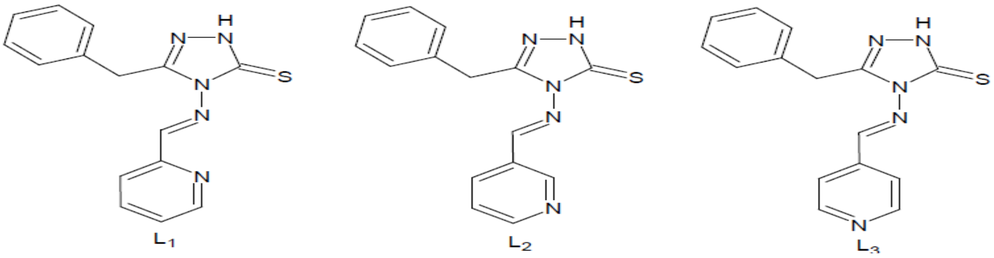
The ligands: 4-(2-pyridylmethylenamino) -3-mercapto-5-benzayl-1,2,4-triazole(L_1), 4-(3-pyridylmethylenamino)-3-mercapto-5-benzayl-1,2,4-triazole(L_2), 4-(4-pyridyl methylenamino)-3-mercapto-5-benzayl-1,2,4-triazole (L_3) were synthesized according to the literature methods [11-19]. The structures of ligands are shown in Scheme1.

2.3. Synthesis of Cu(II), Ni(II), Co(II) and Cd(II) Mixed Ligand Complexes

To 1 mmol of $CuCl_2\cdot 2H_2O$, $NiCl_2.6H_2O$, $CoCl_2.6H_2O$ or $CdCl_2.2.5H_2O$ in 10 mL hot ethanol, a solution of L_1, L_2 or L_3 (1 mmol in 40 mL hot ethanol) was added dropwise with constant stirring in one direction. When a precipitate was formed, 1mmol in 10 mL hot ethanolic solution of (bipy) or (phen) was added. The pH was adjusted to 7.2 – 8.2 using dilute ammonia solution. Refluxing of the resulting solution carried for 8 hours. The product obtained was left overnight, filtered through sintered glass, washed with ethanol and dried in vacuum over P_4O_{10}.

2.4. Physical Measurements

The carbon, hydrogen, nitrogen and sulfur content of the solid complexes were obtained by elemental analyzer system Gmbh Vario El. Conductivity measurements for the various complexes were carried out using Jenway 4320 meterlab conductivity meter in DMF solutions at 10^{-3}M concentrations at room temperature. Electronic spectra of the solid complexes were run on a Perkin Elmer UV/VIS spectrophotometer Lambda 40 using 1-cm matched silica cells. Magnetic susceptibility measurements were carried out at room temperature using a magnetic susceptibility balance of the type MSB-Mk1. Molar susceptibilities were corrected for diamagnetism of the component atoms by the use of Pascal's constants. The infrared spectra of the free ligands and the metal complexes were recorded on a Shimadzu 470 infrared spectrophotometer (4000-400 cm^{-1}) using KBr discs. Thermogravimetric studies of the various complexes were carried out using a Shimadzu DTG-60Hz thermal analyzer, at a heating rate of 10^oC/min in a dynamic nitrogen atmosphere. TEM pictures were taken using a JEOL transmission microscope (model JEM-100CXII ELCTRON MICROSCOPE) with an acceleration voltage of 80KV.



Scheme 1: Structure of the ligands

3. Results and discussion

3.1. Elemental Analyses and Conductivity Measurements

Elemental analysis data of the prepared mixed ligand complexes are listed in Table1. The data indicate formation of complexes with a 1:1:1 ratio between the metal and ligands with the general formula$[M(L)(L')Cl_2].nH_2O$ where M= Cu(II), Ni(II), Co(II) or Cd(II), except the two complexes $[Ni(L_1)(bipy)(H_2O)Cl]Cl.3H_2O$ and $[Co(L_2)(phen)(H_2O)Cl]Cl.H_2O$. The mixed ligand complexes, $[M(L)(L')Cl_2].nH_2O$ have molar conductance values in the range 12.2 – 34.7 Ohm^{-1} cm^2 mol^{-1} (Table 1) corresponding to a nonelectrolyte nature of their DMF solutions [20]. While the molar conductance values of DMF solutions of the complexes $[Ni(L_1)(bipy)(H_2O)Cl]Cl.3H_2O$ and $[Co(L_2)(phen)(H_2O)Cl]Cl$ are 70.1 and 68.3 Ohm^{-1} cm^2 mol^{-1} respectively, indicating that these two complex solutions are 1:1 electrolytes [20].

3.2. IR Spectra

The IR spectral data of the free ligands and their complexes are given in (Tables 2 and 3).The IR spectrum of the free (bipy) ligand exhibits a series of significant IR absorption bands as appearing in the vibration regions 3040, 1575, 1550 and 750 cm^{-1}, these bands are apparently the characteristic absorptions of the free (bipy) ligand[21, 22]. These bands suffer a positive shift to a higher wavenumbers on complexation. This shift has been attributed to the coordination of the (bipy) ligand to form the mixed ligand complexes. The IR spectrum of the free (phen) ligand in the absorption region 1417–1580 cm^{-1},which is concerned with ring vibration modes (C-C) and (C-N), consists of three intense significant bands; one close to 1580 cm^{-1}, the second in the neighborhood of 1500 cm^{-1} and the third is located at 1417 cm^{-1}, the first and the second bands usually split into doublet and triplet bands respectively [23]. These bands were shifted to higher frequencies in the mixed ligand complexes. The free (phen) ligand consistently exhibit two intense bands at 750 and 870 cm^{-1}, the bands related to C–H out-of-plane deformation modes of phen molecules [24, 25] these are situated almost at the same position in the mixed ligand complex spectra. The ligands L_1, L_2 and L_3 ligands show four bands at 1520–1588 cm^{-1}, 1300–1400 cm^{-1}, 1008–1040 cm^{-1} and 700-850 cm^{-1} which are assignable to thioamide I, II, III, IV vibrations, respectively [26] with contributions from δ(C-H) + δ(N-H), υ(C=S) + υ(C-N) + δ(C-H), υ(C-N) + υ(C-S) and υ(C=S) modes of vibrations, respectively. These bands are expected to be affected differently by the modes of coordination to the metal ions. In the complexes, these bands shift to lower frequency, suggesting the coordination of the sulfur atom to the metal ions [27].The presence of crystallization water in the complexes [28] is indicated by a broad trough band in the region 3323 – 3441 cm^{-1} related to υ_{OH} and two weaker bands in the region 800 – 750 and 610 – 625cm^{-1} due to rocking and wagging modes of the OH group vibration, respectively [29].

Table 1: Analytical and physical data for the mixed ligand complexes of α,ά-bipyridyl and 1,10-phenanthroline ligands.

No.	**Complexes** **[Empirical formula]** **(Formula weight)**	**Colour**	**Analytical Data**				Λ_m^* **Ohm^{-1}cm^{2}mol^{-1}**	μ_{eff} **B.M.**
			%Found (Calculated)					
			C	H	N	S		
1	[Cu(L_1)(bipy)Cl_2].H_2O $CuCl_2C_{25}H_{23}N_7SO$ M.wt = 602.03	Green	49.4 (49.83)	4.14 (3.85)	16.04 (16.28)	5.74 (5.31)	31.7	2.32
2	[Cu(L_3)(bipy)Cl_2].3.5H_2O $CuCl_2C_{25}H_{28}N_7SO_{3.5}$ M.wt. = 647.06	Brown	46.37 (46.36)	3.84 (4.36)	15.77 (15.14)	4.85 (4.94)	34.7	2.17
3	[Cu(L_2)(phen)Cl_2]1.5H_2O $CuCl_2C_{27}H_{24}N_7SO_{1.5}$ M.wt = 635.04	Pale Green	51.18 (51.02)	3.12 (3.80)	15.52 (15.43)	5.33 (5.03)	34.6	1.77
4	[Cu(L_3)(phen)Cl_2].H_2O $CuCl_2C_{27}H_{23}N_7SO$ M.wt. = 626.03	Green	51.10 (51.75)	3.16 (3.70)	14.84 (15.65)	5.07 (5.10)	22.1	1.71
5	[Ni(L_1)(bipy)(H_2O)Cl]Cl.3H_2O $NiCl_2C_{25}H_{29}N_7SO_4$ M.wt. = 651.07	Yellow	46.26 (46.07)	4.64 (4.48)	15.87 (15.05)	5.21 (4.91)	70.1	3.16
6	[Ni(L_2)(bipy)Cl_2].4H_2O $NiCl_2C_{25}H_{29}N_7SO_4$ M.wt. = 651.07	Yellow	46.82 (46.07)	4.37 (4.48)	15.71 (15.05)	5.07 (4.91)	30.9	3.43
7	[Ni(L_3)(bipy)Cl_2].3H_2O $NiCl_2C_{25}H_{27}N_7SO_3$ M.wt. = 633.07	Yellow	47.52 (47.38)	4.12 (4.29)	15.67 (15.48)	4.78 (5.05)	23.9	3.42
8	[Ni(L_1)(phen)Cl_2].H_2O $NiCl_2C_{27}H_{23}N_7SO$ M.wt. = 621.04	Yellow Green	52.80 (52.17)	3.40 (3.73)	15.83 (15.78)	5.35 (5.14)	23.6	4.25
9	[Ni(L_2)(phen)Cl_2].2H_2O $NiCl_2C_{27}H_{29}N_7SO_4$ M.wt. = 675.05	Green	47.14 (47.99)	4.46 (4.32)	14.81 (14.52)	4.62 (4.72)	24.6	3.33
10	[Co(L_2)(bipy)Cl_2].1.5H_2O $CoCl_2C_{25}H_{24}N_7SO_{1.5}$ M.wt. = 607.04	brown	49.17 (49.41)	4.19 (3.98)	16.94 (16.14)	5.86 (5.26)	14.4	4.45
11	[Co(L_3)(bipy)Cl_2].H_2O $CoCl_2C_{25}H_{23}N_7SO$ M.wt. = 598.03	brown	49.22 (50.16)	3.45 (3.87)	16.72 (16.39)	5.48 (5.36)	23.2	4.43
12	[Co(L_2)(phen)Cl(H_2O)]Cl.H_2O $CoCl_2C_{27}H_{25}N_7SO_2$ M.wt. = 640.04	brown	50.27 (50.62)	3.70 (3.93)	15.73 (15.31)	4.73 (4.99)	68.3	4.83
13	[Co(L_3) (phen)Cl_2].2H_2O $CoCl_2C_{27}H_{25}N_7SO_2$ M.wt. = 640.04	brown	50.95 (50.62)	4.26 (3.93	15.48 (15.31)	4.26 (4.99)	18.6	4.57
14	[Cd (L_2)(bipy)Cl_2].4H_2O $CdCl_2C_{25}H_{29}N_7SO_4$ M.wt. = 707.04	White	42.55 (42.43)	4.57 (4.13)	14.16 (13.86)	4.35 (4.52)	12.6	-

Table 1: Analytical and physical data for the mixed ligand complexes of α,ά-bipyridyl and 1,10-phenanthroline ligands(Continue).

No.	Complexes [Empirical formula] (Formula weight)	Colour	Analytical Data %Found (Calculated)				Λ_m^* Ohm^{-1}cm^{2}mol^{-1}	μ_{eff} B.M.
			C	H	N	S		
15	[Cd $(L_3)(bipy)Cl_2].4H_2O$ $CdCl_2C_{25}H_{29}N_7SO_4$ M.wt. = 707.04	White	42.7 (42.43)	4.36 (4.13	13.78 (13.86)	4.64 (4.52)	27.8	-
16	$[Cd(L_2)(phen)Cl_2].4.5H_2O$ $CdCl_2C_{27}H_{30}N_7SO_{4.5}$ M.wt. = 740.04	White	43.49 (43.78)	4.70 (4.08)	13.63 (13.24)	4.10 (4.32)	12.2	-
17	[Cd $(L_3)(phen)Cl_2].4H_2O$ $CdCl_2C_{27}H_{29}N_7SO_4$ M.wt. = 731.04	White	44.35 (44.32	3.97 (3.99)	13.79 (13.40)	3.98 (4.37)	14.2	-

Table 2: IR frequency bands (cm^{-1}) of bipyridyl and its mixed ligand complexes

complexes	υ(H_2O)	υ(N–H)	υ(C=N)	Thioamide bands I δ(C-H) δ(N-H)	II δ(C-H) υ(C=S) υ(C-N)	III υ(C-N) υ(C-S)	IV υ(C=S)	bpiy characteristic bands			
bipy	-	-	-	-	-	-	-	3040	1575	1550	750
$[Cu(L_1)(bipy)Cl_2].H_2O$	3378	3011	1607	1598	1345	1050	853	2974	1534	1516	728
$[Cu(L_3)(bipy)Cl_2].3.5H_2O$	3413	3020	1613	1602	1327	1025	817	2919	1534	1500	730
$[Ni(L_1)(bipy)(H_2O)Cl]Cl.3H_2O$	3387	3070	1630	1596	1317	1023	817	3028	1560	1508	745
$[Ni(L_2)(bipy)Cl_2].4H_2O$	3340	3020	1595	1594	1336	1032	820	3011	1560	1542	728
$[Ni(L_3)(bipy)Cl_2].3H_2O$	3323	3075	1607	1596	1320	1030	817	2985	1551	1539	730
$[Co(L_2)(bipy)Cl_2].1.5H_2O$	3369	3050	1611	1605	1345	1022	817	2930	1560	1533	736
$[Co(L_3)(bipy)Cl_2].H_2O$	3423	3046	1600	1595	1336	1023	820	2985	1520	1506	736
[Cd $(L_2)(bipy)Cl_2].4H_2O$	3397	3053	1605	1593	1328	1027	821	2916	1560	1543	727
[Cd $(L_3)(bipy)Cl_2].4H_2O$	3441	3056	1596	1590	1329	1005	823	3003	1543	1523	745

Table 3: Some IR frequency bands (cm^{-1}) of 1,10-phenanthroline and its mixed ligand complexes

Complexes	υ(H_2O)	υ(N–H)	υ(C=N	Thioamide bands				phen characteristic bands				
				I	II	III	IV					
				δ(C-H) δ(N-H)	δ(C-H) υ(C=S) υ(C-N)	υ(C-N) υ(C-S)	υ(C=S					
phen	-	-	-	-	-	-	-	1580	1500	1417	870	750
[Cu(L_2)(phen)Cl_2]1.5H_2O	3426	3012	1616	1534	1328	1026	760	1590	1508	1430	846	733
[Cu(L_3)(phen)Cl_2].H_2O	3418	3023	1616	1520	1311	1028	768	1592	1520	1423	855	722
[Ni(L_1)(phen)Cl_2].H_2O	3403	3055	1614	1515	1360	1030	735	1595	1518	1421	815	723
[Ni(L_2)(phen)Cl_2].2H_2O	3367	3010	1630	1517	1347	1050	780	1586	1530	1440	821	723
[Co(L_2)(phen)Cl(H_2O)]Cl.H_2O	3380	3012	1641	1550	1373	1015	784	1591	1530	1450	820	728
[Co(L_3) (phen)Cl_2].2H_2O	3375	3045	1615	1546	1346	1029	760	1595	1515	1448	845	732
[Cd(L_2)(phen)Cl_2].4.5H_2O	3395	3055	1603	1555	1352	1058	791	1585	1514	1454	815	729
[Cd (L_3)(phen)Cl_2].4H_2O	3426	3055	1622	1549	1344	1041	780	1591	1526	1426	856	723

Table 4: Electronic spectral data of mixed ligand complexes of the bipyridyl and 1,10-phenanthroline(1×10^{-3}-1×10^{-4} M in DMF solution).

No.	Complex	υ_{max} (k.K) (ϵ_{max} cm^2 mol^{-1})	Assignment
1	[Cu(L_1)(bipy)Cl_2].H_2O	35.08(24418) 25.31(95029) 15.26(232.09)	intraligand LMCT d – d
2	[Cu(L_3)(bipy)Cl_2].3.5H_2O	34.48(18831.2) 25.64(34953.5) 14.98(299.91)	intraligand LMCT d – d
3	**[Cu(L_2)(phen)Cl_2].1.5H_2O**	**36.36(97899)** **33.00(11121)** **14.83(144.14)**	intraligand intraligand d – d

Table 4: Electronic spectral data of mixed ligand complexes of the bipyridyl and 1,10-phenanthroline (1×10^{-3}-1×10^{-4} M in DMF solution)(Continue).

No.	Complex	υ_{max} (k.K) (ϵ_{max} cm^2 mol^{-1})	Assignment
4	$[Cu(L_3)(phen)Cl_2].H_2O$	36.36(65607) 21.73(148.77) 15.60(13.19)	intraligand LMCT d – d
5	$[Ni(L_1)(bipy)(H_2O)Cl]Cl.3H_2O$	34.48(625341) 16.31(3386)	intraligand d – d
6	$[Ni(L_2)(bipy)Cl_2].4H_2O$	35.33(12795.7) 27.02(28328) 16.52(456.47)	intraligand LMCT d – d
7	$[Ni(L_3)(bipy)Cl_2].3H_2O$	33.89(60103) 15.74(313.26)	intraligand d – d
8	$[Ni(L_1)(phen)Cl_2].H_2O$	35.97(101146) 23.58(45002) 16.39(483.23)	intraligand LMCT d – d
9	$[Ni(L_2)(phen)Cl_2].2H_2O$	35.97(38732) 24.33(15357) 16.94(169.96)	intraligand LMCT d – d
10	$[Co(L_2)(bipy)Cl_2].1.5H_2O$	31.25(23331.5) 25.57(6556) 16.66(394.79) 14.92(316.76)	intraligand LMCT d – d d – d
11	$[Co(L_3)(bipy)\ Cl_2].H_2O$	36.36(44292) 30.30(7837) 16.52(275.83) 14.97(265.72)	intraligand intraligand d – d d – d
12	$[Co(L_2)\ (phen)(H_2O)Cl]Cl.H_2O$	37.03(172436) 28.73(8544) 16.73(529.9) 14.74(183.62)	intraligand LMCT d – d d – d
13	$[Co(L_3)\ (phen)Cl_2].2H_2O$	37.03(29519) 16.39(432.5) 15.38(498.08)	intraligand d – d d – d
14	$[Cd(L_2)(bipy)Cl_2].4H_2O$	34.48(82029) 25.64(54594)	intraligand LMCT
15	$[Cd(L_3)(bipy)Cl_2].4H_2O$	35.71(25010.1) 30.25(18918.3)	intraligand LMCT
16	$[Cd(L_2)(phen)Cl_2].4.5H_2O$	37.45(45352) 34.84(29863) 22.47(2632)	intraligand intraligand LMCT
17	$[Cd(L_3)(phen)Cl_2].4H_2O$	34.96(27640) 24.81(136)	intraligand LMCT

3.3. Electronic Spectra and Magnetic Measurements

The electronic spectra of DMF solution of the mixed ligand complexes are recorded in the wavelength range 200-1100 nm. The υ_{max}(kK) and ε_{max}(cm^2 mol^{-1}) values of the different absorption bands are recorded in Table 4. The first set with υ_{max} in the range 31.25 –37.45 kK could be attributed to intraligand charge transfer transitions [30]. The second set includes bands having υ_{max} in the range 21.73 – 28.73 kK. These bands are assigned as LMCT transitions[30].The third set of bands of Cu(II) mixed ligand complexes (1), (2), (3) and (4) has υ_{max} in the range 14.83 – 15.60 kK is assigned for a d-d transition which is typical for Cu(II) distorted octahedral complexes [31]. These bands are assigned to all the three transitions $^2B_{1g}\rightarrow {}^2B_{2g}$, $^2B_{1g}\rightarrow {}^2A_{1g}$ *and* $^2B_{1g}\rightarrow {}^2E_g$ which are usually found in tetragonal Cu(II) complexes [30]. The room temperature magnetic moment values of Cu(II) mixed ligand complexes (1), (2), (3) and (4) are 2.32, 2.17, 1.77 and 1.71 B.M. respectively (Table 1) that are in harmony with the proposed geometry of Cu(II) ions [31, 32]. The d-d transition bands observed for Ni(II) mixed ligand complexes (5), (6), (7), (8) and (9) are found to have υ_{max} in the range 15.74 – 16.94 kK could be attributed to $^3A_{2g(E)}\rightarrow {}^3T_{1g(F)}$ transitions, suggesting octahedral geometry for the Ni(II) complexes[33].

3.4 Transmission electron microscopy (TEM)

Electron images from the (TEM) can be used to achieve different information, for example for crystallographic or compositional studies etc. Transmission electron microscope (TEM) examination was used to check the nanostructure and to estimate particle size of the prepared complexes. Transmission electron microscopy (TEM) is used to determine actual particle sizes. The TEM images shows that the particle diameter is 35.2 - 32.8 nm with a mean particle size of 34 nm (see Fig. 1).The average crystal size is estimated by considering the few number of crystals shown in the TEM image (Fig. 1). The prepared material shows the existence of nano-particle with spherical shape. It is apparent that the diameter of the smallest particle is equal to the diameter of a spherical particle because the particles have been grown by nucleation growth of smaller particles [37,38].

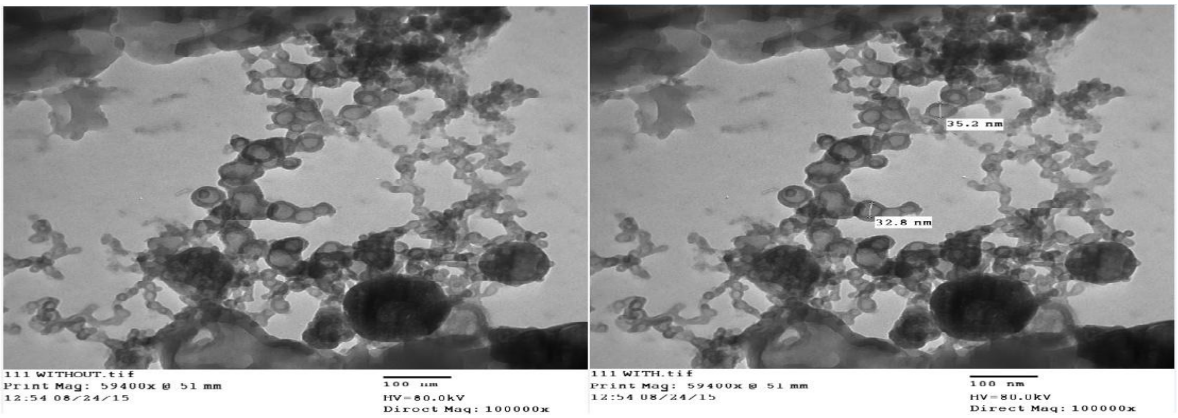


Fig. 1: TEM image of [Co(L$_3$)(phen)Cl$_2$].2H$_2$O nanoparticle.

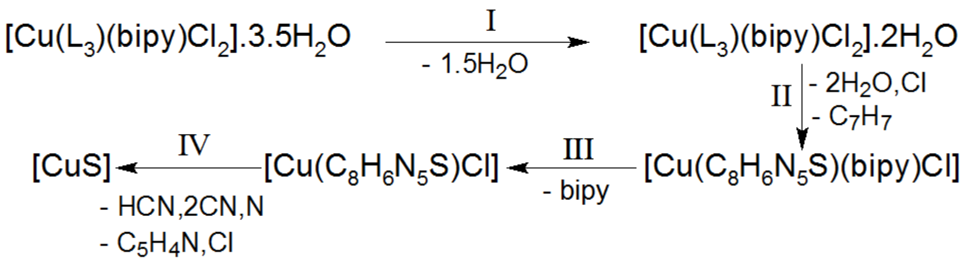
3.5. Thermal Decomposition Studies

Thermogravimetric studies have been made in the temperature range 43–750 °C. The thermal stability data of all the complexes are listed in (Table 5). Thermal decomposition curves of the complexes showed a similar sequence of three decomposition steps [39-41], given in (Figures.2a, 2b and 3a, 3b). The first decomposition step for all the complexes occurred in the temperature range of 43–299°C. The observed mass losses obtained for Cu(II) complexes were (3.17%), (4.33%), (4.59%) and (2.34%) and Ni(II) (8.83%), (5.25%), (8.69%), (2.14%) and(5.64) for Co(II) complexes (4.20%), (3.56%), (5.24%) and (5.74%) for complexes Cd(II) were (10.87%), (20.23%), (10.74%) and (14.16%) which were attributed to the decomposition of absorbed water molecules (Table 5). Water of hydration is associated with complex formation and is found outside the coordination sphere formed around the central metal ion as in equation(1).

The second decomposition step occurred in the temperature range of 122–526°C corresponding to observed mass losses for Cu(II) complexes were (58.61%), (25.44%), (39.55%) and (18.44%) for Ni(II) complexes were (55.36%), (29.48%), (30.08%), (17.44%) and (31.60%) for Co(II) were (50.99%), (21.61%), (19.52%), and (22.94%). for Cd(II) were (59.23%), (36.24%), (9.59%) and (13.34%)due to the decomposition of phen and bipy ligand and partial decomposition of triazole ligand or chlorine atom as in equation(2).

The third decomposition step occurred in the temperature range of 265–750 °C corresponds to observed mass losses for Cu(II) complexes were (16.44%), (24.19%), (26.82%) and (28.38%) for Ni(II) complexes were (11.31%), (24.67%), (26.57%), (20.40%) and (42.77%) for Co(II) complexes were (14.14%), (53.03%), (20.01%), and (28.43%). for Cd(II) complexes were (7.65%), (24.52%), (10.10%) and (49.16%). due to the decomposition of phen and bipy ligand and partial decomposition of triazole ligand as in equation(3).

The four decomposition step occurred in the temperature range of 370–751°C corresponds to observed mass losses for Cu(II) complexes were (31.83%) and (20.63%) for Ni(II) complexes were (28.24%) and (20.19%) for Co(II) were (34.64%) and (29.59%)for Cd(II) complex was (36.17%).The final decomposition of traizole ligand from metal chelates to different moieties, partial decomposition of triazole ligand C_7H_7, HCN and 2CN mioeties.The final decomposition corresponds to a metal sulphide residue or metal with part from organic compound incomplete (Table 5) as in equation(4).



(1)

$$\begin{tikzcd}
{[Ni(L_3)(bipy)Cl_2].3H_2O} \arrow[r, "\mathrm{I}", "-3H_2O"'] & {[Ni(L_3)(bipy)Cl_2]} \arrow[r, "\mathrm{II}", "-bipy,Cl"'] & {[Ni(L_3)Cl]} \arrow[d, "\mathrm{III}"', "\begin{matrix}-C_7H_7\\-C_5H_4N\end{matrix}"] \\
 & {[NiS]} & {[Ni(C_3H_2N_4S)]} \arrow[l, "\mathrm{IV}"', "-Cl,CN,2HCN,N"]
\end{tikzcd} \tag{2}$$

$$\begin{tikzcd}
{[CdL_3)(phen)Cl_2].4H_2O} \arrow[r, "\mathrm{I}", "-4H_2O,Cl"'] & {[Cd(L_3)(phen)Cl]} \arrow[r, "\mathrm{II}", "-C_5H_4N,Cl"'] & {[Cd(C_{10}H_9N_4S)(phen)]} \arrow[d, "\mathrm{III}"', "\begin{matrix}-C_7H_7,2HCN\\-phen,CN,N\end{matrix}"] \\
 & & {[CdS]}
\end{tikzcd} \tag{3}$$

$$\begin{tikzcd}
{[CoL_2)(phen)(H_2O)Cl]Cl.H_2O} \arrow[r, "\mathrm{I}", "-2H_2O"'] & {[Co(L_2)(phen)Cl_2]} \arrow[r, "\mathrm{II}", "-C_7H_7,Cl"'] & {[Co(C_8H_6N_5S)(phen)Cl]} \arrow[d, "\mathrm{III}"', "\begin{matrix}-Cl\\-C_5H_4N\end{matrix}"] \\
 & {[CoS]} & {[Co(C_3H_2N_4S)(phen)]} \arrow[l, "\mathrm{IV}"', "\begin{matrix}-2HCN,N\\-phen,CN\end{matrix}"]
\end{tikzcd} \tag{4}$$

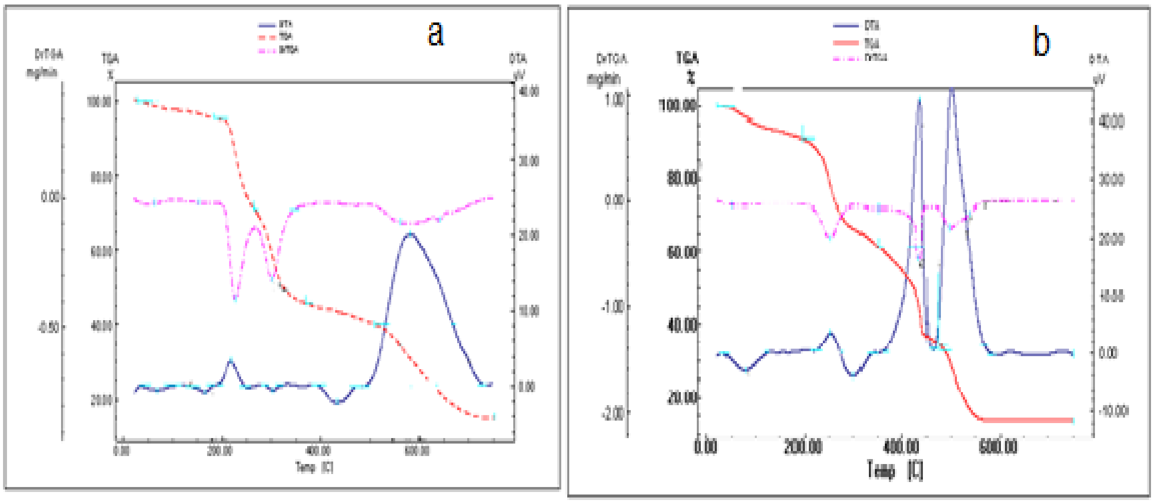


Fig. 2: TG-DTG curves of complex a=$[Cu(L_3)(bipy)Cl_2].3.5H_2O$, b=$[Ni(L_3)(bipy)Cl_2].3H_2O$

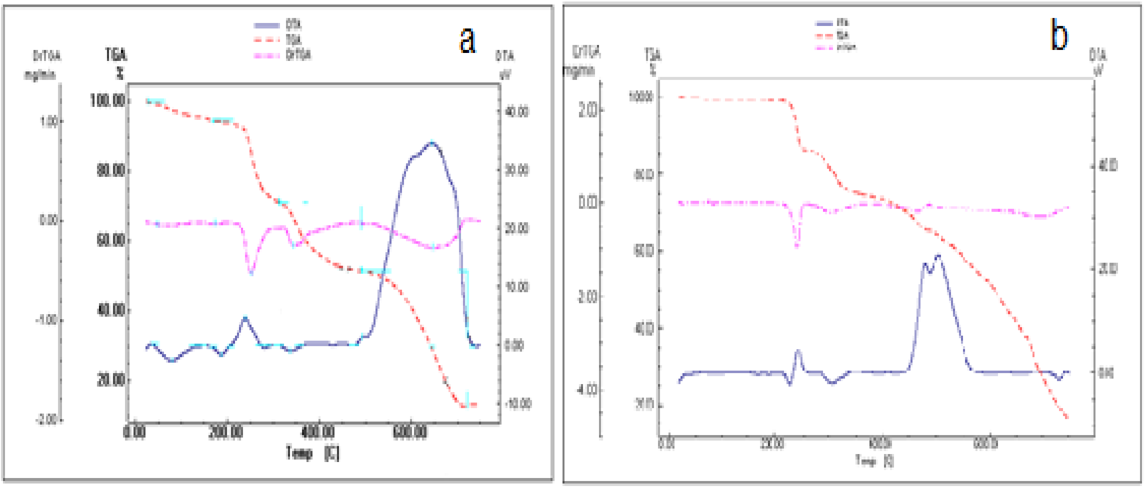


Fig. 3: TG-DTG curves of complex a=$[Co(L_2)$ $(phen)(H_2O)Cl]Cl.H_2O$, b=$[Cd(L_3)(phen)Cl_2].4H_2O$

Table 5: Thermal data for mixed ligand complexes of α,ά-bipyridyl and 1,10-phenanthroline ligand.

Complexes	**steps**	**Temp. Range °C**	**Weight loss %**		**Loss moiety**	**Process**	**Residue**	
			Calcd.	Found			Calcd.(Found) %	Nature
[Cu(L_1)(bipy)Cl_2].H_2O	I	50-134	2.99	3.17	H_2O	dehydration	22.29(21.63)	[Cu(CN_2S)]
	II	136-412	58.47	58.61	bipy,C_7H_7,$C_6H_5N_2$	decomposition		
	III	415-738	16.11	16.44	HCN,2Cl	decomposition		
[Cu(L_3)(bipy)Cl_2].3.5H_2O	I	47-162	4.17	4.33	1.5H_2O	dehydration	14.86(14.32)	[CuS]
	II	163-264	25.03	25.44	C_7H_7, 2H_2O, Cl	decomposition		
	III	265-368	24.11	24.19	bipy	decomposition		
	IV	370-751	31.83	31.57	Cl, C_5H_4N,2CN N,HCN	decomposition		
[Cu(L_2)(phen)Cl_2].1.5H_2O	I	56-119	4.25	4.59	1.5H_2O	dehydration	29.75(28.87)	[Cu($C_3H_2N_4S$)]
	II	122-526	39.39	39.55	2Cl, phen	decomposition		
	III	528-750	26.61	26.82	C_5H_4N,C_7H_7	decomposition		
[Cu(L_3)(phen)Cl_2].H_2O	I	51-126	2.87	2.34	H_2O	dehydration	30.21(30.01)	Cu($C_3H_2N_4S$)]
	II	128-317	18.05	18.44	C_5H_4N, Cl	decomposition		
	III	320-493	28.75	28.38	phen	decomposition		
	IV	498-749	20.12	20.63	Cl, C_7H_7	decomposition		
[Ni(L_1)(bipy)(H_2O)Cl]Cl.3H_2O	I	52-185	8.29	8.83	3H_2O	dehydration	24.28(23.98)	[Ni($C_2H_2N_3S$)]
	II	187-495	55.45	55.36	H_2O, 2Cl, C_7H_7 CN, bipy	decomposition		
	III	498-750	11.98	11.31	C_5H_4N	decomposition		
[Ni(L_2)(bipy)Cl_2].4H_2O	I	48-148	5.52	5.25	2H_2O	dehydration	11.54(12.13)	[Ni(NS)]
	II	149-320	29.49	29.48	bipy, 2H_2O	decomposition		
	III	322-465	24.73	24.67	C_7H_7,2Cl	decomposition		
	IV	467-739	28.72	28.24	C_5H_4N,2HCN,CN,N	decomposition		
[Ni(L_3)(bipy)Cl_2].3H_2O	I	51-174	8.53	8.69	3H_2O	dehydration	14.24 (14.32)	[NiS]
	II	176-351	30.17	30.08	bipy, Cl	decomposition		
	III	353-472	26.69	26.57	C_7H_7,C_5H_4N	decomposition		
	IV	474-750	20.37	20.19	2HCN,CN, Cl ,N	decomposition		
[Ni(L_1)(phen)Cl_2].H_2O	I	54-126	2.87	2.14	H_2O	dehydration	21.58 (21.10)	[Ni(CN_2S)]
	II	130-317	17.45	17.44	C_5H_4N,Cl	decomposition		
	III	320-493	20.12	20.40	C_7H_7,Cl	decomposition		
	IV	498-749	37.38	37.52	2CNH, phen	decomposition		
[Ni(L_2)(phen)Cl_2].2H_2O	I	52-157	5.54	5.63	2H_2O	dehydration	19.27(19.86)	[Ni(NS)]
	II	158-341	31.85	31.60	phen,Cl	decomposition		
	III	342-738	43.34	42.77	C_5H_4N, ClC_7H_7, CN,2CHN	decomposition		
[Co(L_2)(bipy)Cl_2].1.5H_2O	I	51-135	4.44	4.20	1.5H_2O	dehydration	30.49(30.34)	[Co($C_3H_2N_4S$)]
	II	136-460	50.08	50.99	C_5H_4N,2Cl, bipy	decomposition		
	III	462-748	14.99	14.16	C_7H_7	decomposition		
[Co(L_3)(bipy) Cl_2].H_2O	I	48-127	3.01	3.56	H_2O	dehydration	21.54 (21.42)	[Co(NS)]
	II	130-424	21.07	21.61	C_7H_7,Cl	decomposition		
	III	426-742	53.84	53.03	HCN, Cl, bipy, CN,$C_6H_5N_2$	decomposition		
[Co(L_2) (phen)(H_2O)Cl]Cl.H_2O	I	47-167	5.62	5.24	2H_2O	dehydration	19.71(20.43)	[CoS]
	II	169-311	19.68	19.52	C_7H_7, Cl	decomposition		
	III	313-491	20.46	20.01	C_5H_4N, Cl,	decomposition		
	IV	465-738	34.53	34.64	2HCN, CN,N phen	decomposition		

Table 5: Thermal data for mixed ligand complexes of α,ά-bipyridyl and 1,10-phenanthroline ligand(Continued).

			Weight loss %				**Residue**	
Complexes	**steps**	**Temp. Range °C**	Calcd.	Found	**Loss moiety**	**Process**	Calcd.(Found) %	Nature
[Co(L$_3$) (phen)Cl$_2$].2H$_2$O	I	48-137	5.62	5.74	$2H_2O$	dehydration	14.08(13.67)	[CoS]
	II	138-272	23.28	22.94	2Cl ,C_5H_4 N	decomposition		
	III	274-412	28.12	28.43	phen	decomposition		
	IV	414-737	28.90	29.54	C_7H_7, N 2HCN, CN	decomposition		
[Cd(L$_2$)(bipy)Cl$_2$].4H$_2$O	I	54-169	10.18	10.87	$4H_2O$	dehydration	22.65(22.13)	[Cd(NS)]
	II	172-471	59.68	59.23	C_5H_4N, C_7H_7 HCN, 2Cl, bipy	decomposition		
	III	473-745	7.49	7.65	HCN, CN	decomposition		
[Cd(L$_3$)(bipy)Cl$_2$].4H$_2$O	I	46-299	20.22	20.23	$4H_2O$,2Cl	Dehy.+decom.	18.97(19.00)	[CdS]
	II	300-520	36.77	36.24	$C_6H_5N_2$,bipy	decomposition		
	III	522-731	24.04	24.52	C_7H_7,HCN,2CN	decomposition		
[Cd(L$_2$)(phen)Cl$_2$].4.5H$_2$O	I	43-170	10.94	10.74	$4.5H_2O$	dehydration	32.01(33.12)	[Cd($C_3H_2N_4S$)]
	II	175-391	9.89	9.59	2Cl	decomposition		
	III	393-510	10.54	10.1	C_5H_4 N	decomposition		
	IV	512-745	36.62	36.17	C_7H_7, phen	decomposition		
[Cd(L$_3$)(phen)Cl$_2$].4H$_2$O	I	53-169	14.63	14.16	$4H_2O$, Cl	Dehy.+decom.	21.99 (22.13)	[CdS]
	II	170-420	13.45	13.34	Cl, C_5H_4N	decomposition		
	III	421-742	49.93	49.16	C_7H_7, phen 2HCN,CN,N	decomposition		

The different kinetic parameters were computed from thermal decomposition data using the Coats-Redfern and Horwitz-Metzger methods [42, 43].The thermodynamic parameters, enthalpy $\Delta H^{\#}$, entropy $\Delta S^{\#}$ and free energy $\Delta G^{\#}$ of activation were calculated using standard equations and the values are given in (Table 6). The kinetic and thermodynamic parameters of the various decomposition stages were determined from TGA thermogram using the Coats-Redfern equation [42] in the following forms:

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right]=\frac{M}{T}+B \quad \text{for } n\neq1 \qquad (1)$$

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

Where α is the fraction of material decomposed, n is the order of the decomposition reaction, M = $E^{\#}/R$ and B = $ZR/\phi E^{\#}$ where $E^{\#}$, R, Z and ϕ are the activation energy, molar gas constant, pre-exponential factor (collision factor) and heating rate, respectively. Horwitz-Metzger equation[43] in the forms(3),(4). Where θ = T-T_s, T_s is the temperature at the DTG peak. The correlation coefficient, r, was computed using the least square method for different values of the order of the reaction, n, by plotting the left hand side of equations 1, 2 against 1/T and against 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≈l) was chosen as the order parameter for the decomposition stage of interest. From the intercept and linear slope of each stage, the Z and E values were determined. The thermodynamic parameters, $\Delta H^{\#}$, $\Delta S^{\#}$and $\Delta G^{\#}$ were calculated using the relationships (5), (6), (7).

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{1-n}\right]=\ln\frac{ZRT_s^2}{\phi E^{\#}}-\frac{E^{\#}}{RT_s}+\frac{E^{\#}\theta}{RT_s^2} \quad \text{for} \quad n \neq 1 \qquad (3)$$

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

$$\Delta S^{\#} = R\ [\ln Zh / kT_s] \qquad (5)$$

$$\Delta H^{\#} = \Delta E^{\#} - RT_s \qquad (6)$$

$$\Delta G^{\#} = \Delta H^{\#} - T_s\Delta S^{\#} \qquad (7)$$

Where: h, Planck's constant, k, Boltzman constant, R, gas constant and T_s, temperature at the DTG peak.The $\Delta S^{\#}$ values were found to be negative, which indicates a more ordered activated state that may be possible through the chemisorption of decomposition products [44]. The values of the activation energy for the second stage of decomposition were found to be higher than that for the first stage (Table 6) which indicates that the rate of decomposition of the second stage is lower than that of the first stage, this may be attributed to the structural rigidity of the mixed ligands as compared with H_2O, which requires more energy for its rearrangement before undergoing any compositional change [45]. The values of the entropy for all degradation steps of all the complexes are negative. The significantly negative $\Delta S^{\#}$supports the assignment of an associative mechanism. However, the activation process in the studied systems seems to be strongly dominated by bond formation [46]. The positive sign of $\Delta H^{\#}$ indicates that the decomposition stages are endothermic processes for both of them. On the other hand, the positive sign of $\Delta G^{\#}$ reveals that all the decomposition steps are non-spontaneous.

5. Conclusion

New nano-sized materials based on mercaptotriazoles derivatives, bipyridyl,1,10-phenanthroline and their Co(II), Ni(II) and Cu(II) complexes were synthesized and characterized. Based on the results obtained of the elemental analysis, UV–Vis., IR spectral data, magnetic measurements and conductance measurements it is possible to determine the type of coordination of the ligands in their complexes. Crystallization water molecule and chloride ion are found in all the divalent complexes. On the basis of analytical, magnetic and electronic spectral data mixed ligand complexes octahedral geometries have been proposed for all the complexes(ligand: metal: ligand ratio of 1:1:1). Thermal property measurements show that the complexes have good thermal stability. The stability of complexes was explained and kinetic parameters ($E^{\#}$, Z, $\Delta H^{\#}$, $\Delta S^{\#}$ *and* $\Delta G^{\#}$) of all thermal decomposition stages have been evaluated using the Coats–Redfern and Horwitz-Metzger methods.

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Table 6: Thermogravimetric parameters for the thermal degradation of the process.

		Coats-Redfern equation (Kinetic parameters)				**Thermodynamic parameters**			**Horowitz-Metzger equation (Kinetic parameters)**			**Thermodynamic parameters**		
	Stp.	**n**	**R**	**$E^{\#}$**	**Z**	**$\Delta S^{\#}$**	**$\Delta H^{\#}$**	**$\Delta G^{\#}$**	**r**	**$E^{\#}$**	**Z**	**$\Delta S^{\#}$**	**$\Delta H^{\#}$**	**$\Delta G^{\#}$**
1	1st	0.33	1.0000	27.54	12.13×10^{4}	-148.67	44.72	95.26	0.9975	27.07	8.71	-228.00	24.25	101.7
	2nd	0.00	1.0000	58.00	14.80×10^{2}	-188.80	53.66	152.05	1.0000	47.40	108.13	-210.61	43.07	152.8
	3rd	0.00	0.9996	59.90	48.35×10^{4}	-180.51	54.72	148.78	0.9994	68.42	11.62×10^{4}	-192.36	63.25	183.0
2	1st	0.66	0.9988	7.60	64.87×10^{5}	-115.80	4.7	45.11	0.9997	12.90	24.58×10^{-3}	-277.02	10.00	106.6
	2nd	1.00	1.0000	41.84	42.51×10^{3}	-160.99	37.49	121.88	0.9999	37.72	8.11	-232.19	33.37	155.0
	3rd	2.00	0.9999	37.08	23.77×10^{4}	-148.92	31.38	133.54	1.0000	56.08	71.27	-216.37	50.38	198.8
	4th	0.00	0.9898	25.67	52.04×10^{5}	-124.31	19.19	116.03	1.0000	50.72	3.37	-242.79	44.25	233.3
3	1st	0.66	0.9998	6.41	17.88×10^{6}	-106.68	3.75	37.99	0.9999	11.59	17.1×10^{-3}	-279.35	8.93	98.6
	2nd	1.00	1.0000	33.01	26.64×10^{6}	-145.93	28.55	106.6	0.9899	44.39	45.73	-218.02	39.93	157.0
	3rd	0.00	0.9970	35.18	71.33×10^{6}	-139.62	29.68	123.5	0.9973	48.78	6.61	-235.98	43.14	201.9
4	1st	0.33	0.9973	9.02	42.43×10^{5}	-118.59	6.37	44.1	0.9950	12.81	21.01×10^{-3}	-258.44	10.16	92.6
	2nd	0.50	0.9999	30.97	15.77×10^{5}	-149.70	26.82	101.6	0.9911	37.65	9.10	-230.85	35.50	150.9
	3rd	0.50	0.9934	38.04	97.09×10^{5}	--154.94	33.22	122.9	0.9967	41.89	9.67	-231.56	37.08	171.1
	4th	0.66	1.0000	19.01	84.95×10^{5}	-120.70	12.17	111.5	1.0000	47.08	1.70	-262.04	40.24	251.9
5	1st	0.50	0.9997	21.69	13.90×10^{4}	-147.75	18.79	70.35	0.9956	27.11	7.75	-229.17	24.21	104.1
	2nd	0.50	0.9999	37.08	18.88×10^{4}	-150.03	31.83	125.3	1.0000	46.26	14.25	-228.95	40.99	183.6
	3rd	0.00	0.9987	38.98	15.76×10^{5}	-134.70	32.13	142.9	0.9934	31.39	43.63×10^{-3}	-279.39	24.55	254.4
6	1st	2.00	0.9993	18.82	72.71×10^{5}	-114.85	15.92	56.00	0.9997	14.21	47.96×10^{-2}	-271.46	11.31	106.0
	2nd	2.00	1.0000	60.86	39.02×10^{2}	-180.84	56.51	151.2	1.0000	50.44	281.12	-202.72	46.09	152.1
	3rd	2.00	0.9999	37.08	23.77×10^{4}	-148.92	31.38	133.5	1.0000	56.08	71.27	-216.37	50.38	198.8
	4th	0.00	0.9998	28.56	62.04×10^{4}	-126.31	22.19	119.0	0.9999	45.32	3.89	-237.79	39.14	228.2
7	1st	0.50	0.9999	19.25	61.85×10^{3}	-153.82	16.58	66.1	1.0000	27.54	3.13	-236.05	23.58	100.8
	2nd	2.00	0.9999	120.77	19.45×10^{4}	-148.36	116.41	194.2	0.9999	112.7	15.77×10^{8}	-73.52	108.3	151.2
	3rd	0.00	0.9998	77.02	98.53×10^{5}	-153.82	71.14	180.0	0.9999	84.63	35.53×10^{2}	-184.12	78.75	209.1
	4th	5.00	1.0000	26.62	34.05×10^{5}	-127.73	20.23	118.4	0.9999	51.39	5.90	-238.02	45.00	228.0
8	1st	0.00	1.0000	13.31	31.25×10^{3}	-161.15	10.04	73.7	0.9999	16.61	33.13×10^{-3}	-275.53	13.35	121.6
	2nd	2.00	0.9981	89.38	14.39×10^{5}	-132.06	84.84	157.08	0.9982	56.46	702.30	-140.37	51.92	128.7
	3rd	2.00	0.9976	47.54	60.81×10^{3}	-160.51	41.66	155.30	0.9978	71.35	788.67	-196.64	65.47	204.6
	4th	0.00	1.0000	3.80	24.38×10^{6}	-112.39	-3.42	94.35	0.9998	21.29	26.68×10^{-2}	-293.28	14.07	269.2
9	1st	1.00	0.9988	10.51	91.26×10^{5}	-112.70	7.70	45.79	0.9999	16.07	86.19×10^{-3}	-266.33	13.26	103.2
	2nd	0.33	1.0000	43.74	35.30×10^{3}	-163.31	38.96	132.86	1.0000	46.24	22.21	-224.60	41.46	170.6
	3rd	1.00	0.9990	73.22	18.68×10^{5}	-131.98	67.37	160.29	0.9987	58.24	875.33	-195.72	41.32	179.1
10	1st	0.66	0.9949	32.87	66.64×10^{2}	-172.74	30.06	88.44	0.9998	38.76	26.42×10^{4}	-142.14	30.85	89.17
	2nd	2.00	0.9975	34.70	35.26×10^{3}	-162.47	30.38	114.86	0.9985	55.72	6.99	-233.35	51.40	172.7
	3rd	0.33	0.9997	63.71	20.47×10^{2}	-131.47	58.58	139.82	0.9995	71.12	26.78×10^{2}	-185.35	65.99	158.5
11	1st	2.00	1.0000	57.05	11.56×10^{3}	-167.98	54.31	109.91	0.9972	47.69	34.72×10^{3}	-158.84	44.94	97.51
	2nd	0.00	0.9998	79.87	51.21×10^{6}	-101.81	75.61	127.73	0.9998	61.184	48.84×10^{2}	-173.78	56.933	148.4
	3rd	0.00	0.9996	30.61	94.16×10^{4}	-136.69	25.96	101.81	0.9929	3.22	13.36	-228.59	8.57	166.3
12	1st	0.33	0.9987	20.31	54.59×10^{3}	-154.63	18.79	67.181	0.9988	26.18	173.5	-199.76	23.21	87.12
	2nd	0.00	0.9985	21.32	13.66×10^{5}	-186.86	16.97	14.69	0.9979	31.24	26.68×10^{-2}	-205.84	26.90	134.5
	3rd	0.50	0.9943	25.67	13.27×10^{5}	-121.05	20.55	101.49	0.9958	34.65	1.13	-247.25	34.65	184.7
	4th	0.00	1.0000	1.90	15.41×10^{6}	-115.70	-4.90	89.86	0.9998	18.87	7.72	-293.73	12.07	252.6
13	1st	0.66	0.9965	57.72	11.70×10^{5}	-129.75	54.92	98.6	0.9848	64.29	14.37×10^{6}	-108.87	61.49	98.18
	2nd	0.66	0.9990	62.76	10.11×10^{5}	-134.42	58.52	127.0	0.9990	49.51	669.58	-195.27	45.27	145.1
	3rd	2.00	0.9998	188.2	95.89×10^{13}	36.14	183.33	161.78	0.9971	167.1	2.87×10^{15}	-8.75	162.8	115.0
	4th	0.50	0.9986	98.89	50.36×10^{3}	-159.32	93.07	204.74	0.9976	86.46	26.23×10^{3}	-167.41	80.64	198.0
14	1st	0.00	1.0000	146.44	23.5×10^{11}	-32.40	141.80	159.8	1.0000	148.6	38.9×10^{10}	-28.22	144.0	159.8
	2nd	2.00	0.9999	185.43	11.88×10^{12}	-0.6422	180.80	181.1	0.9999	173.6	10.05×10^{12}	-2.03	168.4	169.7

	3rd	2.00	1.0000	185.43	11.88×10^{12}	-1.15	179.98	180.7	0.9995	196.2	86.69×10^{12}	15.36	190.7	180.7

Table 6: Thermogravimetric parameters for the thermal degradation of the process(Continue).

			Coats-Redfern equation (Kinetic parameters)			**Thermodynamic parameters**			**Horowitz-Metzger equation (Kinetic parameters)**			**Thermodynamic parameters**		
	Stp.	**n**	**R**	**$E^{\#}$**	**Z**	**$\Delta S^{\#}$**	**$\Delta H^{\#}$**	**$\Delta G^{\#}$**	**r**	**$E^{\#}$**	**Z**	**$\Delta S^{\#}$**	**$\Delta H^{\#}$**	**$\Delta G^{\#}$**
15	1st	2.00	1.0000	38.22	93.12×10^{3}	-165.19	35.59	87.79	0.9929	31.57	125.95	-205.19	28.94	93.78
	2nd	0.50	0.9978	49.44	25.18×10^{3}	-166.99	43.13	149.8	0.9982	60.49	419.11	-201.04	54.18	182.6
	3rd	0.00	0.9993	50.40	20.38×10^{3}	-168.45	45.27	149.2	0.9993	58.28	156.72	-208.93	53.16	182.0
16	1st	0.00	0.9995	38.44	61.91×10^{3}	-157.82	34.10	116.4	0.9164	48.52	57.05	-215.93	44.19	156.6
	2nd	1.00	0.9809	63.71	16.26×10^{2}	-189.07	59.28	58.83	0.9853	64.16	15.36×10^{2}	-189.54	59.28	170.5
	3rd	0.50	1.0000	20.92	67.22×10^{5}	-121.69	14.82	89.32	0.9999	40.13	0.5×10^{-3}	-254.20	34.03	220.6
	4th	0.00	0.9963	6.65	23.18×10^{6}	-111.83	0.2296	86.67	1.0000	23.24	24.9×10^{-3}	-283.51	16.83	235.9
17	1st	2.00	0.9994	32.33	13.07×10^{4}	-151.43	28.09	105.47	0.9996	29.39	1.06	-248.87	25.15	152.32
	2nd	1.00	0.9996	19.96	64.14×10^{5}	-120.08	15.17	84.45	0.9996	26.17	18.69×10^{-2}	-264.34	31.38	173.9
	3rd	0.33	0.9998	10.46	21.20×10^{7}	-112.18	4.16	86.95	0.9989	26.04	42.26×10^{-2}	-278.75	19.91	224.9

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