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Snythesis, characterization and thermal dissociation of cobalt(II) complexes of the photoproducts of octacyanomolybdate(IV) and -tungstate(IV) with ethylenediamine

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Abstract

Photosubstituted mixed ligand complexes of Co(II) with irradiated solutions of $Mo(CN)_8{}^{4-}$ and $W(CN)_8{}^{4-}$ with ethylenediamine have been synthesized. The complexes have been isolated and characterized by their elemental analysis and IR spectroscopy. The assigned formulae are $Co_2[Mo(CN)_2(C_2H_8N_2)_2(OH)_2]Cl_4.2H_2O$ **I** and $Co[W(CN)_2(C_2H_8N_2)_2(OH)_2]Cl_2.2H_2O$ **II** for Mo(IV) and W(IV) complexes, respectively. The IR peaks observed for both the complexes show N–H stretching, H–N–H bending and stretching vibrations of the C–N and C–C bonds. Depending on the nature of the absorption bands, complex **I** is assigned as *-trans* and complex **II** as *-cis* configuration. The thermal decomposition of these complexes has been studied by TG and DSC techniques. The reaction scheme for decomposition of each complex has been proposed. The activation energy (E_a), pre-exponential factor (A) and entropy of activation ($\Delta S^{\#}$) have been calculated by employing the integral methods like Arrhenius, Coats–Redfern and Doyle. Enthalpy (ΔH) values for each transition are obtained from DSC data. © 1998 Elsevier Science B.V.

Keywords: Photosubstituted complex; Octacyanomolybdate(IV); Octacyanotungstate(IV); Ethylenediamine complexes; Thermal dissociation

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1. Introduction

Complexes containing ethylenediamine as ligand have been widely discussed in the literature [1]. The great complexing capacity of the amine group makes ethylenediamine most versatile in the synthesis of inorganic complexes [2]. Thermal studies of tetracyanonickelates having the general formula $Ni(en)_m$-$Ni(CN)_4.nH_2O$ (m=1, 2 or 3 and n>0) whose composition is affected by the pH value of the medium result in varying numbers of ethylenediamine ligands and the amount of water present [3]. Thermogravimetric studies of numerous ethylenediamine complexes of transition metals have been reported [1]. The octacyanomolybdate(IV) and -tungstate(IV) in alkaline solutions lead primarily to the substitution of one cyanide ligand by irradiation in the ligand field band [4], which undergoes thermal substitution of a hydroxyl group with ethylenediamine [5]. The thermal behaviour of cyano compounds is complicated due to the variety of the chemical species (cyanogen, cyanate, isocyanate, carbonate etc) which is related to nitrite or cyanide and which can be formed in

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thermally induced intramolecular reactions with or without participation of the surrounding atmosphere [6].

In this paper, we report the complex formation of the photoproducts of octacyanomolybdate(IV) and -tungstate(IV) and ethylenediamine with cobalt(II) chloride, their characterization and thermal dissociation.

2. Experimental

Potassium octacyanomolybdate(IV) and -tungstate(IV) were prepared by the method of Leipoldt et al. [7]. Ethylenediamine and cobalt chloride $CoCl_2.6H_2O$ were of AR grade. All the solutions were prepared in doubly distilled water.

2.1. Synthesis of complexes

Aqueous solutions of $K_4M(CN)_8$ (M=Mo or W) and ethylenediamine were mixed in the ratio of 1:2 of 0.1 M each. The solution mixtures were subjected to ultraviolet radiation through a mercury lamp for about 15 min until the yellow colour of the solution changed to deep red. Irradiation was stopped and an aqueous solution of cobalt chloride was added dropwise until a reddish black precipitate (Mo) and a light green precipitate (W) were formed. The precipitate was washed and separated by centrifugation and dried over fused $CaCl_2$. The chemical analysis gave – found: C=11.52; H=3.18; N=13.45; (%) against calculated – C=12.00; H=3.56; N=13.80; (%) The empirical formulae for the complexes are:

$$Co_2[Mo(CN)_2(C_2H_8N_2)_2(OH)_2]Cl_4.2H_2O \quad \textbf{\textit{I}}$$

and

$$Co[W(CN)_2(C_2H_8N_2)_2(OH)_2]Cl_2.2H_2O \quad \textbf{\textit{II}}$$

for which the chemical analysis carried out gave – found: C=13.5; H=3.5; N=16.0; (%) against calculated – C=13.0; H=4.0; N=15.2;(%).

2.2. Physical measurements

Determination of carbon, hydrogen, nitrogen and metal was carried out by micro-analysis methods. IR spectra of the solid complexes were recorded on a Perkin Elmer 1710 Fourier transform spectrometer in the range of 400–4000 cm^{-1} using KBr disc technique. TG was conducted on a Du Pont 2000 thermal analyser. DSC was also carried out on a Du Pont TA 2000 system with a DSC attachment. Nitrogen flow was maintained at 60 cm^3 min^{-1}. Scanning was done at the rate of 10°C min^{-1}. An aluminium pan was used under a dynamic nitrogen atmosphere. DSC calibration was effected by indium (99.99% purity). Temperature repeatability of the instrument is ±0.1°C and of ΔH is ±0.0 2mW.

3. Results and discussion

3.1. IR studies

The photoexcitation of $M(CN)_8{}^{4-}$ (where M=Mo(IV) or W(IV)) with ethylenediamine at 366 nm produces a photoproduct in solution in which cyanide ions are substituted by ethylenediamine molecules [5]. Addition of cobalt (II) chloride to the photoproduct results in the formation of a complex which is assigned $Co_2[Mo(CN)_2(C_2H_8N_2)_2(OH)_2]Cl_4.2H_2O$ on the basis of elemental analysis. IR spectra of the complex show a very strong peak at 3400 and 1600 cm^{-1}, indicating the asymmetric and symmetric OH stretching and bending vibrations, respectively, due to water molecules. The presence of a strong band at 2200 cm^{-1} implies the presence of cyano group with the mode M–C=N, showing cyanide as a bridging ligand analogous to a polynuclear complex $[Na_2Co(CN)_5X]$, in which the band due to C=N stretching vibration of the cyanide bridge is found at 2202 cm^{-1} and that of terminal cyanide is at 2130 cm^{-1} [8]. The four principal regions of absorption observed at 1600, 1400, 800 cm^{-1} can be assigned as asymmetric deformation, symmetric deformation and NH_3 rocking mode, are supportive of the metal–amine complex. The bands observed correspond to the ethylenediamime complexes [9]. The main bands observed are between 3300 and 3077 cm^{-1}, which can be due to the NH stretching region. The band in the region of 1400 cm^{-1} is due to vibrations of the $–CH_2$ group. The band at 1040–1000 cm^{-1} may be the result of stretching vibrations of either the C–N or the C–C bond. The complex formation with W(IV) is assigned the formula $Co[W(CN)_2 (C_2H_8N_2)_2(OH)_2] Cl_2.2H_2O$

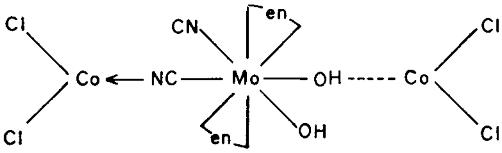
on the basis of elemental analysis. The band position is similar to those in the case of Mo(IV). The presence of the water molecules in the complex is supported by the strong peak at 3400 cm^{-1}. The absorption band at 2100 cm^{-1} shows the presence of cyanide in the terminal mode. The other principal regions of absorption are at 1620, 1400 and 840 cm^{-1}, which can be assigned as asymmetric deformation, symmetric deformation and NH_3 rocking mode. The band at 1125 cm^{-1} is due to NH_2 bending vibration. The peak at 1050 cm^{-1} is due to vibrations of the CH_2 group. All the peaks correspond to the reported peaks for the complex of cobalt–ethylenediamine in which ethylenediamine is in gauche configuration [9]. Free ethylenediamine exhibits the bands of bending vibration of the NH_2 group at 1608 and 1597 cm^{-1} [10]. The bands due to N–H vibrations are shifted to lower frequencies in the complexes, which suggest the formation of the amine complex showing the nitrogen of the amine groups coordinated to the metal atom [10].

The position of ethylenediamine can result in the formation of two structures for each complex, *cis* and *trans*. In cobalt ethylenediamine complexes, the most consistent variation between the spectra of *cis*- and *trans*-isomers have been found in the CH_2 rocking region, i.e. 870–900 cm^{-1}. The complexes with a *cis*-configuration show two bands, while those with a *trans*-structure show one. It has also been reported that the position of the bands in the compounds of the type $[Co(en)_2AB]X$ are not dependent on any one of the groups [11].

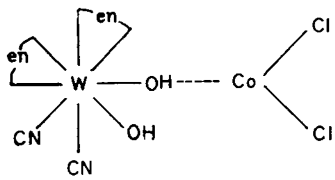
For complex **I**, the spectrum between 870–900 cm^{-1} shows only a single band, suggesting the configuration to be *trans* one, while in complex **II** this band is split, showing the configuration to be a *cis* one. Moreover, Merrit and Wiberly [12] reported the difference in the spectra of *cis* and *trans* complexes of the type $[Co(en)_2Cl_2]X$ at 1600 cm^{-1}. In the *trans*-bisethylenediamine complexes a single sharp band occurs in the range of 1605–1575 cm^{-1}, whereas in the *cis* form of trisethylenediamine complex, the band structure is more complex and occurs over a wider range 1634–1527 cm^{-1}. For the bisethylenediamine complex (**I**), a sharp absorption peak is observed at 1600 cm^{-1}, confirming the structure to be *trans*, while in **II**, the same band is observed at a comparatively wider range of 1620 cm^{-1} justifying it as a *cis*–configuration.

On the basis of the above discussion the possible structure of the complexes is:

trans- $Co_2[Mo(CN)_2(C_2H_8N_2)(OH)_2]Cl_4.2H_2O$



cis- $Co[W(CN)_2(C_2H_8N_2)_2(OH)_2]Cl_2$ $2H_2O$



3.2. TA studies

3.2.1. trans-$Co_2[Mo(CN)_2(C_2H_8N_2)(OH)_2]Cl_4.2H_2O$

The complexes were subjected to TG and DSC analysis. The thermograms obtained are shown in Figs. 1 and 2 respectively. The TG was obtained in a nitrogen atmosphere. The results are tabulated in Table 1. The thermogram of **I** indicates three different mass loss ranges. The first mass loss is from ambient temperature 76–172°C, due to the release of OH and H_2O, two moles each in the form of water. The observed mass loss is 11.60% as against the calculated value of 11.71%. In the second stage, one mole of the ethylenediamine along with one mole of cyanide split off with a mass loss of 12.74% as against the calculated value of 14.4% in the temperature range of 190–349°C with the onset temperature of 222.12°C and DTG peak at 225.80°C. The third stage occurs in the range of 356–471°C with DTG maximum at 379.10°C, which results in the removal of another mole of cyanide along with one mole of ethylenediamine. The observed mass loss is 14.54% as against calculated value of 14.4%. The residue has the observed mass 59.48% as against the calculated value of 61.12%. Thermal dissociation is represented in Scheme 1. Calculated and observed mass loss percentages are given with and without parenthesis, respectively.

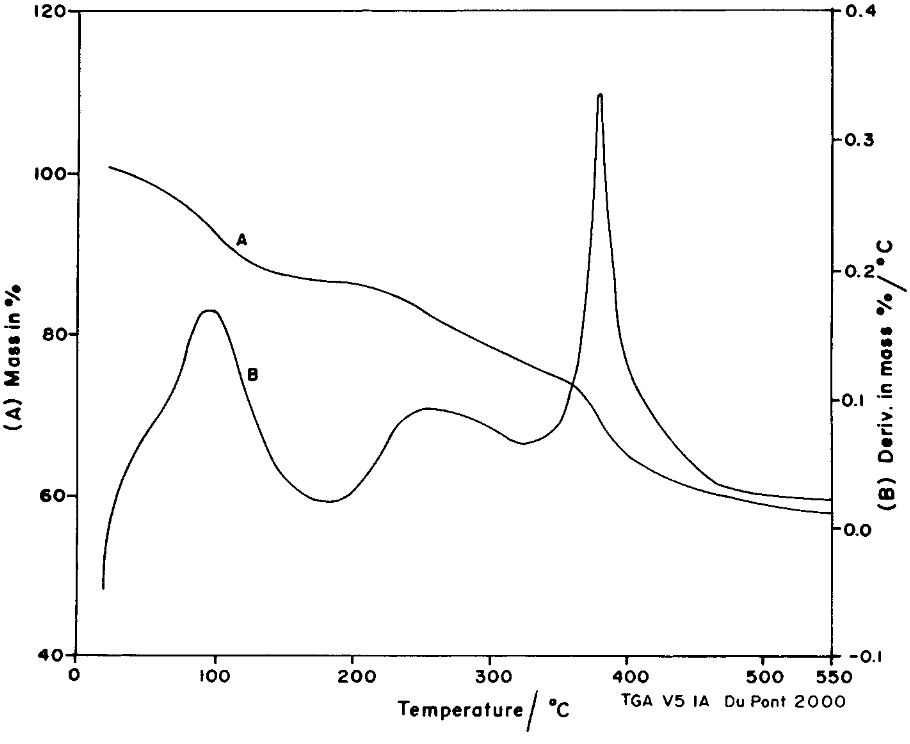


Fig. 1. The TG and DTG curves of complex I.

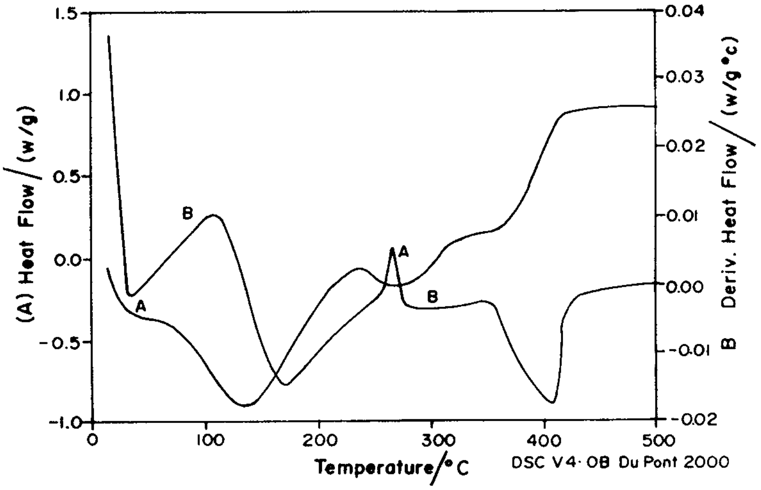


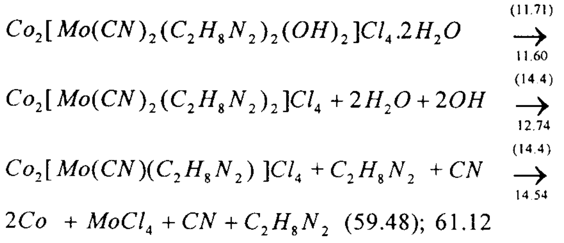
Fig. 2. The DSC curve of complex I.

3.2.2. *cis-Co[W(CN)$_2$(C$_2$H$_8$N$_2$)$_2$(OH)$_2$]Cl$_2$ 2H$_2$O*

The TG and DTG curve for the **II** Co [W(CN)$_2$-(C$_2$H$_8$N$_2$)$_2$ (OH)$_2$] Cl$_2$.2H$_2$O is shown in Fig. 3. Decomposition of the complex is completed in three steps. In the first stage of decomposition two moles of H_2O along with one mole of ethylenediamine are removed in the temperature range of 60–218°C with the DTG maximum at 93°C. The observed mass

Table 1
Thermoanalytical data for the decomposition of the complexes:$Co_2[Mo(CN)_2(C_2H_8N_2)_2(OH)_2]Cl_4.2H_2O$ **I** and Co $[W(CN)_2(C_2H_8N_2)_2(OH)_2]Cl_2.2H_2O$**II**

Temp. range °C	Max. temp. in DTG °C	Obsd. mass loss %	Calc. mass loss %	Remarks Removal of
Complex **I**				
76–172	96.14(1)	11.60	11.71	2 mol H_2O+2 mol OH
222–349	255.80(1)	12.74	14.40	1 mol$C_2H_8N_2$+1 mol CN
372–471	379(1)	14.54	14.40	1 mol CN+1 mol$C_2H_8N_2$
				Residue 2Co+$MoCl_4$; calc. (59.48) obsd. 61.12%
Complex **II**				
60–218	93(I)	17.54	17.3	2 mol H_2O+1 mol $C_2H_8N_2$
272–379	327(1)	11.89	10.89	1 mol $C_2H_8N_2$
414–518	426(1)	14.26	15.16	2 mol OH+2 mol CN
				Residue Co+WCl_2; calc. (56.62) obsd. 56.31%



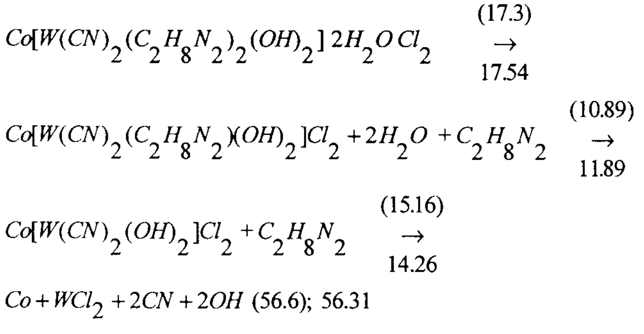
$$Co_2[Mo(CN)_2(C_2H_8N_2)_2(OH)_2]Cl_4.2H_2O \xrightarrow[11.60]{(11.71)}$$
$$Co_2[Mo(CN)_2(C_2H_8N_2)_2]Cl_4+2H_2O+2OH \xrightarrow[12.74]{(14.4)}$$
$$Co_2[Mo(CN)(C_2H_8N_2)]Cl_4+C_2H_8N_2+CN \xrightarrow[14.54]{(14.4)}$$
$$2Co+MoCl_4+CN+C_2H_8N_2\ (59.48);\ 61.12$$

Scheme 1.

loss is 17.54% as against calculated mass loss of 17.3%. The second stage occurs at 272–379°C which corresponds to the removal of another mole of ethylenediamine resulting in the observed mass loss of 11.89% as against a calculated loss of 10.89%. In the final stage two moles of hydroxyl along with two moles of cyanide are removed in the temperature range of 414–518°C with DTG maximum at 416°C. The observed mass loss is 14.26 as against a calculated loss of 15.16%. The observed mass of the residue is 56.62% as against 56.31%. Scheme 2 shows the thermal decomposition steps:

3.3. Differential scanning calorimetry

The DSC curve for **I** (Fig. 2) displays two sharp peaks, a broad exothermic peak starting at 75°C up to 217°C with an enthalpy change of 297.8 J g^{-1} due to the expulsion of OH and H_2O molecules along with cyanide and ethylenediamine moiety. The second peak is endothermic at ca. 322°C up



$$Co[W(CN)_2(C_2H_8N_2)_2(OH)_2]2H_2O\,Cl_2 \xrightarrow[17.54]{(17.3)}$$
$$Co[W(CN)_2(C_2H_8N_2)(OH)_2]Cl_2+2H_2O+C_2H_8N_2 \xrightarrow[11.89]{(10.89)}$$
$$Co[W(CN)_2(OH)_2]Cl_2+C_2H_8N_2 \xrightarrow[14.26]{(15.16)}$$
$$Co+WCl_2+2CN+2OH\ (56.6);\ 56.31$$

Scheme 2.

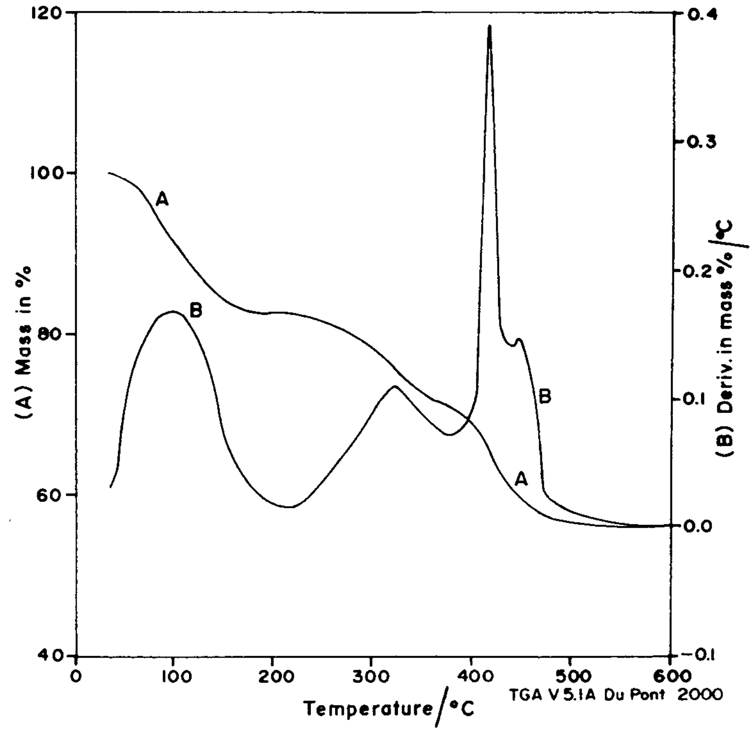


Fig. 3. The TG and DTG curve of complex **II**.

to 427°C with a maximum at 367°C with ΔH= 57.88 J g^{-1} involving the expulsion of the remaining moiety (Scheme 3).

The DSC curve of **II** is shown in Fig. 4 which shows the complex to melt at 76.88°C. The expulsion of two moles of H_2O takes place along with the overlapping of ethylenediamine. The enthalpy change for these overlapping processes is established to be 371.8 J g^{-1}. The next step involves the dissociation of another ethylenediamine molecule with enthalpy change of 178.9 J g^{-1}. The loss of the remaining ligands occurs in another endothermic stage, with a low enthalpy value implying expulsion of the cyanide and hydroxyl ligands (ΔH=31.12 J g^{-1}). The successive stages can be represented in the Scheme 4.

3.4. Kinetic parameters

Thermal decomposition of both complexes **I** and **II** takes place in three steps. The order of the reaction '*n*,'

$$Co_2[Mo(CN)_2(C_2H_8N_2)_2(OH)_2]Cl_4.2H_2O \xrightarrow{75\text{-}217^{\circ}C}$$

$$Co_2[Mo(CN)(C_2H_8N_2)]Cl_4 + CN + C_2H_8N_2 + 2H_2O + 2OH \quad \Delta H = 297.8J/g$$

$$Co_2[Mo(CN)(C_2H_8N_2)\,]Cl_4 \xrightarrow{322\text{-}427^{\circ}C}$$

$$2Co + MoCl_4 + CN + C_2H_8N_2 \; \Delta H = 57.88J/g$$

Scheme 3.

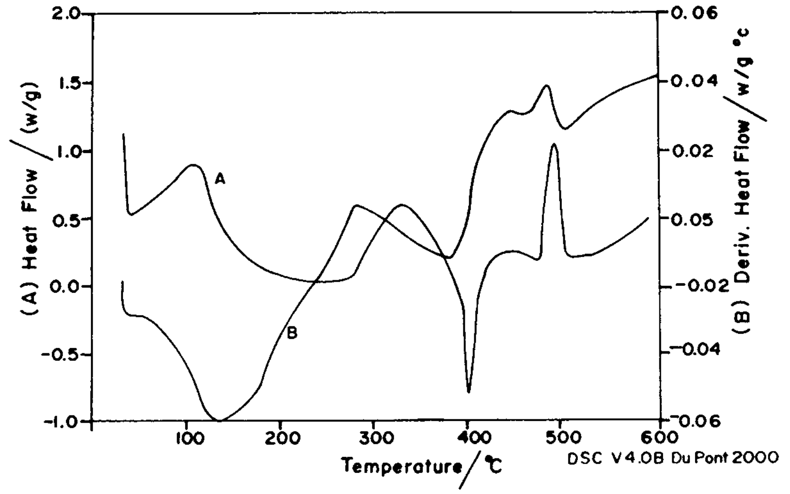


Fig. 4. The DSC curve of complex **II**.

activation energy (E_a) and entropy of activation ($\Delta S^{\#}$) were calculated using different methods:

By Doyle's method [13], the values of E_a and pre-exponential factor (A) can be calculated from the slope and intercept of the least square plots of

$$\log\frac{\sigma_T}{W}\ \text{vs.}\ \frac{1}{T}\ \text{using}\ \log\frac{\sigma_T}{W}=\frac{E_a}{4.6T}+\log\frac{A}{RH}$$

where RH: heating rate, $\sigma_T : t/RH : -\mathrm{d}w/\mathrm{d}t$. The entropy of activation, $\Delta S^{\#}$, was calculated from the equation:

$$A=\mathrm{k}\frac{T_s}{h\exp}\left(\frac{\Delta S^{\#}}{R}\right)$$

where k: Boltzmann constant, h: Planck's constant, $\Delta S^{\#}$: entropy of activation and T_s is the DTG peak temperature. The activation energies calculated for stages I, II and III in complex **I**(Fig. 5) were found to be 24.6, 11.4 and 23.5 and in complex **II**(Fig. 6) 22.9, 9.8 and 13.1 kJ mol^{-1}, respectively. The Arrhenius method [14] was used in calculating the kinetic parameters on the basis of fundamental equation:

$$\frac{-\mathrm{d}X}{\mathrm{d}t}=\mathrm{k}X^n \qquad \text{(A)}$$

where X: amount of sample undergoing the reaction, n: order of the reaction and k: specific rate constant. Entropy of activation $\Delta S^{\#}$ can be calculated from Eq. (A). By measuring k at several temperatures the graph of log k against $1/T$ gives a straight line whose slope is $-E_a/2.3\ R$ and intercept is 2.3 log A. The activation energy for **I** for three steps was found to 26.4, 13.0 and 36.9 and for **II**, 20.9, 11.6 and 26.4 kJ mol^{-1} respectively. TG data were also analysed by the Coats and Redfern [15] treatment where the plot of $\log[-\log(1-\alpha)//T^2]$ versus $1/T\times10^3$

$$Co[W(CN)_2(C_2H_8N_2)_2(OH)_2]\,2H_2O\,Cl_2 \xrightarrow{77-208^{\circ}\mathrm{C}}$$

$$Co[W(CN)_2(C_2H_8N_2)(OH)_2]\,Cl_2+C_2H_8N_2+2H_2O \quad \Delta H=371.8J/g$$

$$Co\ [W(CN)_2(\mathrm{OH})_2]Cl_2 \xrightarrow{248-371^{\circ}\mathrm{C}} Co[W(CN)_2(OH)_2]Cl_2+C_2H_8N_2 \quad \Delta H=178.9J/g$$

$$\xrightarrow{466-498^{\circ}\mathrm{C}} Co+WCl_2+2CN+2OH\,\Delta H=31.12J/g$$

Scheme 4.

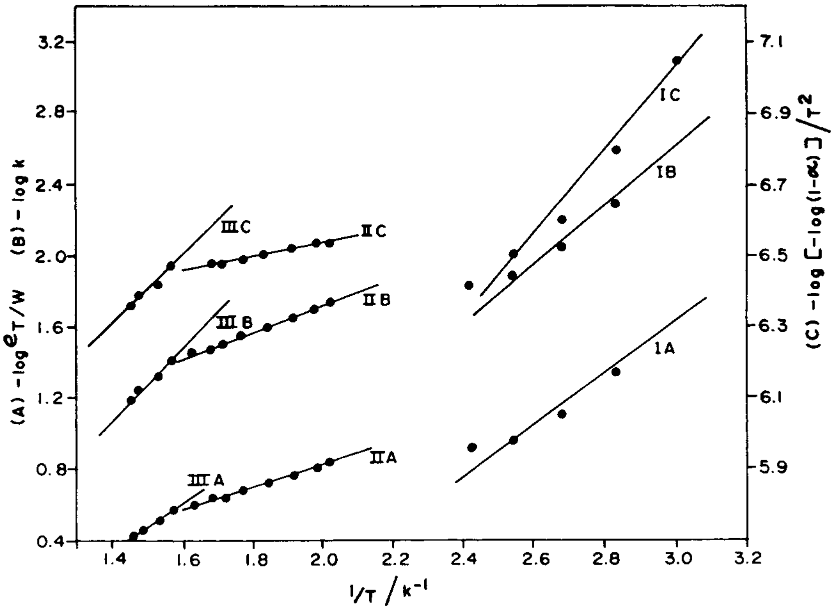


Fig. 5. Plot of (A) $-\log\sigma_T/w$; (B) $-Log[-\log(1-\alpha)]/T^2$; (C) $-\log k$ *vs.* $1/T \times 10^3 \mathrm{K}^{-1}$ of complex **I**.

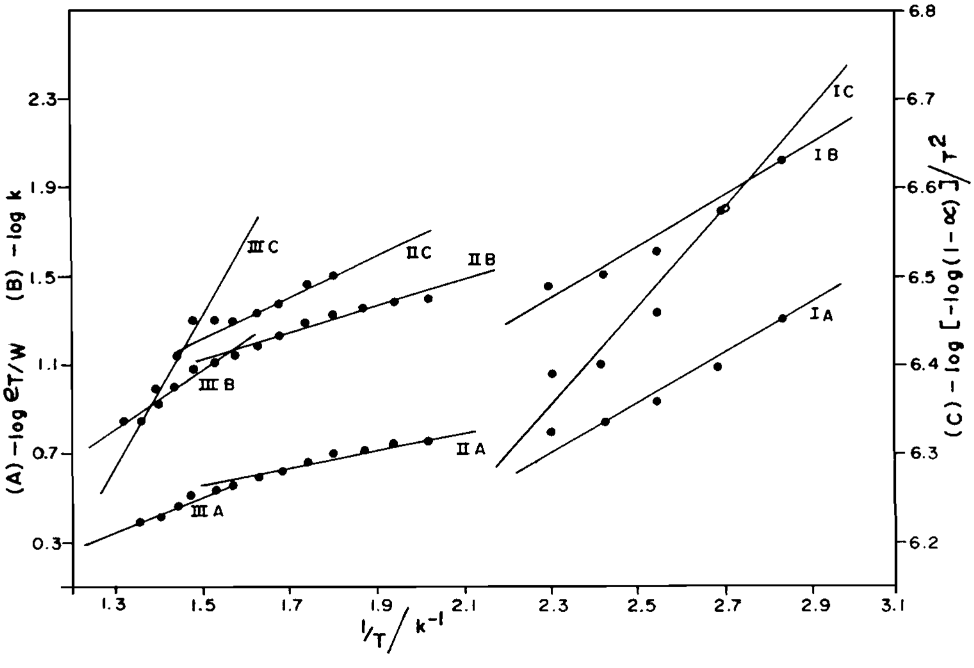


Fig. 6. Plot of (A) $-\log\sigma_T/w$; (B) $-Log[-\log(1-\alpha)]/T^2$; (C) $-\log k$ *vs.* $1/T \times 10^3 \mathrm{K}^{-1}$ of complex **II**.

Table 2
Activation energy (E_a), frequency factor (A) and entropy of activation ($\Delta S^{\#}$) for complex **I** – $Co_2[Mo(CN)_2(C_2H_8N_2)_2(OH)_2]Cl_4$. $2H_2O$

Stage	Parameters	Doyle	Coats and Redfern	Arrhenius
I	E_a (kJ mol^{-1})	24.6	15.0	26.4
	A (s^{-1})	2.3	4.5	1.6
	$\Delta S^{\#}$ (JK^{-1} mol^{-1})	−240.0	−234.2	−242.9
II	E_a (kJ mol^{-1})	11.4	3.4	13.0
	A (s^{-1})	0.4	6.2	0.3
	$\Delta S^{\#}$ (JK^{-1} mol^{-1})	−258.0	−234.6	−258.8
III	E_a (kJ mol^{-1})	23.5	17.8	36.9
	A (s^{-1})	1.4	5.0	1.6
	$\Delta S^{\#}$ (JK^{-1} mol^{-1})	−248.9	−238.1	−247.5

Table 3
Activation energy (E_a), frequency factor (A) and entropy of activation ($\Delta S^{\#}$) for complex **II** $Co[W(CN)_2(C_2H_8N_2)_2(OH)_2]Cl_2$.2 –$H_2O$

Stage	Parameters	Doyle	Coats and Redfern	Arrhenius
I	E_a (kJ mol^{-1})	22.9	13.7	20.9
	A (s^{-1})	1.9	4.7	1.1
	$\Delta S^{\#}$ (JK^{-1} mol^{-1})	−241.3	−233.9	−245.8
II	E_a (kJ mol^{-1})	9.8	4.4	11.6
	A (s^{-1})	0.3	6.1	0.2
	$\Delta S^{\#}$ (JK^{-1} mol^{-1})	−262.3	−231.7	−264.0
III	E_a (kJ mol^{-1})	13.0	14.8	26.4
	A (s^{-1})	0.5	5.3	1.0
	$\Delta S^{\#}$ (JK^{-1} mol^{-1})	−257.4	−238.2	−252.1

gives a straight line(Figs. 5 and 6), indicating that the order of the reaction for the decomposition of all the complexes is one. The slope of the line is taken as $-E_a/2.3R$. The entropy of activation is again calculated from Eq. (A). The activation energy for the three stages of complex **I** is 15.0, 3.4 and 17.8 and complex **II** is 13.7, 4.4 and 14.8 kJ mol^{-1}, respectively. The activation energy (E_a), frequency factor (A) and entropy of activation ($\Delta S^{\#}$) for complexes **I** and **II** are listed in Table 2Table 3 respectively. From the overall kinetic data, it is evident that all the values obtained by these methods are quite comparable although those obtained from the Arrhenius method are more divergent.

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