

## Physicochemical Studies and Thermal Decomposition Kinetics of Cobalt(II) and Nickel(II) Complexes of Acetylacetonaminofluorene

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Cobalt(II) and nickel(II) complexes of a new Schiff base, acetylacetonaminofluorene [LH] have been synthesized. On the basis of spectral, magnetic and thermal data, octahedral structure was assigned to both complexes  $[ML_2(H_2O)_2]$ . Thermal decomposition of these complexes was studied by TG. Kinetic parameters, *viz.* activation energy,  $E$ , pre-exponential factor,  $A$ , and order of reaction,  $n$ , were calculated from the TG curves using mechanistic and non-mechanistic integral equations.

Transition metal complexes of Schiff bases have important technical applications. Some workers<sup>1-7</sup> have studied thermal stabilities of metal chelates with azomethine ligands. In continuation of our work<sup>8-11</sup> on thermal decomposition kinetics of metal chelates, we report here the preparation, characterization and thermoanalytical data of cobalt(II) and nickel(II) complexes of a novel Schiff base, acetylacetonaminofluorene. Interpretation and mathematical analysis of the data and evaluation of the order of reaction and energy and entropy of activation, based on the integral method

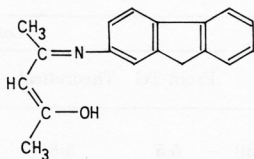


Figure 1.

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using Coats-Redfern equation<sup>12</sup> and the approximation method using Horowitz-Metzger equation,<sup>13</sup> are given. Mechanistic integral equations<sup>14,15</sup> are also used for evaluating kinetics and mechanism.

## EXPERIMENTAL

Metal complexes of acetylacetonaminofluorene [LH] were prepared by refluxing 1 M methanolic solution of the metal chloride and 2 M methanolic solution of the ligand and 1.5 g of sodium acetate for one hour. Precipitates were filtered off, washed with an ethanolic solution of the reagent and dried in a vacuum desiccator. The purity of the samples was checked by elemental analysis for the metal and C, H, N analyses and spectral and thermal studies.

### Instrumental

Infrared spectra were recorded using a Perkin-Elmer Model 283 infrared spectrophotometer. Thermal studies were carried out using a Perkin Elmer 7 series thermal analysis system. A constant heating rate of 10 °C min<sup>-1</sup> and sample mass ~5 mg were employed for the entire study. Computational work was done with a Horizon III mini computer using the programming language FORTRAN.

### Data Processing

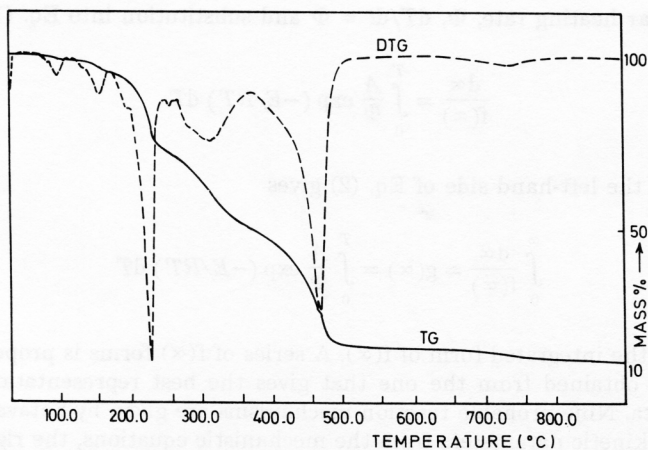
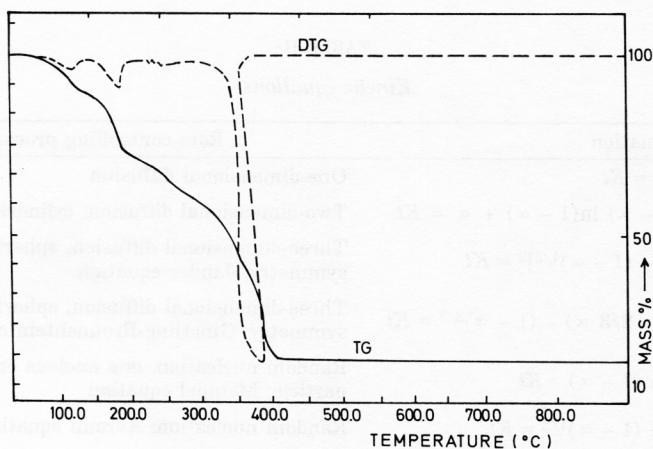
Instrumental TG curves were redrawn as mass *vs.* temperature (TG) curves and also as the rate of loss of mass *vs.* temperature curve. The decomposition temperature ranges in DTG for the metal chelates are presented in Table I. The curves for Co(II) and Ni(II) complexes exhibited a three stage decomposition pattern. Thermograms are represented in Figures 2 and 3. Mechanistic and non-mechanistic methods were used to determine kinetic data from TG curves.

### Thermal Decomposition Kinetics

Kinetic parameters, *viz.* activation energy *E*, pre-exponential factor *A*, and order parameter *n*, for the thermal decomposition of the Co(II) and Ni(II) complexes were determined from the TG data. Fractional decomposition,  $\alpha$ , for respective temperatures, was calculated from TG curves.

TABLE I  
Thermal decomposition data

Substance	Peak temp. in DTG °C	Temp. ranges in DTG °C	Loss of mass %			
			From TG	Theoretical	Pyrolysis	Probable assignments
[CoL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]						
I Stage	120	50 – 130	5.5	5.8		Loss of H <sub>2</sub> O
II Stage	190	130 – 250	27	27.1		Loss of acetylacetonone
III Stage	380	250 – 420	54.5	54.4	87.4	Loss of aminofluorene
[NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]						
I Stage (a & b)	100, 150	75 – 175	6	5.8		Loss of H <sub>2</sub> O
II Stage	220	175 – 280	27	27.15		Loss of acetylacetonone
III Stage (a & b)	310, 460	280 – 480	55.2	55.27	88.5	Loss of aminofluorene

Figure 2. TG and DTG of  $[\text{CoL}_2(\text{H}_2\text{O})_2]$ .Figure 3. TG and DTG of  $[\text{NiL}_2(\text{H}_2\text{O})_2]$ .

Determination of the mechanism of reactions from non-isothermal methods has been discussed by Sestak and Berggren and Satava.<sup>14,15</sup> The procedure is based on the assumption that the non-isothermal reaction proceeds isothermally in an infinitesimal time interval, so that the rate can be expressed by an Arrhenius-type equation

$$\frac{d\alpha}{dt} = A \exp(-E/RT) f(\alpha) \quad (1)$$

where  $A$  is the pre-exponential factor,  $t$  is the time and  $f(\alpha)$  depends on the mechanism of the process.

For a linear heating rate,  $\Phi$ ,  $dT/dt = \Phi$  and substitution into Eq. (1) gives

$$\frac{d\alpha}{f(\alpha)} = \int_0^T \frac{A}{\Phi} \exp(-E/RT) dT \quad (2)$$

Integration of the left-hand side of Eq. (2) gives

$$\int_0^\infty \frac{d\alpha}{f(\alpha)} = g(\alpha) = \int_0^T \frac{A}{\Phi} \exp(-E/RT) dT \quad (3)$$

where  $g(\alpha)$  is the integrated form of  $f(\alpha)$ . A series of  $f(\alpha)$  forms is proposed, and the mechanism is obtained from the one that gives the best representation of the experimental data. Nine probable reaction mechanisms are given by Satava<sup>15</sup> (Table II). To determine kinetic parameters from the mechanistic equations, the right-hand side of Eq. (3), the temperature integral which is an incomplete gamma function, was used in the form given by Coats and Redfern, which produces one of the best solutions and is recommended by several authors.<sup>16,17</sup>

TABLE II  
Kinetic equations

Function	Equation	Rate-controlling process
D <sub>1</sub>	$\alpha^2 = Kt$	One-dimensional diffusion
D <sub>2</sub>	$(1 - \alpha) \ln(1 - \alpha) + \alpha = Kt$	Two-dimensional diffusion, cylindrical symmetry
D <sub>3</sub>	$[1 - (1 - \alpha)^{1/3}]^2 = Kt$	Three-dimensional diffusion, spherical symmetry: Jander equation
D <sub>4</sub>	$(1 - 2/3 \alpha) - (1 - \alpha)^{2/3} = Kt$	Three-dimensional diffusion, spherical symmetry: Ginstling-Brounshtein equation
F <sub>1</sub>	$-\ln(1 - \alpha) = Kt$	Random nucleation, one nucleus on each particle; Mampel equation
A <sub>2</sub>	$-\ln(1 - \alpha)^{1/2} = Kt$	Random nucleation; Avrami equation I
A <sub>3</sub>	$-\ln(1 - \alpha)^{1/3} = Kt$	Random nucleation; Avrami equation II
R <sub>2</sub>	$1 - (1 - \alpha)^{1/2} = Kt$	Phase boundary reaction, cylindrical symmetry
R <sub>3</sub>	$1 - (1 - \alpha)^{1/3} = Kt$	Phase boundary reaction; spherical symmetry

The general form of the equation used is

$$\ln \frac{g(\alpha)}{T^2} = \ln \frac{AR}{\Phi E} - \frac{E}{RT} \quad (4)$$

Along with the mechanistic equations, two non-mechanistic methods suggested by Coats and Redfern and Horowitz and Metzger were also used for comparison. The reaction order can easily be estimated by comparing the values using  $n = 0.33, 0.5, 0.66$  and  $1$  in equations



$$1 - (1 - \alpha)^{1-n} / (1 - n)T^2 \quad \text{vs.} \quad 1/T \text{ for } n \neq 1 \quad (5)$$

$$\log [-\log (1 - \alpha)] / T^2 \quad \text{vs.} \quad 1/T \text{ for } n = 1 \quad (6)$$

Coats-Redfern equation

$$\ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{(1 - n)T^2} \right] = \ln \left[ \frac{AR}{\Phi E} \frac{(1 - 2RT)}{E} \right] - \frac{E}{RT} \quad (7)$$

Horowitz-Metzger equation

$$\ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{(1 - n)} \right] = \ln \frac{ART_s^2}{\Phi E} - \frac{E}{RT_s} + \frac{E\Theta}{RT_s^2} \quad (8)$$

where  $\Theta = T - T_s$ . From the slope and intercept,  $E$ ,  $A$  and  $\Delta S$  were calculated.

### RESULTS AND DISCUSSION

The structure of the two complexes was found to be  $[ML_2(H_2O)_2]$ . Analytical, molar conductance and magnetic data are presented in Table III. The complexes exhibit molar conductance in the range 1-10  $\text{ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$  in nitrobenzene. The magnetic and electronic spectral data are also consistent with an octahedral structure in both complexes.

The IR spectrum of the ligand shows a band of medium intensity at about 1610  $\text{cm}^{-1}$ , which may be attributed to  $\nu C=N$  of Schiff base.<sup>18</sup> This band shifts to lower frequencies at 1600  $\text{cm}^{-1}$  in the complexes indicating a reduction of electron density in the

TABLE III  
Analytical Data and Characteristics of  $[CoL_2(H_2O)_2]$  and  $[NiL_2(H_2O)_2]$

Substance	M %	C %	H %	N %	Magnetic susceptibility B.M.	Molar conductance $\text{ohm}^{-1} \text{ mol}^{-1} \text{ cm}^2$
$[CoL_2(H_2O)_2]$	9.40 (9.52)	69.72 (69.79)	5.79 (5.82)	4.40 (4.52)	5.2	8
$[NiL_2(H_2O)_2]$	9.36 (9.48)	69.78 (69.82)	5.80 (5.82)	4.48 (4.52)	3.61	5

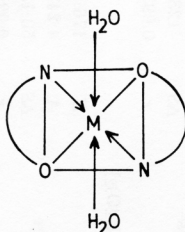


Figure 4. M = Co(II) or Ni(II).

TABLE IV  
Kinetic parameters for the decomposition of  $[\text{CoL}_2(\text{H}_2\text{O})_2]$  and  $[\text{NiL}_2(\text{H}_2\text{O})_2]$  from DTG using mechanistic equations

Substance	Parameter	1	2	3	4	5	6	7	8	9
$[\text{CoL}_2(\text{H}_2\text{O})_2]$										
II Stage	$E$	71.8062	81.1846	92.8023	85.0191	48.8698	20.7499	11.3568	39.8707	42.7295
	$A$	$3.3990 \times 10^5$	$3.0114 \times 10^6$	$2.2632 \times 10^7$	$2.1440 \times 10^6$	$1.622 \times 10^3$	$4.487 \times 10^3$	$2.4688 \times 10^6$	$1.3233 \times 10^4$	$9.239 \times 10^3$
	$\Delta S$	-142.8001	-124.6490	-107.8647	-127.4749	-187.284	-178.8096	-126.3012	-169.8100	-172.799
	$r$	0.9729	0.9778	0.9823	0.9796	0.9829	0.9759	0.9645	0.9765	0.9790
III Stage	$E$	116.2554	124.9953	135.2003	128.3725	67.9453	28.9673	15.9725	60.0759	62.5944
	$A$	$4.6145 \times 10^6$	$1.6175 \times 10^7$	$3.4406 \times 10^7$	$3.0895 \times 10^6$	$2.088 \times 10^3$	$1.1747 \times 10^6$	$7.1055 \times 10^6$	$1.9816 \times 10^4$	$1.8080 \times 10^4$
	$\Delta S$	-123.9579	-113.5213	-107.2408	-127.2962	-188.0326	-135.3423	-120.3661	-169.3117	-170.0743
	$r$	0.9979	0.9966	0.9941	0.9959	0.9893	0.9860	0.9808	0.9948	0.9933
$[\text{NiL}_2(\text{H}_2\text{O})_2]$										
II Stage	$E$	176.1546	195.3943	221.4608	203.8859	121.1219	56.3448	34.7797	99.3043	106.5625
	$A$	$4.2473 \times 10^{15}$	$3.0542 \times 10^{17}$	$5.4262 \times 10^{17}$	$6.0174 \times 10^{19}$	$2.2886 \times 10^{10}$	$2.503 \times 10^3$	$4.9959 \times 10^4$	$4.8401 \times 10^7$	$1.7247 \times 10^8$
	$\Delta S$	50.1304	85.7064	128.8089	91.3492	-50.8142	-184.1863	-159.2782	-102.0620	-91.4885
	$r$	0.9250	0.9420	0.9611	0.9490	0.9738	0.9695	0.9645	0.9487	0.9579
III Stage	$E$	82.9922	89.1131	96.2670	91.4767	46.2638	17.8153	8.2685	40.9522	42.7149
	$A$	$2.023 \times 10^3$	$2.635 \times 10^3$	$2.828 \times 10^3$	$3.369 \times 10^3$	$2.4262 \times 10^5$	$9.4275 \times 10^6$	$2.1513 \times 10^7$	$2.059 \times 10^3$	$1.2468 \times 10^6$
	$\Delta S$	-189.2608	-187.0618	-186.4722	-185.0167	-149.3495	-118.9748	-112.1094	-189.1145	-135.8084
	$r$	0.9271	0.9367	0.9459	0.9401	0.9439	0.9039	0.8233	0.9261	0.9317

$E$  in  $\text{kJ mol}^{-1}$ ;  $A$  in  $\text{S}^{-1}$ ;  $\Delta S$  in  $\text{J mol}^{-1}\text{K}^{-1}$ .

azomethine linkage as the nitrogen coordinates to the metal ion.<sup>19</sup> The C–O stretch at  $\sim 1280\text{ cm}^{-1}$  is redshifted to  $\sim 1250\text{ cm}^{-1}$ , which is an evidence of the participation of phenolic –OH in complexation.<sup>20</sup>

In both complexes, the presence of coordinated water is confirmed by the observation of a broad band at  $3300\text{ cm}^{-1}$ . However, conclusive evidence regarding the bonding of nitrogen and oxygen was provided by the occurrence of  $\nu\text{M–N}$  and  $\nu\text{M–O}$  in the  $460\text{--}560\text{ cm}^{-1}$  and  $350\text{--}400\text{ cm}^{-1}$  regions, respectively, in the metal complexes.<sup>21</sup> The IR data suggest that the ligand behaves as a bidentate chelating agent coordinating through enolic oxygen and azomethine nitrogen. Its probable structure is shown in Figure 4.

The decomposition temperature ranges for the metal chelates are given in Table I. Data from independent pyrolytic experiments are also included in this table. The kinetic parameters calculated from the nine mechanistic equations are given in Table IV. The corresponding values of  $E$ ,  $A$  and  $r$  from non-mechanistic equations (Coats-Redfern, Horowitz-Metzger) are given in Table V.

The activation energies obtained in the present complexes are comparable to those of the coordination compounds of 3d transition metals having similar structure. In both complexes  $2\text{H}_2\text{O}$  molecules are lost around  $130\text{--}150^\circ\text{C}$ . According to Nikolaev *et al.*,<sup>22</sup> water eliminated at this temperature can be considered as coordinated water.

### Decomposition Kinetics

From Tables IV and V it can be seen that more than one equation gives good linear curves with high values of correlation coefficients, so it may become difficult to assign the reaction mechanisms unequivocally from the linearity of the curve alone. In such cases, some authors have chosen the function  $f(\infty)$ , which gives kinetic parameters in agreement with those obtained by the numerical method. In the present

TABLE V

Substance		Coats-Redfern	Horowitz-Metzger	n
[CoL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]				
II Stage	$E$ (kJ mol <sup>-1</sup> )	48.8698	60.2676	1
	$A$ (S <sup>-1</sup> )	$1.620 \times 10^3$	$3.5124 \times 10^4$	
	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	-187.284	-161.6851	
	$r$	0.9829	0.9836	
III Stage	$E$ (kJ mol <sup>-1</sup> )	58.4865	70.5551	1/3
	$A$ (S <sup>-1</sup> )	$1.3772 \times 10^4$	$1.447 \times 10^3$	
	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	-172.3389	-191.0833	
	$r$	0.9972	0.9965	
[NiL <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]				
II Stage	$E$ (kJ mol <sup>-1</sup> )	121.1215	123.7760	1
	$A$ (S <sup>-1</sup> )	$2.2887 \times 10^{10}$	$1.3025 \times 10^{11}$	
	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	-50.8142	-36.3448	
	$r$	0.9738	0.9698	
III Stage	$E$ (kJ mol <sup>-1</sup> )	46.2638	68.1434	1
	$A$ (S <sup>-1</sup> )	$2.4252 \times 10^5$	$1.81 \times 10^2$	
	$\Delta S$ (J mol <sup>-1</sup> K <sup>-1</sup> )	-149.3495	-209.3458	
	$r$	0.9439	0.9326	

case, it is observed that for the second stage of Co(II) complex and for the second and third stages of Ni(II) complex, the  $F_1$  mechanism based on Mampel model equation gives the highest correlation. For the third stage of decomposition of Co(II) complex, the  $R_2$  mechanism based on phase boundary reaction, cylindrical symmetry gives values that agree with  $E$  and  $A$  values obtained from the Coats-Redfern equation.

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#### SAŽETAK

##### Fizikalno-kemijska istraživanja i kinetika termalnog raspada acetilacetaminofluorenskih kompleksa kobalta(II) i nikla(II)

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Pripremljeni su kompleksi kobalta(II) i nikla(II) s novom Schiffovom bazom, acetilacetaminofluorenom (LH). Na temelju spektralnih, magnetskih i termičkih podataka za oba kompleksa,  $ML_2(H_2O)_2$ , pretpostavljena je oktaedarska struktura. Termalni raspad kompleksa istraživani je TG metodom, a iz TG krivulja izračunani su kinetički parametri: energija aktiviranja, pred-eksponencijalni faktor i red reakcije.