

# Studies on energetic compounds part 37: kinetics of thermal decomposition of perchlorate complexes of some transition metals with ethylenediamine

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## Abstract

Five bis(ethylenediamine)metal perchlorate (BEMP) complexes like  $[M(en)_2](ClO_4)_2$  (where  $M = Mn, Co, Ni, Cu, Zn$  and  $en =$  ethylenediamine) have been prepared and characterized by gravimetric methods, infrared spectroscopy (IR) and elemental analysis. Thermal decomposition studies have been undertaken using simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) in nitrogen atmosphere. Non-isothermal TG and DTA studies have also been carried out separately in air to examine the effect of atmosphere on thermolysis of these complexes. Thermal stability of the complexes was found to decrease in the order:  $[Zn(en)_2](ClO_4)_2 > [Mn(en)_2](ClO_4)_2 > [Ni(en)_2](ClO_4)_2 > [Cu(en)_2](ClO_4)_2 > [Co(en)_2](ClO_4)_2$ .

Isothermal TG over the temperature range of decomposition of all these complexes, has been done to evaluate the kinetics of decomposition. Both model fitting and model free isoconversional methods have been used to analyse the kinetics. Isoconversional method has been found to be superior over the conventional model fitting method and is able to describe the complex decomposition of these complexes. It indicates that the values of activation energy vary with the extent of conversion ( $\alpha$ ) while model fitting method results in a single value of  $E$  for overall decomposition process which cannot be attributed to any process under such a complex decomposition reaction. Explosion delay ( $D_E$ ) measurement has been carried out to investigate the response of these complexes under the condition of rapid heating.

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## 1. Introduction

During the past few decades, there has been a spate of keen interest in the thermal decomposition studies of the transition metal complexes containing both monodentate and bidentate amine ligands [1–6]. The reason for this undoubtedly being the enormous array of applications of these complexes. Out of the various types of bidentates, ethylenediamine ( $en$ ) is a very common ligand for complexation to transition metal ions [7–9]. During complexation to the central metal ions,  $en$  donates its lone pairs of electrons present on two nitrogen atoms of the amine groups and thus acts as a neutral bidentate ligand. Maslowska and Szmich [7] have studied the thermal decomposition of some  $en$  complexes with metal nitrates in air atmosphere and found that the

decomposition occurs in multisteps and all the steps gave endothermic peaks in DTA thermograms. The kinetics and mechanisms of thermolysis of  $en$  complexes of copper(II) chloride/bromide monohydrates [8] and recently studied copper(II) complexes of  $en$  with various counter anions (nitrate, chloride, sulphate, acetate, oxalate) [9] well described their thermal decomposition trend, relative thermal stability and effect of different anions on thermolysis. In all these studies, which are undertaken in different atmosphere, the corresponding metal oxides have been obtained at the end of the thermal decomposition reactions. Thus, a survey of literature shows that although the details of thermal studies on  $en$  complexes with different counter anions are reported prior to this work, the thermolysis, kinetics and mechanism of thermal decomposition for  $en$  complexes of  $Mn, Co, Ni, Cu$  and  $Zn$  having  $ClO_4^-$  as counter anion are not yet available in open literature. Such complexes fall in category of high energetic compounds because on thermal treatment these complexes undergo highly exothermic self-propogative

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decomposition reactions due to simultaneous presence of both oxidizing ( $\text{ClO}_4$ ) and reducing (en) groups in the same complex molecule [9]. In this way, complexes release chemical energy in the form of heat and produce gaseous decomposition products and solid residues [10]. On the basis of nature of their explosivity, these amine complexes are categorized to lie between those of primary and secondary explosives [11,12]. These energetic complexes may find applications in propellants, explosives and pyrotechnic compositions. As it is pointed out previously that transition metal amine complexes decompose to respective metal oxides, these ultrafine oxides may have interesting electrical, magnetic and catalytic properties. A large number of semi-conducting oxides (e.g.  $\text{CuO}$ ,  $\text{MnO}$ ,  $\text{ZnO}$  etc.) find interesting applications in preparation of environmental sensors for detecting trace level pollutants such as  $\text{H}_2\text{S}$ ,  $\text{CO}$ ,  $\text{NO}_x$ ,  $\text{NH}_3$  etc. in atmospheric air [13–16]. It is suggested [17] that the use of ultrafine metal oxides increases the sensing capability of the sensors. Naturally, the nanocrystalline metal oxides, formed during thermolysis of the complexes, may be better substitute for this application than the commercial aged ones. One of the most important technological applications of such energetic complexes is their incorporation in composite solid propellant (CSP) formulations in which they perform the activities of burning rate modifiers. Transition metal oxides (TMOs) are well-known catalysts for solid rocket propellants [18–21]. However, some energetic transition metal complexes [22–25] and salts of NTO (5-nitro-2,4-dihydro-3H-1,2,4-triazol-3-one) [26] have been proved to be potential ballistic modifiers for CSPs. These complexes and NTO salts produce highly reactive TMO particles during combustion, which act as better catalysts than the less reactive commercial ones in CSPs. Additionally, the exothermic decomposition of these compounds is also supportive for burn rate enhancement, as the heat release may add to the surface temperature of the propellants.

We have already reported the studies on thermal decomposition, kinetics and mechanism of some hexammine metal perchlorates (HAMP) [23,27], bis(ethylenediamine)metal nitrates (BEMN) [25,28] and bis(propylenediamine)metal nitrates (BPMN) [29] complexes. HAMP [22,23] and BEMN [24,25] were found to be potential additives for CSPs. Thus, in view of the exciting potential for various applications, we are reporting in this paper, the preparation, characterization, kinetics and mechanism of thermal decomposition of bis(ethylenediamine)metal perchlorate complexes. Simultaneous TG-DTA, non-isothermal TG and DTA, isothermal TG and explosion delay measurements have been carried out to examine the effect of slow and rapid heating of complexes in different conditions. In our earlier studies, we have evaluated [23,25,27,28] the kinetic parameters for thermolysis of various energetic complexes by conventional model fitting method. By making use of a model free, isoconversional approach, recently we were able to estimate activation energy corresponding to different processes [29,30].

## 2. Experimental

### 2.1. Materials

Following AR grade commercially available chemicals (sources given in parentheses) were used as received without any further purification.

Carbonates of manganese, cobalt, copper (BDH), nickel, zinc (Thomas Baker), 70% perchloric acid, methanol (Ranbaxy), ethanol (Hayman), ethylenediamine, silica gel (S.D. Fine Chemicals) and petroleum ether (Merck).

### 2.2. Preparation of the complexes

Firstly, the metal carbonates were treated with 70% perchloric acid at room temperature to obtain respective metal perchlorate hexahydrates, which were washed with petroleum ether, recrystallized from distilled water and dried over fused  $\text{CaCl}_2$  in a desiccator. The various BEMP complexes were prepared by reacting ethanolic solutions of metal perchlorate hexahydrates with ethylenediamine in equimolar ratios as per the standard literature procedures [31–35]. Thus, precipitated complexes of different colours were separated from mother liquor by decantation and washed with methanol. All of these complexes were recrystallized from aqueous ethanolic solutions and dried over fused  $\text{CaCl}_2$  in a desiccator.

### 2.3. Thermal decomposition studies

All the non-isothermal analyses (e.g. TG-DTA in  $\text{N}_2$  and TG and DTA in air atmosphere) were undertaken at a heating rate of  $10^\circ\text{C min}^{-1}$ . The simultaneous TG-DTA thermograms on the complexes (mass  $\approx 1$ – $2$  mg) were obtained on Mettler Toledo Star system under inert atmosphere (flowing  $\text{N}_2$  at a rate of  $100 \text{ ml min}^{-1}$ ). Non-isothermal TG thermograms were recorded on our indigenously fabricated TG apparatus [36] in static air (sample mass  $\approx 20$  mg, 100–200 mesh). DTA thermograms were taken under flowing air atmosphere (at a rate of  $100 \text{ ml min}^{-1}$ ) using an instrument supplied by Universal Thermal Analysis instruments, Mumbai (sample mass  $\approx 10$  mg). Isothermal TG on these complexes (mass  $\approx 20$  mg) was done in static air using above stated indigenously fabricated TG apparatus at appropriate temperatures of decomposition. Explosion delay ( $D_E$ ) was measured using the tube furnace (TF) technique as reported in earlier [37–40].

## 3. Results

### 3.1. Characterization

The purity of all these complexes was checked by thin layer chromatography (TLC) using a mixture of *n*-butanol, chloroform and glacial acetic acid in the volume ratio of

2:1:1 as mobile phase (eluent). All the complexes gave yellow coloured spots and  $R_f$  values for each complex are presented in Table 1. The metal contents (%) were estimated gravimetrically by well-established methods [41]. The percentage mass of other elements (C, H, N) was obtained on Fission Instruments DP 200 series 2 systems. The complexes were further characterized by their infrared spectra (Impact 400) in the form of their nujol mulls. The deduced molecular formulae of the complexes and their physical, elemental and spectral parameters are reported in Table 1.

### 3.2. TG-DTA

The simultaneous TG-DTA thermograms are demonstrated in Fig. 1 and the corresponding data are listed in Table 2. It is clear that all these complexes (except copper complex) decompose in a single step. Mass loss for these complexes occurs in the temperature range of 235–360 °C, which approach a maximum of 79–80% of the initial weight. This single step weight loss corresponds to simul-

taneous losses of two molecules of ligands (en) and counter anion ( $\text{ClO}_4^-$ ). The mass of final residue corresponds to the formation of respective metal oxides. In the case of the copper complex, a plateau is observed for a short range of temperature after a mass loss of 16.0%, which indicates that the thermolysis of this complex occurs at multisteps. This initial mass loss (temperature range 230–292 °C) corresponds to the removal of one en molecule and thus, mono(ethylenediamine)copper perchlorate is formed. On progressive heating, this monoligand intermediate is further decomposed explosively to CuO and other gaseous products. The rate of thermolysis reaction is fast and highly exothermic that is evident by sharp exothermic DTA peaks presented in Fig. 1. Both the steps of decomposition of copper complex are exothermic in nature.

### 3.3. Non-isothermal TG and DTA in air atmosphere

To detect the effect of atmospheric change on thermolysis of these energetic complexes, TG and DTA studies have

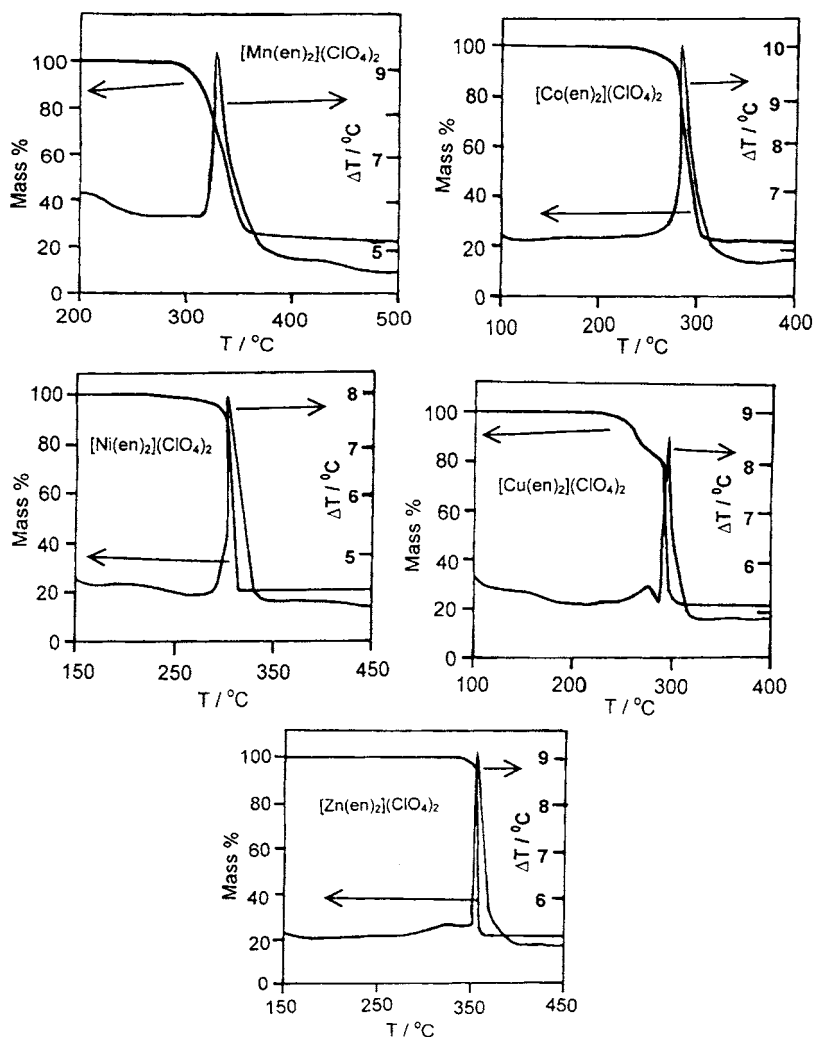


Fig. 1. TG-DTA thermograms of BEMP complexes under nitrogen atmosphere.

Table 1  
Physical, elemental and spectral parameters of BEMP complexes

Complex	Colour	TLC <sup>a</sup>		Observed, % (calculated)				IR <sup>b</sup>					
		Eluent	R <sub>f</sub>	C	H	N	Metal	ν <sub>en</sub>	ν <sub>M–N</sub>	ν <sub>H<sub>2</sub>N–CH<sub>2</sub></sub>	ν(Cl=O)	ν(Cl–O <sup>–</sup> )	ClO <sub>4</sub> <sup>–</sup>
[Mn(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	Brown	2a:b:c	0.80	12.2 (12.8)	3.9 (4.3)	14.1 (15.0)	13.8 (14.7)	1055 (m)	442 (s)	1045 (m)	540 (s)	1105 (w)	619 (s)
[Co(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	Light pink	2a:b:c	0.74	11.8 (12.7)	3.5 (4.2)	13.7 (14.8)	13.9 (15.6)	1085 (m)	439 (s)	1054 (m)	620 (s)	1065 (w)	618 (s)
[Ni(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	Violet	2a:b:c	0.69	11.7 (12.7)	3.7 (4.2)	13.9 (14.8)	14.4 (15.5)	1110 (m)	437 (s)	1107 (m)	590 (s)	1072 (w)	620 (s)
[Cu(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	Dark blue	2a:b:c	0.76	11.8 (12.5)	3.4 (4.1)	13.6 (14.6)	15.5 (16.6)	1072 (m)	435 (s)	1085 (m)	587 (s)	1120 (w)	623 (s)
[Zn(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	White	2a:b:c	0.74	11.6 (12.5)	3.3 (4.2)	13.7 (14.5)	15.6 (16.9)	1107 (m)	443 (s)	1089 (m)	630 (s)	1098 (w)	620 (s)

<sup>a</sup> a: *n*-butanol; b: chloroform; c: glacial acetic acid; R<sub>f</sub>: retention factor; locating reagent: iodine.

<sup>b</sup> m: medium; s: sharp; w: wide.

Table 2  
TG-DTA phenomenological data on BEMP complexes under inert atmosphere

Complex	TG <sup>a</sup>				DTA (exothermic peak temperature) (°C)
	T <sub>i</sub> (°C)	T <sub>s</sub> (°C)	T <sub>f</sub> (°C)	% Decomposition	
[Mn(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	280	330	355	80.0	325
[Co(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	235	295	307	79.5	290
[Ni(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	260	298	310	80.0	295
[Cu(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	230	260	292	20.0	270
	292	298	305	78.0	295
[Zn(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	330	350	360	79.5	352

<sup>a</sup> T<sub>i</sub>: onset temperature, T<sub>s</sub>: inflection temperature, T<sub>f</sub>: endset temperature.

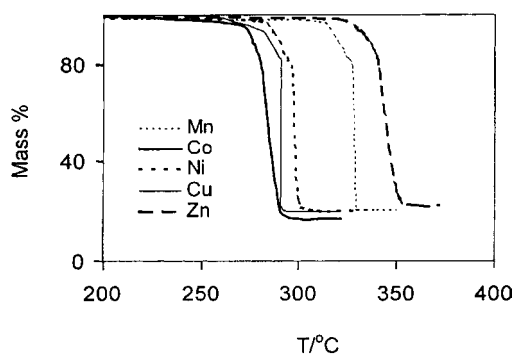


Fig. 2. Non-isothermal TG thermograms of complexes recorded in air atmosphere.

been carried out in static and flowing air atmosphere, respectively. Non-isothermal TG thermograms are demonstrated in Fig. 2 and data corresponding to this are collected in Table 3. Evidently, all of these complexes, including that of copper, undergo thermolysis via a single and fast step of decomposition. Single step fast decomposition of these complexes can also be seen in DTA thermograms shown in Fig. 3 and data summarized in Table 3, which are found to be exothermic in nature.

### 3.4. Isothermal TG

Isothermal TG thermograms were obtained over a short range of temperature, because thermal decomposition is slow at lower temperatures and quite fast at higher temperatures. Therefore, an optimum range was selected and for this study,

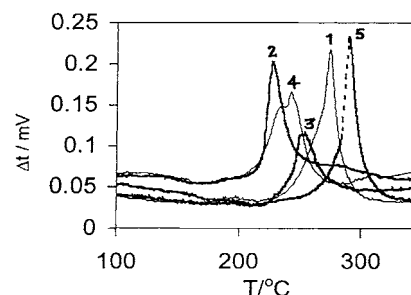


Fig. 3. DTA thermograms obtained in air atmosphere: 1, [Mn(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>; 2, [Co(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>; 3, [Ni(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>; 4, [Cu(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>; and 5, [Zn(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>.

the desired temperature was maintained within  $\pm 1^\circ\text{C}$  and mass loss readings were taken after suspending the sample into the furnace. The isothermal TG thermograms are shown in Fig. 4, which indicate an induction period followed by acceleration period as the common feature of decomposition of all these complexes.

### 3.5. Mathematical treatment of isothermal TG data

Following two methods were employed to evaluate kinetic parameters.

#### 3.5.1. Model fitting method

The following general equation is used to describe kinetics of thermally induced reactions in the solid state:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

Table 3  
TG and DTA data profile on complexes under air atmosphere<sup>a</sup>

Complex	TG			DTA (exothermic peak temperature) (°C)
	SDT (°C)	FDT (°C)	% Decomposition	
[Mn(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	312	330	79.0	275
[Co(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	270	295	83.0	228
[Ni(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	285	312	79.5	253
[Cu(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	284	298	78.0	243
[Zn(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	320	360	77.5	291

<sup>a</sup> SDT: starting decomposition temperature, FDT: final decomposition temperature.

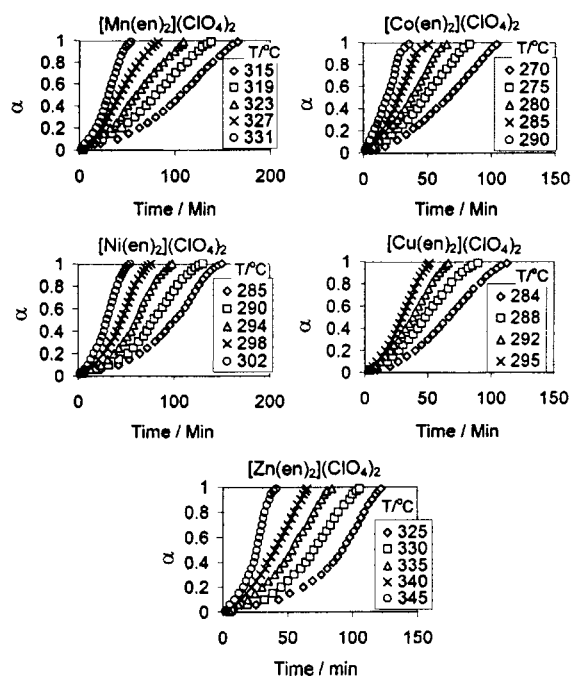


Fig. 4. Isothermal TG thermograms of BEMP complexes in air.

where  $\alpha$  is the degree of conversion,  $t$  the time,  $T$  the absolute temperature,  $k(T)$  the temperature dependent rate constant and  $f(\alpha)$  a function called the reaction model. The values of  $\alpha$  were calculated from the isothermal TG data. A list of various commonly used reaction models is given in Table 4. It is assumed that the rate constant depending on the temperature obeys Arrhenius expression:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where  $A$  is the pre-exponential (Arrhenius) factor,  $E$  the activation energy and  $R$  the gas constant. The integral form of Eq. (1) is generally applied for kinetic analysis, which changes to following expression for isothermally simulated reactions:

Table 5  
Arrhenius parameters for isothermal decomposition of  $[\text{Mn}(\text{en})_2](\text{ClO}_4)_2$  obtained from model fitting method

Model <sup>a</sup>	$E$ (kJ mol <sup>-1</sup> )	$\ln(A)$ (min <sup>-1</sup> )	$r$
1	214.2	41.2	0.9910
2	216.9	42.8	0.9908
3	217.5	39.1	0.9810
4	212.0	38.2	0.9920
5	214.2	38.6	0.9892
6	218.9	40.7	0.9854
7	221.1	39.5	0.9936
8	220.5	40.4	0.9872
9	211.1	42.5	0.9918
10	215.0	38.4	0.9834
11	221.9	39.3	0.9876
12	213.3	38.3	0.9823
13	217.1	41.3	0.9879
14	219.9	39.6	0.9865

<sup>a</sup> Enumeration of the model is as given in Table 4.

$$g(\alpha) \equiv \int_0^\alpha [f(\alpha)]^{-1} d\alpha = k(T)t \quad (3)$$

where term  $g(\alpha)$  represents the integrated form of the reaction model (Table 4). Thus, having substituted a particular reaction model in Eq. (3) one can estimate corresponding rate constant from the slope of  $g(\alpha)$  vs.  $t$  plots. For every reaction model selected, the rate constants are determined at several temperatures and Arrhenius equation in its logarithmic form (Eq. (4)) is used to evaluate Arrhenius parameters:

$$\ln k(T) = \ln A - \frac{E}{RT} \quad (4)$$

Arrhenius parameters evaluated for the isothermal TG data of Mn, Co, Ni, Cu and Zn complexes along with correlation coefficient ( $r$ ) are collected in Tables 5–9, respectively.

### 3.5.2. Isoconversional method

In this method, it is assumed that the reaction model in Eq. (1) is independent of temperature. Under isothermal

Table 4  
Various mechanism based kinetic models generally used to describe thermal decomposition of solids

Model	$f(\alpha)$	$g(\alpha)$
(1) Power law	$4\alpha^{3/4}$	$\alpha^{1/4}$
(2) Power law	$3\alpha^{2/3}$	$\alpha^{1/3}$
(3) Power law	$2\alpha^{1/2}$	$\alpha^{1/2}$
(4) Power law	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
(5) One-dimensional diffusion	$1/2\alpha^{-1}$	$\alpha^2$
(6) Mampel (first order)	$1 - \alpha$	$-\ln(1 - \alpha)$
(7) Avrami–Erofeev	$4(1 - \alpha)[-\ln(1 - \alpha)]^{3/4}$	$[-\ln(1 - \alpha)]^{1/4}$
(8) Avrami–Erofeev	$3(1 - \alpha)[-\ln(1 - \alpha)]^{2/3}$	$[-\ln(1 - \alpha)]^{1/3}$
(9) Avrami–Erofeev	$2(1 - \alpha)[-\ln(1 - \alpha)]^{1/2}$	$[-\ln(1 - \alpha)]^{1/2}$
(10) Contracting sphere	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
(11) Three-dimensional diffusion	$2(1 - \alpha)^{2/3}(1 - (1 - \alpha)^{1/3})^{-1}$	$[1 - (1 - \alpha)^{1/3}]^2$
(12) Contracting cylinder	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
(13) Prout–Tomkins	$\alpha(1 - \alpha)$	$\ln(\alpha/1 - \alpha)$
(14) Ginstling–Bronshtein	$3/2[(1 - \alpha)^{-1/3} - 1]^{-1}$	$[1 - (2\alpha/3)] - (1 - \alpha)^{2/3}$

Table 6  
Arrhenius parameters for isothermal decomposition of [Co(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> obtained from model fitting method

Model <sup>a</sup>	<i>E</i> (kJ mol <sup>-1</sup> )	ln( <i>A</i> ) (min <sup>-1</sup> )	<i>r</i>
1	139.4	26.6	0.9988
2	130.1	24.0	0.9980
3	133.4	24.9	0.9981
4	134.6	25.2	0.9982
5	140.0	27.6	0.9987
6	133.4	24.8	0.9992
7	134.1	25.2	0.9983
8	129.4	24.6	0.9991
9	136.4	25.2	0.9994
10	141.5	26.9	0.9979
11	134.9	25.1	0.9983
12	132.2	24.8	0.9982
13	134.6	25.0	0.9993
14	138.3	24.7	0.9986

<sup>a</sup> Enumeration of the model is as given in Table 4.

conditions, we may combine Eqs. (3) and (4) to obtain:

$$-\ln t_{\alpha,i} = \ln \left[ \frac{A}{g(\alpha)} \right] - \frac{E_{\alpha}}{RT_i} \quad (5)$$

where  $E_{\alpha}$  (activation energy at a particular  $\alpha$ ) is determined from the slope of  $-\ln t_{\alpha,i}$  vs.  $T_i^{-1}$  plot. Thus, the values of  $E_{\alpha}$  for all the complexes were evaluated at various  $\alpha_i$ . The dependencies of  $E_{\alpha}$  on extent of conversion ( $\alpha$ ) are shown in Fig. 5.

### 3.6. Explosion delay measurements

Explosion delays ( $D_E$ ) at various high temperatures were measured on the complexes (mass  $\approx$  20 mg) and the values are summarized in Table 10. The  $D_E$  data were fitted in the following equation [42–44]:

$$D_E = A \exp \left( \frac{E^*}{RT} \right) \quad (6)$$

Table 7  
Arrhenius parameters for isothermal decomposition of [Ni(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> obtained from model fitting method

Model <sup>a</sup>	<i>E</i> (kJ mol <sup>-1</sup> )	ln( <i>A</i> ) (min <sup>-1</sup> )	<i>r</i>
1	166.0	30.8	0.9977
2	170.6	31.2	0.9970
3	164.3	30.4	0.9968
4	166.5	30.9	0.9966
5	169.3	31.9	0.9978
6	165.6	29.5	0.9973
7	164.8	29.2	0.9976
8	171.3	32.4	0.9970
9	166.4	30.4	0.9898
10	172.2	31.2	0.9899
11	165.0	30.3	0.9963
12	176.5	36.5	0.9900
13	166.0	30.5	0.9897
14	170.0	30.2	0.9989

<sup>a</sup> Enumeration of the model is as given in Table 4.

Table 8  
Arrhenius parameters for isothermal decomposition of [Cu(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> obtained from model fitting method

Model <sup>a</sup>	<i>E</i> (kJ mol <sup>-1</sup> )	ln( <i>A</i> ) (min <sup>-1</sup> )	<i>r</i>
1	150.0	27.3	0.9974
2	145.3	26.5	0.9976
3	152.6	28.3	0.9974
4	155.2	28.9	0.9976
5	148.0	28.4	0.9982
6	158.7	29.5	0.9968
7	157.3	29.4	0.9964
8	145.9	26.1	0.9973
9	151.8	27.7	0.9979
10	157.1	28.3	0.9983
11	150.9	27.7	0.9977
12	157.9	32.2	0.9987
13	149.5	29.4	0.9974
14	151.9	26.7	0.9985

<sup>a</sup> Enumeration of the model is as given in Table 4.

Table 9  
Arrhenius parameters for isothermal decomposition of [Zn(en)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> obtained from model fitting method

Model <sup>a</sup>	<i>E</i> (kJ mol <sup>-1</sup> )	ln( <i>A</i> ) (min <sup>-1</sup> )	<i>r</i>
1	227.0	40.2	0.9898
2	217.4	38.6	0.9924
3	223.9	39.9	0.9992
4	228.0	40.8	0.9899
5	211.4	38.7	0.9972
6	229.1	41.0	0.9984
7	217.2	38.8	0.9966
8	215.8	38.9	0.9990
9	226.1	40.0	0.9947
10	224.9	39.3	0.9951
11	231.4	41.2	0.9996
12	215.3	41.5	0.9982
13	231.7	43.5	0.9969
14	217.1	37.2	0.9971

<sup>a</sup> Enumeration of the model is as given in Table 4.

where  $E^*$  is the activation energy for thermal explosion. Eq. (6), in its logarithmic form, is used to determine  $E^*$  from the slope of a plot of  $\ln(D_E)$  vs.  $T^{-1}$ . The plot of  $\ln(D_E)$  vs.  $T^{-1}$  for these BEMP complexes are

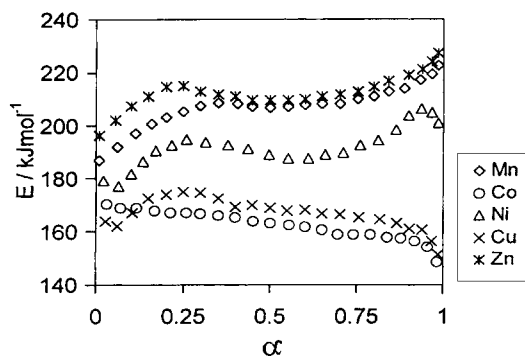


Fig. 5. Dependencies of activation energy on extent of conversion for these complexes (each atomic symbol with a marker represents the graph of respective metal complex).

Table 10  
Explosion delay ( $D_E$ ), activation energy for thermal explosion ( $E^*$ ) and correlation coefficient ( $r$ ) for BEMP complexes

Complex	$D_E$ (s) at					$E^*$ (kJ mol <sup>-1</sup> )	$r$
	350 °C	400 °C	450 °C	500 °C	550 °C		
[Mn(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	110.08	90.25	42.21	17.57	16.94	29.7	0.9899
[Co(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	99.74	84.93	34.53	14.61	13.40	27.3	0.9989
[Ni(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	108.50	89.79	38.88	15.64	14.91	28.4	0.9997
[Cu(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	101.25	85.65	34.76	14.90	13.85	28.0	0.9990
[Zn(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	110.78	92.72	43.47	19.02	18.07	30.5	0.9989
[Co(en) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub> <sup>a</sup>	–	95.69	60.50	25.72	15.98	31.8	0.9976

<sup>a</sup> Sample mass ≈ 10 mg.

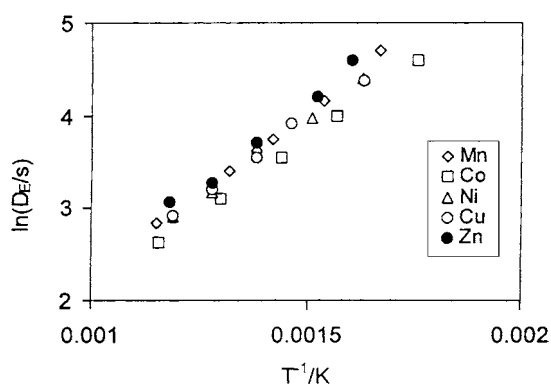


Fig. 6. Plot of  $\ln(D_E)$  vs.  $1/T$  for BEMP complexes (each atomic symbol with a marker represents the graph of respective metal complex).

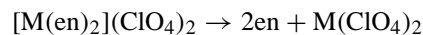
presented in Fig. 6 whilst calculated  $E^*$  are reported in Table 10.

#### 4. Discussion

The analytical data listed in Table 1 clearly indicate that estimated values of percentage mass of each element are in good agreement to those of calculated values and thus the formation of all these complexes is confirmed. Additionally, the values of characteristic absorption frequencies of different groups, present in the complexes match well with those reported in standard texts [45,46]. All these complexes are anhydrous and metal:ligand ratio is found to be 1:2. These features as well as spectral data are close to those of earlier studies [47–50] reported on similar complexes. As can be seen from TG-DTA thermograms (Fig. 1) and corresponding data (Table 2), the complexes of Mn, Co, Ni and Zn undergo decomposition in single step while that of Cu decomposes in two steps, first step corresponds to removal of one molecule of ligand i.e. en and second due to decomposition of intermediate species. Obviously, mono(ethylenediamine)copper perchlorate is formed as intermediate and separation of stages is due to relatively higher thermal stability of this monoligand intermediate in comparison to that of other complexes. The formation and stability of such monoligand intermediate compounds have also been seen earlier during thermal studies of bis(ethylenediamine)copper chloride/bromide

monohydrates [8] and bis(ethylenediamine)copper nitrates [25,28]. The fast decomposition of all these complexes, except that of the complex of Cu, is attributable to a redox reaction between bound/free en and oxidizing group (ClO<sub>4</sub><sup>-</sup>). Corresponding metal oxides were obtained as final decomposition product at the end of thermal decomposition reactions. Such observations have also been made earlier during thermal studies of amine complexes of copper(II) nitrate [9,28] and nickel(II) nitrate [28,51,52]. The thermal decomposition of all the present complexes is highly exothermic as evidenced by sharp exothermic peak in corresponding DTA.

Atmosphere (N<sub>2</sub>/air) affects decomposition modes of the complexes. The rate of decomposition of all these complexes is fast in air than that in N<sub>2</sub>. Decomposition of Cu complex takes place in single step during TG in air, which is a two-step process in N<sub>2</sub> atmosphere. This change in mode of decomposition for these complexes is due to oxidative nature of air atmosphere. DTA thermograms for all these complexes gave a single exothermic peak except that of Cu complex for which there is an exothermic hump at 236 °C. This feature of thermogram for Cu complex is indicative of partial removal of en just prior to fast decomposition. Though the mode of decomposition of these compounds is a complex process, it may be speculated that the first step in the decomposition process may be dissociation of the compounds into en and metal perchlorate, M(ClO<sub>4</sub>)<sub>2</sub>:



However, such a dissociation occurring in these perchlorates is difficult to detect by TG and DTA at atmospheric pressure. The reason for this being the unstable nature of the metal perchlorate at higher temperatures, which would decompose instantaneously by exothermic reactions. The expected endotherm corresponding to dissociation process may thus be completely overshadowed by exothermic process resulting in an overall exothermic effect. In order to ascertain the contributions from endothermic dissociation and exothermic decomposition processes, DTA thermograms were recorded under various conditions with a constant sample mass. Although, similar DTA experiments were carried out with all these metal complexes, that of Co is reported in Fig. 7 as representative. The reduction in the exothermic peak intensity can be seen in the case of DTA taken under



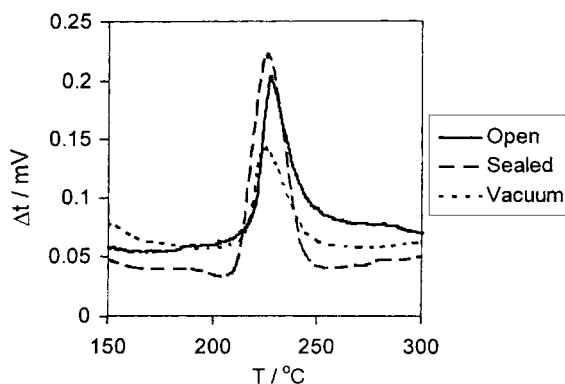


Fig. 7. DTA thermograms of Co complex in various conditions.

vacuum than that of air, which may be due to predominance of dissociation over the exothermic decomposition. Thus, it seems that removal of en molecules precedes the exothermic decomposition reactions of these complexes. Fig. 7 exhibits an increase of exothermic peak intensity recorded in sealed cups than that in open, which may be due to decomposition of the complexes at early stages and an increasing contribution from decomposition of gaseous products in later stage. Similar is the case with other complexes of this series also. The thermal stability of these complexes, as indicated by TG (both in air as well as in inert atmosphere), decreases in the order:  $[\text{Zn}(\text{en})_2](\text{ClO}_4)_2 > [\text{Mn}(\text{en})_2](\text{ClO}_4)_2 > [\text{Ni}(\text{en})_2](\text{ClO}_4)_2 > [\text{Cu}(\text{en})_2](\text{ClO}_4)_2 > [\text{Co}(\text{en})_2](\text{ClO}_4)_2$ . It was found that exothermic peak temperatures in DTA decrease in the same order.

Though, the decomposition of all these samples is complex, the analysis of kinetics from isothermal TG using model fitting method leads to uncertainty. In this method, the kinetics of thermal decomposition reactions is analysed choosing a 'best fit' model, based on the value of ' $r$ '. Various mechanism based kinetic model (Table 4) are fitted in isothermal TG data and the model that gives the value of ' $r$ ', close to 1, is selected as 'the best fit'. As it is shown in Tables 5–9, there are many models, which have equal or nearly equal values of ' $r$ '. Obviously, it is, therefore, not reasonably correct to choose a model as 'the best fit' on the basis of ' $r$ '. Moreover, values of  $E$  obtained from different models for particular sample are nearly equal irrespective of the equations used. An average value of 216.7, 135.2, 168.1, 152.3 and 222.6  $\text{kJ mol}^{-1}$  have been obtained as activation energy for isothermal decomposition of Mn, Co, Ni, Cu and Zn complexes (Tables 5–9). It is difficult to assign this value of activation energy to a particular step in the decomposition process in such a complex reaction. A plot (Fig. 8) of all the values of  $E$  against respective  $\ln(A)$  from Tables 5–9 indicate that all these values fall in a almost straight line, showing the existence of kinetic compensation effect.

Realistic kinetic parameters can only be extracted in a way that is independent of the reaction model. Isoconversional method is known to permit estimation of apparent activation energy independent of the model. In this method, activation

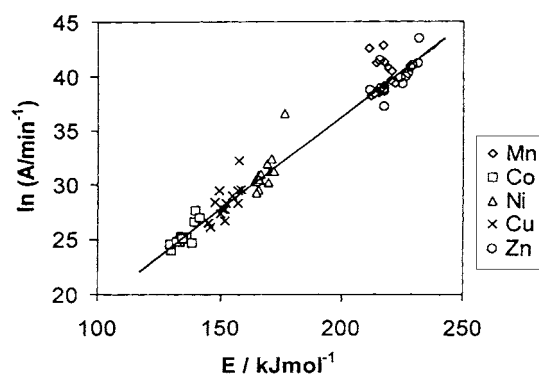


Fig. 8. The linear dependence of  $\ln(A)$  with  $E$  for all the complexes (each atomic symbol with a marker represents the graph of respective metal complex).

energy corresponding to extent of conversion of the sample is evaluated. In our case, we have adopted the isoconversional method reported by Vyazovkin [53]. This approach indicates that the decomposition of these complexes is not simple as indicated by model fitting method. As can be seen from Fig. 5, initially the  $E$  values for thermal decomposition of Mn, Ni, and Zn complexes are lower in  $\alpha$  range 0.009–0.28, which increase to 223, 206 and 227  $\text{kJ mol}^{-1}$  for Mn, Ni and Zn complexes, respectively. The initial low value of  $E$  may be attributed to the removal of en at early stage of decomposition reactions which are partially governed by dissociation process while finally higher values of  $E$  may correspond to decomposition of anionic part ( $\text{ClO}_4^-$ ) to respective metal oxides. In the case of Co complex, fairly constant value of  $E$  (163  $\text{kJ mol}^{-1}$ ) in  $\alpha$  range 0.07–0.91 was obtained which may be due to highly explosive reactions and overlapping of different processes during decomposition of the complex. The  $E$  for decomposition of Cu complex has higher value at early stage ( $\alpha = 0.15$ –0.35), which decreases gradually to 151  $\text{kJ mol}^{-1}$  ( $\alpha = 0.4$ –0.98) at later stage of decomposition. This feature may be due to formation and stability of mono(ethylenediamine)copper perchlorate initially and further its explosive decomposition causing the decrease of  $E$  at later stage.

Since, the mechanism of any reaction depends largely on different factors e.g. temperature, endothermic or exothermic nature of process, crystal structure, packing, catalysis or other effect [54], it is difficult to draw reasonable conclusion about a unique mechanism to be applicable to all the decomposition reactions.

To examine the response of complexes in a condition of rapid heating,  $D_E$  was measured. The  $D_E$  data reported in Table 10 indicate that the time required for thermal explosion at a particular temperature decreases in the order:  $[\text{Zn}(\text{en})_2](\text{ClO}_4)_2 > [\text{Mn}(\text{en})_2](\text{ClO}_4)_2 > [\text{Ni}(\text{en})_2](\text{ClO}_4)_2 > [\text{Cu}(\text{en})_2](\text{ClO}_4)_2 > [\text{Co}(\text{en})_2](\text{ClO}_4)_2$ . It is interesting to note that the  $D_E$  data also show a trend similar to the thermal decomposition results and thus showing the relative thermal stability of the complexes in the same order under the condition of rapid heating. It may

further be noted that there appears to be a direct correlation between thermal decomposition and explosion. The values of activation energy for decomposition (Tables 5–9) and that of explosion (Table 10) are in agreement with this order. The values of the decomposition temperature,  $E$ , time for explosion at a particular temperature and  $E^*$  are lowest for Co complex and highest for that of Zn, out of all the studied complexes. The contributing factors for this trend may be due to the ionic size of central atom, their electron affinity, oxidation number etc. but in absence of any firm data, these explanation remain conjectural. A decrease of sample mass (from 20 to 10 mg) causes an increase of time required for thermal explosion at a particular temperature (Table 10). The variation of explosion time with the amount of the sample taken seems to indicate self-heating. All the studied complexes show similar variation of explosion time with the amount of the sample taken.

## 5. Conclusions

The thermal studies carried out using TG-DTA (in  $N_2$ ) and non-isothermal TG and DTA in air; indicate that all these BEMP complexes undergo decomposition reactions in a single and rapid step that is highly exothermic. However, Cu complex decomposes in two steps in nitrogen and in a single step in air atmosphere. The rate of decomposition of these complexes is relatively high in air in comparison to that in nitrogen. Kinetic analysis of isothermal TG data by model fitting method is not reasonably correct, since this method fails to explain the complex processes involved in decomposition of the complexes. A single value of  $E$  was obtained corresponding to decomposition reactions, which cannot be assigned for a particular process. Isoconversional method, on the other hand, describes well the complexity of single step decomposition that yields a series of  $E$  values as a function of extent of conversion. The decomposition temperature,  $E$ ,  $D_E$  and  $E^*$  have been found to be maximum for Zn complex and minimum for Co complex.

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