Asian Journal of Chemistry Vol. 13, No. 1 (2001), 177–184

Synthesis, Characterisation and Thermal Decomposition Kinetics of Some Azo Dye Complexes of Chromium(III)

SHERIF RAWTHER* and K. MOHANAN†
Department of Chemistry, Government College for Women, Trivandrum-695 014, India

Chromium(III) complexes of 2,3-dimethyl-1-phenyl-4-(2-hydroxy-naphthylazo)-5-pyrazolone; 2,3-dimethyl-1-phenyl-4-(2,4-dihydroxy-phenylazo)-5-pyrazolone and 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-methylphenylazo)-5-pyrazolone have been synthesised and characterised on the basis of elemental analysis, molar conductance, magnetic susceptibility measurements, infrared and electronic spectral studies. Thermal decomposition kinetics of these complexes in nitrogen atmosphere was investigated by TG and DTG techniques. Kinetic parameters such as activation energy E, pre-exponential factor A and entropy of activation ΔS were calculated.

INTRODUCTION

Thermal properties of metal chelates with different types of complexing agents have been extensively investigated by several workers.[1–5] However, very few studies are reported showing the relationship between thermal stability of metal chelates and structure of the chelating agents.[6] In this connection we report the thermal decomposition kinetics and relative thermal stabilities of some chromium(III) complexes with 2,3-dimethyl-1-phenyl-4-(2-hydroxy-naphthylazo)-5-pyrazolone (HNAAP), 2,3-dimethyl-1-phenyl-4-(2,4-dihydroxyphenylazo)-5-pyrazolone (HRAAP) and 2,3-dimethyl-1-phenyl-4-(2-hydroxy-5-methylphenylazo)-5-pyrazolone (HCAAP).

EXPERIMENTAL

The ligands were prepared by a reported method.[7] The metal complexes were prepared by the following general procedure. To the finely powdered ligand (0.01 mol) in methanol the metal salt solution (0.005 mol) in methanol was added gradually in small amounts with constant shaking. The colour was changed at once heralding the formation of the complex. The contents were refluxed for 3 h on a water bath in order to ensure completion of the reaction. The complex formed was suction filtered, washed with distilled water and finally with ethanol. The complex was dried in vacuum over P_4O_{10}.

The TG and DTG analyseis of the complexes were carried out using a Du Pont

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†Department of Chemistry, University College, Trivandrum-695 034, Kerala, India.

2000 thermal analyser system, with a heating rate of 10°C min^{-1} and a sample size of 5–6 mg in an atmosphere of nitrogen using a platinum crucible.

RESULTS AND DISCUSSION

The analytical data, molar conductance and magnetic susceptibility of the three compounds are given in Table-1.

TABLE-1
ANALYTICAL DATA OF Cr(III) COMPLEXES

Complex	% Analysis, Found (Calcd.)			Molar conductance*	μ_{eff} (B.M.)
	M	Cl	N		
$Cr(NAAP)_2Cl$	6.31 (6.49)	4.37 (4.42)	13.56 (13.97)	6.77	3.62
$Cr(RAAP)_2Cl$	6.26 (6.68)	4.29 (4.83)	14.12 (14.38)	23.0	3.70
$Cr(CAAP)_2Cl$	7.00 (7.12)	4.60 (4.86)	14.92 (15.36)	30.0	3.81

*Measured in nitrobenzene.

The IR spectra of HNAAP, HRAAP and HCAAP exhibit a broad medium intensity band around 2900 cm^{-1} which can be assigned to the hydrogen bonded OH group. Another very strong band at *ca.* 1660 cm^{-1} in the spectra of the free ligands may be attributed to the C═O stretching vibration. A band around 1460 cm^{-1} may be attributed to the N═N group.

In all the complexes, the band around 2900 cm^{-1} is absent, showing that the ligand reacts with the metal in the enol form with the elimination of replaceable hydrogen. The broad band of medium intensity around 3400 cm^{-1} in HRAAP is retained in all the Cr(III) complexes with HRAAP showing the presence of free OH group. The frequency at 1660 cm^{-1} due to C═O group in the ligand is shifted to a lower frequency of *ca.* 1600 cm^{-1} in the spectra of all the three complexes. This shows the participation of the C═O group in coordination. The frequency at 1460 cm^{-1} assigned to N═N of the ligand undergoes a downward shift in the spectra of all the complexes indicating the participation of these groups in complexation.

In electronic spectra of the free ligands HNAAP, HRAAP and HCAAP show intense bands at 43010 cm^{-1}, 39525 cm^{-1} and 40650 cm^{-1} respectively. This may be assigned to $\pi^* \leftarrow \pi$ transition. The bands at 24270, 26246 and 26595 cm^{-1} for the above ligands may be attributed to $\pi^* \leftarrow n$ transition. The electronic spectra of the complexes are almost alike.The bands due to $\pi^* \leftarrow \pi$ transition in the spectra of complexes do not undergo any appreciable change. But the $\pi^* \leftarrow n$ transition observed at around 24000 underges a blue shift in all the complexes. This leads to the conclusion that the 'n' electrons involved in the transition are bonded to the metal during complex formation.

The TG and DTG curves of the three complexes are given in Fig. 1–3. The kinetic parameters[8] for the decomposition of the complexes obtained from different equations are presented in Table-2. The kinetic data and mathematical analysis of the decomposition kinetics are given in Tables-3–5. The behaviour of the complexes including peak temperature, mass loss and stability ranges can be obtained from Tables 6 and 7.

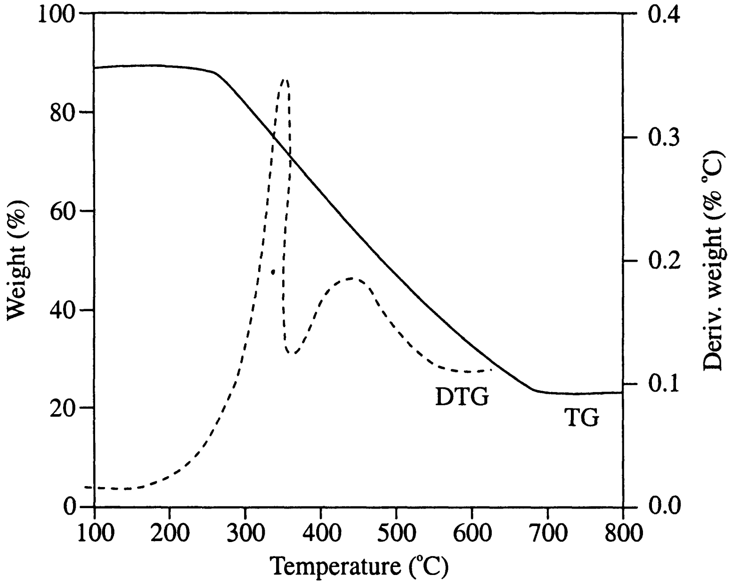

Fig. 1. TG and DTG curves of [Cr(RAAP)$_2$]Cl

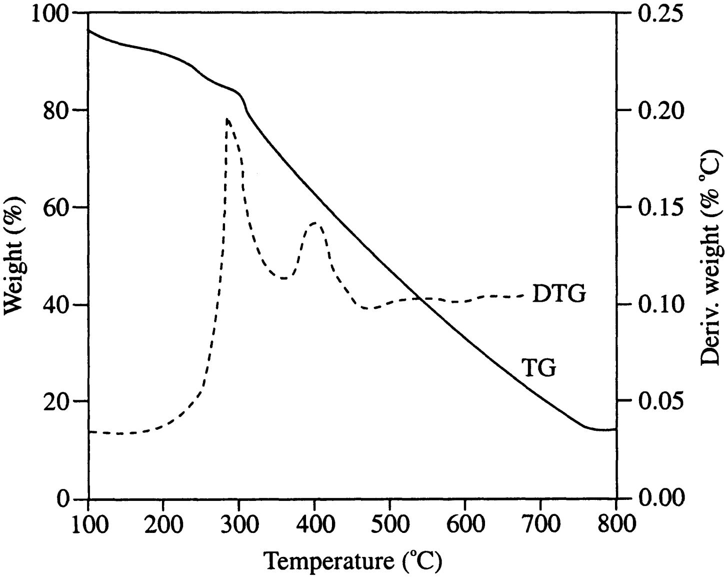

Fig. 2. TG and DTG curves of [Cr(CAAP)$_2$]Cl

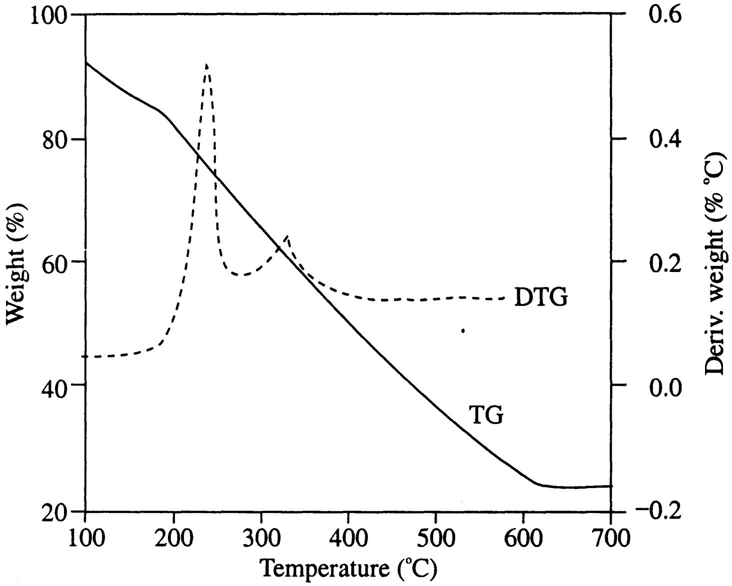

Fig. 3. TG and DTG curves of $[Cr(NAAP)_2]Cl$

TABLE-2
KINETIC PARAMETERS OF Cr(III) COMPLEXES OF PYRAZOLONES

Equation	Complex	E ($kJ\ mol^{-1}$)	A (S^{-1})	ΔS ($KJ\ mol^{-1}$)	r
Coats Redfern[9]	$[Cr(NAAP)_2]Cl$	105.00	4.73×10^7	−104	0.9992
Madhusudanan *et al.*[10, 11]	$[Cr(NAAP)_2]Cl$	106.00	1.80×10^8	−92	0.9992
Horowitz Metzger[8]	$[Cr(NAAP)_2]Cl$	127.50	1.20×10^8	−88	0.9988
Freeman Carroll	$[Cr(NAAP)_2]Cl$	75.60	6.4×10^5	−130	0.9890
Coats Redfern[9]	$[Cr(CAAP)_2]Cl$	82.90	4.10×10^7	−103	0.9844
Madhusudanan *et al.*[10, 11]	$[Cr(CAAP)_2]Cl$	82.40	6.30×10^7	−99	0.9842
Horowitz Metzger[8]	$[Cr(CAAP)_2]Cl$	89.00	4.80×10^8	−124	0.9988
Coats Redfern[9]	$[Cr(RAAP)_2]Cl$	71.20	3.30×10^5	−144	0.9815
Madhusudanan *et al.*[10, 11]	$[Cr(RAAP)_2]Cl$	71.90	6.50×10^5	−133	0.9850
Horowitz Metzger[8]	$[Cr(RAAP)_2]Cl$	77.50	4.60×10^4	−160	0.9787

TABLE-3

KINETIC DATA FOR THE DECOMPOSITION OF Cr(III) COMPLEXES OF 2,3-DIMETHYL-1-PHENYL-4-(2-HYDROXYNAPHTHYLAZO)-5-PYRAZOLONE

Temp (K)	Wt (mg)	$C=\frac{W_t-W_f}{Wo-Wf}=(1-\alpha)$	Coats Redfern method $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$	Madhusudanan *et al.* method $\ln\left[\frac{-\ln(1-\alpha)}{T^{1.925}}\right]$	$\frac{1}{T}\times 10^3$	$\theta=T-T_s$	Horowiz-Metzger method $\ln[-\ln(1-\alpha)]$
563	5.276	0.9336	−15.346	−14.898	1.7760	−65	−2.6781
583	5.187	0.8447	−14.516	−14.016	1.7152	−45	−1.7790
603	5.065	0.7141	−13.892	−13.389	1.6580	−25	−1.0880
623	4.834	0.4668	−13.141	−12.636	1.6050	−05	−0.2720

$W_0=5.332$ mg, $W_f=4.398$ mg, $T_s=628$ K, n = 1

TABLE-4

KINETIC DATA FOR THE DECOMPOSITION OF Cr(III) COMPLEX OF 2,3-DIMETHYL-1-PHENYL-4-(2,4-DIHYDROXYPHENYLAZO)-5-PYRAZOLONE

Temp (K)	Wt mg	$C=\frac{W_t-W_f}{Wo-Wf}=(1-\alpha)$	Coats Redfern method $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$	Madhusudanan *et al.* method $\ln\left[\frac{-\ln(1-\alpha)}{T^{1.925}}\right]$	$\frac{1}{T}\times 10^3$	$\theta=T-T_s$	Horowitz-Metzger method $\ln[-\ln(1-\alpha)]$
543	4.695	0.7534	−13.8565	−13.3620	1.8416	−36	−1.2620
553	4.655	0.7006	−13.6643	−13.1680	1.8083	−26	−1.0334
563	4.593	0.6251	−13.4222	−12.9250	1.7761	−16	−0.7555
573	4.479	0.4817	−13.0160	−12.5170	1.7452	−06	−0.3142
583	4.301	0.2578	−12.4325	–	1.6715	+04	+0.3040

$W_0=4.891$, $W_f=4.096$, $T_s=579$ K, n = 1.

TABLE-5
KINETIC DATA FOR THE DECOMPOSITION OF Cr(III) COMPLEXES OF 2,3-DIMETHYL-1-PHENYL-4-(2-HYDROXY-5-METHYLPHENYLAZO)-5-PYRAZOLONE

Temp (K)	Wt mg	$C = \frac{W_t - W_f}{Wo - Wf} = (1 - \alpha)$	Coats Redfern method $\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right]$	Madhusudanan *et al.* method $\ln\left[\frac{-\ln(1-\alpha)}{T^{1.925}}\right]$	$\frac{1}{T} \times 10^3$	$\theta = T - T_s$	Horowitz-Metzger method $\ln[-\ln(1-\alpha)]$
493	5.253	0.6967	−13.419	−12.933	2.020	−31	−1.0180
503	5.219	0.6419	−13.254	−12.766	1.988	−21	−0.8137
513	5.150	0.5306	−13.114	−12.446	1.949	−11	−0.4560
523	5.042	0.3564	−12.488	−12.033	1.912	−1	0.0305
533	4.928	0.1725	−11.990	−11.500	1.876	+9	0.5630

$W_0 = 5.441$ mg, $W_f = 4.821$, $T_s = 524$ K, n = 1

TABLE-6
TG AND DTG DATA OF Cr(III) COMPLEXES OF PYRAZOLONES

Complex	Ambient temperature (K)	First decompositon (K)	Peak temperature (K)	Second decomposition (K)	Peak temperature (K)
$[Cr(NAAP)_2]Cl$	520	520–630	628	645–730	689
$[Cr(CAAP)_2]Cl$	490	490–650	524	660–700	694
$[Cr(RAAP)_2]Cl$	470	470–600	579	610–770	679

TABLE-7
PYROLYSIS DATA OF Cr(III) COMPLEXES OF PYRAZOLONES

Complex	Final residue	Percentage loss of mass after final stage	
		From TG	From independent pyrolysis
$[Cr(NAAP)_2]Cl$	Cr_2O_3	78.4	77.8
$[Cr(CAAP)_2]Cl$	Cr_2O_3	80.8	79.2
$[Cr(RAAP)_2]Cl$	Cr_2O_3	81.5	79.8

The $[Cr(NAAP)_2]Cl$ complex is stable up to 520 K. It shows the first stage of decomposition between 520–630 K. This is represented by a DTG peak at 628 K. The second stage decomposition takes place between 645–730 K and is represented by a DTG peak at 689 K. In $[Cr(CAAP)_2]Cl$ complex, the different stages of decomposition take place at lower temperature ranges. The first stage occurs between 660–700 K which is represented by the DTG peak at 694 K.

In $[Cr(RAAP)_2]Cl$ complex both the stages of decomposition take place at slightly lower temperature ranges. The first stage occurs between 470–600 K and the final decomposition between 610–770 K. The DTG peaks for these steps are at 579 K and 679 K respectively.

The losses observed in the TG studies of all the chromium complexes correspond to the formation of Cr_2O_3 which is stable beyond 870 K. This agrees fairly well with the mass loss obtained in independent pyrolysis experiments. The final decomposition product was analysed being Cr_2O_3.

On the basis of the foregoing discussion the relative thermal stabilities of the chelates may be represented as

$$[Cr(NAAP)_2]Cl > [Cr(CAAP)_2]Cl > [Cr(RAAP)_2]Cl$$

The first stage in all the three complexes were studied in detail to evaluate kinetic parameters. Analysis of data obtained using the Horowitz-Metzger[8] and Coats Redfern equation[9] indicated that the first stage of decomposition in all the three complexes follows first order kinetics. The value of 'n' determined with the aid of master curve[10] is *ca.* 1. Accordingly the kinetic parameters were evaluated using the Coats Redfern[9], Madhusudanan *et al.*[10, 11] and Horowitz-Metzger[8] equations. The results are listed in Tables 2–4. The satisfactory values of r in all cases (r *ca.* 1) indicate good agreement with the experimental data. The values of the kinetic parameters obtained from the various equations are reasonable and in good agreement. For the three complexes under consideration, the first stage of decomposition is very low. The entropy of activation values varies from −90 to −136 J K^{-1} mol^{-1}. The negative values of activation entropy indicate that in all the three cases, the activated complex has a more ordered structure than the reactants and the reactions are slower than normal.[12]

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(*Received:* 11 August 2000; *Accepted:* 1 November 2000) AJC-2147