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TG, DTA AND ELECTRICAL CONDUCTANCE PROPERTIES OF SOME Cu(II) AND Mn(II) BISAZO-DIANILS COMPLEXES

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Abstract

The TG and DTA of a new series of Mn(II) and Cu(II) complexes with a number of newly prepared bisazo-dianil ligands were studied in the temperature range (20–700°C). The TG and DTG curves display to main steps, the first one within the temperature range (25–330°C) correspond to the elimination of water or and ethanol from the complexes. The second step within the range (350–625°C) is due to the decomposition of the complexes yielding the metal oxides as the final product. The rate constants of the dehydration and decomposition reactions were determined, from which some kinetic parameters were evaluated. The DTA curves show that the dehydration of the metal complexes is an endothermic reaction. In all cases the anhydrous metal complexes undergo exothermic decomposition reactions to give the metal oxide.

The thermodynamic parameters (ΔE, ΔH, ΔS, ΔG) for the occurring processes are calculated. The electrical conductivities of the solid complexes were measured and the activation energy of the complex and its free ligand are also calculated.

Keywords: bisazo-dianils, Cu(II) and Mn(II) complexes, electrical conductivity, thermal analysis

Introduction

TG is the simplest thermal analysis method. It can be utilized to determine the mode of thermal decomposition of a given substance, the temperature ranges for its stability, the determination of the rate constant of the thermal reactions and as well the evaluation of thermal kinetic parameters.

DTA is a technique by which the chemical reactions can be followed through observation of heat absorbed or liberated. It is especially suited for studies of structural changes within a solid at elevated temperature, where few other methods are available. Both methods are quite suitable to get a good idea about dehydration, dehydroxylation and amorphization of metal complexes [1].

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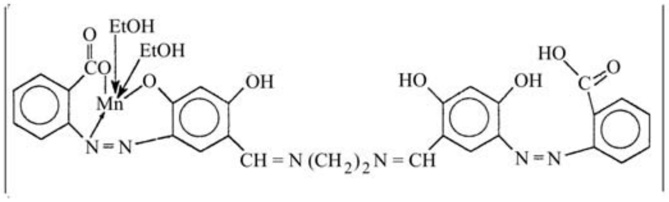
Differential thermal analysis studies are quite suitable for characterization of the composition of many organic compounds particularly for investigation of solid substrates [2]. The DTA quantitave measurement successfully determines the heat capacity changes as well as the heat of reaction and heat of evaporation, which all occur during the enthalpy changes of the material subjected to decomposition [3]. The stoichiometry of thermal decomposition and the relationship between the thermal parameters of complexes were studied by some authors [4]. Also the thermal behaviour of synthetic pyroaurite – like anionic clay with molar ratio Mg/Fe=2 was studied [5]. Thermal dissociation processes for clathretes [6], thermal analysis of fly ash-based zeolites [7] and TG/DTA/MS of poly(methyl methacrylate) [8].

The thermal analysis study of azo and azomethine complexes has been the subject of intense research in our laboratory for several years. Recently, the TG behaviour and also the electrical conductivity of solutions of the complexes containing two azo and two azomethine group in the same molecule were studied within the characterization of these complexes [9]. The bonding between the dianils ligand and some metal ions of certain biological importance was investigated. These metal complexes with dianils and bisazodianils were used as catalysts for oxygen reduction at the rotating carbon cathodes [10] and for hydrogenation of unsaturated hydrocarbons [11]. The thermodynamic parameters for the decomposition steps were calculated [11, 12].

Experimental

The preparations and structure of the complexes of bisazo dianil have been described before [9]. The DTA curves were recorded on DuPont instruments 990, 1200 DTA cell within the temperature range 20–700°C. The TG of the solid complexes were recorded on TA 50 WS1 thermal analysis TG cell and the electrical conductivity of the solid compounds was measured using a RM170 super megometec electrometer; compressed pellet 1.44 cm^2 in area and 0.42 cm thick were molded at 25°C at a pressure of 10 tons.

The complexes under investigation have the following structures:



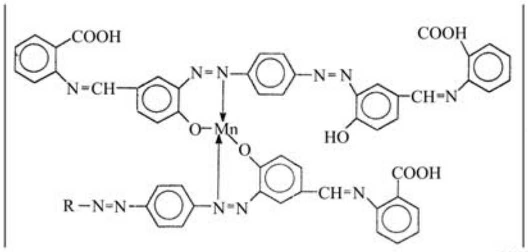
Square pyramidal

Results and discussion

TG and DTA study

Thermogravimetric analysis of the metal complexes under study was investigated before [9]. The results showed that the complexes lost their hydration water

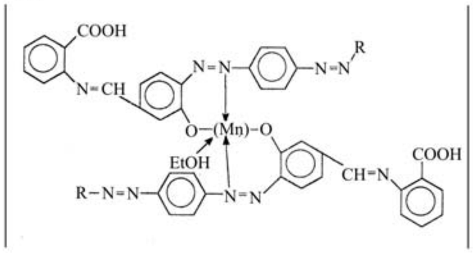
II)



2EtOH

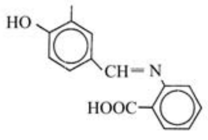
square planer

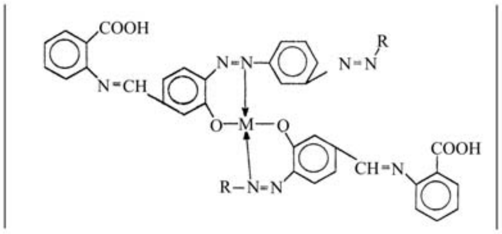
III)



square pyramidal

(II-V)R=

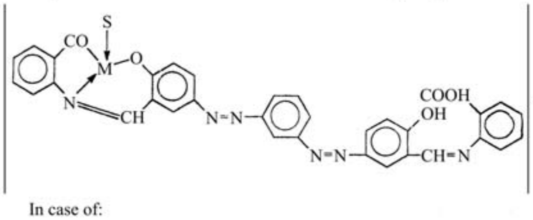




·n

In case of:

M	n	Geometrical structure
IV)=Cu^{2+}	=$5H_2O$	Square planar
V)=Mn^{2+}	=EtOH	Square planar



·n

In case of:

M	S	n	Geometrical structure
VI)=Cu^{2+}	=EtOH	=$2H_2O$	Square planar
VII)=Mn^{2+}	=2EtOH	O	Square planar

below 100°C. Within the temperature range 100–330°C, the coordinated water molecules were eliminated. The anhydrous complexes displayed the decomposition of the organic ligand within the temperature range 350–625°C leading to the metal oxide. The metal contents were calculated from the residue and were found to be in good agreement with the results of elemental analysis. The reactions representing the three steps in the thermal decomposition can be given as follows:

$$[MLS]\cdot n\mathrm{H_2O}\rightarrow[MLS]+n\mathrm{H_2O}\ \text{(below 100°C)}$$

$$[MLS]\rightarrow ML+S\ \text{(100–330°C)}\ S\text{=water or ethanol coordinated}$$

$$ML\rightarrow MO+[\mathrm{CO_2}+\mathrm{H_2O}]\ \text{(350–625°C) decomposition products of the ligand.}$$

The first step, with DTG peak in the 41–65°C range (Fig. 1), is related to volatilization of lattice water or ethanol molecules type and/or ethanol of coordination. In most complexes, a plateau is obtained after the first step which corresponds to the formation of stable dehydrated or desolvated metal complexes. In the second step of decomposition, the organic ligand is lost in the 350–611°C range with the formation of a stable metal oxide. The metal content was determined from the mass of the residual oxide which was found to agree well with analytical results within appropriate experimental errors.

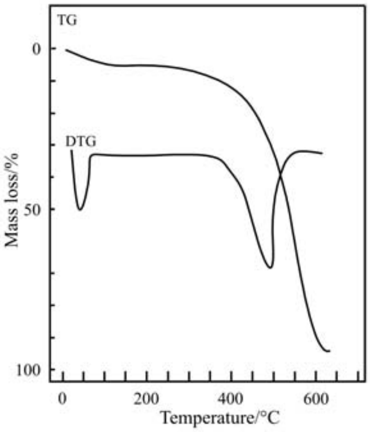


Fig. 1 TG and DTG curves of complex V

The order, n, and heat of activation, E^*, of the decomposition steps were determined using Coats–Redfern equations in the form [13, 14].

$$\ln\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right]=\frac{M}{T}+B\ \text{for}\ n\neq1 \tag{1}$$

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right]=\frac{M}{T}+B\ \text{for}\ n\neq1 \tag{2}$$

where $M = -E^*/R$ and $B = \ln AR/\Phi E^*$; E^*, R, A and Φ are the heat of activation, gas constant, pre-exponential factor and heating rate, respectively; the correlation factor, r, is computed using the least squares method for Eqs (1) and (2). Linear curves were drawn for values of n ranging from 0 to 2 in increments of 0.2. The value of n, which gave the best linear plot was chosen as the order parameter, for the decomposition stage of interest and the heat of activation was calculated from it's slope. The other activation parameters (ΔH^*, ΔS^* and ΔG^*) were calculated using standard equations [15]. The data are collected in Tables 1 and 2.

Table 1 Thermal data of the complexes investigated

Complex	Step	T_i	T_m	T_f	Mass loss (calcd.)/%
I $[MnH_4L(EtOH)_2]$	1st	25	62	100	12.40 (12.58)
	2nd	180	342	411	92.7 (93.1)
II $[Mn(H_3L)_2]\cdot 2EtOH$	1st	25	38	56	6.7 (7.3)
	2nd	173	550	589	95.3 (96.1)
III $[Mn(H_3L)_2]\cdot EtOH$	1st	27	48	70	3.4 (4.4)
	2nd	198	511	588	95.1 (95.4)
IV $[Cu(H_3L)_2]\cdot 3EtOH$	1st	25	46	58	9.6 (9.2)
	2nd	145	416	585	94.4 (96.5)
V $[Mn(H_3L)_2]\cdot EtOH$	1st	25	58	112	3.4 (4.6)
	2nd	350	480	611	95.1 (94.7)
VI $[Cu(H_2L(EtOH)_2]\cdot H_2O$	1st	25	50	110	4.7 (4.9)
	2nd	198	450	596	89.9 (91)
VII $[Mn(H_2L(EtOH)_2]$	1st	25	65	141	12.1 (11.6)
	2nd	203	465	575	91.4 (92.2)

The negative values of the activation entropy $\Delta\Sigma^*$ indicate a more activated complex than the reactants and/or the reactions are slower than normal [16].

There are no obvious trends in the values of E^* or the activation enthalpy ΔH^* However, the values of activation energy ΔG^* for the second stage of decomposition are higher than for the first stage which indicates that the rate of decomposition of the second stage is slower than that of the first [17]. This reflects the importance of $T\Delta S^*$ term, which is incorporated in ΔG^* in the decomposition of the complexed chelating agent. This may be attributed to the structural rigidity of chelating ligands as compared with H_2O and EtOH which requires more energy (i. e. $T\Delta\Sigma^*$) to get the correct ordered activated complex [15].

The DTA curves of all the solid complexes, represented in Fig. 2, indicate that the Cu(II) complexes show a weak endothermic peak at (33–41°C) and (45–55°C) assigned to the loss of EtOH and water molecules included in the crystal lattice for complexes IV and VI, respectively. Complex VI shows, a second endothermic peak at (70–240°C) due to the loss of coordinated EtOH molecules. Also, the exothermic peaks at (378–500°C)

Table 2 Kinetic parameters of the complexes investigated

Complex	Step	*n*	*r*	E^*/ kJ mol^{-1}	ΔH^*/ kJ mol^{-1}	ΔS^*/ kJ mol^{-1} K^{-1}	ΔG^*/ kJ mol^{-1}
I [$MnH_4L\cdot(EtOH)_2$]	1st	1.00	0.98696	47.79	45.01	–0.14	91.91
	2nd	2.00	0.98437	24.53	19.41	–0.19	136.26
II [$Mn(H_3L)_2\cdot 2EtOH$]	1st	1.00	0.99466	82.08	79.49	–0.11	113.40
	2nd	0.33	0.97932	46.59	39.57	–0.20	204.35
III [$Mn(H_3L)_2$]$\cdot$EtOH	1st	1.00	0.99751	102.60	99.93	–0.13	141.66
	2nd	1.00	0.99923	79.31	72.79	–0.19	221.75
IV [$Cu(H_3L)_2$]$\cdot$3EtOH	1st	1.00	0.98899	89.85	87.20	–0.11	122.29
	2nd	1.00	0.99353	23.87	18.14	–0.19	149.05
V [$Mn(H_3L)_2$]$\cdot$EtOH	1st	1.00	0.99588	37.27	34.52	–0.14	80.86
	2nd	1.00	0.99981	29.14	23.34	–0.20	162.94
VI [$CuH_2L\cdot(EtOH)_2$]$\cdot H_2O$	1st	1.00	0.98204	62.27	59.58	–0.12	98.34
	2nd	1.00	0.99327	84.09	78.08	–0.19	215.45
VII [$Mn(H_2L\cdot(EtOH)_2$]	1st	0.66	0.98524	35.755	32.95	–0.13	67.89
	2nd	1.00	0.99548	63.33	57.19	–0.21	212.17

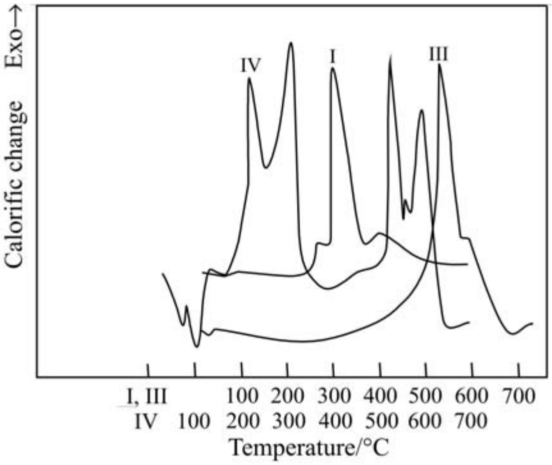


Fig. 2 DTA of the solid Cu(II) and Mn(II) complexes

and (500–600°C) for complexes IV and VI denote the decomposition and loss of the organic portion with subsequent formation of the metal oxide (CuO).

The DTA curves of the Mn(II) complexes II and III display broad endothermic peaks at (33–41°C) due to the loss of EtOH molecule included in the crystal lattice and at (51–180°C), (160–180°C) and (57–109°C) for the Mn(II) complexes I, V and VII due to the loss of coordinated EtOH and H_2O molecules. The strong exothermic peaks at (258–350°C), (300–525°C), (300–525°C), (400–430°C) and (260–460°C) for the Mn(II) complexes I, II, III, V and VII, respectively include the decomposition and loss of the organic portion with the formation of the metal oxide.

The thermodynamic parameters for the various decomposition steps are calculated according to the following equations:

$$\ln K = \ln A - \frac{E_a}{RT}$$

K is the reaction constant, A is the frequency factor, R=gas constant, and E_a the activation energy. Thus, $\ln K$ will vary linearly with $1/T$. This plot yields E_a from the slope.

Also

$$\ln\left(\frac{K}{T}\right) = \ln\left(\frac{K_B}{h}\right) + \frac{\Delta S}{R} - \frac{\Delta H}{RT}. \qquad [15, 16]$$

where K_B is Boltzmann's constant; h Planck's constant, R the gas constant. A plot of $\ln K/T$ will be a linear function of $1/T$; the slope yields ΔH. The intercept, after allowance for $\ln K_B/h=23.76$, provides the value of ΔS. The Gibbs free energy can be calculated from the equation.

$$\Delta G = \Delta H - T\Delta S$$

The data obtained are collected in Table 3. The curves and the calculated thermal parameters for the complexes show that the stability of these complexes depends on the nature of both the central metal ion and the ligand.

Effect of nature of the central ion

It can be seen from the curves that the thermal stability of Cu(II) complexes is higher than that for the corresponding Mn(II) complexes with the same ligands. The decomposition temperature of Cu(II) complexes IV and VI lies at 489 and 534°C, respectively but the Mn(II) complexes V and VII decompose to the oxide at 426 and 453°C, respectively. The thermal stability of the metal complexes was found to increase periodically with increase in atomic number of the metal and the larger value of charge/radius ratio [20].

Effect of nature of the ligand

The present study established some relationships between thermal stability and position of the functional group. The curves of Mn(II) complexes show that the complexes formed on terminal azo groups (I) are less stable than complexes formed on internal azo groups. Also complexes with two azo groups in *p*-position, as in complexes II, III, have higher thermal stability than complexes for ligands of two azo groups in the *m*-position; complex (V). The complexes formed through coordination with azo groups participated in chelation are less stable than complexes formed through coordination with the Schiff base part of the molecules i.e. bonding with the C=N group on complexation [9].

Electrical conductivity

The electrical conductivity of organic molecular solids differs in several important ways from that of its metal complexes. The electrical conductivity (σ) of a solid normally varies with temperature according to the Arrhenius equation.

$$\sigma = \sigma_0 \exp^{-(\Delta E / K_B T)}$$

where σ_0, ΔE and K_B are conductivity constants, the activation energy and the Boltzman constant, respectively.

The conductivity of the sample σ was obtained using the general formula [21].

$$\sigma = \frac{I}{vc} \frac{d}{a}$$

where (I) is the current in ampere, (vc) is the potential drop across the sample of cross-section area (a) and thickness (d).

Figure 3 shows the electrical conductivity as a function of (1000/T) of complex IV and its free ligand to compare between the conductivity of the free ligand and its complex and also the electrical conductivity of the free ligand of complex III to study the effect of position N=N groups on the electrical conductivity.

Table 3 The thermodynamic parameters (Δ*E*, Δ*H*, Δ*S*, Δ*G*) for the Cu(II) and Mn(II) complexes

Process	Thermal nature of process	T_{peak}/°C	Δ*E*/kJ mol^{-1}	Δ*H*/kJ mol^{-1}	Δ*S*/kJ mol^{-1}	Δ*G*/kJ mol^{-1}
I) $[MnH_4L(EtOH)_2]\rightarrow MnH_4L$	endo	51	9.8	8.4	–86	$46.7\cdot 10^3$
$MnH_4L\rightarrow MnO$	exo	314				
II) $[Mn(H_3L)_2]\cdot 2EtOH\rightarrow Mn(H_3L)_2$	endo	41	26.27	22.4	–182	$100.3\cdot 10^3$
$[Mn(H_3L)_2]\rightarrow MnO$	exo	498				
III) $[Mn(H_3L)_2]\cdot EtOH\rightarrow Mn(H_3L)_2$	endo	33	47.4	34.5	–181	$100.2\cdot 10^3$
$Mn(H_3L)_2\rightarrow MnO$	exo	448				
IV) $[Cu(H_3L)_2]\cdot 3EtOH\rightarrow Ca(H_3L)_2$	endo	107	38.4	37.35	–178	$106.8\cdot 10^3$
$Cu(H_3L)_2\rightarrow CuO$	exo	489				
V) $[Mn(H_3L)_2\cdot EtOH]\rightarrow Mn(H_3L)_2$	endo	180	47.9	39.6	–189	$16.5\cdot 10^3$
$Mn(H_3L)_2\rightarrow MnO$	exo	426				
VI) $[CuH_2L(EtOH)_2]\cdot H_2O\rightarrow [CuH_2L(EtOH)_2]$	endo	50	24.5	19.5	–49	53
$[CuH_2L(EtOH)_2]\rightarrow CuH_2L$	exo	93				
$CuH_2L\rightarrow CuO$	exo	534				
VII) $[MnH_2L(EtOH)_2]\rightarrow MnH_2L$	endo	57	49.8	41.5	–199.8	84
$MnH_2L\rightarrow MnO$	exo	453				

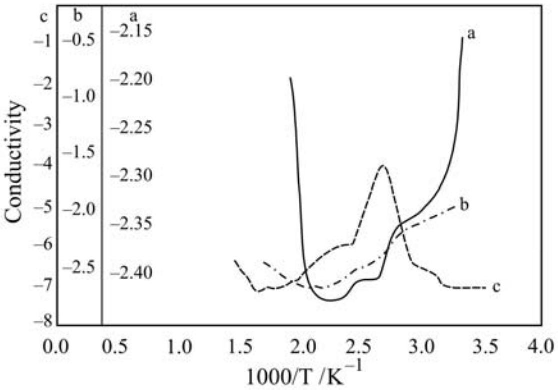


Fig. 3 D.c. Electrical conductivity *vs.* 1000/*T*. a – ligand of complex III, b – ligand of complex IV, c – complex IV

The electrical conductivity curve for the free ligand of complex IV shows that electrical conductivity decreased with increasing temperature up to 143°C (1000/*T*=2.4); above this temperature the electrical conductivity remained constant with incraesing temperature up to 220°C (1000/*T*=2.028). The conductivity of complex IV increased with temperature to 100°C (1000/*T*=2.7) after that the electrical conductivity decreased with increasing temperature up to 277°C (1000/*T*=1.82). The electrical conductivity remained constant with increasing temperature up to 330°C (1000/*T*=1.66), above which increase of conductivity with temperature was observed.

The electrical conductivity of the free ligand of complex III decreased with increasing temperature up to 144°C. The electrical conductivity was constant from 144–160°C, above 160°C the electrical conducivity increased.

The results show that the activation energy Δ*E* (3.39 eV) of the metal complex (IV) is higher than the activation energy Δ*E* (2.48 eV) of the free ligand, while the activation energy Δ*E* for the free ligand having N=N in *p*-position Δ*E* (1.99 eV) is lower than if N=N is in *m*-position Δ*E* (2.48) in the ligand.

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