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THERMAL AND MAGNETIC STUDIES OF MIXED LIGAND COMPLEXES OF CHROMIUM(III) CONTAINING DITHIOCARBAMATE AND ACETYLACETONE /OXINE /GLYCINE MOIETIES

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Chromium(III) complexes of the type $Cr(A)(A')_2$, $Cr(A)_2(A')$ and $Cr(A)_3$ have been prepared (where *A* is either piperidyldithiocarbamate or morpholyldithiocarbamate and *A'* is glycine or oxine or acetylacetone moiety). The mixed ligand complexes have been characterized by elemental analyses, magnetic susceptibility measurements and thermal studies. The complexes show magnetic moment in the range of 3.5–4.3 B.M. which corresponds to three unpaired electrons. TG studies have also been carried out, in order to study the mode of decomposition of the complexes and to evaluate various kinetic parameters.

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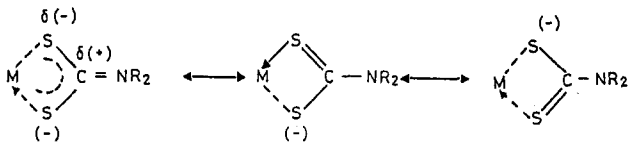
The dithiocarbamate ligand can stabilize higher oxidation states of transition metals in their complexes [1]. These ligands have a special feature. There is an additional π–electron flow from nitrogen to sulphur via a planar delocalized π–orbital system. The dithiocarbamato moiety in its complexes, $M(S_2CNR_2)_n$ (*M* = metal atom and *n* = valency) have several canonical forms:



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This effect results in strong electron donation and hence a high electron density on the metal leading to its next higher oxidation state.

Chromium is the element which has been extensively implicated as both an animal and human carcinogen. Baefjer [2] reported that chromatic workers had a higher lung cancer incidences than did the population as a whole. The compound, $Cr(R_2dtc)_3$, first reported by Delepine [3] has been studied extensively and an excellent review on similar compounds has appeared [4]. Metal complexes of dithiocarbamates are well known for their structural and biochemical importance [1, 4, 5]. Klopping and Kerk [6] investigated the data on fungicidal activities of various dialkyldithiocarbamates. Kaushik *et al.* [7] tested the antifungal activity of ammonium N–(*m*–chlorophenyl) dithiocarbamate and its complexes with Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) against aspergillus niger. The clinical applications [8], toxicological [9, 10] and inhibitory [11, 12] action and herbicidal activity [13] of dithiocarbamates are also well known. The dithiocarbamate ligands have also proved useful in analytical chemistry, particularly for the estimation of metal ions, for example iron, cobalt and nickel were determined gravimetrically as their diethyldithiocarbamate complexes in the presence of tartarate as masking agent [14]. Triarylbenzylammonium dithiocarbamates are plant growth regulators, especially suitable for chemical pinching. They are also plant disciccants and defoliants [15]. In this manuscript we report the synthesis and spectral characterization, together with magnetic and thermal measurements on mixed chromium(III) dithiocarbamates.

Experimental

Preparation

All the chemicals used were of Analar grade. The dithiocarbamate ligands were obtained as sodium salts. Sodium morpholyldithiocarbamate was prepared by the method of Gleu and Schwab [16]. The sodium salt was recrystallized from ethanol. The purity of the ligands was checked by elemental analysis and TLC technique.

Complexes were isolated by reacting chromium(III) salt with sodium salt of morpholine dithiocarbamic acid (Na–morph–dtc) or of piperidine dithiocarbamic acid (Na–pip–dtc) and acetylacetone / 8–hydroxyquinoline / glycine in stoichiometric ratios.

$Cr(pip\text{–}dtc)_2(acac)$ and $Cr(pip\text{–}dtc)_2(oxine)$

Aqueous solution of chromic(III) chloride, sodium piperidyldithiocarbamate and ethanolic solution of acetylacetone/oxine were allowed to react in 1:2:1 molar ratio. The compounds were separated out on vigourous shaking after some time. The separated compounds were filtered, washed with water, ethanol and ether and dried in vacuum over P_2O_5.

$Cr(pip\text{–}dtc)(acac)_2$ and $Cr(pip\text{–}dtc)(oxine)_2$

These compounds were obtained by the similar method as described above by reacting $CrCl_3 \cdot 6H_2O$, Na-pip-dtc and acac/oxine in 1:1:2 molar ratio.

$Cr(pip\text{–}dtc)_2(gly)$ and $Cr(pip\text{–}dtc)(gly)_2$

To an aqueous solution of chromic(III) chloride was added a mixture of aqueous solution of sodium piperidyldithiocarbamate and aqueous solution of glycine in stoichiometric ratios. The compounds separated out, on stirring for some time, were filtered, washed with water, ether and dried in vacuum over P_2O_5.

$Cr(pip\text{–}dtc)_3$

To an aqueous solution of chromic(III) chloride an aqueous solution of sodium piperidyldithiocarbamate was added in 1:3 molar ratio. The compounds separated, on stirring for 5 to 7 min, were filtered, washed with water, ethanol, ether and dried in vacuum over P_2O_5.

The complexes were recrystallized from chloroform solution. Similarly more complexes were prepared by the methods as described above with sodium morpholyldithiocarbamate. These are:

$Cr(morph\text{–}dtc)(gly)_2$, $Cr(morph\text{–}dtc)_2(gly)$, $Cr(morph\text{–}dtc)(acac)_2$, $Cr(morph\text{–}dtc)_2(acac)$, $Cr(morph\text{–}dtc)(oxine)_2$, $Cr(morph\text{–}dtc)_2(oxine)$ and $Cr(morph\text{–}dtc)_3$

Physical measurements

Microanalysis for carbon and hydrogen (Table 1) were performed at the USIC, University of Delhi, India. Analysis of chromium was done by atomic absorption spectroscopic method and that of sulphur by standard methods.

Magnetic susceptibility measurements were carried out by Gouy method using mercury tetrathiocyanatocobaltate(II), $Hg[Co(CNS)_4]$ as calibrant ($\chi_g = 16.44 \cdot 10^{-6}$ c.g.s.). The diamagnetic correction were calculated using Pascal's constants.

Table 1 Analytical data of chromium(III) complex

Complexes	Analysis / % Found (Calc.)			
	C	H	Cr	S
$Cr(pip\text{-}dtc)(gly)_2$	33.64 (33.33)	5.32 (5.00)	14.93 (14.44)	18.46 (17.77)
$Cr(pip\text{-}dtc)_2(gly)$	38.32 (37.58)	6.02 (5.59)	12.32 (11.63)	30.48 (28.63)
$Cr(pip\text{-}dtc)(oxine)_2$	57.94 (57.37)	5.23 (4.38)	11.13 (10.35)	12.89 (12.74)
$Cr(pip\text{-}dtc)_2(oxine)$	49.32 (48.74)	5.86 (5.22)	10.87 (10.05)	25.46 (24.75)
$Cr(pip\text{-}dtc)(acac)_2$	47.03 (46.60)	6.81 (6.31)	13.34 (12.62)	16.19 (15.53)
$Cr(pip\text{-}dtc)_2(acac)$	43.76 (43.22)	6.29 (5.93)	11.45 (11.01)	29.21 (27.11)
$Cr(pip\text{-}dtc)_3$	41.35 (40.60)	6.36 (5.63)	10.32 (9.77)	36.81 (36.09)
$Cr(morph\text{-}dtc))(gly)_2$	30.28 (29.83)	4.49 (4.41)	13.69 (14.36)	20.32 (17.67)
$Cr(morph\text{-}dtc)_2(gly)$	32.36 (31.92)	4.89 (4.65)	11.62 (11.52)	29.47 (28.38)
$Cr(morph\text{-}dtc)(oxine)_2$	55.18 (54.76)	4.80 (4.36)	10.79 (10.31)	13.36 (12.69)
$Cr(morph\text{-}dtc)_2(oxine)$	43.83 (43.76)	4.99 (4.41)	10.22 (9.98)	24.38 (24.56)
$Cr(morph\text{-}dtc)(acac)_2$	44.73 (43.47)	6.33 (5.79)	12.93 (12.56)	15.29 (15.45)
$Cr(morph\text{-}dtc)_2(acac)$	38.32 (37.81)	5.89 (5.04)	11.46 (10.92)	30.00 (26.89)
$Cr(morph\text{-}dtc)_3$	34.12 (33.45)	5.02 (4.46)	9.87 (9.66)	36.24 (35.68)

Table 2 Magnetic moments / B.M. and physical properties

Complexes	Colour	μ_{eff} / B.M.	M.P. / °C
Cr(pip–dtc)(gly)$_2$	bluish grey	3.5	No change upto 250
Cr(pip–dtc)$_2$(gly)	bluish grey	3.5	No change upto 250
Cr(pip–dtc)(oxine)$_2$	dark green	4.2	120 dec.
Cr(pip–dtc)$_2$(oxine)	green	4.1	185 dec.
Cr(pip–dtc)(acac)$_2$	bluish grey	3.7	No change
Cr(pip–dtc)$_2$(acac)	bluish grey	3.7	153 dec.
Cr(pip–dtc)$_3$	grey	3.8	No change upto 250
Cr(morph–dtc)(gly)$_2$	bluish grey	4.3	295 dec.
Cr(morph–dtc)$_2$(gly)	bluish grey	3.8	235 dec.
Cr(morph–dtc)(oxine)$_2$	green	4.0	135 dec.
Cr(morph–dtc)$_2$(oxine)	light green	3.9	160 dec.
Cr(morph–dtc)(acac)$_2$	dark grey	4.1	234 dec.
Cr(morph–dtc)$_2$(acac)	dark grey	3.7	213 dec.
Cr(morph–dtc)$_3$	grey	3.8	168 dec.

Thermal studies were made on a SETARAM (Lyon, France) G–70 Thermobalance (sample size 20–40 mg) heating rate 7 deg·min^{-1}, flow rate of gas 10 ml·min^{-1}).

Thermogravimetric analysis

Thermogravimetric analysis provides rapid information concerning the thermal stability, composition of intermediates and the composition of the final product. The weight change is plotted on the ordinate with decreasing weight downwards and temperature (T) on the abscissa increasing from left to right. From TG trace, kinetic parameters such as activation energy and reaction order can be calculated. The method of Coats and Redfern [17] has been used for deriving kinetic parameters. This method assumes a rate law of the type:

$$\frac{d\alpha}{dt} = K(1-\alpha)^n \tag{i}$$

and an Arrhenius equation of the type

$$k = Z \cdot e^{-E/RT} \tag{ii}$$

to be valid, where α stands for the fraction transformed, n for the reaction order, K for the rate constant, E is the activation energy, R the gas constant and Z stands for pre-exponential or frequency factor and is independent of temperature T.

Integrating a combination of equations (i) and (ii) Coats and Redfern derived the equation:

$$\log\frac{F(\alpha)}{T^2} = \log\frac{ZR}{\beta E}\cdot\left(1-\frac{2RT}{E}\right) - \frac{E}{2.303RT} \tag{iii}$$

where β is the linear heating rate. The function $F(\alpha) = -\log(1-\alpha)$ for $n = 1$ and thus a plot of

$$-\log\left[\frac{-\log(1-\alpha)}{T^2}\right] \quad vs. \quad 1/T \quad \text{for } n = 1 \tag{iv}$$

results in a straight line of slope $-E/2.303R$ for the correct value of n, since for most values of E and for the temperature range over which reactions generally occur, the expression:

$$\log\frac{ZR}{\beta E}\cdot\left(1-\frac{2RT}{E}\right)$$

is constant.

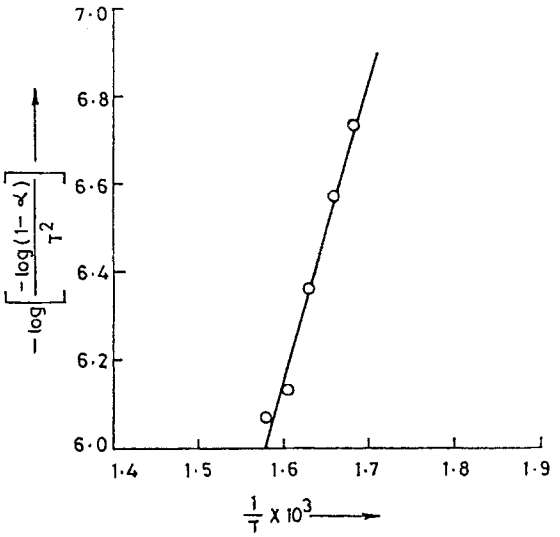

Fig. 1a Kinetic parameters from TG; Cr(pip–dtc)(glycine)$_2$

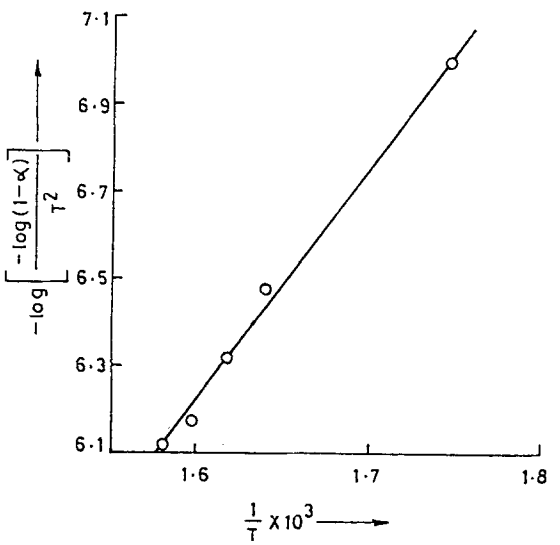

Fig. 1b Kinetic parameters from TG; Cr(pip–dtc)$_2$(glycine)

The complexes $Cr(pip\text{–}dtc)(gly)_2$, $Cr(pip\text{–}dtc)_2(gly)$, $Cr(pip\text{–}dtc)(oxine)_2$, $Cr(pip\text{–}dtc)_2(acac)$, $Cr(pip\text{–}dtc)_3$, $Cr(morph\text{–}dtc)(gly)_2$, $Cr(morph\text{–}dtc)_2(gly)$, $Cr(morph\text{–}dtc)(acac)_2$, $Cr(morph\text{–}dtc)_3$ remain stable up to 553, 523, 393, 423, 563, 573, 513, 513 and 413 K, respectively, then they

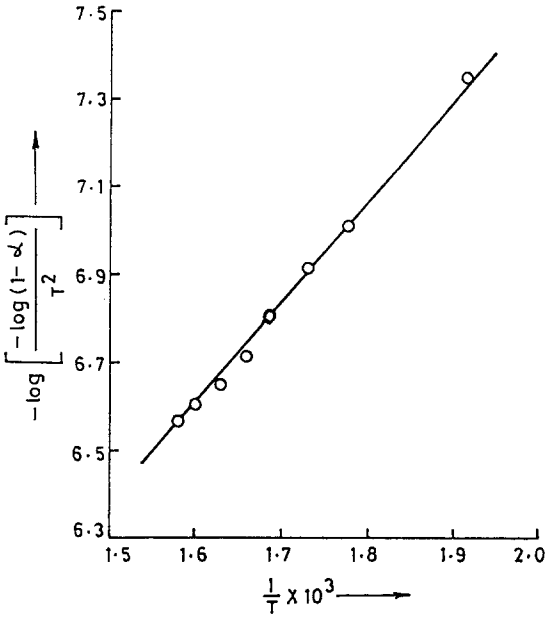

Fig. 1c Kinetic parameters from TG; $Cr(pip\text{–}dtc)(oxine)_2$

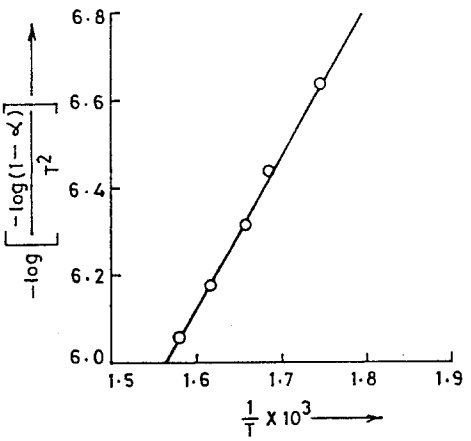

Fig. 1d Kinetic parameters from TG; $Cr(pip\text{–}dtc)_2(acac)$

start decomposing. The decomposition of these complexes continues upto 973, 913, 1203, 1033, 893, 873, 993, 953 and 973 K, respectively. The weight loss of 78.19% (calc. 78.88%) for $Cr(pip\text{–}dtc)(gly)_2$, 82.01% (calc. 82.93%) for $Cr(pip\text{–}dtc)_2(gly)$, 82.98% (calc. 84.77%) for $Cr(pip\text{–}dtc)(oxine)_2$,

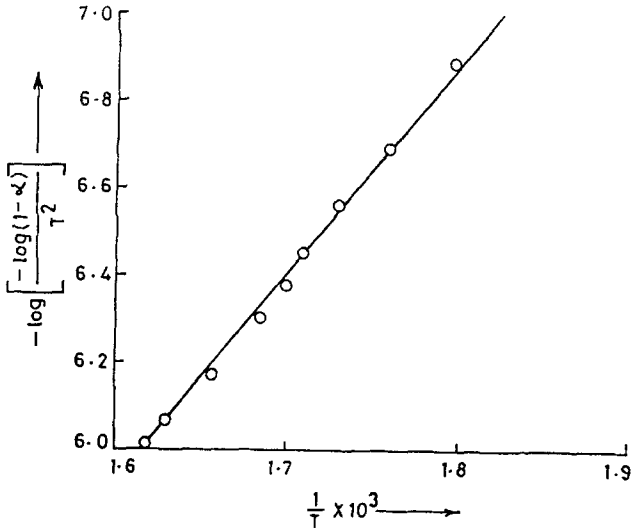

Fig. 1e Kinetic parameters from TG; $Cr(pip\text{–}dtc)_3$

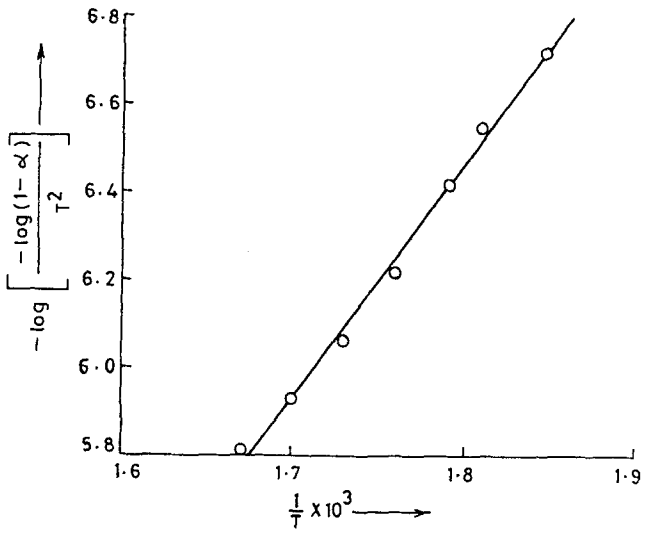

Fig. 1f Kinetic parameters from TG; $Cr(morph\text{–}dtc)(acac)_2$

Table 3a Kinetic parameters from TG for Cr(III) complex

T /	Cr(pip–dtc)(gly)$_2$			Cr(pip–dtc)$_2$(gly)			Cr(pip–dtc)(oxine)$_2$			Cr(pip–dtc)$_2$(acac)			Cr(pip–dtc)$_3$		
K	x	y	z	x	y	z	x	y	z	x	y	z	x	y	z
493	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
523	–	–	–	–	–	–	0.029	1.910	7.35	–	–	–	–	–	–
533	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
542	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
543	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
553	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
558	–	–	–	–	–	–	–	–	–	–	–	–	0.09	1.792	6.89
563	–	–	–	–	–	–	0.058	1.776	7.10	–	–	–	–	–	–
568	–	–	–	–	–	–	–	–	–	–	–	–	0.14	1.760	6.69
573	–	–	–	0.06	1.745	7.10	–	–	–	0.16	1.745	6.64	–	–	–
578	–	–	–	–	–	–	0.088	1.730	6.92	–	–	–	0.19	1.730	6.56
583	–	–	–	–	–	–	–	–	–	–	–	–	0.24	1.710	6.45
588	–	–	–	–	–	–	–	–	–	–	–	–	0.28	1.700	6.38
593	0.14	1.686	6.73	–	–	–	0.117	1.686	6.81	0.25	1.686	6.44	0.33	1.686	6.30
598	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
603	0.20	1.658	6.57	–	–	–	0.147	1.658	6.72	0.33	1.658	6.32	0.43	1.658	6.17
608	–	–	–	0.25	1.640	6.48	–	–	–	–	–	–	–	–	–
613	0.31	1.630	6.36	–	–	–	0.176	1.630	6.65	–	–	–	0.52	1.630	6.07
618	–	–	–	0.34	1.618	6.32	–	–	–	0.44	1.618	6.18	0.57	1.618	6.01
623	0.48	1.605	6.13	0.44	1.605	6.18	0.200	1.600	6.60	–	–	–	–	–	–
633	0.54	1.579	6.07	0.50	1.579	6.12	0.220	1.579	6.57	0.55	1.579	6.06	–	–	–
663	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–

where $x = \alpha; y = 1/T \cdot 10^3; z = -\log\left[\frac{-\log(1-\alpha)}{T^2}\right]$

Table 3b Kinetic parameters from TG for Cr(III) complex

T /	Cr(morph–dtc)(gly)$_2$			Cr(morph–dtc)$_2$(gly)			Cr(morph–dtc)(acac)$_2$			Cr(morph–dtc)$_3$		
K	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
493	–	–	–	0.05	2.021	7.05	–	–	–	–	–	–
533	–	–	–	0.09	1.876	6.80	–	–	–	–	–	–
542	–	–	–	–	–	–	0.12	1.845	6.72	–	–	–
543	–	–	–	–	–	–	–	–	–	0.20	1.841	6.48
553	–	–	–	0.14	1.808	6.67	0.18	1.808	6.55	0.24	1.760	6.41
558	–	–	–	–	–	–	0.30	1.792	6.42	–	–	–
563	0.04	1.776	7.25	–	–	–	–	–	–	–	–	–
568	–	–	–	–	–	–	0.36	1.760	6.22	–	–	–
573	0.08	1.745	6.96	0.19	1.745	6.55	–	–	–	–	–	–
578	–	–	–	0.23	1.730	6.46	0.48	1.730	6.07	0.35	1.730	6.25
583	0.12	1.715	6.79	–	–	–	–	–	–	–	–	–
588	–	–	–	–	–	–	0.60	1.700	5.93	–	–	–
593	0.16	1.686	6.67	0.41	1.686	6.18	–	–	–	0.45	1.686	6.13
598	0.20	1.672	6.57	–	–	–	0.72	1.672	5.81	–	–	–
603	0.24	1.658	6.48	–	–	–	–	–	–	–	–	–
608	0.32	1.644	6.34	–	–	–	–	–	–	–	–	–
613	0.36	1.631	6.29	–	–	–	–	–	–	–	–	–
618	0.44	1.618	6.18	–	–	–	–	–	–	–	–	–
623	–	–	–	0.46	1.605	6.16	–	–	–	–	–	–
663	–	–	–	0.53	1.508	6.12	–	–	–	–	–	–

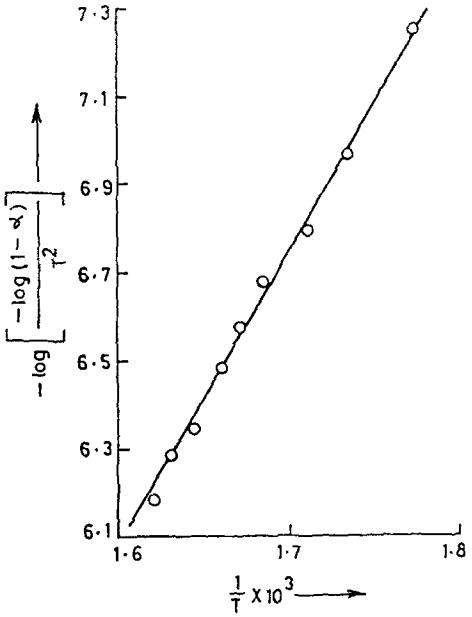

Fig. 2a Kinetic parameters from TG; Cr(morph–dtc)$_3$

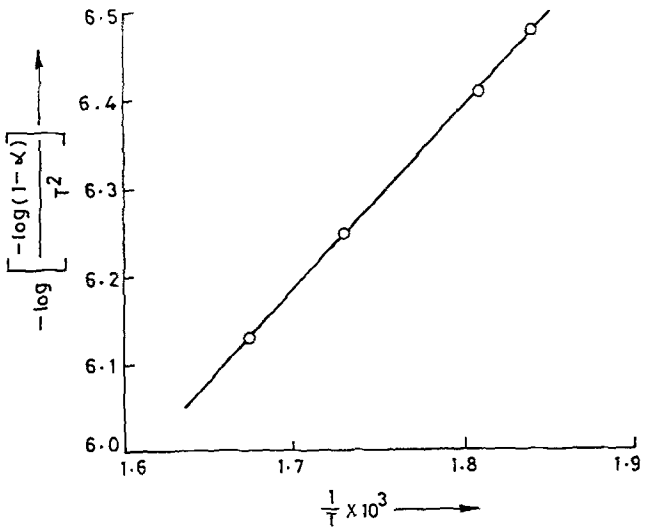

Fig. 2b Kinetic parameters from TG; Cr(morph–dtc)$_2$(glycine)

82.68% (calc. 83.88%) for Cr(pip–dtc)$_2$(acac), 84% (calc. 85.7%) for Cr(pip–dtc)$_3$, 76% (calc. 76.3%) for Cr(morph–dtc)(gly) 83.59% (calc.

83.14%) for Cr(morph–dtc)$_2$(gly), 81.95% (calc. 81.5%) for Cr(morph–dtc)(acac), (84.03% calc. 85.85%) for Cr(morph–dtc)$_3$ corresponds to the formation of Cr_2O_3 finally. The relevant data needed for plotting the linearization curves are recorded in Tables 3(a) and 3(b) and the linearization plot is shown in Fig. 1a-f and Fig. 2a-c.

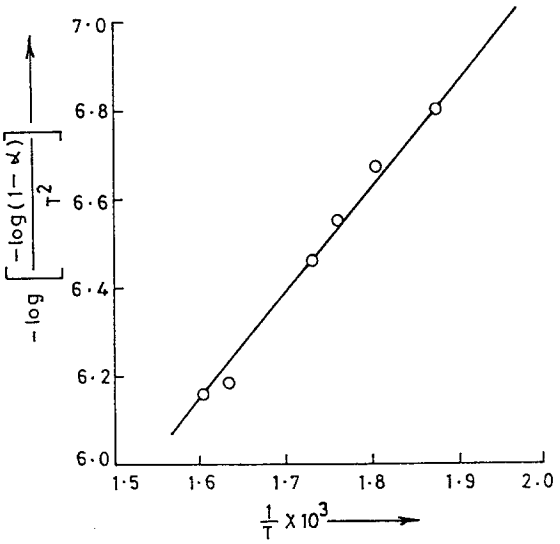

Fig. 2c Kinetic parameters from TG; Cr(morph–dtc)(gly)$_2$

The thermal data of all the complexes together with activation energy values are given in Table 4. The order of reaction in each case is one. The complexes Cr(pip–dtc)(oxine)$_2$ and Cr(morph–dtc)$_2$(gly) and Cr(morph–dtc)$_2$(gly) have the lowest value of activation energy.

Table 4 Thermal data for mixed ligand chromium(III) complexes

Complex	Temp. range / K	Order of reaction / n	E / kcal·mol^{-1}
Cr(pip–dtc)(gly)$_2$	553– 973	1	27.45
Cr(pip–dtc)$_2$(gly)	523– 913	1	24.40
Cr(pip–dtc)(oxine)$_2$	393–1203	1	10.98
Cr(pip–dtc)$_2$(acac)	423–1033	1	16.01
Cr(pip–dtc)$_3$	563– 893	1	23.53
Cr(morph–dtc)(acac)$_2$	513– 953	1	25.62
Cr(morph–dtc)(gly)$_2$	573– 873	1	31.37
Cr(morph–dtc)$_3$	413– 973	1	18.30
Cr(morph–dtc)$_2$(gly)	513– 993	1	10.98

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Zusammenfassung — Es wurden Chrom(III)-komplexe des Typs $Cr(A)(A')_2$, $Cr(A)_2(A')$ und $Cr(A)_3$ (wobei A entweder Piperidyldithiocarbamat oder Morpholyldithiocarbamat und A' Glycin, Oxin oder Acetylaceton ist) hergestellt. Die Mischligandenkomplexe wurden mittels Elementaranalyse, Messungen der magnetischen Suszeptibilität und durch thermische Untersuchungen beschrieben. Die Komplexe weisen ein magnetisches Moment im Bereich 3.5–4.3 B.M. auf, was drei ungepaarten Elektronen entspricht. Es wurden auch TG-Untersuchungen durchgeführt, um die Art und Weise der Zersetzung der Komplexe zu untersuchen und verschiedene kinetische Parameter zu bestimmen.