COBALT, NICKEL AND COPPER COMPLEXES OF BENZYLAMINO-*p*-CHLOROPHENYLGLYOXIME
Thermal and thermodynamic data

H. Arslan

Department of Chemistry, Faculty of Arts and Sciences, Mersin University, Mersin, Turkey

Abstract

Vic-dioxime ligands and their metal complexes are used in analytical, bio, pigment and medicinal chemistry. Complexes of nickel(II), copper(II), and cobalt(II) with benzylamino-*p*-chlorophenyl-glyoxime (B*p*CPG) are synthesised. Thermal behaviour of these complexes was studied in dynamic nitrogen atmosphere by DTA, DTG and TG techniques. GC-MS combined system was used to identify the products during pyrolytic decomposition. The pyrolytic end products were identified by X-ray powder diffraction. Thermoanalytical data of these complexes are presented in this communication. Interpretation and mathematical analysis of these data and evaluation of order of reaction, the energy and entropy of activation based on the integral method using the Coats–Redfern equation and the approximation method using the Horowitz–Metzger equation are also given. The metal complexes undergo decomposition in three stages and metal oxides remained as end products of the complexes.

Keywords: benzylamino-*p*-chlorophenylglyoxime, complexes, thermal behaviour, thermal decomposition kinetics, thermodynamics

Introduction

Thermal analysis, although an old technique, is now proving useful in the interpretation and determination of different physical parameters such as inorganic and organic thermodynamics and reaction kinetics in different fields of study such as chemistry, polymer science, biology, medicine and pharmaceutics [1–7].

Metal complexes of the ligands containing sulfur and nitrogen as donor atoms are known to possess antiviral, bactericidal and carcinostatic activities [8, 9]. Vic-dioxime metal complexes are important as coordination compounds. These complexes have been of particular interest as biological model compounds [10, 11]. The synthesis of vic-dioxime and some of their transition metal complexes has been reported [12–14]. Vic-dioxime ligands and their metal complexes are used in analytical, bio, pigment and medicinal chemistry and the number of studies on the synthesis and properties of this kind of derivative compounds of oximes is increasing.

In previous studies vic-dioxime derivatives having such properties and their metal complexes are synthesised and their thermal behaviours are examined [15]. In this paper three typical complexes' of Ni(II), Cu(II) and Co(II) (benzylamino-*p*-chlorophenylglyoxime complexes) thermoanalytical data have been presented. Interpretation and mathematical analysis of those data and the energy and entropy of activation have been done based on the integral method using the Coats–Redfern equation [16], and the aproximation method using the Horowitz–Metzger equation [17].

Experimental

The synthesis of ligand and metal complexes is made as given in literature [18]. Metal solutions of Co(II), Ni(II) and Cu(II) ions are prepared from analytical purity reagents of $CoCl_2 \cdot 6H_2O$, $NiCl_2$ and $CuCl_2 \cdot 2H_2O$ salts. Metal complexes are obtained from the reactions of metal solutions with the alcoholic ligand solutions and solid complexes are filtered out from the liguid phase [18].

Apparatus

DTA and TG curves are obtained with Shimadzu DT-40 model simultaneously with DTA and TG apparatus. The heating rate and other characteristics are given below: heating rate: 10 K min^{-1}, atmosphere: nitrogen, flow rate of furnace atmosphere: 60 mL min^{-1}, crucible: platinum, sample size: 4 to 8 mg, reference substance: α-Al_2O_3.

A GC-MS system VG-ZabSpect model DFMS, was used to identify pyrolysis products evolved during heating. Microanalyses were obtained using a Carlo Erba MOD 11016 instrument. Infrared spectra were recorded in the region 4000–400 cm^{-1} on a Shimadzu 435 spectrophotometer, using KBr pellets. X-ray powder diffraction analyses of the final residues were made with a Siemens F model diffractometer. X-ray generator is Phillips, PW-1010 model and ranging from 20 to 40 kV and 6 to 50 mA while using fine focus CuK_α radiation (λ=1.5406 Å).

Thermal behaviour

The thermal behaviour of the above chelates were studied in detail. TG traces exhibit a three-stage decomposition pattern. Mass loss considerations and X-ray diffraction data indicated the products to be oxides.

TG curves were redrawn as % mass loss *vs*. temperature (TG) curves and also as the rate of loss of mass *vs*. temperature (DTG) curves. Typical TG, DTG and DTA curves are presented in Fig. 1 and the temperature ranges and percentage mass losses of the decomposition reaction are given in Table 1, together with the temperature of greatest rate of decomposition (DTG$_{max}$) and the theoretical percentage mass losses.

Table 1 Thermoanalytical results (TG/DTG/DTA) of Ni(II), Cu(II) and Co(II) of B*p*CPG complexes in nitrogen atmosphere

Complex	TG results		DTG results peak temp./K	DTA results peak temp./K	Mass loss/%		Evolved moiety
	Temp. range/K	Stage			found	calcd	
Ni(B*p*CPG)$_2$	382–524	I	504	500	29.16	29.54	C$_6$H$_5$–CH$_2$–NH–C≡N+2OH
	524–698	II	631	659	18.51	17.79	C$_6$H$_5$–CH$_2$–N=CH+NO
	698–912	III	848	833	41.03	41.42	2Cl–C$_6$H$_4$≡CN
	>912	residue			11.30	11.25	NiO
Cu(B*p*CPG)$_2$	403–511	I	452	442	31.75	29.32	C$_6$H$_5$–CH$_2$–NH–C≡N+2OH
	511–581	II	575	574	16.10	17.66	C$_6$H$_5$–CH$_2$–N=CH+NO
	581–810	III	720	718	39.90	41.13	2Cl–C$_6$H$_4$≡CN
	>810	residue			12.25	11.89	CuO
Co(B*p*CPG)$_2$ ·2H$_2$O	410–533	I	471	451	23.46	24.01	C$_6$H$_5$–CH$_2$–NH–C≡N+2H$_2$O
	533–590	II	574	576	27.00	26.01	C$_6$H$_5$–CH$_2$–N=CH+NO+2OH
	590–758	III	691	688	38.98	39.28	2Cl–C$_6$H$_4$≡CN
	>758	residue			10.56	10.70	CoO

Results and discussions

The thermal decomposition of the complexes was studied to investigate their thermal stability, purity and fragmentation pattern in the temperature range 298–1473 K. The thermal behaviour of the investigated compound in terms of intermediate and volatiles, based on the correspondence the calculated and the found values, are given in Table 1. The overall loss of mass from the TG curves is 87.8% for Cu(B*p*CPG)$_2$, 88.7% for Ni(B*p*CPG)$_2$ and 89.4% for Co(B*p*CPG)$_2$·2 H$_2$O.

Ni(II) complex underwent three steps decomposition (Fig. 1). In the first step, a loss in mass of 29.2% was observed in the temperature range 382–524 K, indicating the loss of C$_6$H$_5$–CH$_2$–NH≡CN and two OH groups from the system. In the 2nd step, a mass loss of 18.5% is involved due to the elimination of C$_6$H$_5$–CH$_2$–N=CH+NO from the system in temperature range 524–698 K. In the final step (698–912 K) 2Cl–C$_6$H$_4$–C≡N was eliminated causing a mass loss of 11.3%.

Cu(II) complex decomposes in three stages (Fig. 1). The first decomposition occurs between 403 and 511 K with 31.8% mass loss, the second decomposition occurs between 511 and 581 K with 16.1% mass loss and the third decomposition occurs between 581 and 810 K with 39.9% mass loss.
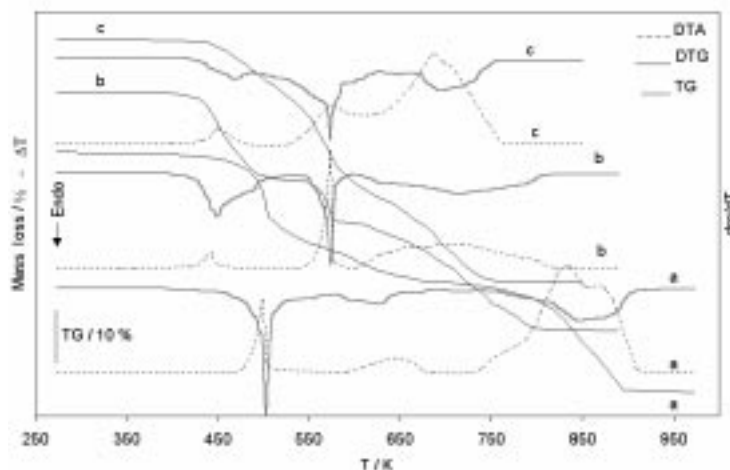

Fig. 1 Typical thermoanalytical curves of a – Ni(B*p*CPG)$_2$, b – Cu(B*p*CPG)$_2$ and c – Co(B*p*CPG)$_2$·2H$_2$O complexes in nitrogen atmosphere

B*p*CPG complexes of both Ni(II) and Cu(II) have a similar thermal decomposition mechanism which is expected since they both have a square-planar structure. These complexes do not contain any water molecule and there is no detectable change in TG curves upto 373 K. It may also be noted here the absence of dehydration peaks in the DTG curves and the absence of hydroxyl bands in the IR spectra indicate Ni(II) and Cu(II) complexes are anhydrous (Fig. 2). The microanalysis also supports these results (found: C, 54.3%, H, 3.9%, N, 12.3%; C$_{30}$H$_{26}$N$_6$O$_4$Cl$_2$·Ni re-
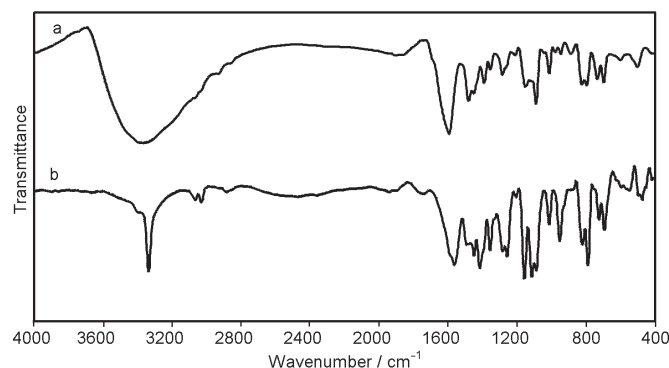
Fig. 2 IR spectra of a – Co(II)- and b – Ni(II)-benzylamino-*p*-chlorophenylglyoxime complexes

quires: C, 54.3%; H, 3.9%; N, 12.7% – found: C, 53.5%, H, 3.6%, N, 12.9%; $C_{30}H_{26}N_6O_4Cl_2 \cdot Cu$ requires: C, 53.9%; H, 3.9%; N, 12.6%).

The stages of decomposition for the nickel and copper complex which are in agreement with that of Arslan *et al.* and Burakevic *et al.* [15, 19, 20] and confirmed by GC-MS data (C_6H_5–CH_2–NH–C=N (132 *m/z*), C_6H_5–CH_2–N–CH (118 *m/z*), Cl–C_6H_4C=N (137 *m/z*)), TG data and X-ray powder diffraction data [21]. Figure 3 shows X-ray powder diffraction patterns of the end product of the Cu(II) complex as a sample data (ASTM, File No=5-661).
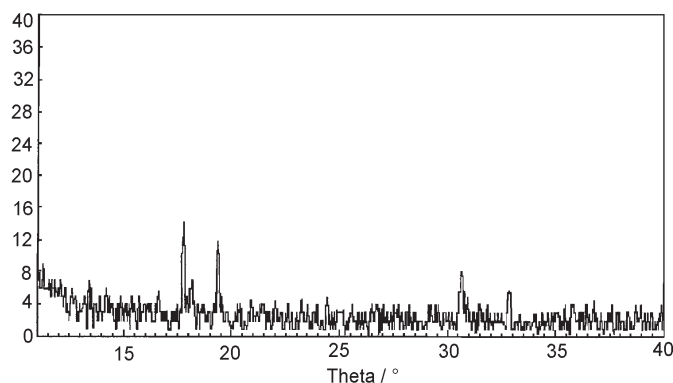

Fig. 3 X-ray powder diffraction pattern of CuO

Three-step decomposition was observed for Co(B*p*CPG)$_2$·2H$_2$O (Fig. 1). In the first step a 23.5% loss in mass due to loss of C_6H_5–CH_2–NH≡CN+2H$_2$O, in 2nd step a 27.0% loss in mass due to C_6H_5–CH_2–N=CH+NO+2OH groups whereas in 3rd step a 39.0% loss in mass due to 2 Cl–C_6H_4–C≡N group were observed in the temperature range 410–533, 533–590 and 590–758 K, respectively.

Co(II) complex which has an octahedral structure undergoes thermal decomposition in three stages and turns to CoO but gives different intermediate products (Table 1). CHN analysis of Co(II) complex shows that it has two moles hydrate water (found: C, 51.4%, H, 4.6%, N, 12.2%; $C_{30}H_{26}N_6O_4Cl_2 \cdot Co \cdot 2H_2O$ requires: C, 51.4%; H, 4.3%; N, 12.0%). IR measurements also support this result. The coordinated H_2O molecules of the Co(II) complex are identified by broad –OH absorption bands around 3350–3480 cm^{-1} which keep their intensities constant after heating at 110°C for 24 h (Fig. 2). These results are in good agreement with the theoretical decomposition mechanism. Beginning and end products were confirmed via IR spectrometric and X-ray diffraction data.

Decomposition kinetics

Two methods are mentioned in literature related to decomposition kinetics studies which are Coats–Redfern and Horowitz–Metzger and we used these two methods in our study. From the TG curves, the order *n*, activation energy E^*, entropies ΔS^*, and
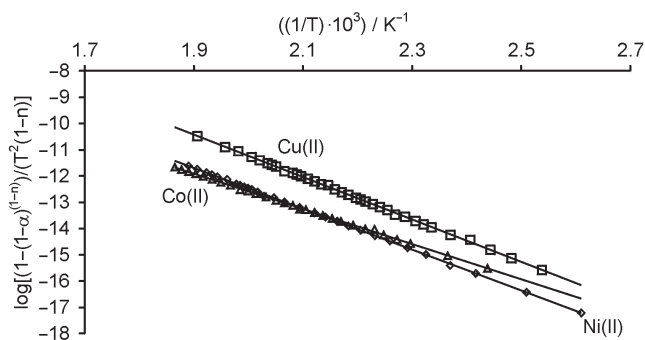

Fig. 4 Linearisation curves of the first decomposition steps of Coats–Redfern method for Co(II)-, Ni(II)-, Cu(II)-benzylamino-*p*-chlorophenylglyoxime complexes
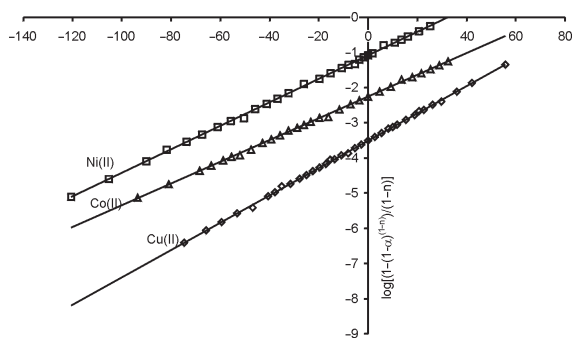

Fig. 5 Linearisation curves of the first decomposition steps of Horowitz–Metzger method for Co(II)-, Ni(II)-, Cu(II)-benzylamino-*p*-chlorophenylglyoxime complexes

pre-exponential factor *A*, of the thermal decomposition have been elucidated by the well-known methods.

Table 2 Kinetic data on the investigation compounds, obtained with the Coats–Redfern and the Horowitz–Metzger equation

Complexes	Radius of metal ion/ pm	Stage	Reaction order/*n*	Parameters*	Coats– Redfern equation	Horowitz– Metzger equation
Cu(II) complex	70	I	0.970	E^*	67.3	70.9
				A	189689.8	519710.4
				ΔS^*	−147.5	−139.3
				r	0.9985	0.9995
		II	0.889	E^*	77.8	93.3
				A	42695.9	218445.3
				ΔS^*	−161.6	−128.9
				r	0.8521	0.8856
		III	0.968	E^*	73.3	84.7
				A	435.7	2732.5
				ΔS^*	−173.1	−186.7
				r	0.9968	0.9942
Ni(II) complex	72	I	0.693	E^*	64.6	70.3
				A	27998.5	108019.3
				ΔS^*	−164.1	−152.9
				r	0.9760	0.9797
		II	0.708	E^*	79.9	78.5
				A	42654.8	16983.1
				ΔS^*	−134.9	−170.0
				r	0.9660	0.9757
		III	0.752	E^*	75.3	103.9
				A	44.6	3358.4
				ΔS^*	−192.0	−156.1
				r	0.9878	0.9919
Co(II) complex	74	I	0.890	E^*	55.9	64.9
				A	2699.4	27649.8
				ΔS^*	−157.9	−164.2
				r	0.9972	0.9969
		II	0.899	E^*	65.0	70.2
				A	3090.6	9281.3
				ΔS^*	−156.8	−174.5
				r	0.9938	0.9961
		III	0.654	E^*	65.6	84.8
				A	194.3	6923.3
				ΔS^*	−179.8	−178.5
				r	0.9984	0.9960

*Unit of parameters: E^*/kJ mol^{-1}, A/s^{-1}, ΔS^*/J mol^{-1} K^{-1}, *r* – correlation coefficient of the linear plot

The linearisation curves of Coats–Redfern and Horowitz–Metzger methods are shown in Figs 4 and 5, respectively. Kinetic parameters calculated by employing the Coats–Redfern and Horowitz–Metzger equations are summarised in Table 2, together with the radii of metal ions. The results show the values obtained by various methods are comparable.

The reaction order values are around one for each stage for complexes. The kinetic data reached by both of the methods are in harmony with each other. The activation energy of Co(II), Ni(II) and Cu(II) complexes is expected to increase in relation with decreasing in their radius [22]. Among these two complexes (nickel and copper) having the same square-planar geometry and similar decomposition steps, the smaller size of Cu(II) permits a closer approach of the ligand as compared to Ni(II). Hence E^* value for the Cu(II) complex higher than that of Ni(II) [23–26]. The same decomposition kinetics is also true for the second and third stages values, E^*.

The negative values of ΔS^* in these complexes indicate that the reactions are slower than normal, this trend has been supported by Özpozan *et al.* [27] and Arslan [20] studies [28]. In addition to that the activated complexes have a more ordered structure than the reactants [26].

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