This method mainly used for the determination of water particle in the complexes the evolution of water, the ignition of precipitate often result in thermal decomposition reactions involving the dissociation of complex in to its metal oxide. The decomposition temperatures will be obviously be related to the thermal stabilities. The temperature at which precipitates may dried, or ignited to the required chemical form, can be determined from a study of the thermo gravimetric(TG) curves[1]. The thermogravimetry are the particular important to analyze the purity of the complexes and thermal stability of the complexes. The investigation of correct drying temperatures and the suitability of various weighing form for gravimetric analysis, the determination of the composition of the complex mixture. The results may be presented as a thermo gravimetric(TG) curve in which the weight changes is recorded as a function of temperature or time, or as a derivative thermo gravimetric (DTG) curve where the first derivative of the TG curve is plotted with respect to either temperature of time [2].

The most widely application of thermogravimetry in analytical chemistry has been in the study of the recommended drying temperatures of gravimetric precipitates. Duval studies over the thousand gravimetric precipitate by this method [3]. A slow rate of heating is to be proffered with the sample weight over the temperatures in which chemical changes take place. Thermo gravimetric curve must be interpreted with due regard to the fact that while they are being obtained the temperature is changing at a uniform rate, to a specified temperature and maintained at that temperature for a definite time [4]. The of thermogravimetric data to evaluate kinetic parameters of solid-state reactions involving weight loss (or gain) has been investigated by a number of workers[5].

Freeman and Carroll[6] have stated some of the advantages of this method over conventional isothermal studies. In this reasons may be added the advantages of using one single sample for investigation. However, importance of procedural details, such as crucible geometry, heating rate, pre-history of sample, and particle size, on the parameters has yet to be fully investigated. It is also necessary to ensure accurate temperature measurement, both for precision and also to detect any departure from a linear heating rate due to endo-or exothermic reactions. Thermogravimetric analysis (TGA) has come into wide use in the last few decades for rapidly assessing the thermal stability of various substances.

A new mathematical interpretation of thermogravimetric traces enables one to determine conveniently the kinetic parameters of pyrolysis curve[7]. The slope of straight line, plot of function of the weight fraction left vs. the temperature gives the activation energy of pyrolysis. The good agreement between values of activation energy obtained by the new equations and reported literature values for some polymers, complexes and hydrated salts serves to validate the new approach[8].

A prior knowledge of the value of the order of reaction is assumed in most derivation, while the method[9] which allows for the determination of both the activation energy and the order of reaction suffers from a number of disadvantages. In the reaction aA+bB = cC, the rate of disappearance of A is expressed by.

$$\frac{dC}{dt} = -kC^n \ldots (1)$$

Where C is concentration of A decomposed at time‘t’, n = order of reaction and k = rate constant given by expression.

$$k = Ae^{-E/RT} \ldots (2)$$

Where A – Arrhenius frequency factor and E = activation energy of the reaction. For a linear heating rate of say α min^{-1}.

$$\alpha = dT/dt \ldots (3)$$

Combining equations (1), (2) and (3) rearranging and integrating wet get

$$\int_a^{\alpha} \frac{dc}{(1-\alpha)^n} = \frac{A}{a} \int_O^T \bar{e}^{E/RT}\, dT \ldots (4)$$

The right hand side of equation (4) has no exact integral, but the making the substitution u = E/RT and using the relation.

$$\int_u^{\infty} \bar{e}^u u^{-b}\, du \cong u^{1-b}\, e^{-u} \sum_{n=o}^{\infty} \frac{(-1)^{\alpha} (b)_n}{u^n + 1}$$

Equation (4) becomes

$$\frac{1-(1-\alpha)^{1-n}}{1-n} = \frac{ART^2}{\alpha E}\left[1 - \frac{2RT}{E}\right]\bar{e}^{E/RT} \ldots (5)$$

Taking logs

$$\log_{10}\left[\frac{1-c(1-\alpha)^{1-n}}{T^2(1-n)}\right]=\log_{10}\frac{AR}{\alpha E}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.303RT} \qquad \ldots(6)$$

for all values of n except n=1 in which base equation (4) after taking logs becomes.

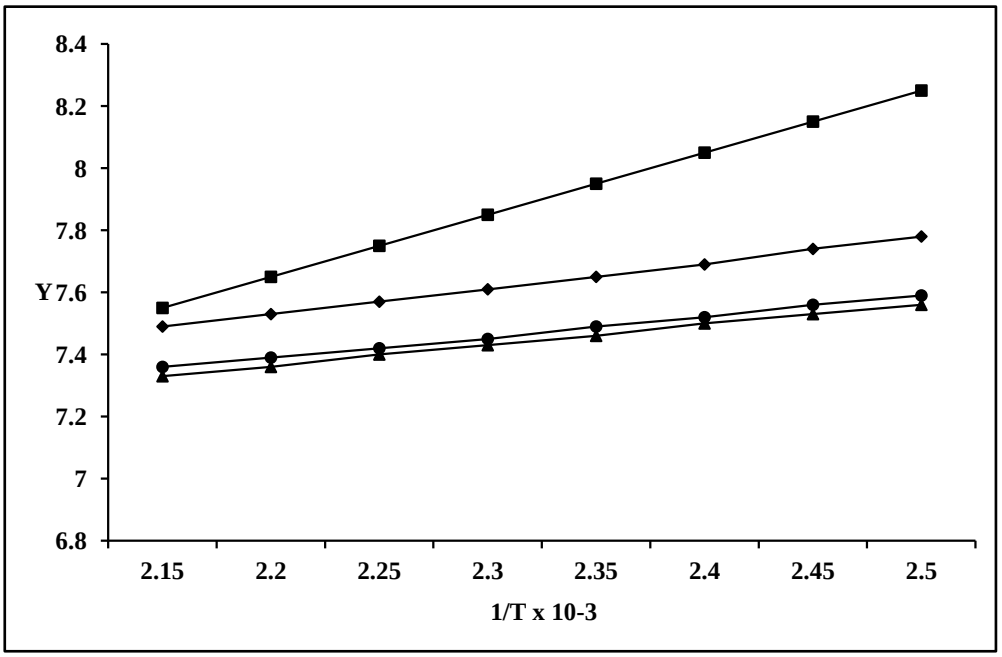
$$\log_{10}\left[-\log_{10}\frac{(1-\alpha)}{T^2}\right]=\log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right]-\frac{E}{2.303RT} \qquad \ldots(7)$$

Thus a plot of either $\log_{10}\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]$ against $\frac{1}{T}$ or where n=1,

$$\log_{10}\left[\frac{-\log(1-\alpha)}{T^2}\right] \text{ against } \frac{1}{T}$$

Should result in a straight line of slope –E/2.303R for the correct value of n, since it may be shown that for most value of E and for the temperature range over which reactions generally occur the expression.

$$\log_{10}\frac{AR}{aE}\left[1-\frac{2RT}{E}\right] \text{ is sensibly constant}$$



The equations may be applied by simple graphical techniques. Since there is theoretical justification for orders of reaction of 0, 1/2, 2/3 and 1 in solid state kinetics[10], it is possible to substitute these in,

$$Y = -\log\left[\frac{1-(1-\alpha)^{1-n}}{T(1-n)}\right] \text{ for } n = 0,\ 1/2 \text{ and } 2/3$$

and $$-\log\left[\frac{-\log(1-\alpha)}{T^2}\right] \text{ for } n = 1$$

into equation (6) (or equation (7) when n=1 to obtain the appropriate plots. It is also possible to use a computational approach to select a value of 'n' which gives the best straight line through the points on the assumption that the order is constant throughout the reaction[11].

Results and discussion

Thermogravimetric studies of the Cu(II, Co(II), Ni(II), Zn(II), Cd(II) and Hg(II) complexes were carried on the Perkin Elmer thermal analysis instrument at a heating rate of 10°C per minute in nitrogen atmosphere from 28 - 800°C. The thermograms, TG-DTA of the complex are depicted in Fig. 5(1) and (2) respectively. The range of temperature and the experimental and calculated weight losses of decomposition with probable assignment are given in the Table 5(1).

Thermal decomposition study of Cu(II) complex of the ligand [BCAP]

The **$[Cu(BCAP)Cl_2]_n$** complex with the general formula $[Cu(C_{16}H_{13}N_3O_2)Cl_2]_n$ is thermally decomposed in single step. The estimated weight loss of 43% corresponds to loss of one chloride[12] molecule and $(C_7H_7N)_n$ species at the temperature 333.37°C. This practical weight loss of 43% is in accordance with the theoretical weight loss of 42.71%. The complex showed a gradual degradation up to 800°C and onwards. The weight of the residue 15.42% corresponds to the formation of the Cu oxide.

Thermal decomposition study of Ni(II) complex of the ligand [BCAT]

The thermal stability of the Ni(II) complex of the ligand [BCAT] was studied in the in the temperature ranges from 28 - 800°C at a heating rate of 10°C per minute. The thermograms, TG-DTA of the complex are depicted in Fig. 5(3) and 5(4) respectively. The range of temperature and the experimental and calculated weight losses of decomposition with probable assignment are given in the Table 5(2).

The **$[Ni(BCAT)_2 2H_2O]$** complex with the general formula $[Ni(C_{15}H_{11}O_2N_2S)_2 2H_2O]$ is thermally decomposed in two successive decomposition steps. The first estimated weight loss of 6% corresponds to loss of two coordinated water molecules at the temperature 184.24°C. This practical weight loss of 6% is in

accordance with the theoretical weight loss of 5.4%. The resultant intermediate complex underwent further decomposition and gave another break at 284.40°C with weight loss of 95% which corresponds to the decomposition of complex to expel $(C_{15}H_{11}N_2O_2S)_2$ species. This practical weight loss of 95% is in accordance with the theoretical weight loss of 94.54%. The complex showed a gradual degradation up to 800°C and onwards. The weight of the residue 8.89% corresponds to the formation of the Ni oxide.

Thermal decomposition study of Cd(II) complex of the ligand [BCACP]

The thermal stability of the Cd(II) complex of the ligand [BCACP] was studied in the in the temperature ranges from 28 - 800°C at a heating rate of 10°C per minute. The thermograms, TG-DTA of the complex are depicted in Fig. 5(5) and 5(6) respectively. The range of temperature and the experimental and calculated weight losses of decomposition with probable assignment are given in the Table 5(3).

The **[Cd(BCACP)**Cl_2**]** complex with the general formula $[Cd(C_{17}H_{14}N_2O_2)Cl_2]$ is thermally decomposed in two successive decomposition steps. The first estimated weight loss of one chloride molecule and (C_8H_8) species at the temperature 322.07°C. This practical weight loss of 38% is in accordance with the theoretical weight loss of 37.92%. The complex underwent further decomposition and gave another break at 555.34°C with weight loss of 38% which corresponds to the decomposition of complex to expel $(C_9H_6N_2O_2)$ species. This observed weight loss 38% is in accordance with the theoretical weight loss of 37.74%. The complex showed a gradual degradation up to 800°C and onwards. The weight of the residue 24.38% corresponds to the formation of the Cd oxide.

Thermal decomposition study of Zn(II) complex of the ligand [BCMeOACP]

The thermal stability of the Zn(II) complex of the ligand [BCMeOACP] was studied in the temperature ranges from 28 - 800°C at a heating rate of 10°C per minute. The thermograms, TG-DTA of the complex are depicted in Fig. 5(7) and (8) respectively. The range of temperature and the experimental and calculated weight losses of decomposition with probable assignment are given in the Table 5(4).

The **[Zn(BCMeOACP)**Cl_2**]** complex with the general formula $[Zn(C_{18}H_{16}N_2O_3)Cl_2]$ is thermally decomposed in single step. The estimated weight loss of 43% corresponds to loss of one chloride[13] molecule and (C_9H_{10}) species at the temperature 259.74°C. This practical weight loss of 43% is in accordance with the

theoretical weight loss of 42.56%. The complex showed a gradual degradation up to 800°C and onwards. The weight of the residue 14.72% corresponds to the formation of the Zn oxide.

Thermal decomposition study of Zn(II) complex of the ligand [BCClACP]

The thermal stability of the Zn(II) complex of the ligand [BCClACP] was studied in the in the temperature ranges from 28 - 800°C at a heating rate of 10°C per minute. The thermograms, TG-DTA of the complex are depicted in Fig. 5(9) and (10) respectively. The range of temperature and the experimental and calculated weight losses of decomposition with probable assignment are given in the Table 5(5).

The **[Zn(BCClACP)**Cl_2**]** complex with the general formula [$Zn(C_{17}H_{13}N_2O_2Cl)Cl_2$] is thermally decomposed in two successive decomposition steps. The first estimated weight loss of one chloride molecule at the temperature 289.76°C. This practical weight loss of 16% is in accordance with the theoretical weight loss of 15.81%. The complex underwent further decomposition and gave another break at 329.60°C with weight loss of 31% which corresponds to the decomposition of complex to expel (C_8H_7Cl) species. This practical weight loss 31% is in accordance with the theoretical weight loss of 30.63%. The complex showed a gradual degradation up to 800°C and onwards. The weight of the residue 14.56% corresponds to the formation of the Zn oxide.

Thermal decomposition study of Cd(II) complex of the ligand [BCMeTPC]

The thermal stability of the Cd(II) complex of the ligand [BCMeTPC] was studied in the temperature ranges from 28 - 800°C at a heating rate of 10°C per minute. The thermograms, TG-DTA of the complex are depicted in Fig. 5(11) and (12) respectively. The range of temperature and the experimental and calculated weight losses of decomposition with probable assignment are given in the Table 5(6).

The **[Cd(BCMeTPC)Cl_2]** complex with the general formula [$Cd(C_{15}H_{12}N_2O_2S)Cl_2$] is thermally decomposed in single step. The estimated weight loss of 39% corresponds to loss of one chloride molecule and (C_6H_6S) species at the temperature 271.83°C. This practical weight loss of 39% is in accordance with the theoretical weight loss of 38.75%. The complex showed a gradual degradation up to 800°C and onwards. The weight of the residue 24.06% corresponds to the formation of the Cd oxide.

Thermal decomposition study of Cd(II) complex of the ligand [BCMeTB]

The thermal stability of the Cd(II) complex of the ligand [BCMeTB] was studied in the in the temperature ranges from 28 - 800°C at a heating rate of 10°C per minute. The thermograms, TG-DTA of the complex are depicted in Fig. 6(13) and (14) respectively. The range of temperature and the experimental and calculated weight losses of decomposition with probable assignment are given in the Table 5(7).

The **[Cd(BCMeTB)**Cl_2**]** complex with the general formula [Cd($C_{17}H_{14}N_2O_2S$)Cl_2] [is thermally decomposed in two successive decomposition steps. The first estimated weight loss of one chloride[14] molecule and (C_8H_8S) species at the temperature 297.90°C. This practical weight loss of 42.5% is in accordance with the theoretical weight loss of 41.98%. The complex underwent further decomposition and gave another break at 358.10°C with weight loss of 36% which corresponds to the decomposition of complex to expel ($C_9H_6N_2O_2$) species. This observed weight loss 36% is in accordance with the theoretical weight loss of 35.29%. The weight of the residue 22.79% corresponds to the formation of the Cd oxide.

Thermal decomposition study of Ni(II) complex of the ligand [BCEtHB]

The thermal stability of the Ni(II) complex of the ligand [BCEtHB] was studied in the temperature ranges from 28 - 800°C at a heating rate of 10°C per minute. The thermograms, TG-DTA of the complex are depicted in Fig. 5(15) and (16) respectively. The range of temperature and the experimental and calculated weight losses of decomposition with probable assignment are given in the Table 5(8).

The **[Ni(BCEtHB)Cl_2]** complex with the general formula $[Ni(C_{18}H_{16}N_2O_4)Cl_2]_n$ is thermally decomposed in single step. The estimated weight loss of 49.50% corresponds to loss of one chloride molecule and ($C_9H_{10}O_2$) species at the temperature 326.22°C. This practical weight loss of 49.50% is in accordance with the theoretical weight loss of 48.78%. The complex showed a gradual degradation up to 800°C and onwards. The weight of the residue 12.95% corresponds to the formation of the Ni oxide.

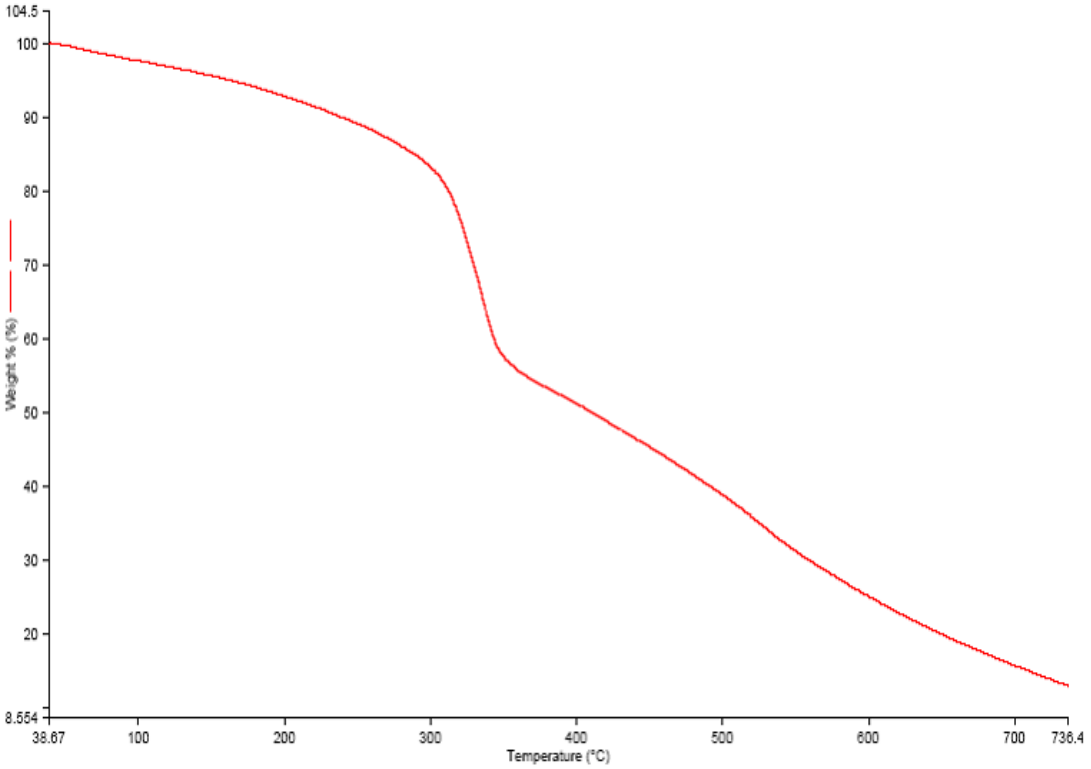


Fig. 5(1) TGA spectrum of Cu(II) complex of the ligand [BCAP]

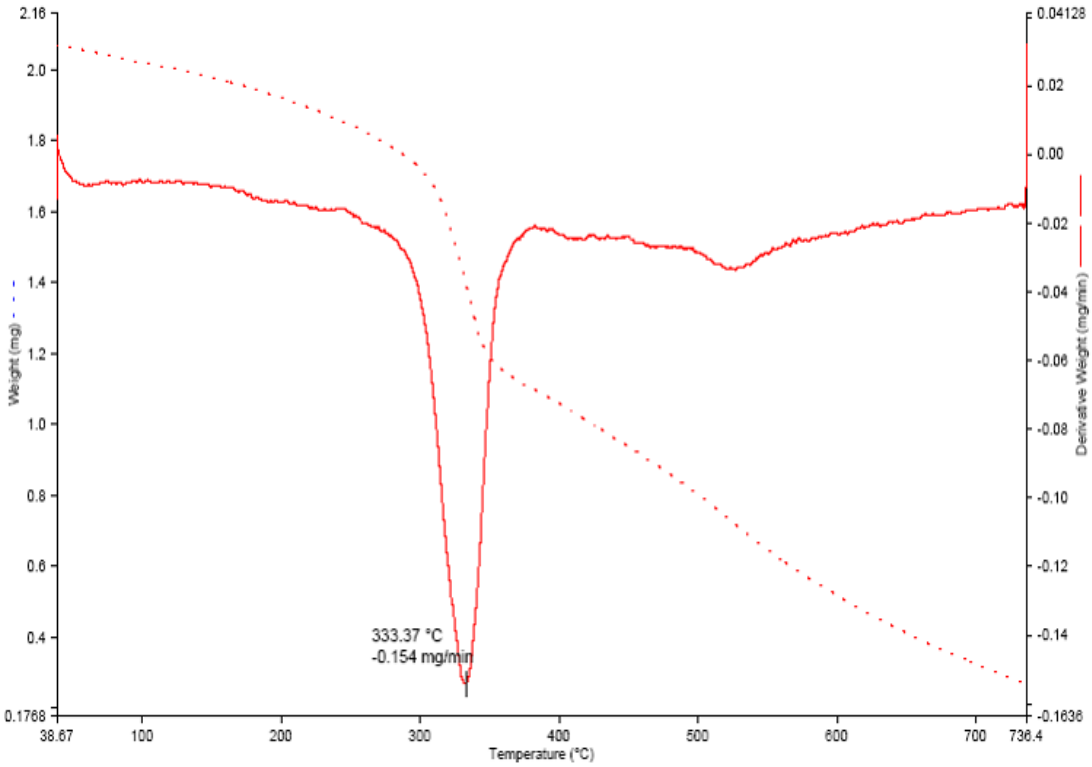


Fig. 5(2) TG-DTA spectrum of Cu(II) complex of the ligand [BCAP]

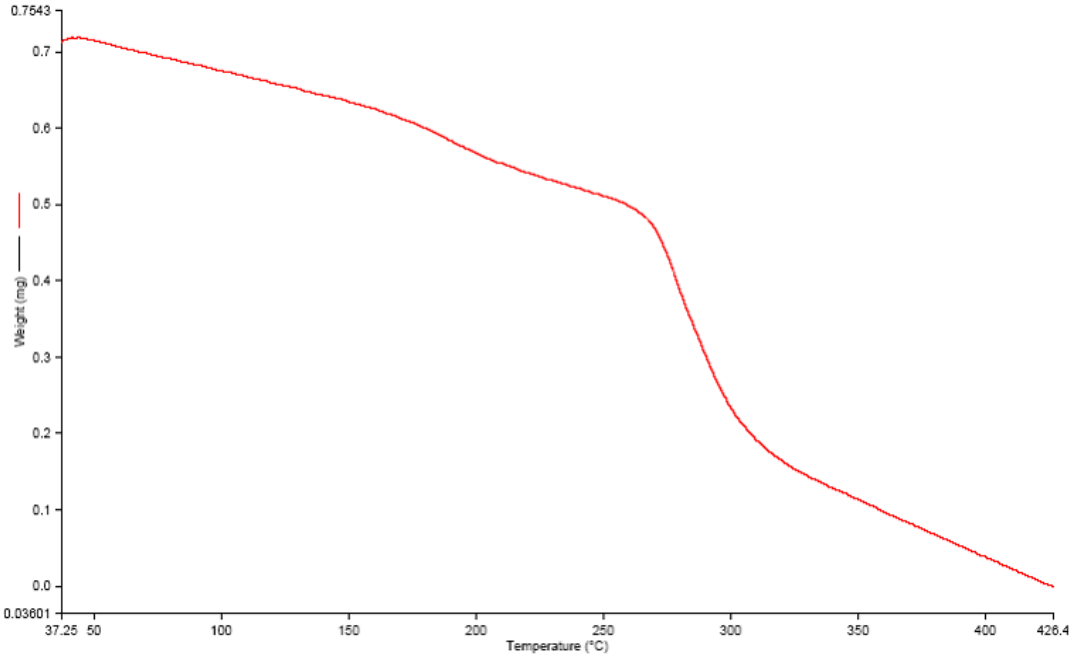


Fig. 5(3) TGA spectrum of Ni(II) complex of the ligand [BCAT]

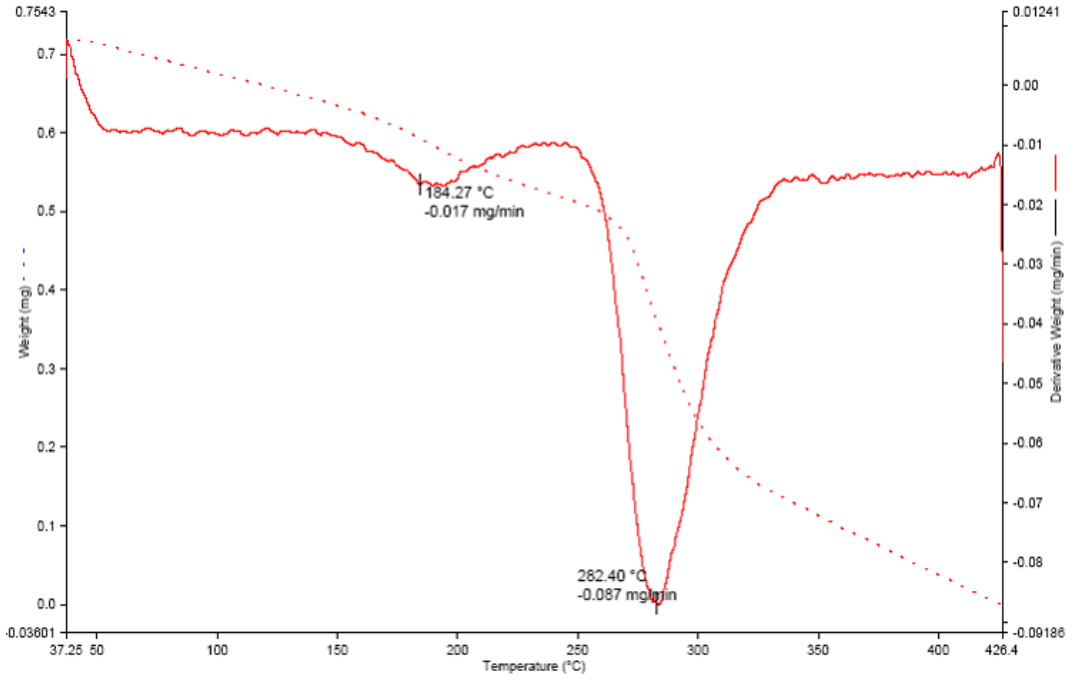


Fig. 5(4) TG-DTA spectrum of Ni(II) complex of the ligand [BCAT]

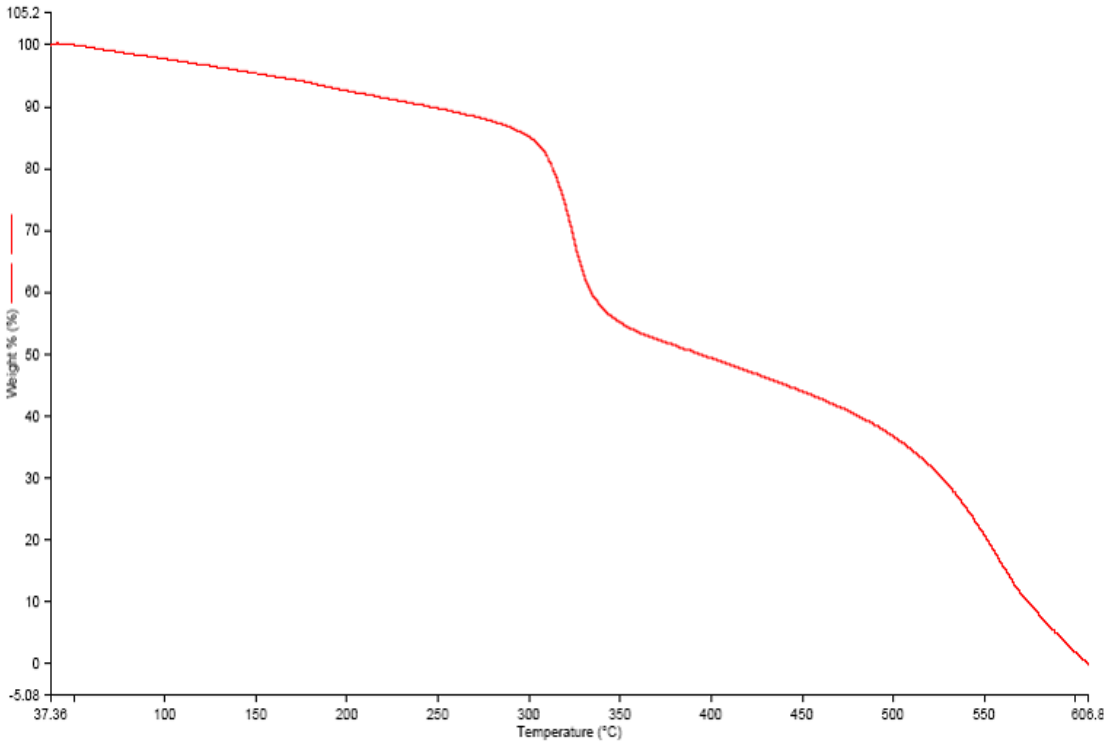


Fig. 5(5) TGA spectrum of Cd(II) complex of the ligand [BCACP]

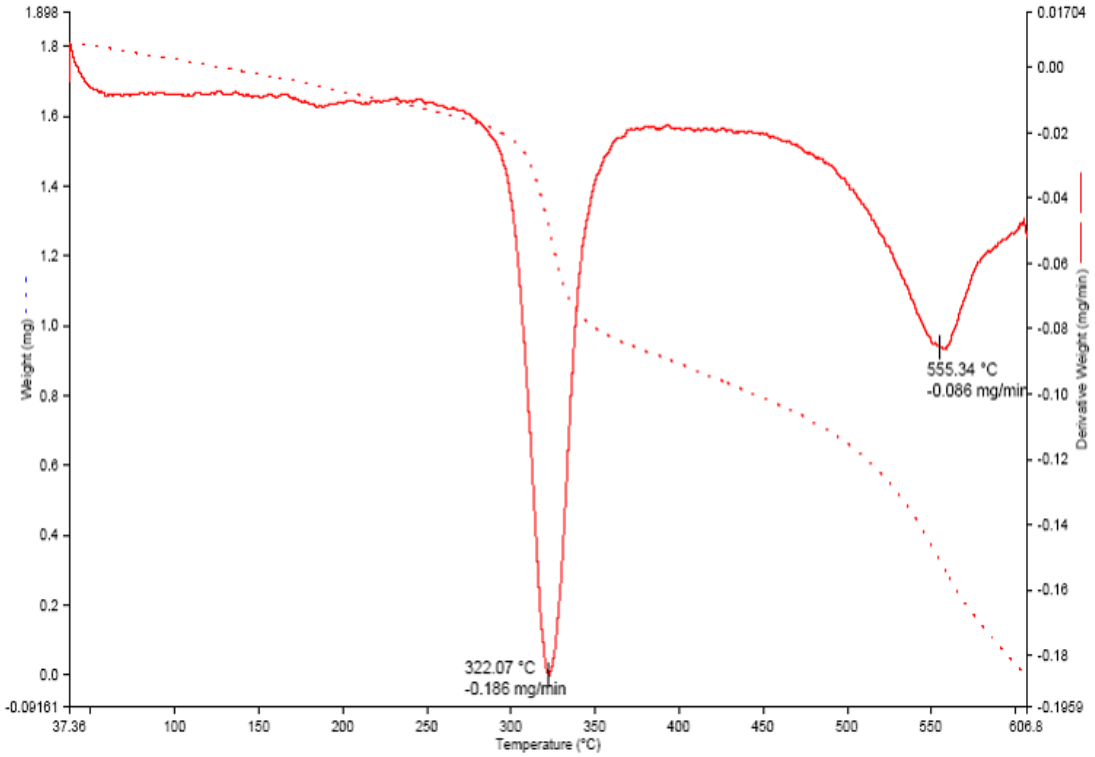


Fig. 5(6) TG-DTA spectrum of Cd(II) complex of the ligand [BCACP]

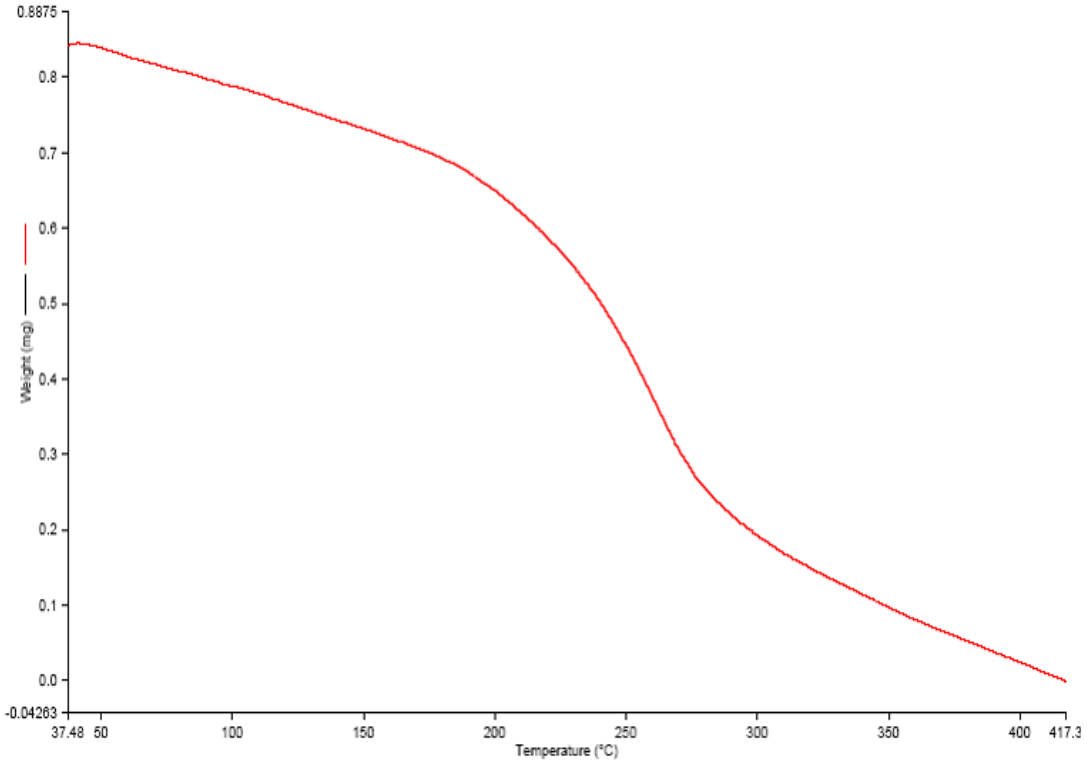


Fig. 5(7) TGA spectrum of Zn(II) complex of the ligand [BCMeOACP]

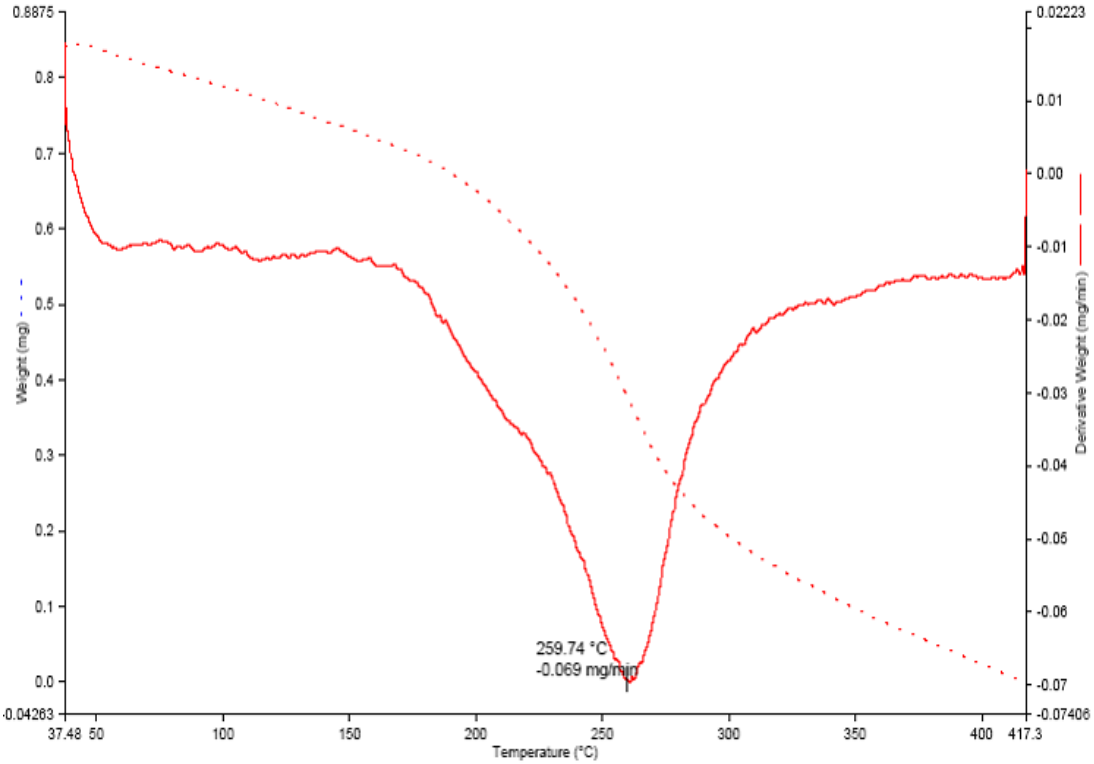


Fig. 5(8) TG-DTA spectrum of Zn(II) complex of the ligand [BCMeOACP]

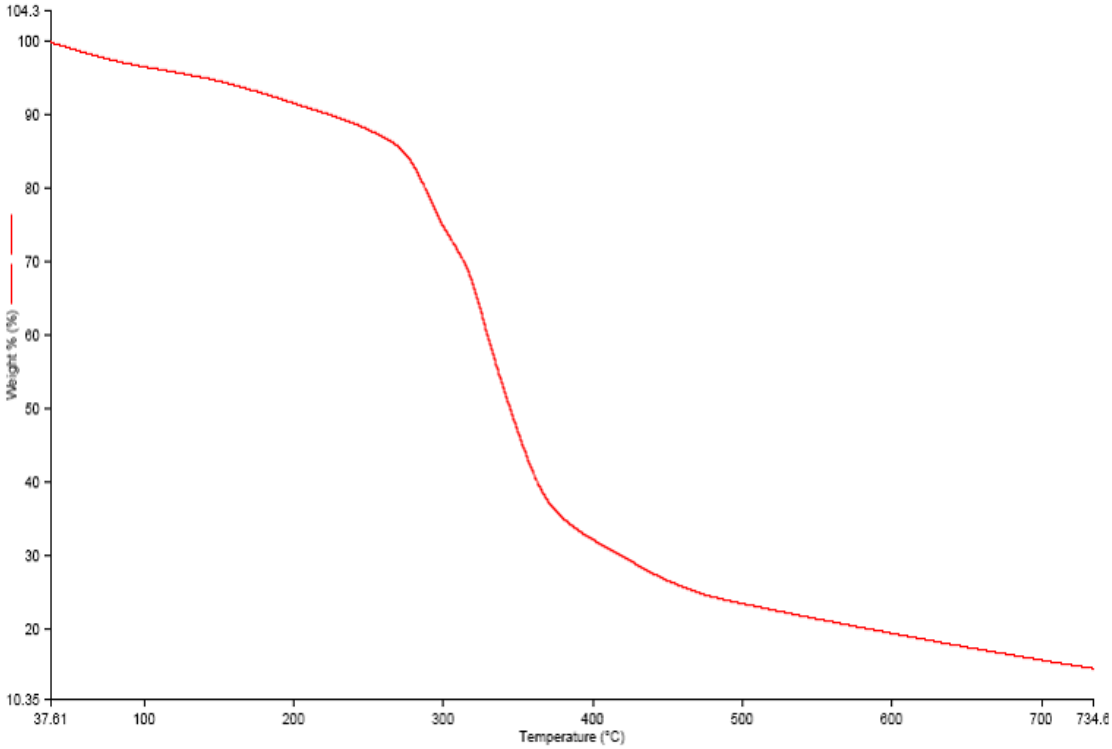


Fig. 5(9) TGA spectrum of Zn(II) complex of the ligand [BCClACP]

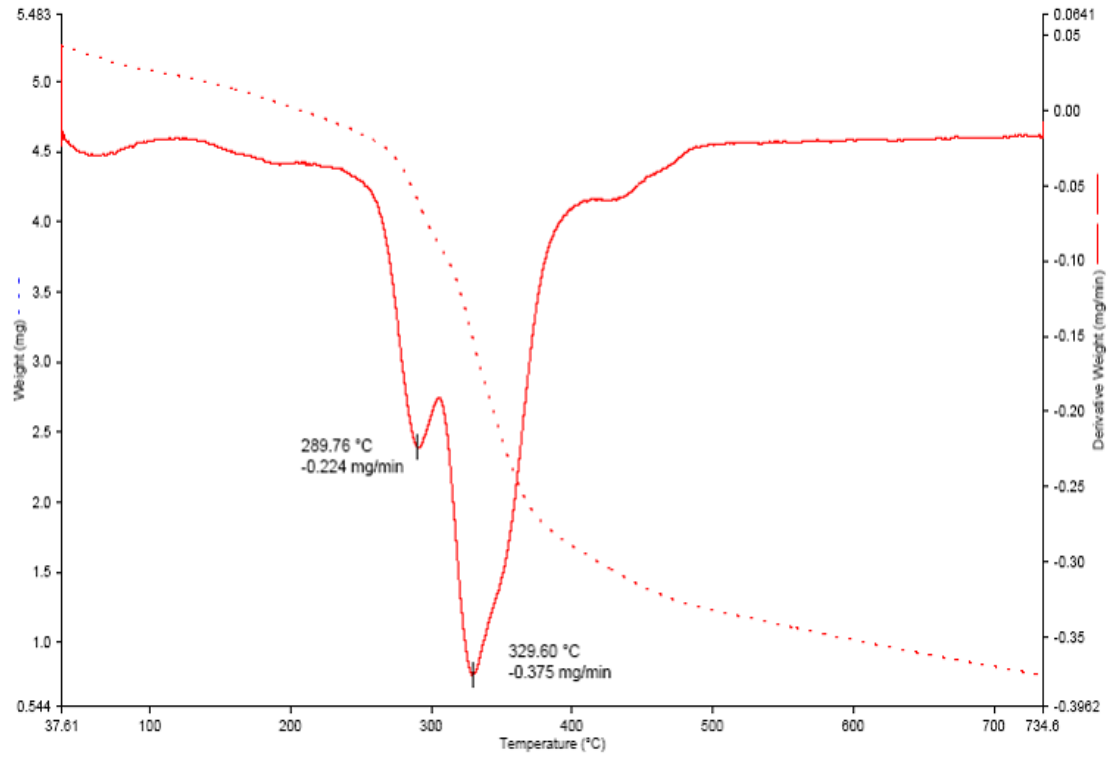


Fig. 5(10) TG-DTA spectrum of Zn(II) complex of the ligand [BCClACP]

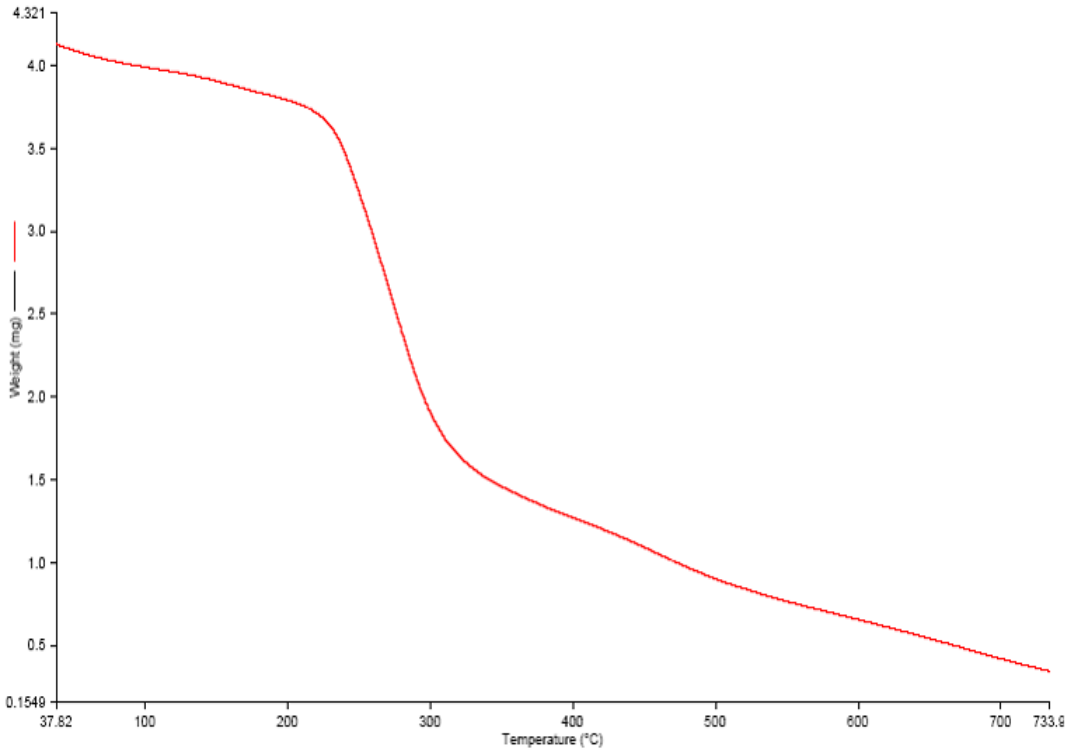


Fig. 5(11) TGA spectrum of Cd(II) complex of the ligand [BCMeTPC]

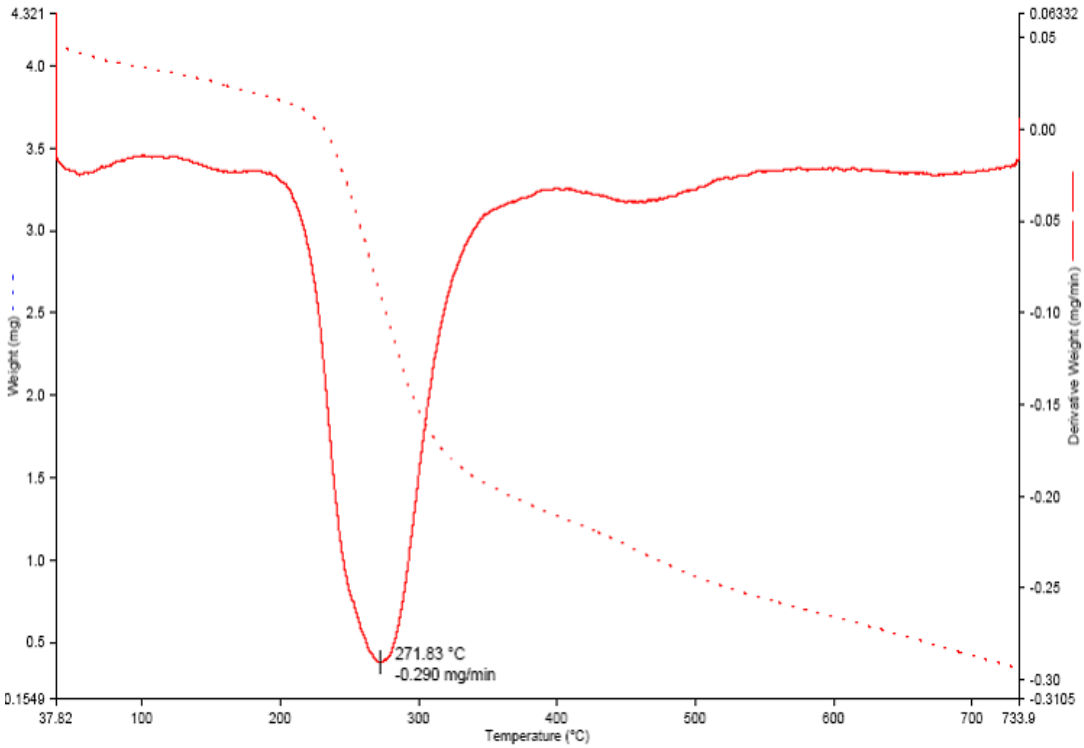


Fig. 5(12) TG-DTA spectrum of Cd(II) complex of the ligand [BCMeTPC]

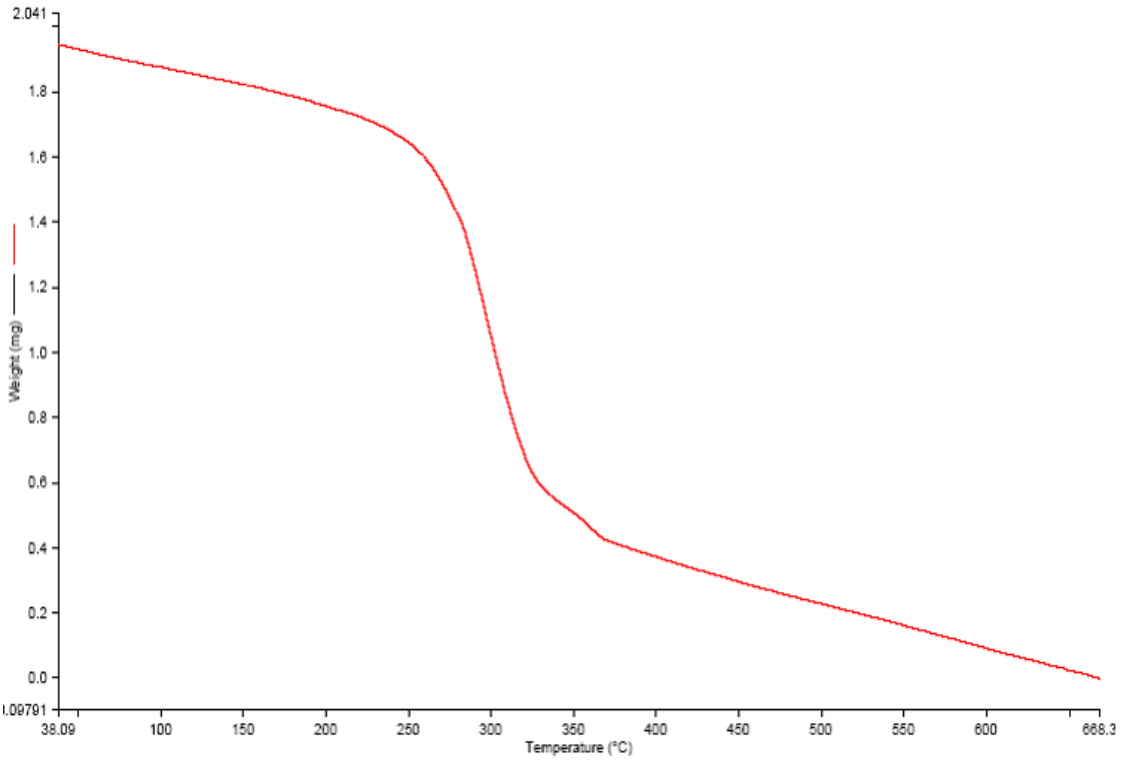


Fig. 5(13) TGA spectrum of Cd(II) complex of the ligand [BCMeTB]

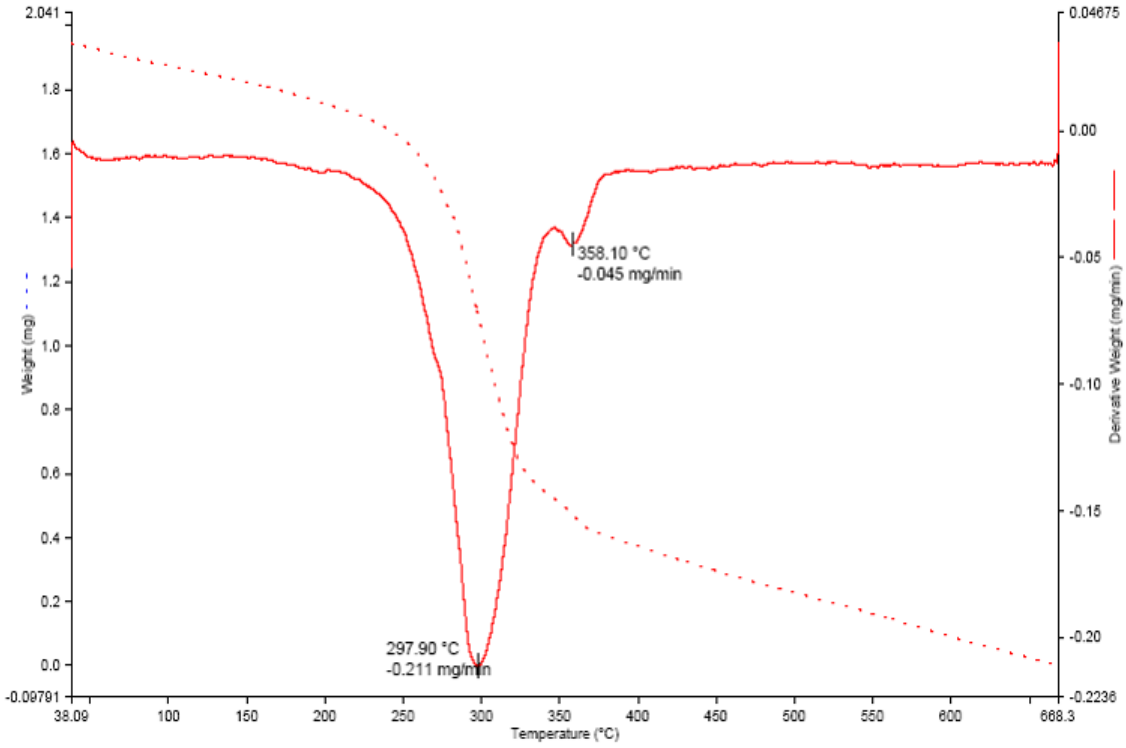


Fig. 5(14) TG-DTA spectrum of Cd(II) complex of the ligand [BCMeTB]

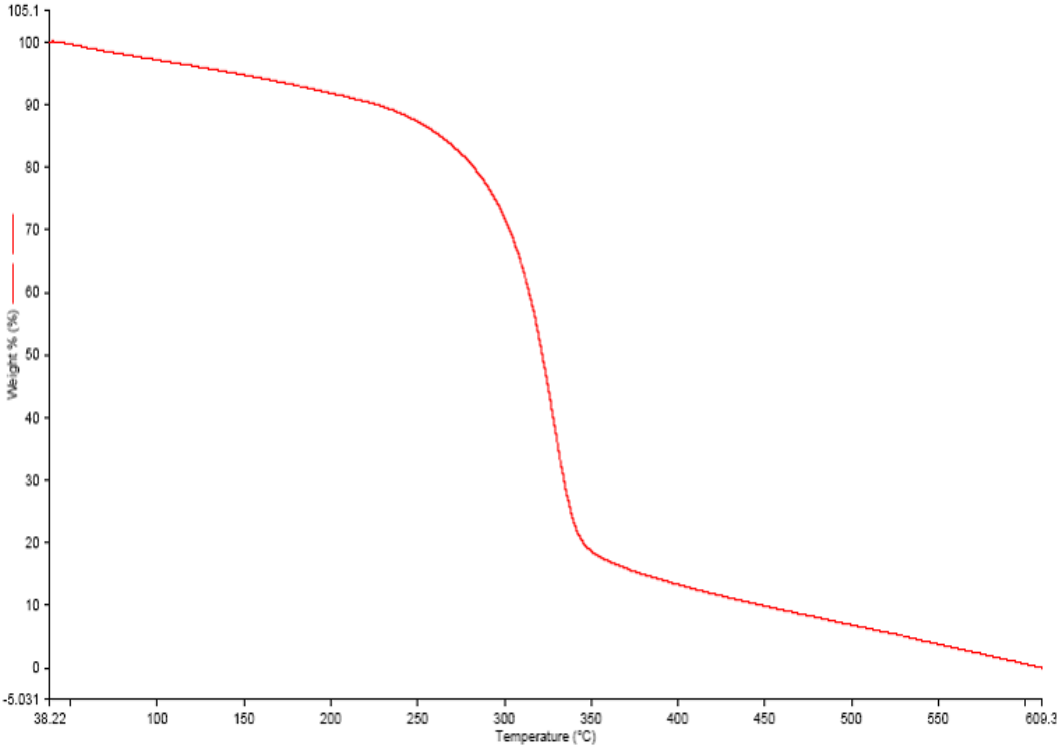


Fig. 5(15) TGA spectrum of NI(II) complex of the ligand [BCEtHB]

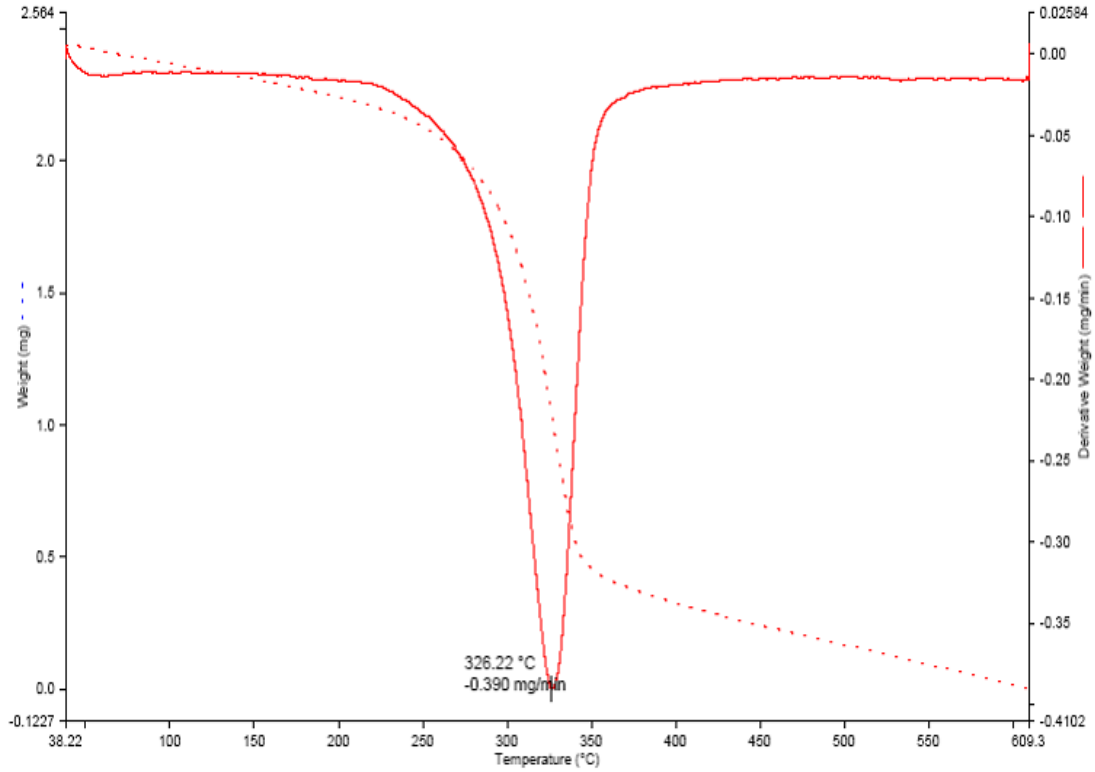


Fig. 5(16) TG-DTA spectrum of NI(II) complex of the ligand [BCEtHB]

Table: 5(1)

Thermal decomposition of Cu(II) complex of the ligand BCAP

Complex	Stage	Peak temp (°C)	Loss in mass (%)		Probable assignment
			Observed	Theoretical	
$[Cu(BCAP)Cl_2]_n$	--	--	--	--	$[Cu(C_{16}H_{13}N_3O_2)Cl_2]$
					↓ - Cl_2 & (C_7H_7N)
	I	333.37	43.0	42.71	$[Cu(C_8H_6N_2O_2)]$
					↓
					CuO

Table: 5(2)

Thermal decomposition of Ni(II) complex of the ligand BCAT

Complex	Stage	Peak temp (°C)	Loss in mass (%)		Probable assignment
			Observed	Theoretical	
$Ni(BCAT)_2 2H_2O$	--	--	--	--	$[Ni(C_{15}H_{11}N_2O_2S)_2 2H_2O]$
					↓ $-2H_2O$
	I	184.27	6.0	5.4	$[Ni(C_{15}H_{11}N_2O_2S)_2]$
					↓ $-(C_{15}H_{11}N_2O_2S)_2$
	II	282.40	95.0	94.54	
					NiO

Table: 5(3)

Thermal decomposition of Cd(II) complex of the ligand BCACP

Complex	Stage	Peak temp (°C)	Loss in mass (%)		Probable assignment
			Observed	Theoretical	
[Cd(BCACP)Cl_2]	--	--	--	--	[Cd($C_{17}H_{14}N_2O_2$)Cl_2]
					↓ -Cl_2 & (C_8H_8)
	I	322.07	38.0	37.92	[Cd($C_9H_6N_2O_2$)]
					↓ -($C_9H_6N_2O_2$)
	II	555.34	38.0	37.74	CdO

Table: 5(4)

Thermal decomposition of Zn(II) complex of the ligand BCMeOACP

Complex	Stage	Peak temp (°C)	Loss in mass (%)		Probable assignment
			Observed	Theoretical	
[Zn(BCMeOACP)Cl_2]	--	--	--	--	[Zn($C_{18}H_{16}N_2O_3$)Cl_2]
					↓ - Cl_2 & (C_9H_{10})
	I	259.74	43.0	42.56	[Zn($C_9H_6N_2O_3$)]
					↓
					ZnO

Table: 5(5)

Thermal decomposition of Zn(II) complex of the ligand BCClACP

Complex	Stage	Peak temp (°C)	Loss in mass (%)		Probable assignment
			Observed	Theoretical	
[Zn(BCClACP)Cl_2]	--	--	--	--	[Zn($C_{17}H_{13}N_2O_2Cl$)Cl_2]
					↓ -Cl_2 & C_8H_7Cl
	I	289.76	47.0	46.65	[Zn($C_9H_6N_2O_2$]
					↓ -$C_9H_6N_2O_2$
	II	329.60	31.0	30.63	ZnO

Table: 5(6)

Thermal decomposition of Cd(II) complex of the ligand BCMeTPC

Complex	Stage	Peak temp (°C)	Loss in mass (%)		Probable assignment
			Observed	Theoretical	
[Cd(BCMeTPC)Cl_2]	--	--	--	--	[Cd($C_{15}H_{12}N_2O_2S$)Cl_2]
					↓ - Cl_2 & (C_6H_6S)
	I	271.83	39.0	38.75	[Cd($C_9H_6N_2O_2$)]
					↓
					CdO

Table: 5(7)

Thermal decomposition of Cd(II) complex of the ligand BCMeTB

Complex	Stage	Peak temp (°C)	Loss in mass (%)		Probable assignment
			Observed	Theoretical	
[Cd(BCMeTB)Cl_2]	--	--	--	--	[Cd($C_{17}H_{14}N_2O_2S$)Cl_2]
					↓ -Cl_2 &(C_8H_8S)
	I	297.90	42.5	41.98	[Cd($C_9H_6N_2O_2$)]
					↓ -($C_9H_6N_2O_2$)
	II	358.10	36.0	35.29	CdO

Table: 5(8)

Thermal decomposition of Ni(II) complex of the ligand BCEtHB

Complex	Stage	Peak temp (°C)	Loss in mass (%)		Probable assignment
			Observed	Theoretical	
[Ni(BCEtHB)Cl_2]	--	--	--	--	[Ni($C_{18}H_{16}N_2O_4$)Cl_2]$_n$
					↓ -Cl_2 & ($C_9H_{10}O_2$)
	I	326.22	49.50	48.78	[Ni($C_9H_6N_2O_2$)]$_n$
					↓
					NiO

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