

PREPARATION, CHARACTERIZATION AND THERMOLYSIS OF METAL NITRATE COMPLEXES WITH 4,4'-BIPYRIDINE

Part 46.

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Two bis(bipyridine) polymeric metal nitrate complexes with 4,4'-bipyridine of simple formula like $[M(\text{bipy})_2](\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (where $M=\text{Co}, \text{Ni}$ and Cu ; $x=4, 2$ and 0 , respectively) have been prepared and characterized. Their thermal decomposition has been undertaken using simultaneous TG-DTG-DTA and DSC in nitrogen atmosphere and non-isothermal TG in air atmosphere. Isothermal TG has been performed at decomposition temperature range of the complexes to evaluate the kinetics of decomposition by applying model-fitting as well as isoconversional method. Possible mechanistic pathways have also been proposed for the thermolysis. Ignition delay measurements have been carried out to investigate the response of these complexes under the condition of rapid heating.

Keywords: *isoconversional method, mechanistic pathway, thermal decomposition*

Introduction

Nitrates are powerful oxidizing agents [1, 2] and decompose exothermically at elevated temperatures. Of the various classes of high energetic compounds (HECs), transition metal complexes find applications in explosives, propellant formulations and pyrotechnique compositions. Moreover, transition metal complexes are known to use as potential burning rate modifier for HTPB-AP propellants [3]. These transition metal complexes are also used as precursors to obtain nano size metal oxides, which can have interesting electrical, magnetic and catalytic properties [4]. Thermal analysis provides realistic information about the thermal stability of compounds. Recently we have undertaken studies on the thermolysis and kinetics of some hexamine metal perchlorates [5, 6], bis(ethylenediamine)metal nitrates [7], bis(diethylenetriamine)metal nitrates [8] and bis(propylenediamine)metal nitrates [9]. In continuation of these studies, here we report the preparation, characterization and thermolysis of the polymeric transition metal nitrate complexes containing 4,4'-bipyridine. For the study of slow decomposition, TG, DTA and DSC have been used. Kinetics of thermolysis has also been evaluated.

Experimental

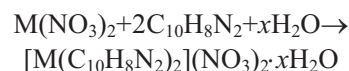
Materials

The following chemicals were used as received; copper carbonate (BDH), nickel and zinc carbonate

(Thomas Baker), 70% nitric acid and methanol (Ranbaxy), ethanol (Hayman), 4,4'-bipyridine (Merck) and silica gel TLC grade (qualigens).

Preparation and characterization of 4,4'-bipyridine metal nitrate complexes

Metal nitrates were prepared according to literature methods [9]. 4,4'-Bipyridine metal nitrate complexes were prepared by reacting an ethanolic solution of corresponding metal nitrates with 4,4'-bipyridine in appropriate stoichiometry.



where $M=\text{Co}, \text{Ni}$ and Cu ; $x=4, 2$ and 0 , respectively.

Precipitated complexes given in Table 1 were washed with methanol, recrystallised from aqueous solution, dried over fused silica and their purity was checked by thin layer chromatography (TLC). The complexes were characterized by standard gravimetric methods [10], infrared (impact 400) [11, 12] mass spectra (JEOL SX 102/DA-6000 mass spectrometer) and elemental analysis (Table 1) (Heraeus Carlo Erba 1108 Instrument). Mass spectra of the complexes are presented in Fig. 1.

Crystallographic study

Crystals of the cobalt complex was obtained by the recrystallization from aqueous solution. The data collection of the crystal was performed at low temperature (198 K) using a Nonius Kappa CCD diffractometer,

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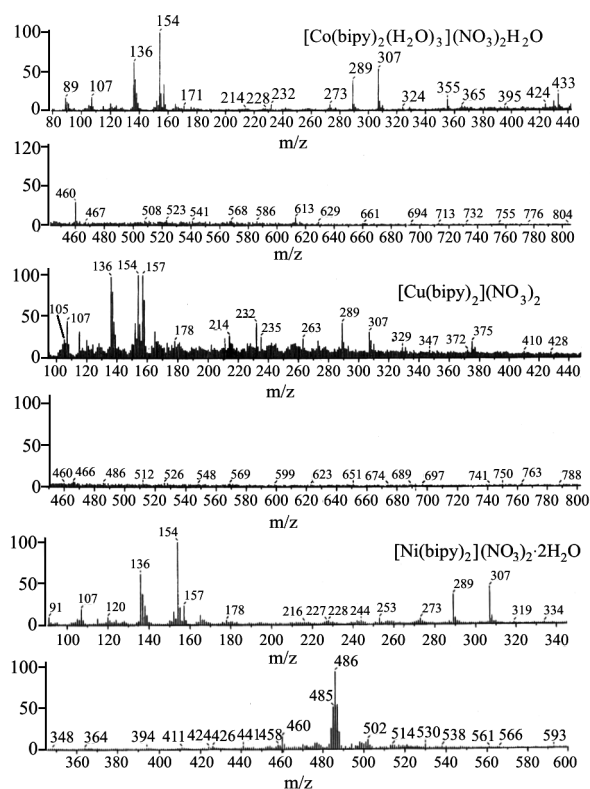


Fig. 1 Mass spectra of the complexes

equipped with a rotating anode generator Nonius FR 591. Programmes used: data collection Collect (Nonius B.V., 1998), data reduction Denzo-SMN [13]. The structure was solved by direct methods (Program SHELXS-97) [14] and refined by full-matrix least squares method on all F^2 data using SHELXL-97 [15]. Hydrogen atoms were in part placed on calculated positions and refined riding, at the water molecules they were located from a difference Fourier map and refined independent. Refinement with anisotropic thermal parameters for non-hydrogen atoms and isotropic parameters for hydrogen atoms led to the R-value of 0.054. The crystal structure (graphics done with Schakal [12]) of the complex is shown in Fig. 2, details of the analysis and crystal parameters in Table 2.

Non-isothermal TG

TG studies on these complexes (mass 30 mg, 100–200 mesh) were undertaken in static air at a heating rate of 5°C min^{-1} using indigenously fabricated TG apparatus [16]. Gold crucible was used as sample holder. The plots of mass% vs. temperature ($^\circ\text{C}$) are given in Fig. 3.

Simultaneous TG-DTG-DTA

Simultaneous TG-DTG-DTA curves on complexes were obtained on a Mettler Toledo Star System in inert nitrogen atmosphere (flow rate 100 mL min^{-1}) at

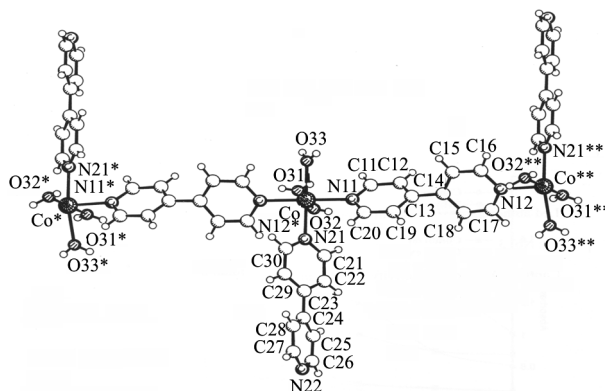


Fig. 2 Crystal structure of the cobalt complex

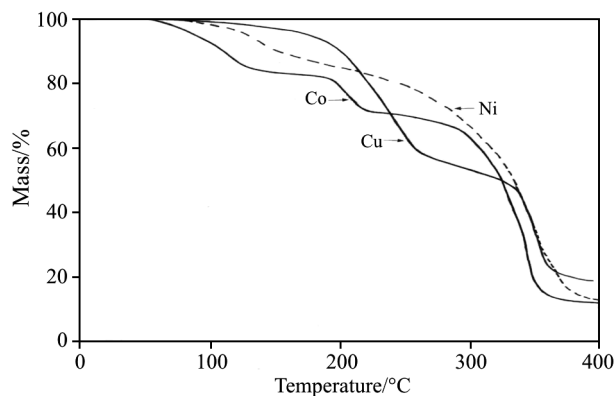


Fig. 3 Non-isothermal TG of the complexes taken in static air atmosphere

Table 1 Physical, elemental and spectral parameters of the complexes

Complex	Color	Observed (calculated)/%				IR, v/cm^{-1}						
		C	H	N	Metal	C–H Str.	C–H Def.	C=C Str.	C=N Str.	C–C Str.	NO_3^-	M–N
$[\text{Co}(\text{bipy})_2](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	pink	42.9 (42.3)	4.41 (3.7)	16.41 (14.8)	9.2 (10.4)	3066	825	1608	1536	1220	1383	485
$[\text{Ni}(\text{bipy})_2](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	sky blue	45.4 (44.7)	3.3 (3.7)	14.8 (15.6)	11.3 (10.9)	3091	871	1635	1559	1281	1383	496
$[\text{Cu}(\text{bipy})_2](\text{NO}_3)_2$	blue	46.1 (47.4)	3.9 (3.2)	16.9 (16.6)	11.2 (12.5)	2990	826	1603	1520	1141	1383	522

Table 2 Crystal data and summary of intensity and structure refinement data

Empirical formula	C ₂₀ H ₂₄ CoN ₆ O ₁₀
CDC deposit no.	245665
Colour	pink
Formula mass	567.38
Temperature/K	198
$\lambda/\text{\AA}$	0.71073
Crystal system	hexagonal
Space group	P6 ₁ (No. 169)
Crystal size/mm	0.40×0.30×0.20
Cell constants	$a=13.653(1)\text{ \AA}$, $\alpha=90^\circ$ $b=13.653(1)\text{ \AA}$, $\beta=90^\circ$ $c=22.535(1)\text{ \AA}$, $\gamma=120^\circ$
Molecules per unit cell, Z	6
Calculated density/g cm ⁻³	1.554
μ/cm^{-1}	7.75
F (000)	1758
Monochromater	graphite
θ range for data collection	1.72 to 26.30 ^o
Limiting indices	$-13 \leq h \leq 17$, $-13 \leq k \leq 14$, $-17 \leq l \leq 28$
Reflections collected/unique	14402/4292 [$R(\text{int})=0.034$]
Data/restraints/parameters	292/11/380
Goodness-of-fit on F^2	1.151
Final R indices [$I > 2\sigma(I)$]	$R1=0.054$, $wR^2=0.086$
R indices (all data)	$R1=0.072$, $wR^2=0.090$
Largest diff. peak and hole/e \AA^{-3}	0.47 and -0.33

a heating rate of 10°C min⁻¹. The curves are shown in Figs 4–6 for cobalt, nickel and copper complexes respectively. TG-DTG and DTA phenomenological data are summarized in Table 3.

DSC studies

DSC curves were undertaken in inert atmosphere (flowing nitrogen at a rate of 50 mL min⁻¹) on Mettler Toledo Star system (sample mass 4 mg, heating rate 10°C min⁻¹). DSC curves are shown in Fig. 7 and data are summarized in Table 3.

Isothermal TG

The isothermal TG on these complexes (mass 30 mg, 100–200 mesh) were carried out in static air using the above said TG apparatus [13] at appropriate temperatures. The isothermal TG curves are presented in Figs 8–10 for cobalt, nickel and copper complexes, respectively in which the extent of conversion (α) is plotted vs. time (min). Kinetic analysis from the

isothermal TG data have been done using the both model fitting method [9, 14] as well as model free isoconversional method [15]. Dependencies of activation energy (E) on the extent of conversion (α) for the complexes are shown in Fig. 11.

Ignition delay (D_i) and ignition temperature (IT) measurement

These studies were undertaken using tube furnace (TF) technique [19] as reported earlier. 20 mg samples

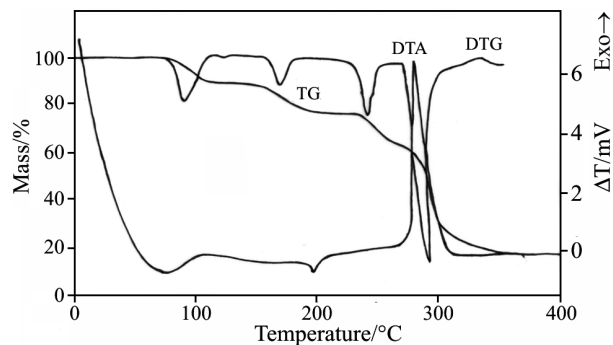


Fig. 4 Simultaneous TG-DTG-DTA curves of the cobalt complex taken in nitrogen atmosphere

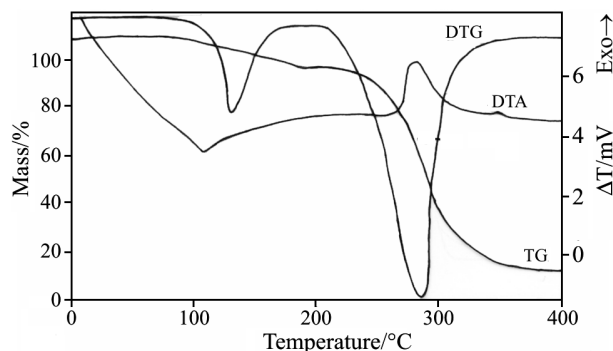


Fig. 5 Simultaneous TG-DTG-DTA curves of the nickel complex taken in nitrogen atmosphere

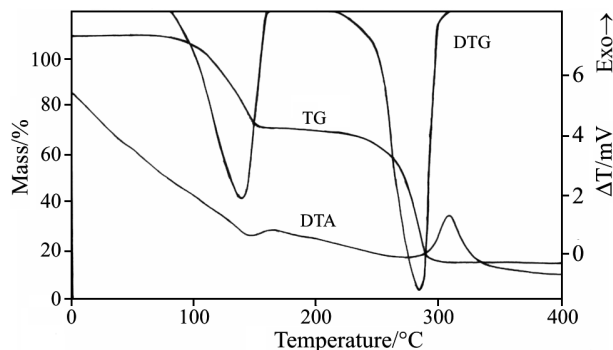


Fig. 6 Simultaneous TG-DTG-DTA curves of the copper complex taken in nitrogen atmosphere

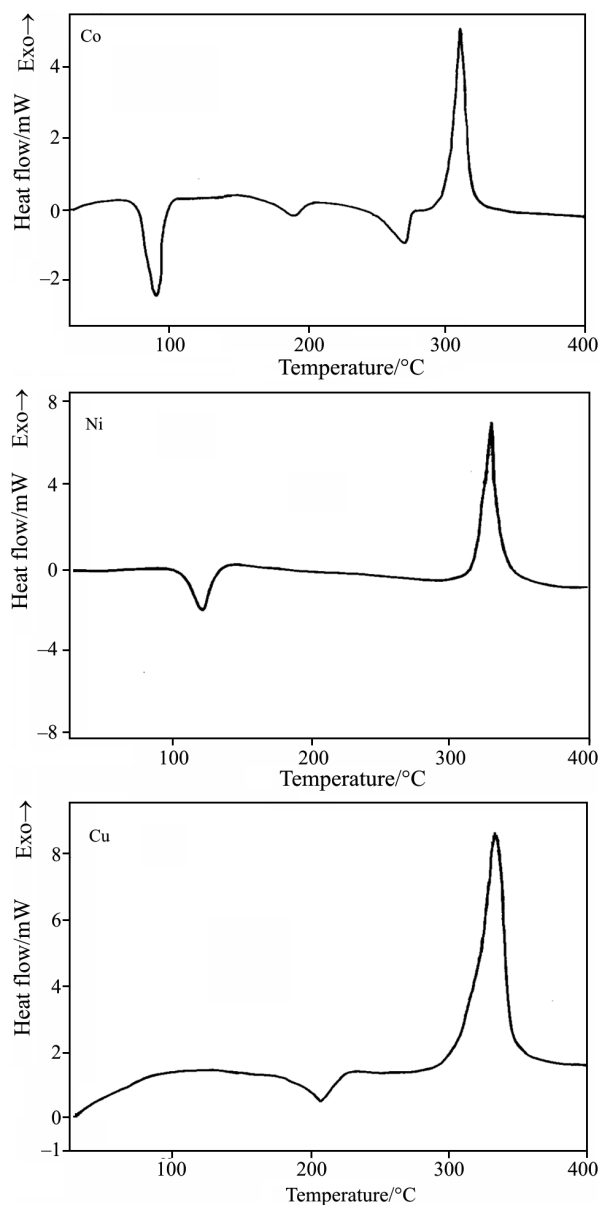


Fig. 7 DSC curves of the complexes taken in flowing nitrogen atmosphere

(100–200 mesh) were taken in an ignition tube ($l=5$ cm, $d=0.4$ cm) and time interval between the insertion of the ignition tube into the TF and the moment of ignition indicated by the removal of fumes with light and noise, noted with the help of a stop watch, gave the value of ignition delay in s. The accuracy of temperature measurement of TF was $\pm 1^\circ\text{C}$. At a selected temperature, this experiment was repeated four times and D_i values are reported in Table 3. D_i data were found to fit in following equation

$$1/D_i = Ae^{E^*/RT}$$

where E^* is the activation energy for ignition and T is the absolute temperature. Typical plots of $\log D_i$ vs. $1/T$ are given in Fig. 12.

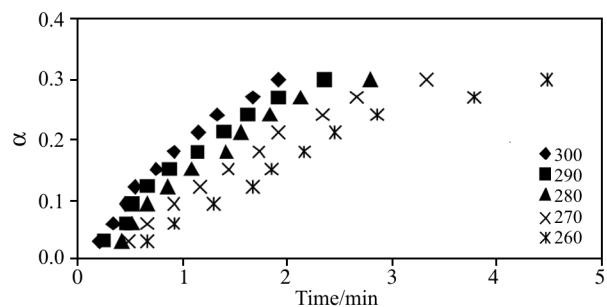


Fig. 8 Isothermal TG curves of the cobalt complex in static air atmosphere

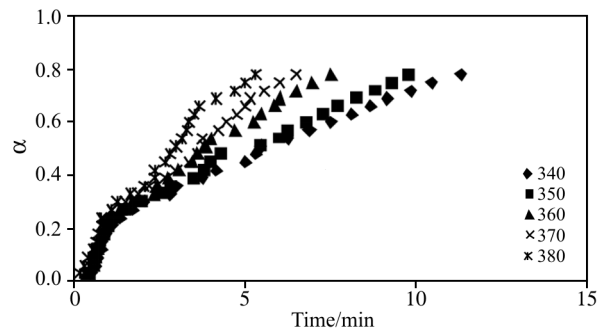


Fig. 9 Isothermal TG curves of the nickel complex in static air atmosphere

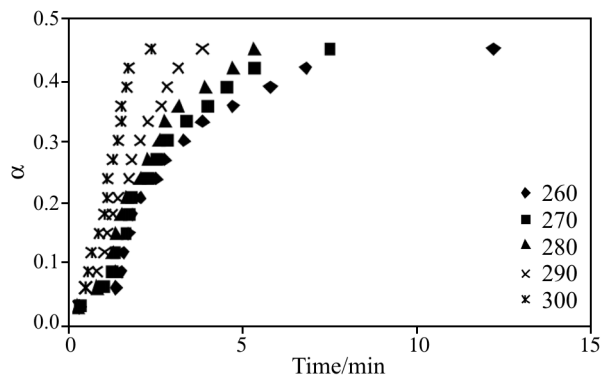


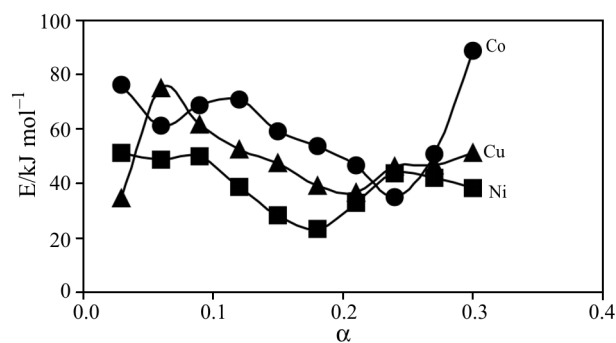
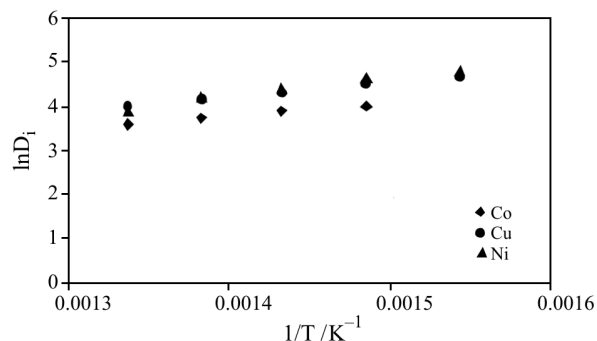
Fig. 10 Isothermal TG curves of the copper complex in static air atmosphere

Results and discussion

The analytical data presented in Table 1, indicate a good agreement between observed and calculated percentage values of each elements, which confirms the metal complex formation. Complexes were found to be polymeric, as indicated by crystal structure of cobalt complex (Fig. 1) and presence of peaks at higher m/z than monomer in the mass spectra of all the three complexes (Fig. 2). On the other hand, IR spectral data (Table 1) also signalize the proposed molecular formula of the complexes. $\nu(\text{M-N})$ and $\nu(\text{C=N})$ peak confirms the metal to ligand bond formation. It is evident that all these complexes undergo decomposition for more than

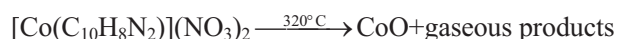
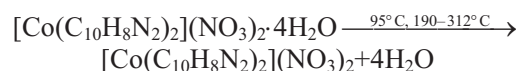
Table 3 TG-DTA phenomenological of the complexes under nitrogen atmosphere

Complex	TG			DTA		DSC	
	Step	$T_{\text{range}} / ^\circ\text{C}$	Decomposition/%	Nature	$T_{\text{range}} / ^\circ\text{C}$	Nature	$T_{\text{range}} / ^\circ\text{C}$
[Co(bipy) ₂](NO ₃) ₂ ·4H ₂ O	I	78–91	9.5	endo	95.9	endo	89.2
	II	155–187	10.07	endo	–	endo	125.6
	III	235–258	11.38	–	225	endo	266
	IV	286–310	42.2	exo	307.5	exo	306
[Ni(bipy) ₂](NO ₃) ₂ ·2H ₂ O	I	125–209	10.0	endo	124	endo	122
	II	273–316	60.3	exo	318	exo	326
[Cu(bipy) ₂](NO ₃) ₂	I	187–218	32.1	endo	213	endo	208
	II	305–324	45.4	exo	332	exo	333

**Fig. 11** Dependencies of activation energy (E) on the extent of conversion (α) for the complexes of the elements shown**Fig. 12** Plot of $\ln D_i$ vs. $1/T$ for the complexes of the elements shown

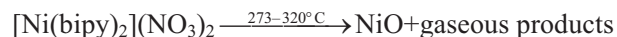
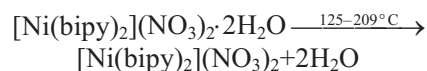
one stage, finally giving metal oxides as residue and other various gaseous decomposition products. TG curve for the cobalt complex shows that it decomposes in four steps in static air as well as in flowing nitrogen atmosphere (Figs 3 and 4). Corresponding to these four steps, four DTG peaks are obtained. In the very first step (78–98°C) four of the water molecules leave out (~13% mass loss). The middle two steps (155–258°C) are due to the removal of one bipyridine molecule (~30% mass loss). In fourth step (235–258°C), residue ignited with light and a sharp mass loss is observed (~40% mass loss) which is due to the exothermic decomposition of [Co(bipy)](NO₃)₂ residue. Finally a residue (~15%) of cobalt oxide is left. Thus the mecha-

nism of thermolysis of the cobalt complex may be proposed as follows.



In DTA and DSC curve of this complex (Fig. 4), an endothermic peak at 97°C is obtained for the removal of four water molecules. For the second step decomposition, one sharp endotherm is obtained due to the removal of half of the bipyridine molecule. For the fourth step decomposition, an exotherm is observed at 307°C which is due to the exothermic decomposition of the residue [Co(bipy)](NO₃)₂. However, there is no DTA peak for the third step mass loss, but in DSC this step appears as an endothermic process at ~196°C (Table 3).

In air as well as in nitrogen atmosphere, Ni complex decomposes in two steps (Figs 3 and 5). The first step is the loss of two water molecules (~10% mass loss) giving an endothermic peak at 124°C in DTA and DSC. The dehydrated complex decomposes between 273–320°C (~60.3% mass loss) giving nickel oxide as residue and an endotherm at 318°C (Figs 5 and 7; Table 3). Thus, the plausible mechanism for the thermolysis of nickel complex may be proposed as

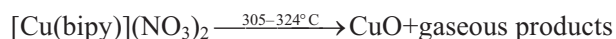
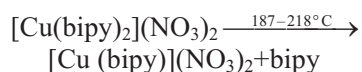


Copper complex also decomposes in two steps in both, static air as well as in flowing nitrogen atmosphere and gives two corresponding DTG peaks (Figs 3 and 6). In the first step (187–218°C), one bipyridine ligand leaves the molecule (~32% mass loss) giving an endotherm at 213°C in DTA and at 208°C in DSC curve. In second step (305–324°C) the residue [Cu(bipy)](NO₃)₂ ignited exothermically and for this mass loss (~45.4%) an exothermic peak at ~332°C was obtained in DTA and DSC curves (Figs 6 and 7; Table 2). Finally, the residue correspond to copper oxide.

Table 4 Ignition delay D_i , activation energy for thermal ignition (E^*) and correlation coefficient (r) for the complexes

Complex	D_i/s at temperature/ $^{\circ}C$					$E^*/kJ\ mol^{-1}$	r
	375 \pm 1	400 \pm 1	425 \pm 1	450 \pm 1	475 \pm 1		
[Co(bipy) ₂](NO ₃) ₂ ·4H ₂ O	74	55	48	42	35	28.6	0.9907
[Ni(bipy) ₂](NO ₃) ₂ ·2H ₂ O	123	102	80	65	49	36.8	0.9944
[Cu(bipy) ₂](NO ₃) ₂	105	88	71	62	53	27.8	0.9986

Thus, the plausible mechanistic pathways for the thermolysis of this complex may be proposed as



Monobipyridine cobalt and copper nitrate is formed as intermediates and separation of stages is due to the relatively higher thermal stability of this monoligand intermediate in comparison to that of nickel complexes. The formation and stability of such monoligand intermediate compounds have also been seen earlier during the thermal studies of bis(ethylenediamine)copper chloride/bromide monohydrates [20], bis(ethylenediamine)copper nitrate [9, 21] and bis(ethylenediamine)metal perchlorate complexes [22].

The analysis of the kinetics from isothermal TG, using model fitting methods lead to uncertainty. However, values of activation energy E , obtained from different models for particular samples are nearly equal irrespective of the equations used. An average value of E equal to 45.6, 116.3 and 59.5 kJ mol⁻¹ have been evaluated for cobalt, nickel and copper complexes, respectively. In case of nickel complex, the value of E is much higher than cobalt and copper complexes because in this case, the E is calculated for the loss of two bipyridine and two water molecules, while in case of cobalt and copper, E is calculated for the loss of one bipyridine ligand along with water molecules.

Application of isoconversional method to the isothermal TG data indicates that the decomposition of these complexes is not simple, as indicated by model fitting methods. Values of E for these complexes are found to vary with α . As we have just studied the kinetics of the removal of water molecules and one bipyridine ligand (~30% mass loss), Fig. 10 represents the dependencies of activation energies on α up to 0.30. The E for nickel complex in this α range is lower than the cobalt copper complexes. For these complexes, E decreases in α range 0.09 to 0.21 which may be due to the predominance of exothermic changes over endothermic changes. However, the variation of activation energy with extent of conversion is changing at every stage, which may be the result of many competing effects and is very difficult

to correlate particular activation energy for a particular process in thermolysis.

To examine the effect of rapid heating on the complexes, D_i data reported in Table 4 indicates that the time required for the thermal ignition at a particular temperature, increases in the order Co < Cu < Ni complex. Thus, showing the relative thermal stability of the complexes in the same order under the condition of rapid heating. Activation energy for the thermal ignition of the complex (Table 4) was found to be in the increasing order as Co < Cu < Ni complex which is also in agreement with the thermal stability order of the complexes. The values of activation energies for slow thermal decomposition (E) and rapid decomposition (E^*) are not same, but the increasing order is same in both the cases. Less stability of the cobalt complex may be attributed to the less nuclear charge and greater ionic size of Co²⁺. Moreover, due to higher nuclear charge and small size of Cu²⁺ than Ni²⁺ the stability of Cu complex should be greater as compared to Ni complex. However, the thermal stability of Ni complexes over Cu complexes is also reported in earlier studies, where [Ni(en)₂](ClO₄)₂ have greater thermal stability than [Cu(en)₂](ClO₄)₂ [22].

Conclusions

The thermal studies carried out on the two bipyridine metal complexes using TG-DTA, DSC (in flowing nitrogen) and non-isothermal TG in air, indicates that all these complexes decomposes in multisteps, last step of which are rapid and exothermic. Both, nickel and copper complex decompose in two steps, whereas cobalt complex decomposes in four steps. Application of model fitting method for the kinetic analysis from isothermal data, fails to explain the complexity of thermolysis as it gives single value of activation energy which can not be assigned to a particular process. On the other hand, isoconversional method describes well the complexity of even single step decomposition that yields a series of E values as a function of extent of conversion. The ignition delay and E^* have been found to be maximum for the nickel complex and minimum for the cobalt and copper complexes.

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