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THERMAL DECOMPOSITION KINETICS OF SOME METAL COMPLEXES OF N,N-DIETHYL-N'-BENZOYLTHIOUREA

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Abstract

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed on the complexes with general formula (M(DEBT)$_n$ (where *M*=Fe, Co, Ni, Cu or Ru; *n*=2, or 3 and DEBT=N,N-diethyl-N'-benzoylthiourea). Derivative thermogravimetric (DTG) curves were also recorded in order to obtain decomposition data on the complexes. The complexes of Fe(III), Co(II), Ni(II), Cu(II) and Ru(III) displayed two- or three-stage decomposition patterns when heated in a dynamic nitrogen atmosphere. Mass loss considerations relating to the decomposition stages indicated the conversion of the complexes to the sulfides or to the corresponding metal alone (Cu, Ru, NiS, CoS or FeS). Mathematical analysis of the TG and DTG data showed that the order of reaction varied between 0.395 and 0.973. Kinetic parameters such as the decomposition energy, the entropy of activation and the pre-exponential factor are reported.

Keywords: kinetics, metal complexes

Introduction

N,N-Diethyl-N'-benzoylthiourea (DEBT) is a selective analytical reagent, especially for the determination of transition metals in complex interfering matrices [1, 2]. The complexation capacity of DEBT has been reported in several papers [3, 4]. However, there is no information on their thermal decomposition in the literature.

In this study, thermoanalytical data (TG, DTA and DTG) were obtained on the Fe(III), Co(II), Ni(II), Cu(II) and Ru(III) complexes of DEBT. The interpretation and the mathematical analysis of these data and the energy and the entropy of activation were based on the integral methods involving the Coats-Redfern equation [5, 6] and the approximation methods involving the Horowitz-Metzger equation [7–9]. The Horowitz-Metzger equation was also used to establish the order of reaction.

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Experimental

Chemicals

DEBT and the complexes $M(DEBT)_n$ (where *M*=Fe(III), Co(II), Ni(II), Cu(II) or Ru(III), *n*=2 or 3) were prepared by the methods described previously [4]. All chemicals used in the syntheses were of analytical reagent grade or extra pure.

Instruments

TG/DTA experiments on the five solid complexes were carried out with a Shimadzu DT-40 thermal analyser equipped with a simultaneous TG/DTA module under a dynamic nitrogen atmosphere (50 ml min^{-1}) at a heating rate of 10 K min^{-1} in the temperature range 298–1273 K. The mass of complexes was 5–10 mg in a platinum crucible; α-Al_2O_3 was used as a reference substance.

X-ray powder diffraction analyses of the final residues were made with a Phillips PW1010 model generator, using CuK_α radiation (λ=1.5406 Å).

GC-MS analyses were carried out by means of a Hewlett-Packard 5890 HP model gas chromatograph and a 5971 HP-1 capillary column at a heating rate of 15 K min^{-1}.

Decomposition kinetics

The thermal behaviour of these chelates was studied in detail. The TG traces exhibited two- and three-stage decomposition patterns. The mass losses and X-ray diffraction data indicated that the end-products were the sulfide or the metal itself.

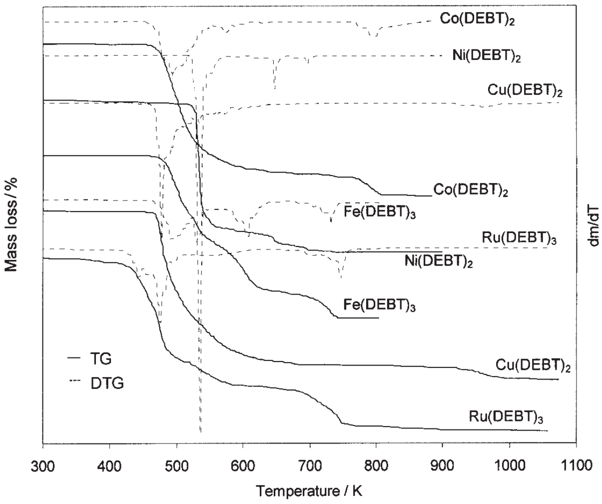

Fig. 1 TG/DTG curves of $Fe(DEBT)_3$, $Co(DEBT)_2$, $Ni(DEBT)_2$, $Cu(DEBT)_2$ and $Ru(DEBT)_3$ in nitrogen

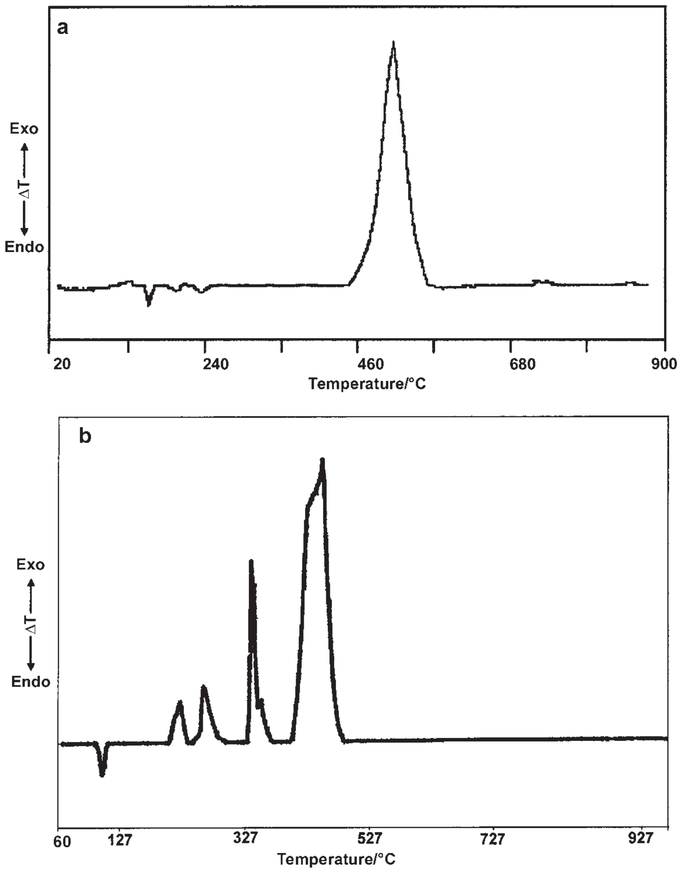

Fig. 2 DTA curves of a – Ru(DEBT)$_3$ and b – Fe(DEBT)$_3$

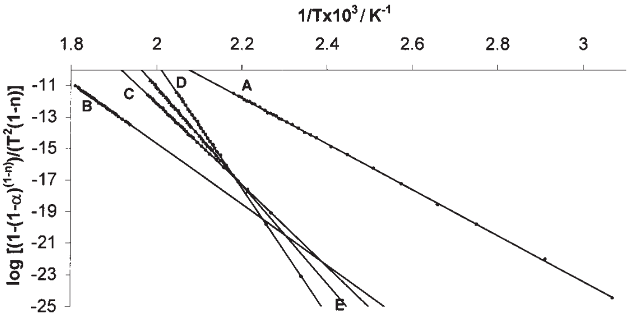

Fig. 3 Coats-Redfern plots of A – Ru(DEBT)$_3$; B – Ni(DEBT)$_2$; C – Fe(DEBT)$_3$; D – Cu(DEBT)$_2$ and E – Co(DEBT)$_2$ for stage Ia

The TG curves were redrawn as the rate of mass loss *vs.* temperature in order to obtain DTG curves. Typical TG/DTG curves for all the metal chelates examined are shown in Fig. 1, with the DTA curves of Ru(DEBT)$_3$ and Fe(DEBT)$_3$ in Fig. 2. The DTG decomposition temperature ranges for the metal chelates are presented in Table 1.

Table 1 Thermal decomposition data

Substance	Stage	Peak temp. in DTG/K	Temp. ranges in TG/K	Mass loss/%		Evolved moiety
				TG	theoret.	
Fe(DEBT)$_3$	Ia	493	441–505	23.33	23.27	DEB
	Ib	530	505–553	23.37	23.27	DEB
	Ic	608	553–617	23.29	23.27	DEB
	II	732	617–751	19.51	18.66	2SCN+CN
	Residue	–	>751	10.5	11.5	FeS
Co(DEBT)$_2$	Ia	493	451–503	33.66	33.48	DEB
	Ib	577	503–595	33.18	33.48	DEB
	II	802	595–884	15.80	15.88	SCN+CN
	Residue	–	>884	17.4	17.2	CoS
Ni(DEBT)$_2$	I	535	516–552	67.03	66.97	2DEB
	II	648	552–656	11.07	10.97	SCN
	III	696	656–749	4.83	4.92	CN
	Residue	–	>749	17.1	17.1	NiS
Cu(DEBT)$_2$	Ia	476	427–488	33.43	33.18	DEB
	Ib	535	488–551	32.93	33.18	DEB
	II	969	551–959	21.58	21.74	2SCN
	Residue	–	>959	12.1	11.9	Cu
Ru(DEBT)$_3$	Ia	446	326–458	22.34	21.96	DEB
	Ib	476	458–571	44.68	43.92	2DEB
	II	748	571–802	20.62	21.59	3SCN
	Residue	–	>802	12.4	12.5	Ru

Two methods were used to evaluate the kinetic data from these TG traces: the Coats-Redfern and Horowitz-Metzger methods. For a first-order process, the Coats-Redfern equation may be written in the form

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right]=\log\left[\frac{AR}{\phi E^*}\left(1-\frac{2RT}{E^*}\right)\right]-\frac{E^*}{2.303RT} \qquad (1)$$

Since the term $1-2RT/E^*$ is ~1, a plot of the left-hand side of Eq. (1) *vs.* $1/T$ was drawn. The E^* values were calculated from the first decomposition step of the slope in Fig. 3 and the A value was determined from the intercept. The Horowitz-Metzger equation may also be written in the form

$$\ln\left[\frac{1-(1-\alpha^{1-n})}{1-n}\right]=\frac{E^{*}\theta}{RT_{s}^{2}} \tag{2}$$

where θ is the difference between the given temperature T and T_s, where T_s is the temperature corresponding to the maximum decomposition rate. A plot of $\ln[(1-(1-\alpha^{1-n}))/(1-n)]$ *vs.* θ was drawn and the slope E^* was calculated for the curve, which was found to be linear. Typical plots for the first decomposition steps are given in Fig. 4.

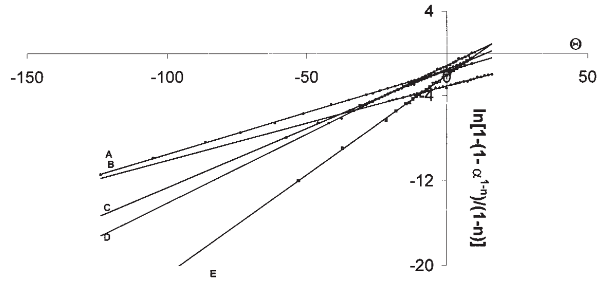

Fig. 4 Horowitz-Metzger plots of A – $Ru(DEBT)_3$; B – $Ni(DEBT)_2$; C – $Fe(DEBT)_3$; D – $Cu(DEBT)_2$ and E – $Co(DEBT)_2$ for stage Ia

Results and discussion

All complexes were studied by TG from ambient temperature to 1273 K under a nitrogen atmosphere. The temperature ranges, the percentage mass losses during the decomposition, the maximum decomposition temperature (DTG max), and the theoretical percentage mass losses are listed in Table 1. The overall loss in mass from the TG curves was 83% for $[Ni(DEBT)_2]$, 88% for $[Cu(DEBT)_2]$, 83% for $[Co(DEBT)_2]$, 90% for $[Fe(DEBT)_3]$, and 88% for $[Ru(DEBT)_3]$. These complexes do not contain

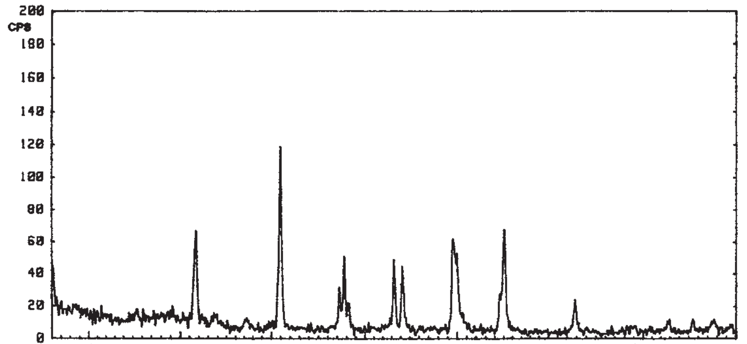

Fig. 5 XRD curves of end-product of $Ni(DEBT)_2$

any water molecule and there is no detectable change in the TG curves up to 373 K. The thermal curves obtained for the five compounds are similar in character.

It was found from TG/DTA on the complexes of Co(II), Ni(II) and Cu(II), which have a square planar structure, that they decompose in two or three stages. The end-products remaining after pyrolysis were identified by X-ray powder diffractometry. They consist of the metal sulfide or the metal itself. The diffraction pattern of the end-product (NiS) of the pyrolysis of the Ni(II) complex can be seen in Fig. 5 as an example.

For kinetic analysis of the pyrolysis reactions revealed by the TG analysis, a computer program in BASIC was written [10]. The program accepts as data only the percentage mass change and the related temperature, and it converts TG data to DTG data. The same program calculates the degree of a pyrolytic reaction, the energy of activation, the pre-exponential factor and the activation entropy through the kinetic methods of Horowitz-Metzger and Coats-Redfern. The computer program was tested with the known data for the pyrolysis of $CaCO_3$.

The results of the analysis showed that the degrees of the main decomposition reactions are close to unity, and the kinetic results obtained with the two methods are in agreement with each other (Table 2).

When the activation energy of thermal decomposition and the ionic radius of Co(II), Ni(II) or Cu(II) are compared, an inverse relationship is to be expected. As the radius decreases, the activation energy should increase [6, 11]. The complexes of Cu(II) and Co(II) decompose through similar mechanisms, and the activation energy does in fact increase with decreasing radius.

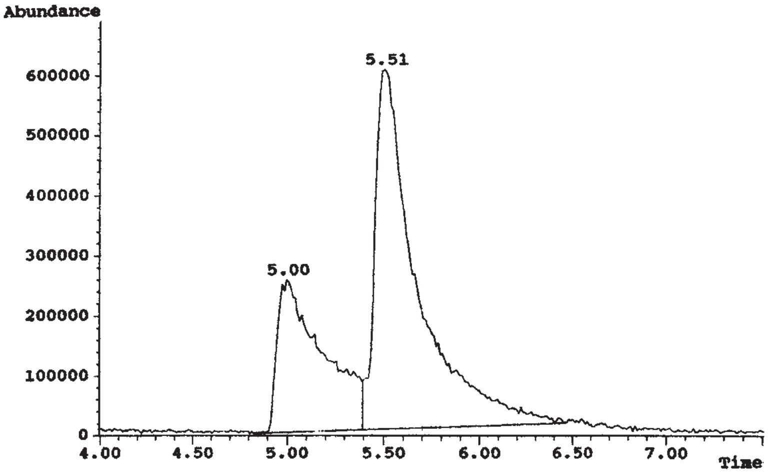

Fig. 6 GC-MS chromatogram of $Ru(DEBT)_3$

The ionic radii and the activation energies obtained by the Coats-Redfern method for the first stage of decomposition of the Cu(II) and Co(II) chelates are given below [12]:

$$E^{*}_{\mathrm{Cu}}=330.3\ \mathrm{kJ\ mol^{-1}}\ (r_{\mathrm{Cu}}=69\ \mathrm{pm}) > E^{*}_{\mathrm{Co}}=258.0\ \mathrm{kJ\ mol^{-1}}\ (r_{\mathrm{Co}}=74\ \mathrm{pm})$$

A decrease in radius of the metal ion allows the ligand to approach the central metal atom more easily, resulting in a stronger bonding interaction between the metal and the ligand. The strengthening of the bonding hampers cleavage of the bond and E^* increases [10, 11].

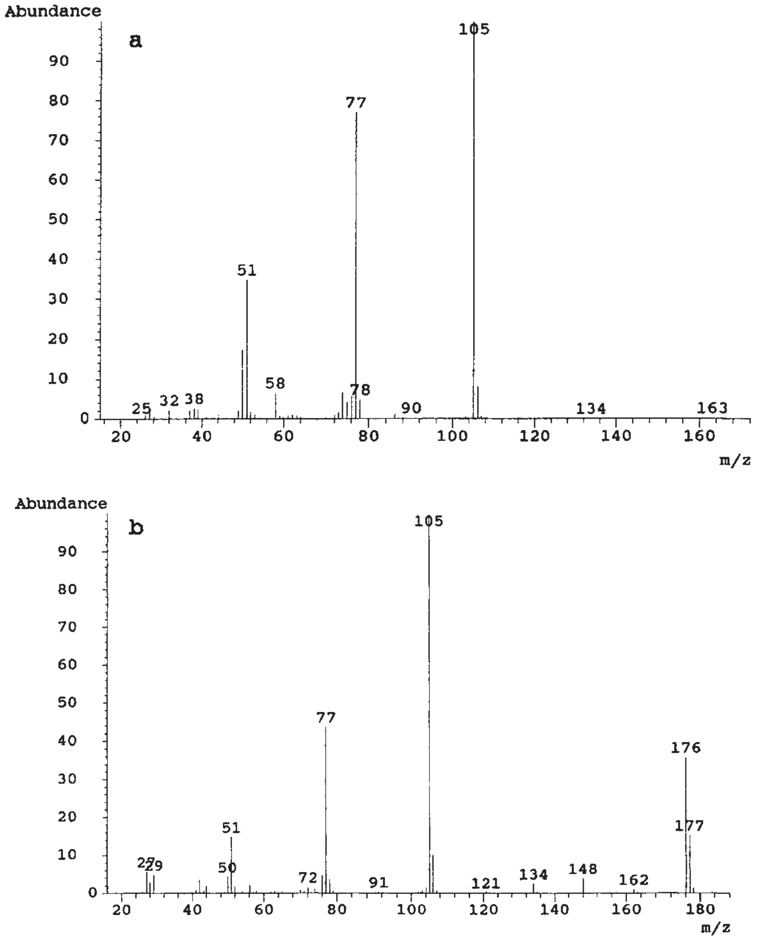

Fig. 7 Mass spectra of Ru(DEBT)$_3$; a – the peak at t_R=5 and b – the peak at t_R=5.51

One molecule of diethylbenzamide ($C_6H_5CON(C_2H_5)_2$; DEB) leaves the Cu(II) and Co(II) complexes in the first decomposition stage. Two molecule of DEB leave the Ni(II) complex in the first decomposition stage. The activation energy of this decomposition stage for the Ni(II) complex is 160.3 kJ mol^{-1}.

The Fe(III) and Ru(III) complexes with octahedral structures, require energies of 215.3 and 121.1 kJ mol^{-1}, respectively, for the loss of 1 molecule of DEB in the first stage. All the complexes under examination were analyzed via their GC chromatograms and the mass spectra in the interval 333–533 K. Because of the similarity in the decomposition processes of these metal chelates, for simplicity only the GC chromatogram and the mass spectrum of Ru(DEBT)$_3$ at different retention times are given in Figs 6 and 7, respectively.

It is observed that the decrease in metal ionic radius on going from Ru(III) to Fe(III) (with the same geometry) led to an increased activation energy of decomposition of the complex. The activation energies of decomposition of the Fe(III) and Ru(III) complexes and the related radii of the metal ions can be compared:

$$E^*_{\mathrm{Fe}}=215.3\ \mathrm{kJ\ mol^{-1}}\ (r_{\mathrm{Fe}}=64\ \mathrm{pm})> E^*_{\mathrm{Ru}}=121.1\ \mathrm{kJ\ mol^{-1}}\ (r_{\mathrm{Ru}}=69\ \mathrm{pm})$$

The first mass loss observed in the TG curves of the complexes relates to the formation of the metal thiocyanate. This occurs for Ni(II) in one step, and for Cu(II), Co(II) and Ru(III) in two steps (Ia and Ib). The corresponding product for the Fe(III) complex is formed in three steps (Ia, Ib and Ic). In general, the decomposition begin at approximately 430 K, with a rapid mass loss above 66%. The calculated mass losses show close agreement with the experimental values. Consequently, the mass loss in this stage is attributed to the evolution of DEB.

Table 2 Kinetic data

Complex	Stage	Reaction order	Parameters	From Coats-Redfern eqn.	From Horowitz-Metzger eqn.
Fe(DEBT)$_3$	Ia	0.804	E^*	215.3	230.0
			A	$7.35\cdot10^{20}$	$2.51\cdot10^{22}$
			ΔS^*	175.9	179.7
			r	0.9991	0.9993
	Ib	0.823	E^*	124.0	129.0
			A	$1.35\cdot10^{10}$	$4.02\cdot10^{10}$
			ΔS^*	–26.6	–46.7
			r	0.9967	0.9966
	Ic	0.785	E^*	149.8	161.2
			A	$8\cdot10^{10}$	$8.71\cdot10^{11}$
			ΔS^*	–41.3	–22.2
			r	0.9991	0.9994
	II	0.727	E^*	199.6	207.6
			A	$1.76\cdot10^{12}$	$5.60\cdot10^{12}$
			ΔS^*	10.8	8.3
			r	0.9943	0.9946

Table 2 Continued

Complex	Stage	Reaction order	Parameters	From Coats-Redfern eqn.	From Horowitz-Metzger eqn.
Co(DEBT)$_2$	Ia	0.794	E^*	258.0	259.8
			A	$7.24\cdot10^{25}$	$6.7\cdot10^{25}$
			ΔS^*	271.4	245.3
			r	0.9972	0.9986
	Ib	0.817	E^*	41.9	44.4
			A	34.4	64.4
			ΔS^*	–194.2	–215.2
			r	0.9978	0.9985
	II	0.924	E^*	261.5	270.7
			A	$1.74\cdot10^{15}$	$6.2\cdot10^{15}$
			ΔS^*	68.1	49.3
			r	0.9981	0.9975
Ni(DEBT)$_2$	I	0.973	E^*	160.4	166.0
			A	$7.9\cdot10^{13}$	$1.71\cdot10^{14}$
			ΔS^*	42.4	22.7
			r	0.9899	0.9890
	II	0.775	E^*	340.2	346.7
			A	$6.5\cdot10^{25}$	$1.8\cdot10^{26}$
			ΔS^*	270.6	251.4
			r	0.9750	0.9734
	III	0.705	E^*	79.6	88.9
			A	2466.7	12923
			ΔS^*	–158.7	–173.4
			r	0.9520	0.9602
Cu(DEBT)$_2$	Ia	0.807	E^*	330.3	359.0
			A	$1.50\cdot10^{34}$	$3.7\cdot10^{37}$
			ΔS*	430.7	470.3
			r	0.9940	0.9285
	Ib	0.897	E^*	78.7	84.5
			A	$44.4\cdot10^{4}$	$187.2\cdot10^{4}$
			ΔS*	–115.5	–129.5
			r	0.9930	0.9946
	II	0.398	E^*	111.77	124.9
			A	$3.2\cdot10^{7}$	$8.9\cdot10^{5}$
			ΔS^*	–79.9	–139.0
			r	0.9991	0.9800

Table 2 Continued

Complex	Stage	Reaction order	Parameters	From Coats-Redfern eqn.	From Horowitz-Metzger eqn.
Ru(DEBT)$_3$	Ia	0.827	E^*	121.1	131.8
			A	$1.5\cdot10^{12}$	$2.7\cdot10^{13}$
			ΔS^*	9.6	8.82
			r	0.9960	0.9972
	Ib	0.943	E^*	67.8	60.6
			A	$28.8\cdot10^{3}$	$12.8\cdot10^{3}$
			ΔS^*	–138.2	–170.4
			r	0.9886	0.9924
	II	0.642	E^*	118.9	136.5
			A	$1.5\cdot10^{6}$	$2.7\cdot10^{7}$
			ΔS^*	–105.35	–109.9
			r	0.9952	0.9967

Units of parameters: E^*=kJ mol^{-1}, A=s^{-1}, ΔS^*=J mol^{-1} K^{-1}, r=correlation coefficient of the linear plot, n=order of reaction

The decomposition of the Cu(II), Co(II), Fe(III) and Ru(III) complexes to metal thiocyanate are observed to occur in one, two or three steps; the first mass loss corresponds to the elimination of 1 DEB molecule, followed by the elimination of the remaining DEB molecules according to the oxidation numbers of the metals.

The activation entropies of pyrolysis of the complexes are all positive in the first decomposition stage. The endothermic peaks observed in the DTA studies stem from the stability of the reactant.

The activation energy of decomposition involving elimination of the second DEB molecule from the Co(II) and Cu(II) complexes increases with decreasing metal ionic radius. Only the activation energies of Co(II) and Cu(II) are compared here, because of the similarities of their second decomposition mechanisms, in which they both decompose in two steps, with elimination of 1DEB molecule in each step. The E^* values are 41.9 kJ mol^{-1} for the Co(II) and 78.7 kJ mol^{-1} for the Cu(II) complex. The E^* value for elimination of the second DEB from the Fe(III) complex is 124.0 kJ mol^{-1}. The corresponding value is 67.8 kJ mol^{-1} for the Ru(III) complex, where 2 molecules of DEB (the second and the third) are evolved simultaneously. 149.8 kJ mol^{-1} is necessary to eliminate the third and last molecule of DEB in the decomposition of the Fe(III) chelate. The second stage, including the elimination of SCN and CN groups, starts at 550–600 K, after the elimination of all DEB molecules in the first stage. The loss of these groups reveals different behaviour for each chelate in the second stage, but all groups leave in one step. The moieties evolved in this stage are 1SCN radical from the Ni(II) chelate, 2SCN radicals from the Cu(II) chelate, 2SCN and 1CN radicals from the Fe(III) chelate, 1SCN and 1CN radicals from the Co(II) chelate and 3SCN radicals from the Ru(III) chelate. Of all these chelates, only that of Ni(II) undergoes a third decomposition stage, in which a CN radical is evolved, leaving NiS behind. Finally, NiS, CoS, FeS, Ru and Cu are the end-products of the pyrolytic decompositions.

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