

Thermal Decomposition Kinetics of Anilino-*p*-chlorophenylglyoxime Complexes of Cobalt (II), Nickel (II) and Copper (II)

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The Co(II), Ni(II) and Cu(II) complexes of anilino-*p*-chlorophenylglyoxime were synthesised. The thermal behaviour of all complexes was studied by DTA and TG. It was found that pyrolytic decomposition occurs with melting in metal complexes and that metal oxides remain as final products of the metal complexes. A GC-MS combined system was used to identify the products during pyrolytic decomposition. The pyrolytic end products were identified by x-ray powder diffraction. The orders, n , the activation energies, E^* , the pre-exponential factors, A , and the entropies, ΔS^* , of thermal decomposition reactions were derived from thermogravimetric and differential thermogravimetric curves. The kinetic analysis of the thermogravimetric data was performed by using the Coats-Redfern and Horowitz-Metzger methods.

Key Words: Anilino-*p*-chlorophenylglyoxime, Cu(II)-, Ni(II)- and Co(II)-complexes, Thermal behaviour, Thermal decomposition kinetic, Pyrolysis, DTA/TG/DTG

Introduction

Metal complexes of the ligands containing S and N as donor atoms are known to possess antiviral, bactericidal¹ and carcinostatic² activities. These ligands are also used as gravimetric reagents for the estimation of semi-noble metals such as Cu, Pd, Ag³, e.g. vic-dioximes.

Vic-dioximes such as dimethylglyoximes yield highly sensitive colour reactions with the transition metals in solutions^{3,4}. The transition metal complexes of vic-dioximes have been in particular interest as biological model compounds^{5,6}. On the other hand, some of the transition metals present in trace quantities (Co, Ni and Cu) are essential elements for biological systems. The synthesis of vic-dioximes and some of their transition metal complexes have been reported⁷⁻¹⁰. Recently, studies in analytical, bio, pigment and medicinal chemistry have increased because of the increasing use of coordination compounds.

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Pekacar et al. have previously reported the preparation of several vic-dioxime derivatives and coordination complexes with these ligands⁷. Some properties of vic-dioximes derivatives have been studied^{11–13}. However, the anilino-*p*-chlorophenylglyoxime (*Ap*CPG) metal complexes were not examined in this earlier work. Here we report the thermal decomposition characteristics of *Ap*CPG complexes of Cu(II), Ni(II) and Co(II). The order, activation energies, entropies and the pre-exponential factors of the thermal decomposition reactions have been determined from the thermogravimetric curves. The kinetic analysis of the data was performed using the Coats-Redfern and Horowitz-Metzger methods.

Experimental

Preparation of samples

The ligand and metal complexes were synthesised as given in the literature⁷. Metal solutions of Co(II), Ni(II) and Cu(II) ions were prepared by using analytical purity reagents of CoCl₂·6H₂O, NiCl₂ and CuCl₂·2H₂O salts. Metal complexes were obtained by mixing the reactions of metal solutions, with the alcoholic ligand solutions, and solid complexes were filtered out from the liquid phase.

Instrumentation

The DTA and TG curves were obtained by a Shimadzu DT-40 model equipped with DTA and TG units. The thermal analysis system was used over the temperature range of 273–1823 K (0–1550 °C). The samples were placed in Pt crucibles and α -Al₂O₃ was used as the reference material. Measurement was performed by using a dynamic nitrogen furnace atmosphere at a flow rate of 60 mL·min⁻¹. The heating rate was 10 K·min⁻¹ and the sample sizes ranged in mass from 6 to 8 mg.

A GC-MS system, VG-ZabSpect model DFMS was used to identify pyrolysis products evolving 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 equipped with an X-ray generator, Phillips, PW-1010 model ranging from 20 to 40 kV and 6 to 50 mA while using a fine focus CuK α radiation ($\lambda = 1.5406 \text{ \AA}$).

Results and discussion

Co(II), Ni(II) and Cu(II) complexes were studied by thermogravimetric analysis from ambient temperature to 800 K in nitrogen atmosphere. The range of temperature and percentage mass losses of the decomposition reaction are given in Table 1, together with the temperature of the greatest rate of decomposition (DTG_{max}) and the theoretical percentage mass losses. The thermal curves obtained for all the complexes examined were similar in character.

Ni(II) complex (C₂₈H₂₂N₆O₄Cl₂·Ni)

The TG studies of the Ni(II) complex of *Ap*CPG showed that the initial mass loss occurs at 455 K. Decomposition ends with a total of 88.5% mass loss at 740 K with a greenish-black solid residue corresponding to a mass of 11.5%. DTA/TG/DTG diagrams of the Ni(II) complex are shown in Figure 1.

Table 1. Thermoanalytical results of metal complexes of anilino-*p*-chlorophenylglyoxime.

Complexes	Stage	Temperature of DTA peak maximum (K)	DTG _{max} (K)	TG temperature range (K)	Mass loss (%)		Evolved moiety
					TG	Theoretical	
Cu(II) Complex	I	476	478	385-486	28.17	28.41	C ₆ H ₅ -NH-C≡N + 2OH + NO
	II	530	529	486-540	38.97	37.71	C ₆ H ₅ -N=CH + Cl-C ₆ H ₄ -C≡N
	III	651	655	540-741	20.51	21.47	Cl-C ₆ H ₄ -C≡N
	Residue	>741	-	-	12.35	12.41	CuO
Ni(II) Complex	I	523	524	455-568	29.63	28.63	C ₆ H ₅ -NH-C≡N + 2OH + NO
	II	589	588	568-609	38.88	38.00	C ₆ H ₅ -N=CH + Cl-C ₆ H ₄ -C≡N
	III	680	687	609-740	19.96	21.63	Cl-C ₆ H ₄ -C≡N
	Residue	>740	-	-	11.53	11.74	NiO
Co(II) Complex	I	450	445	395-514	33.02	32.45	C ₆ H ₅ -NH-C≡N + 2OH + NO + 2H ₂ O
	II	570	571	514-587	36.66	35.95	C ₆ H ₅ -N=CH + Cl-C ₆ H ₄ -C≡N
	III	647	654	587-690	19.43	20.46	Cl-C ₆ H ₄ -C≡N
	Residue	>690	-	-	10.89	11.14	CoO

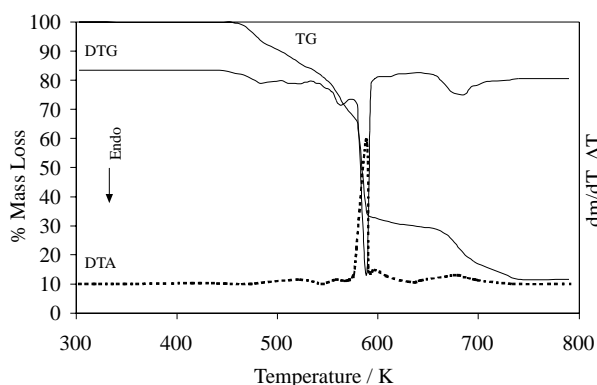
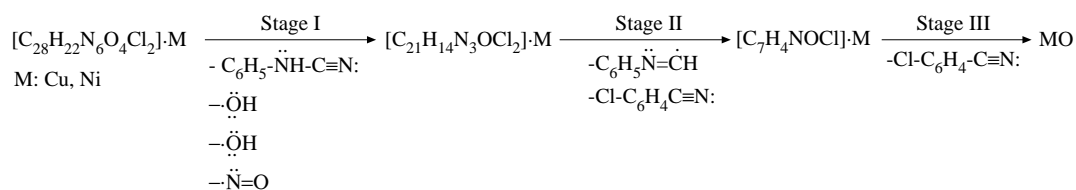


Figure 1. DTA/TG/DTG diagram of anilino-*p*-chlorophenylglyoxime Ni(II) complex.

Examination of the TG curve showed that the sample decomposes in three stages. The sample loses 29.6% of its mass between 455 and 568 K, 38.9% of its mass between 568 and 609 K, and 20.0% of its mass between 609 and 740 K. The DTA profile shows three exothermic peaks at 523, 589, and 680 K, respectively. The theoretical decomposition mechanism is given in Scheme 1 and the identification of greenish-black end product (NiO) of decomposition is obtained by X-ray powder diffraction pattern data (Figure 2).



Scheme 1.

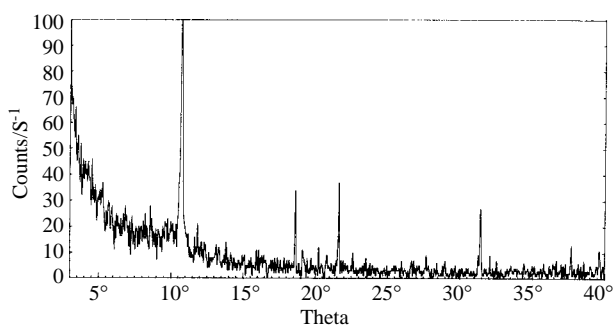


Figure 2. X-ray powder diffraction pattern of NiO.

Cu(II) complex ($C_{28}H_{22}N_6O_4Cl_2 \cdot Cu$)

The Cu (II) complex of the *A_p*CPG is stable up to 385 K, and decomposition begins beyond this temperature as indicated by the first loss step in the TG curve. At this stage the complex simultaneously melts and decomposes and loses 28.2% of its mass. The decomposition reaction occurs in three stages. CuO, the end product of the decomposition reaction, corresponds to an experimental mass of 12.4%, which is equal to the expected theoretical mass. The DTA/TG/DTG data for the Cu(II) complex are shown in Figure 3.

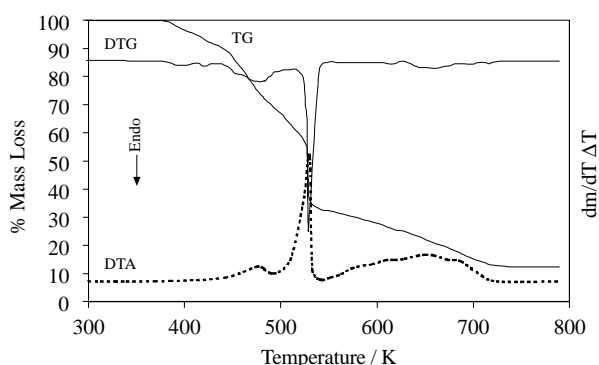


Figure 3. DTA/TG/DTG diagram of anilino-*p*-chlorophenylglyoxime Cu(II) complex.

The first decomposition occurs between 385 and 486 K with a 28.2% mass loss, the second decomposition occurs between 486 and 540 K with a 39.0% mass loss and the third decomposition occurs between 540 and 741 K with a 20.5% mass loss. The DTA study of the complex showed three exothermic peaks. The first peak appeared between 400 and 492 K, the second between 492 and 541 and the third between 541 and 726 K.

Co(II) complex ($C_{28}H_{22}N_6O_4Cl_2 \cdot Co \cdot 2.0 H_2O$)

The complex of Co(II) corresponds to a solid greenish-brown residue in the temperature range between 395 and 690 K with an 89.1% mass loss in nitrogen atmosphere. Both DTA/TG and X-ray powder diffraction studies showed that the residual greenish-brown solid was CoO which corresponds to a theoretical mass of 10.9% of the complex. DTA/TG/DTG diagrams of the Co(II) complex are shown in Figure 4.

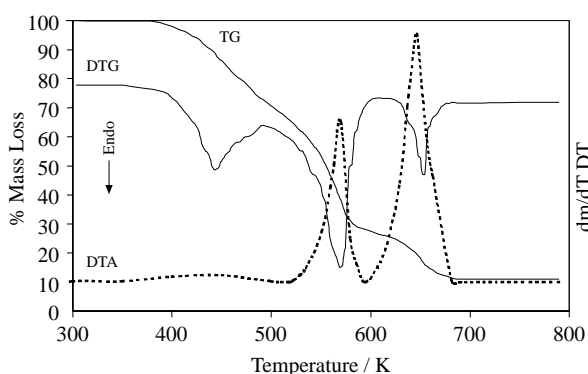


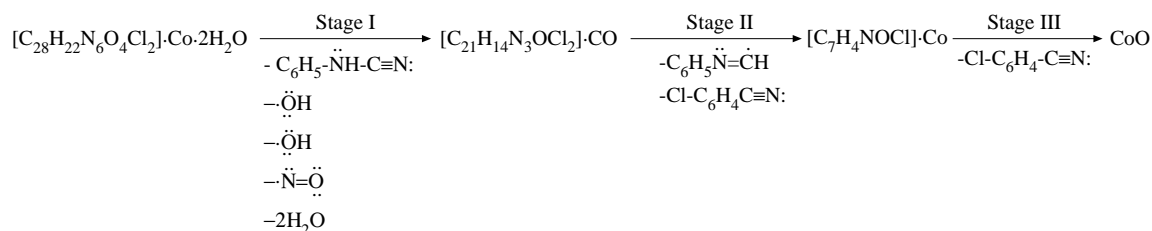
Figure 4. DTA/TG/DTG diagram of anilino-*p*-chlorophenylglyoxime Co(II) complex.

It was observed from the TG curve that the sample decomposes in three stages, losing 33.0%, 36.7% and 19.4% of its mass in each stage. The temperature range during these decompositions was between 395 and 514, 514 and 587 and 587 and 690 K, respectively. The Co(II) complex of ApCPG loses two moles of hydrate waters, which is included in the first stage. The second and third decomposition stages are similar to the complexes of Ni(II) and Cu(II). Three exothermic peaks were observed in the DTA analysis. The maxima of these peaks, two of which are strong and the other weak, are 450, 570, and 647 K, respectively.

Thermal behaviour

The Co(II), Ni(II) and Cu(II) complexes of *Ap*CPG are thermally stable up to 395, 455, and 385 K, respectively. The melting point was not observed in any of the compounds, indicating that melting has been overlapped by the decomposition of the complexes. The decomposition of all the complexes is similar and occurs in three steps.

The theoretical mechanism of decomposition for the complexes of *Ap*CPG, which is in agreement with that of Burakevic et al. and Arslan et al.^{11,14} is possibly as shown in Schemes 1 and 2 and confirmed by GC-MS data, TG data and X-ray powder diffraction data.



Scheme 2.

All of the complexes show three-stage mass loss. Ni(II) and Cu(II) complexes yield decomposition products such as $\text{C}_6\text{H}_5\text{NH-C}\equiv\text{N}+2\text{OH}+\text{NO}$ substances in the first stage, whereas the Co(II) complex yields $\text{C}_6\text{H}_5\text{NH-C}\equiv\text{N}+2\text{OH}+\text{NO}+2\text{H}_2\text{O}$ compounds in the second and third stages, and the products are the same for all of these complexes. In the first and second Schemes, the intermediate products ($\text{C}_6\text{H}_5\text{NH-C}\equiv\text{N}$ (118 m/z), $\text{C}_6\text{H}_5\text{N-CH}$ (104 m/z), $\text{Cl-C}_6\text{H}_4\text{C}\equiv\text{N}$ (137 m/z)) at the theoretical decomposition mechanisms supplied with GC-MS studies are in agreement with our previous studies. The theoretical and the experimental percent mass losses obtained from these decomposition stages are also in agreement.

*Ap*CPG complexes of both Ni(II) and Cu(II) have similar thermal decomposition mechanisms as expected, since they both have a square-planar structure. It may also be noted here that the absence of dehydration peaks in the DTG curves and the absence of hydroxyl bands in the IR spectra indicate that Ni(II) and Cu(II) complexes under investigation are anhydrous. The microanalysis also supports these results (found: C, 53.0%, H, 3.4%, N, 13.2%; $\text{C}_{28}\text{H}_{22}\text{N}_6\text{O}_4\text{Cl}_2\cdot\text{Ni}$ requires: C, 52.9%; H, 3.5%; N, 13.2% - found: C, 52.1%, H, 3.7%, N, 13.0%; $\text{C}_{28}\text{H}_{22}\text{N}_6\text{O}_4\text{Cl}_2\cdot\text{Cu}$ requires: C, 52.5%; H, 3.5%; N, 13.1%).

The Co(II) complex, which has an octahedral structure, undergoes thermal decomposition in three stages and turns to CoO but yields different intermediate products. The CHN analysis of Co(II) complex shows that it has two moles of hydrate molecule (found: C, 50.2%, H, 4.1%, N, 12.6%; $\text{C}_{28}\text{H}_{22}\text{N}_6\text{O}_4\text{Cl}_2\cdot\text{Co}\cdot 2.0\text{H}_2\text{O}$ requires: C, 50.0%; H, 3.9%; N, 12.5%). IR measurements also support this result. The coordinated H_2O molecules of the Co(II) complex are identified by broad -OH absorption bands around $3320\text{-}3400\text{ cm}^{-1}$ whose intensity remain constant after heating at 110°C for 24 h. These results are in agreement with the theoretical decomposition mechanism. The initial compounds and the end products were confirmed via IR spectrometric and X-ray diffraction data. As an example, the X-ray pattern of end product of the Ni(II) complex is shown in Figure 2.

Decomposition kinetics

The result of TG and DTG evaluations are presented in Table 1. In studying the decomposition kinetics, the methods of Coats-Redfern and Horowitz-Metzger were used^{15,16}. From the TG curves, the reaction order n ,

activation energy E^* , entropy ΔS^* , and pre-exponential factor A of the thermal decomposition have been elucidated by the methods mentioned above.

The linearisation curves of the were complexes obtained using Horowitz-Metzger's and Coats-Redfern's methods and are presented in Figure 5 and 6, respectively. The kinetic results of TG-DTG curves are presented in Table 2, together with the radii of metal ions. The results indicate that the values of both methods are comparable.

Table 2. Kinetic data of metal complexes of anilino-*p*-chlorophenylglyoxime.

Complexes	Radius of metal ion/pm	Stage	Reaction order (n)	Parameters ^a	From Coats-Redfern eqn.	From Horowitz-Metzger eqn.	
Cu(II) Complex	70	I	0.897	E^*	68.7	78.0	
				A	3.61×10^5	4.34×10^6	
				ΔS^*	-142.2	-121.5	
		II	0.722	0.722	r	0.9975	0.9985
					E^*	150.8	164.9
					A	5.61×10^{12}	2.34×10^{14}
		III	0.865	0.865	ΔS^*	-5.6	-25.4
					r	0.7425	0.7676
					E^*	73.9	86.0
Ni(II) Complex	72	I	0.888	A	1.68×10^3	1.16×10^4	
				ΔS^*	-161.9	-174.0	
				r	0.9960	0.9980	
		II	0.853	0.853	E^*	46.8	45.2
					A	96.9	60.8
					ΔS^*	-185.6	-215.9
		III	0.433	0.433	r	0.9482	0.9805
					E^*	132.9	138.2
					A	6.88×10^9	1.13×10^{10}
Co(II) Complex	74	I	0.827	ΔS^*	-35.3	-58.1	
				r	0.6103	0.6356	
				E^*	70.9	80.8	
		II	0.686	0.686	A	4.71×10^2	4.29×10^3
					ΔS^*	-172.4	-182.4
					r	0.9150	0.9279
		III	0.457	0.457	E^*	38.9	45.9
					A	0.62×10^2	4.09×10^2
					ΔS^*	-214.6	-198.8
II	0.686	0.686	r	0.9943	0.9954		
			E^*	120.8	128.8		
			A	8.27×10^8	5.01×10^9		
III	0.457	0.457	ΔS^*	-79.6	-64.6		
			r	0.9773	0.9730		
			E^*	66.5	73.9		
III	0.457	0.457	A	0.58×10^3	3.138×10^3		
			ΔS^*	-170.7	-184.5		
			r	0.9828	0.9851		

^aUnit of parameters: E^* in kJ mole^{-1} , A in s^{-1} , ΔS^* in $\text{J mole}^{-1} \text{K}^{-1}$, r -correlation coefficient of the linear plot.

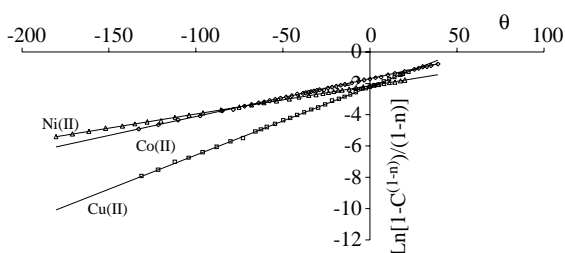


Figure 5. Horowitz-Metzger plots of anilino-*p*-chlorophenylglyoxime Ni(II), Cu(II) and Co(II) complex for stage I.

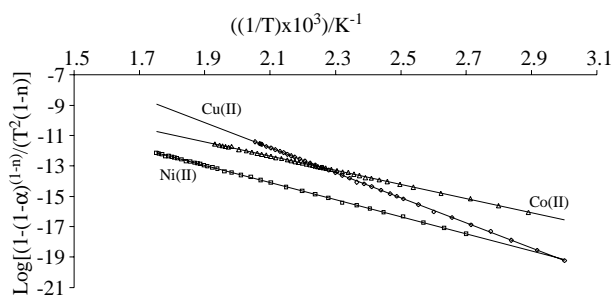


Figure 6. Coats-Redfern plots of anilino-*p*-chlorophenylglyoxime Ni(II), Cu(II) and Co(II) complex for stage I.

The value of correlation coefficients of linearisation curves of the complexes are approximately 1.00, and values of reaction orders are around 1.00 for each decomposition of the complexes. The kinetic data produced by both methods agree with each other.

The activation energy of Co(II), Ni(II) and Cu(II) complexes is expected to increase proportional to the decrease in their radii¹⁷. Complexes of Ni and Cu have a square-planar geometry and show similar decomposition steps. A smaller size of Cu(II) permits a closer approach of the ligand as compared to Ni(II). Hence the E^* value for the Cu(II) complex is higher than that of Ni(II)¹⁸⁻²¹.

The same decomposition kinetics are also true for the E^* values of the second and third stages with respect to the method of Coats-Redfern, and can be placed in descending order:

$$\begin{array}{l}
 \text{Stage I,} \quad E_{Cu}^* = 68.7 \text{ kJ mole}^{-1} > E_{Ni}^* = 46.8 \text{ kJ mole}^{-1} \\
 \text{Stage II,} \quad E_{Cu}^* = 150.8 \text{ kJ mole}^{-1} > E_{Ni}^* = 132.9 \text{ kJ mole}^{-1} > E_{Co}^* = 120.8 \text{ kJ mole}^{-1} \\
 \text{Stage III,} \quad E_{Cu}^* = 73.9 \text{ kJ mole}^{-1} > E_{Ni}^* = 70.9 \text{ kJ mole}^{-1} > E_{Co}^* = 66.5 \text{ kJ mole}^{-1} \\
 r_{Cu}^{2+} = 70 \text{ pm} < r_{Ni}^{2+} = 72 \text{ pm} < r_{Co}^{2+} = 74 \text{ pm}
 \end{array}$$

The negative values of ΔS^* in these complexes indicate that the reaction rates are slower than normal²². This trend has been supported by Indira and Parameswaran's studies²³. In addition, the activated complexes have a more ordered structure than the reactants²¹.

The smaller the metal ions, the greater the metal-ligand bond energies. Therefore, decomposition of the complexes to the metal oxides may be initiated by metal-ligand bond-breaking, since these complexes decompose at higher temperatures proportional to $1/r$ (r = radius of metal ion). On the other hand, the oximes of Cu(II) and Ni(II), which decompose at lower temperatures as $1/r$ increase, may decompose by electron transfer from the oximes to the metal ions. This is supported by the fact that the electron affinities of metal ions, in general, increase with effective nuclear charge^{18,24,25}.

$$T_{Cu} = 385 \text{ K} (r_{Cu}^{2+} = 70 \text{ pm}) < T_{Ni} = 455 \text{ K} (r_{Ni}^{2+} = 72 \text{ pm})$$

Conclusion

The TGA/DTA curves of all the compounds were similar in character. There is a three-stage mass loss on heating. The thermal decomposition mechanism of the metal complexes is summarised in Schemes 1 and 2. The activation energies obtained by non-isothermal methods are compared. The thermal stability of the complexes according to the TG curves follows the sequence: Cu(*Ap*CPG)₂ < Ni(*Ap*CPG)₂. These studies show that there is a relationship between the ionic radius of the metal and the thermal stability of the complex.

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