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Synthesis, characterisation and thermal behaviour of cyano(oxine)-molybdenum(IV) and -tungsten(IV)

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Abstract

A new class of adduct compounds of octacyano-molybdate(IV) and -tungstate(IV) complexes with oxine, of the type $K_4[M(CN)_8]\cdot 8(C_9H_7ON)\cdot 5H_2O$ (where M = Mo or W) was synthesised. FTIR spectra show bands in the range 2000–2200 cm^{-1} and around 1120 cm^{-1}, indicating the presence of the cyano group, $-C\equiv N$, as well as oxine through the $-N{=}O$ mode. The *d* spacing from the X-ray diffraction patterns were determined and compared with those of known compounds. Thermogravimetric analysis indicated the removal of uncoordinated water up to 150 °C. Oxine and cyano molecules were removed stage by stage at higher temperatures. The final products from thermal treatment are oxides of polymeric nature. The kinetic parameters n and E_a were determined by means of TGA and DTG thermograms.

INTRODUCTION

Metal complexes of 8-hydroxyquinoline (oxine) and their adduct compounds have aroused considerable interest in recent years owing to their novel structure and the possibility of their use as antioxidants in petroleum products. Extensive work [1,2] on metal complexes with 8-hydroxyquinoline has been carried out to determine different physico-chemical characteristics, along with structural studies by X-ray diffraction (XRD) and 1R spectra. The thermogravimetric analysis and differential thermal analysis of metal oxinates have been conducted in air [3,4] as well as in an inert environment [5–7]. The zinc oxinate and nickel oxinate adducts with different nitrogen bases were studied [8]. 1,10-Phenanthroline(phen) is substituted in the *trans*-dioxotetracyano-molybdate(IV) ion giving a product of composition $Na[Mo(CN)_3(phen)]\cdot 2(phen)\cdot CH_3OH\cdot H_2O$ as reported by Basson et al. [9]. A little information is available regarding the interaction of octacyanomolybdate(IV) and octacyanotungstate(IV) with nitrogen base ligands. Amine molecules [10] and transition metals [11] interact with octacyanomolybdate(IV), $[(Mo(CN)_8]^{4-}$, and octacyanotungstate(IV),

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$[W(CN)_8]^{4-}$, resulting in the formation of complexes of dodecahedral (D_{2d}) symmetry. Adduct compounds formed by the interaction of octacyano-molybdate(IV) and -tungstate(IV) with 8-hydroxyquinoline have not been reported so far. We report in this paper the synthesis of the adducts of octacyano-molybdate(IV) and -tungstate(IV) complexes with 8-hydroxyquinoline and their characterisation with the help of elemental analysis, Fourier transform (FT) infra-red spectroscopy, XRD studies and thermal behaviour.

MATERIALS AND METHODS

Potassium molybdate, potassium cyanide, potassium tungstate, potassium borohydride, 8-hydroxyquinoline and other chemicals were of A.R. grade and used as such. Potassium octacyano-molybdate(IV) dihydrate, $[K_4Mo(CN)_8] \cdot 2H_2O$, and -tungstate(IV) dihydrate, $[K_4W(CN)_8] \cdot 2H_2O$, were prepared by the method of Leipoldt et al. [12]. The products were purified and crystallised from ethanol–water mixture. 8-Hydroxyquinoline (oxine) (0.1 M) was dissolved in 0.1 N acetic acid, which was neutralised with ammonia solution and then slightly acidified by acetic acid.

Synthesis of complexes

(i) Octacyano(8-hydroxyquinoline)molybdenum(IV) pentahydrate

A solution of 0.1 M 8-hydroxyquinoline was added dropwise into a 0.05 M aqueous solution of octacyanomolybdate (IV) in 8 : 1 molar ratio. A straw coloured precipitate was formed which, on keeping overnight, changed to yellow–orange shining crystals. The crystals were filtered off and washed with ethanol–water mixture. The compound was dried in vacuo over fused $CaCl_2$. The complex thus formed was analysed to establish its stoichiometry by determining Mo gravimetrically and C, H and N by micro-analysis. For $[K_4Mo(CN)_8] \cdot 8(C_9H_7ON) \cdot 5H_2O$: found (%) Mo 5.67, C 56.28, H 3.92, N 13.52; required (%) Mo 5.61, C 56.14, H 3.86, N 13.10.

(ii) Octacyano(8-hydroxyquinoline)tungsten(IV) pentahydrate

A 0.1 M stock solution of 8-hydroxyquinoline was added dropwise into a 0.05 M aqueous solution of octacyano-tungstate(IV) in 8 : 1 molar ratio. The precipitate thus formed was left overnight, and maroon coloured shining crystals were obtained. The crystals were filtered off and washed with ethanol–water mixture. The compound was dried in vacuum. The complex thus formed was analysed for $K_4[W(CN)_8] \cdot 8(C_9H_7ON) \cdot 5H_2O$. Found (%) W 10.36, C 53.37, H 3.89, N 12.52; required (%) W 10.23, C 53.39, H 3.67, N 13.67.

Physical measurements

Fourier transform infra-red spectra were recorded in the range 450–4000 cm^{-1} in a KBr matrix with a Bio-Rad Digilab FTS-40 Fourier Transform Michelson infra-red interferometer equipped with high sensitivity HgCdTe detectors and a KBr beam splitter. The X-ray diffraction patterns were taken on a Philips diffractometer using Cu Kα radiation. Thermal behaviour of the compounds was determined by using a Du Pont 1090 thermal analyser with a TGA module 951 (Du Pont Instruments) at a heating rate of 10 °C min^{-1}, using 10–12 mg of sample. The insolubility of the complex compounds in common organic solvents precluded conductance measurements.

RESULTS AND DISCUSSION

The elemental analysis of the adducts of the complex cyanides of molybdenum and tungsten with oxine shows that they are of the type $K_4[M(CN)_8] \cdot 8(C_9H_7ON) \cdot 5H_2O$. Evidence of the cyanide ligand [13] in these complexes was obtained from FTIR spectra, which show the presence of a very strong band in the region of 2050–2140 cm^{-1}. The $\nu(CN)$ of free CN^- is at 2078 cm^{-1}, and in the adduct the $\nu(CN)$ shifts to higher frequencies. The $\nu(CN)$ in these complexes is changed to higher frequency from 2078 cm^{-1} (vs) in $[Mo(CN)_8]^{4-}$ to 2115.8 cm^{-1} (vs) in $K_4[Mo(CN)_8] \cdot 8(C_9H_7ON) \cdot 5H_2O$ (**I**). The CN^- acts as a σ-donor by donating electrons to metal and as a π-acceptor by accepting electrons from the metal. σ-Donation tends to raise the $\nu(CN)$, since electrons are removed from the 5σ orbital, which is weakly antibonding [14]. A similar frequency of $\nu(CN)$ in $K_4[W(CN)_8] \cdot 8(C_9H_7ON) \cdot 5H_2O$ (**II**) is observed at 2107.8 cm^{-1} (vs). This is consistent with $M-C\equiv N$ bonding. The $\nu(OH)$ in complexes **I** and **II** is in the region 3100–3300 cm^{-1}; it is a broad band and is attributed to the water molecule in uncoordinated form. The frequency in the triplet form around 1600 cm^{-1} indicates the N–H stretching vibration, and the bands at 1569.8 cm^{-1} (s) and 1554.4 cm^{-1} (vs) are due to $\nu(C=N)$ stretching. The presence of oxine in complexes **I** and **II** is indicated by the band in the region 1100–1140 cm^{-1}. Charles et al. [2] reported that, for several metal complexes with oxine, the $\nu(C-O)$ band is observed at 1120 cm^{-1}. The position of this band undergoes a shift depending upon the electronegativity and oxidation state of the metal. In the present investigation, the bands are observed at 1115.5 cm^{-1} (s) in complex I and 1107.8 cm^{-1} (s) in complex II, with a shift of 5 to 12 cm^{-1}. This is attributed to the oxine group linked by its nitrogen and oxygen atoms as a uninegative bidendate ligand. The lower frequency region of the complexes shows the mode of bonding between Mo/W and the ligand. The presence of bands at 465.7 cm^{-1} (m) and 473.6 cm^{-1} (m) is due to M–N. The Mo–O stretch in the complexes is indicated

TABLE 1

Important Fourier transform infra-red frequencies of complexes $K_4[Mo(CN)_8] \cdot 8(C_9H_7ON] \cdot 5H_2O$ (**I**) and $K_4[W(CN)_8] \cdot 8(C_9H_7ON) \cdot 5H_2O$ (**II**) and their assignment

Complex **I** frequencies (cm^{-1})	Assignment	Complex **II** frequencies (cm^{-1})	Assignment
3107 (br)	ν(OH)	3100	ν(OH)
2116 (vs)	br C≡N	2108 (vs)	ν(CN)
1639 (m)	ν_a(C=O)	1631.4 (w)	ν_a(C=O)
1601 (s)	ν_a(N=H)	1578 (m)	ν(OH), ν(N=H),
1570 (vs)	N=H bonding	1554 (vs)	N–H bonding
1408 (vs)	ν(–N=N–)	1392.6 (vs)	ν(–N=N–)
1308 (vs)	ν_{sy}(C–O)	1284 (vs)	ν_{sy}(C–O)
1116 (vs)	ν(N–O)	1108 (s)	ν(N–O) of oxine
820 (vs)		811 (s)	
769 (m)	δ_a(O–C–O)	793 (m)	δ_a(O–C–O)
615 (m)		607 (vw)	
576 (s)		552 (m)	
526 (s)	δ_{sy}(C–C–O)	528.5 (m)	δ_{sy}(C–C–O)
466 (s)	δ_{sy}(O–C–O)	474 (w)	δ_{sy}(O–C–O) M–N

Key: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; br, broad.

by the presence of bands at 882 cm^{-1} and 873 cm^{-1}. The important frequencies of the adduct complexes **I** and **II**, with their assignments of mode, are given in Table 1.

It may be concluded that complexes of the type $K_4[M(CN)_8] \cdot 8(C_9H_7ON) \cdot 5H_2O$ which are formed by the interaction of $[M(CN)_8]^{4-}$ and oxine do not correspond to an increase in the coordination number of molybdenum or tungsten. The simplicity of these spectra (Fig. 1) indicates a dodecahedral (D_{2d}) symmetry [14].

An X-ray diffraction study of the adduct compound $K_4[Mo(CN)_8] \cdot 8(C_9H_7ON) \cdot 5H_2O$ was carried out, and intensity vs. diffraction angle 2θ was recorded in the range 3°–50° using Cu Kα radiation of wavelength 1.5418 Å (Fig. 2). The d spacings calculated vary from 13.27 to 1.98 Å, showing interplanar distance (Table 2). X-ray diffraction study of $Cd_2[Mo(CN)_8] \cdot 2N_2H_4 \cdot 4H_2O$ has shown the decacoordinate bicapped square-anti-prismatic structure [15], which is not found in the adducts **I** and **II**.

THERMAL STUDIES

The complex $K_4[Mo(CN)_8] \cdot 8(C_9H_7ON) \cdot 5H_2O$ is stable up to 70 °C, and loses its five molecules of water in a single step with onset temperature 98.9 °C, which extends up to 145 °C (Fig. 3). That event is observed as a sharp peak in DTG at 113.1 °C. The observed weight loss is 5.04%, as

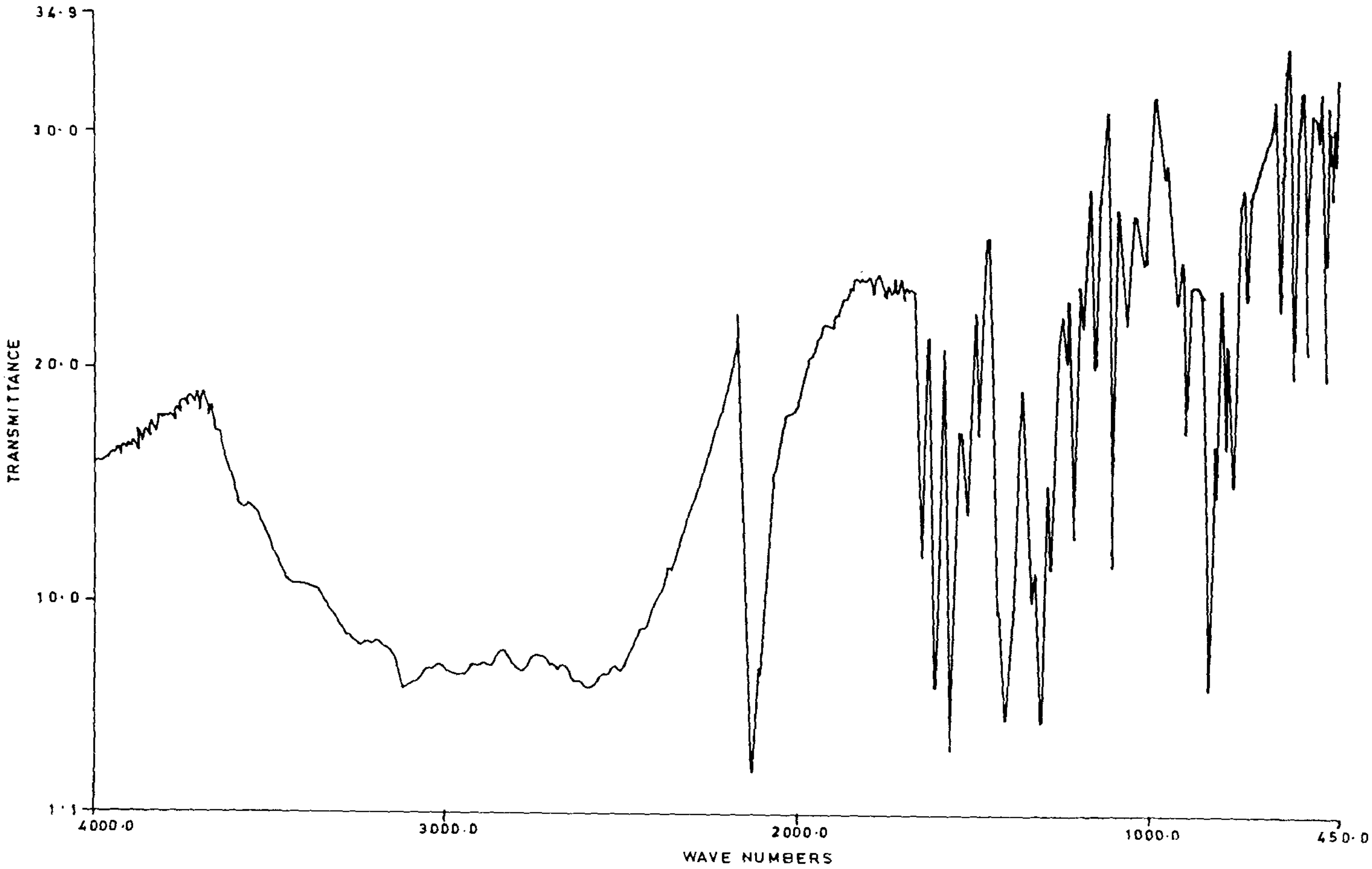

Fig. 1. FTIR spectra of the compound $K_4[Mo(CN)_8 \cdot 8(C_9H_7ON) \cdot 5H_2O$.

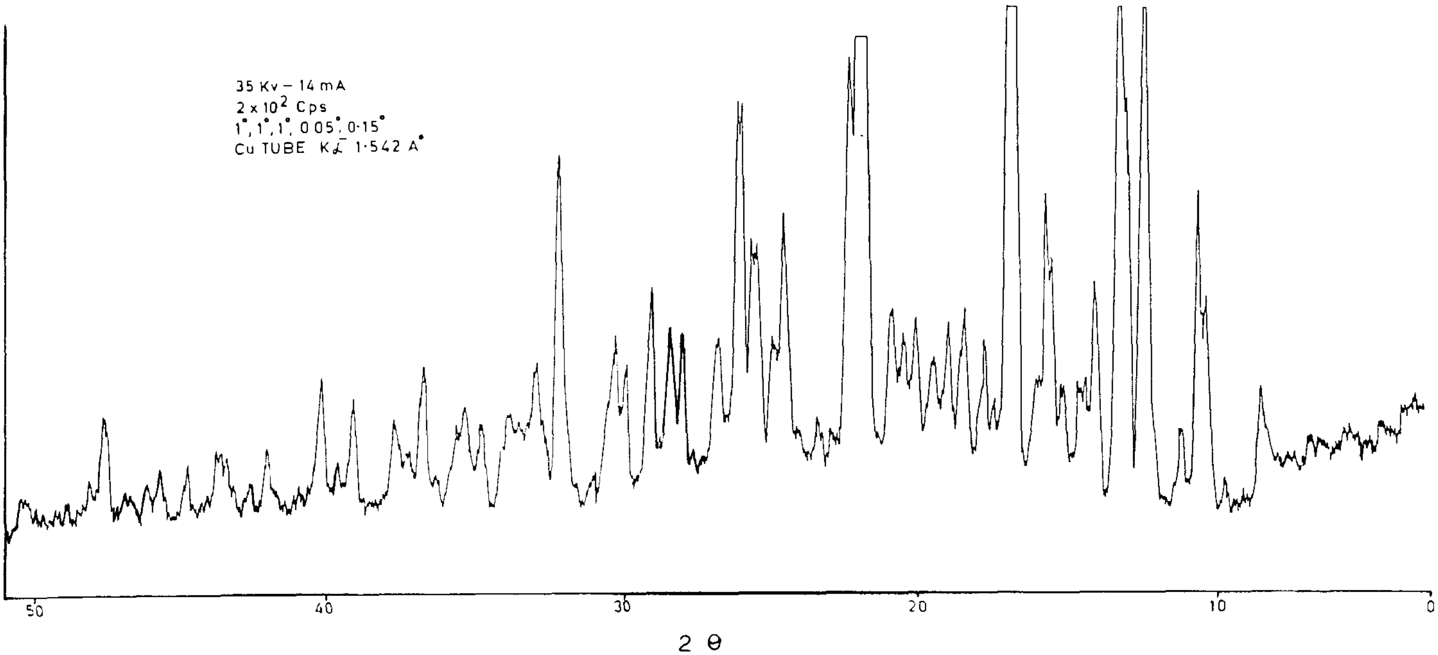

Fig. 2. X-ray powder diffraction patterns of the compound $K_4[Mo(CN)_8]\cdot 8(C_9H_7ON)\cdot 5H_2O$.

TABLE 2

X-ray powder data for $K_4[Mo(CN)_8] \cdot 8(C_9H_7ON) \cdot 5H_2O$

Data pattern 2θ (°)	*d*	Intensity (%)	Data pattern 2θ (°)	*d*	Intensity (%)
8.7	13.27	12	19.6	4.53	24
9.9	8.88	56	22.2	4.01	88
10.6	8.34	58	24.7	3.62	50
10.8	8.19	50	26.2	3.40	76
11.4	7.76	6	29.2	3.06	32
12.7	7.03	85	32.2	2.78	62
13.1	6.81	60	33.0	2.71	15
13.5	6.61	94	36.8	2.44	15
14.2	6.24	36	39.1	2.41	12
15.9	5.61	52	40.2	2.24	14
17.2	5.16	100	47.8	1.98	12
18.6	4.77	26			

against the calculated value of 5.26%. The decomposition of the complex commences from 176.8 ° C and extends up to 240 ° C, whereby 5.2 molecules of oxine are removed as shown in DTG by a peak maximum at 191.1° C. The mass loss observed is 44.74% as against the calculated value of 44.09%. A further 1.2 molecules of oxine (with evolution of hydrogen [16]) are removed in the temperature range 250–465 ° C at a slow rate, with a DTG peak at 343.3° C. The weight loss is found to be 10.30% as against the calculated value of 10.80%. Eight molecules of cyanide are evolved by decomposition in the temperature range 460–810 ° C, with a DTG peak at 686.1° C. This step gives a weight loss of 12.29% as against the calculated value of 12.16%. There is no appreciable change after a temperature of 820 ° C and possibly the polymeric oxide $K_4Mo_2O_8$ is formed [17]; the residual weight was found to be 27.62% of the complex against the calculated value of 27.89% (Table 3). The thermal dissociation is represented in Scheme 1.

The TGA and DTG thermograms of $K_4[W(CN)_8] \cdot 8(C_9H_7ON) \cdot 5H_2O$ show the decomposition in five steps (Fig. 4). Five molecules of water are removed up to 150 ° C, with the DTG peak at 222.0 ° C. The observed weight loss is 4.67% as against the calculated value of 5.0%. The anhydrous adduct loses five molecules of oxine in the range 150–260 ° C, with onset temperature 191.9 ° C. The rate of decomposition in this step is fast, which is obvious from the sharp DTG peak at 210.5 ° C. The observed weight loss is 30.77% as against the calculated value of 32.26%. The difference in the observed and calculated values is due to overlapping of the two steps. $K_4W(CN)_8 \cdot 4(C_9H_7ON)$ loses two molecules of oxine with onset temperature 347.9 ° C for an observed weight loss of 16.13% as against the calculated value of

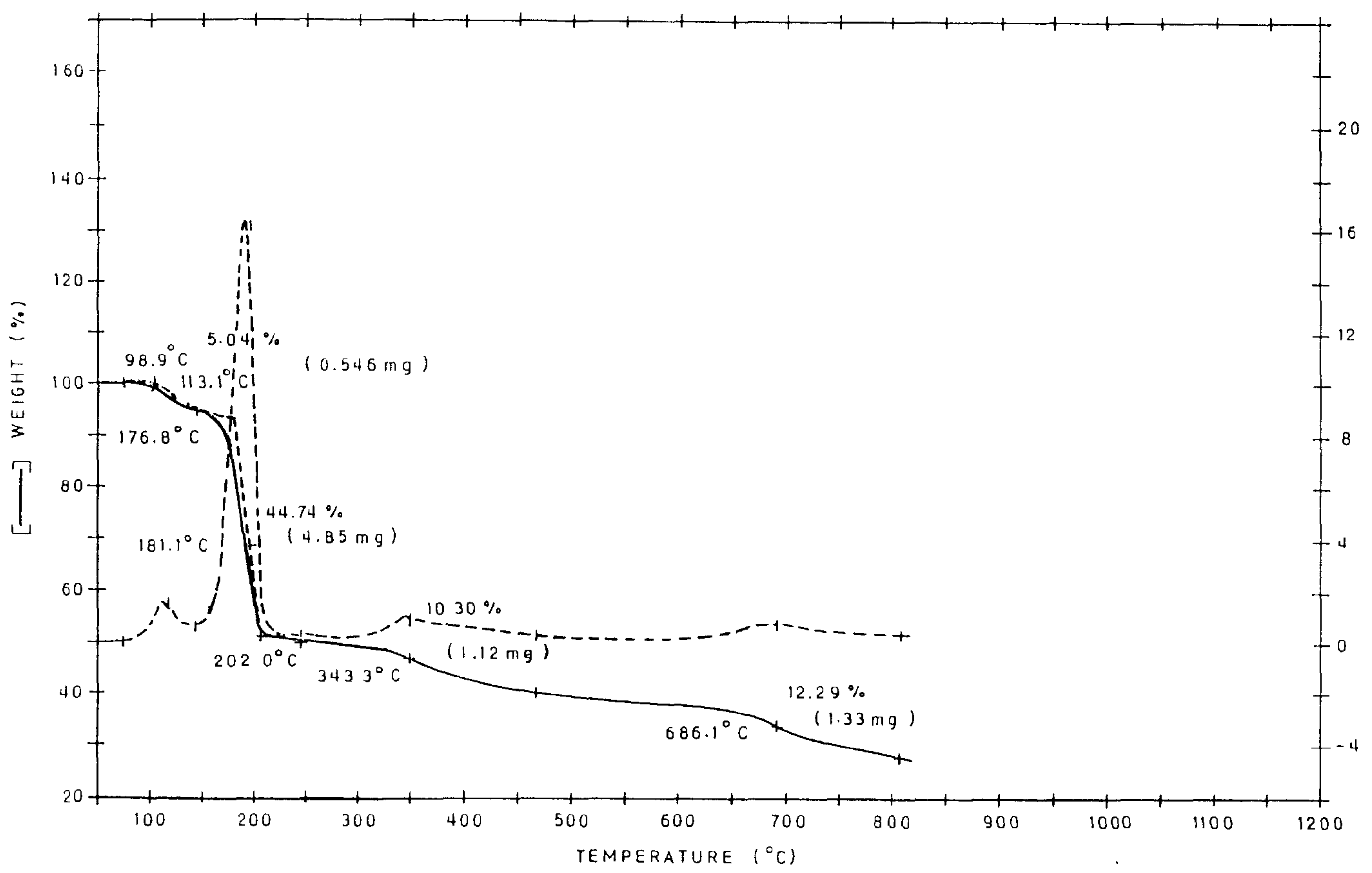

Fig. 3. Thermal curves of the compound $K_4[Mo(CN)_8] \cdot 8(C_9H_7ON) \cdot 5H_2O$.

TABLE 3

Thermoanalytical data for the decomposition of adducts of 8-hydroxyquinoline with octacyano-molybdate $[Mo(CN)_8]^{4-}$ and -tungstate $[W(CN)_8]^{4-}$

Name of complex	Temp. range (°C) in TGA	Maximum temp. in DTG	Weight loss (%)		Remarks
			calcu-ted	observed	
$K_4[Mo(CN)_8]$ $\cdot 8(C_9H_7ON)$ $\cdot 5H_2O$	70–145	113.1	5.26	5.04	5 molecules of water removed
	176.8–240	191.1	44.09	44.74	5.2 molecules of oxine removed
	250–465	343.3	10.80	10.30	1.2 molecules of oxine decomposed
	460–810	686.1	12.16	12.29	8 molecules of CN removed
$K_4[W(CN)_8]$ $\cdot 8(C_9H_7ON)$ $\cdot 5H_2O$	80–150	111	5.00	4.67	6 molecules of water removed
	150–260	210.5	32.26	30.77	4 molecules of oxine removed
	260–410	361.2	14.16	16.13	2 molecules of oxine removed
	410–610	543.9	11.37	10.11	8 molecules of CN decomposed.
	610–810	800.9	4.84	5.02	0.6 mol of oxine is decomposed in the form of CH_4 and N_2

14.16%, with a maximum in DTG at 361.2°C. Eight molecules of cyanide are removed in the range 410–610°C with onset temperature 526.3°C and DTG maximum at 543.9°C with a weight loss of 10.11% as against the calculated value of 11.37%. Partial decomposition (0.6 molecules) of oxine occurs in the form of evolution of hydrogen, methane and carbon monoxide; the observed weight loss is 5.02% as against the calculated value of 4.84%. The end product may be the polymeric oxide $K_4W_2O_8$ (36%). This is represented in Scheme 2.

Octacyano(8-hydroxyquinoline)molybdenum(IV) pentahydrate and the tungsten(IV) analogue, of the type $K_4[M(CN)_8] \cdot 8(C_9H_7ON) \cdot 5H_2O$, show multistep decomposition up to 820°C, whereas the pyrolysis of divalent metal complexes of 8-hydroxyquinoline involves one or two steps [18,19]. These complexes lose water of hydration at around 200°C and beyond. The decomposition temperatures of divalent metal oxinates vary from 275°C for $Cu(C_9H_7ON)_2$ to 460°C for $Cd(C_9H_7ON)_2 \cdot 2H_2O$. The decomposition temperature of oxine molecules in the present investigation (second step) varies from 191 to 211°C, implying the presence of oxine molecules outside the coordination sphere.

$$K_4[Mo(CN)_8] \cdot 8(C_9H_7ON) \cdot 5H_2O \xrightarrow{-5H_2O} K_4[Mo(CN)_8] \cdot 8(C_9H_7ON)$$

$$\xrightarrow{-5.2(C_9H_7ON)} K_4[Mo(CN)_8] \cdot (C_9H_7ON)_{2.8} \xrightarrow{-1.2(C_9H_7ON)} K_4[Mo(CN)_8] \cdot (C_9H_7ON)_{1.6}$$

$$\xrightarrow{-8(CN)} K_4Mo(C_9H_7ON)_{1.6} \rightarrow K_4Mo_2O_8 \ (27.62\%)$$

Scheme 1.

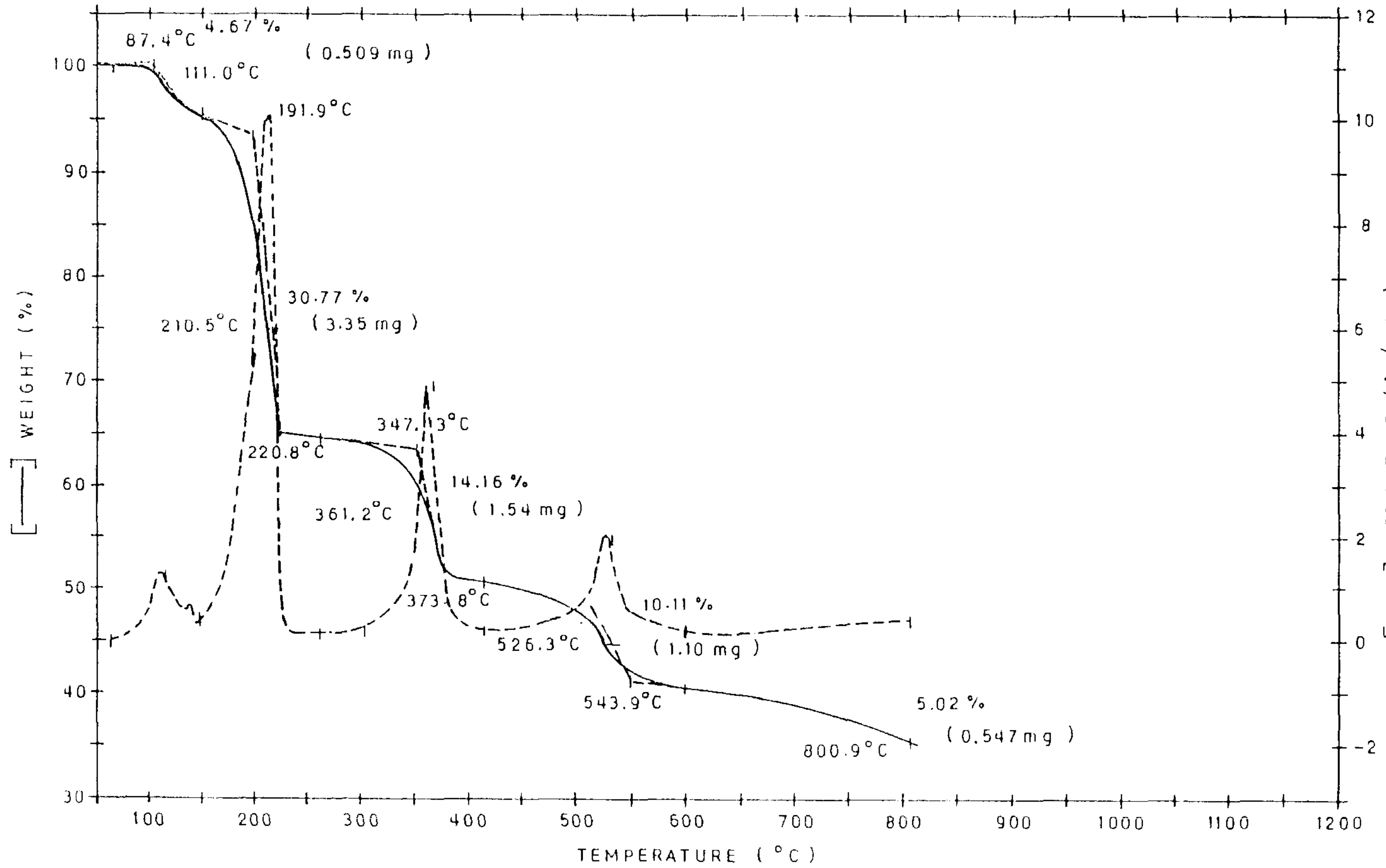

Fig. 4. Thermal curves of the compound $K_4[W(CN)_8] \cdot 8(C_9H_7ON) \cdot 5H_2O$.

$$K_4[W(CN)_8]\cdot 8(C_9H_7ON)\cdot 5H_2O \xrightarrow{-5H_2O} K_4[W(CN)_8]\cdot 8(C_9H_7ON)$$
$$\xrightarrow{-4(C_9H_7ON)} K_4[W(CN)_8]\cdot (C_9H_7ON)_4 \xrightarrow{-2(C_9H_7ON)} K_4[W(CN)_8]\cdot (C_9H_7ON)_2$$
$$\xrightarrow{-8(CN)} K_4W(C_9H_7ON)_2 \xrightarrow{-0.6(C_9H_7ON)} K_4W(C_9H_7ON)_{1.4} \rightarrow K_4W_2O_8$$

Scheme 2.

Evaluation of activation energy

Since the thermal decomposition in step two of complexes **I** and **II** by TGA occurs over a relatively small temperature range, Coats and Redfern [20] suggested that at relatively low conversion, the degree of conversion as a function of temperature is independent of reaction order. For computation of activation energy, the following equation may be used

$$\log\frac{\rho_T}{W} = \frac{E_a}{4.6\,T} + \log\frac{Z}{(RH)}$$

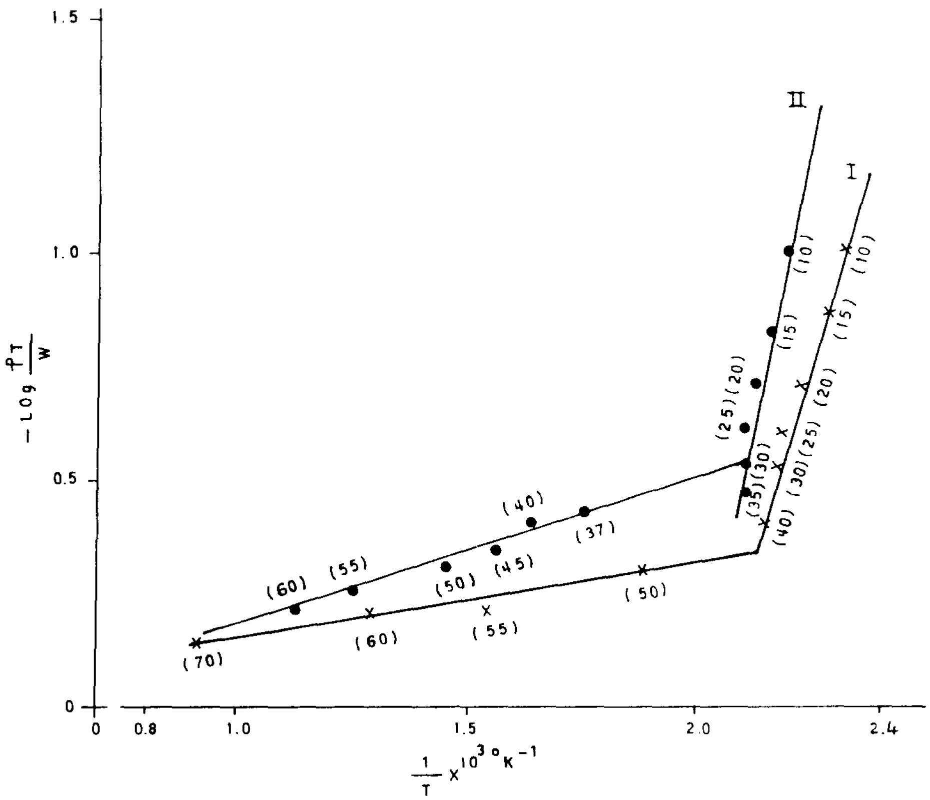

Fig. 5. Plot constructed from thermal curves of compounds $K_4[Mo(CN)_8]\cdot 8(C_9H_7ON)\cdot 5H_2O$ (I) and $K_4[W(CN)_8]\cdot 8(C_9H_7ON)\cdot 5H_2O$ (II).

where $\rho_T = -dW/dT$, (RH) = heating rate and Z is frequency. When $\log \rho_T/W$ is plotted against $1/T$, the value of E_a is calculated by the relation $E_a = 4.6 \times$ slope.

A graph of first order reaction between $\log \rho T/W$ vs. $1 \times 10^3/T$ for complexes **I** and **II** was plotted (Fig. 5) and the activation energy was calculated.

From the graph, the activation energy of $K_4[Mo(CN)_8] \cdot 8(C_9H_7ON) \cdot 5H_2O$ was found to be 17.3 kcal mol^{-1} up to 40% conversion, and after this point the activation energy dropped to 0.77 kcal mol^{-1}; the activation energy of $K_4[W(CN)_8] \cdot 8(C_9H_7ON) \cdot 5H_2O$ was found to be 15.11 kcal mol^{-1} up to 30% conversion and after this point it was reduced to 1.47 kcal mol^{-1}.

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