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Solid State Kinetics Of Cd(II) Complex Derived From Schiff Base Of 5-Amino1,2,3,4 Thiatriazole With-Ortho-Methoxybenzaldehyde.

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Abstract

Thermal analysis has become an established method in the study of thermal behavior of materials and finds wide applications. The cadmium complex ($CdLCl_2$) where L is Schiff base derived from 5-Amino [1,2,3,4] Thiatriazole was synthesized by refluxing the Schiff base with cadmium chloride, and gravimetric analysis. The molecular weight was found to be 403.41mg. Thermal analysis was performed using thermogravimetric Analysis (TGA) Which showed Three distinct stages of weight loss, initial loss of whole ligand moiety and finally loss of moisture and two chloride ion. These steps were analyzed to determine kinetic parameters using freeman-Carroll and zasko's modified Doyle method.

The order of reaction for the main decomposition step was formed to be approximately 0.7M/sec using freemen –Carroll and 1M/sec using zasko's method. The corresponding activation energies were 22.518 kcal/mol and 26.000 kcal/mol respectively.

The apparent entropy of activation (s) was calculated as -48.77981223 e.u and the frequency factor(Z) was found to be 1.4944887×107 sec-1 These results obtained by different methods were in good agreement and support the reliability of the kinetic model. These findings help in understanding the thermal behaviors and stability of cadmium-Schiff base complexes in the solid state.

Keywords: solid state kinetics, thermo gravimetric analysis, Schiff base.

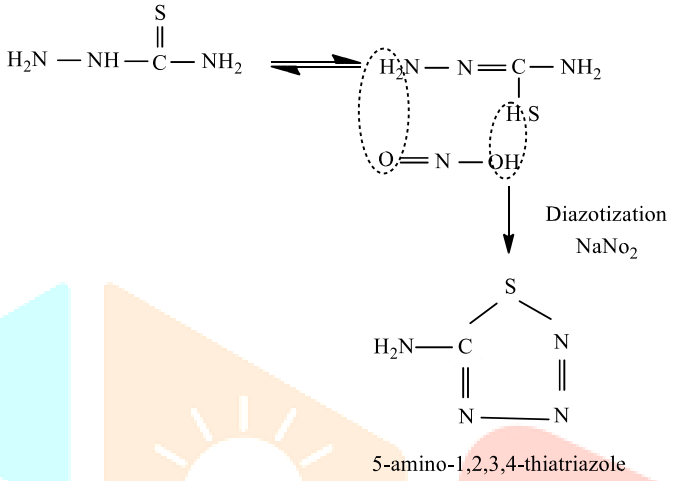
Introduction

In the recent years the coordination chemistry of transition metal and their derivatives have been widely studied due to their biological importance (1-3).A large number of Schiff bases and their complexes have been studied for their important properties e.g. their ability to reversibility bind oxygen transfer of an amino group and complexing ability towards some toxic metal (4-6) chemical parameters of Schiff bases have been determined with the help of thermogravimetric analysis. This technique involve change in weight of a system under examination with increase of temperature at a pre-determine preferably at a linears rate of study the solid state reaction. A number of workers have demonstrated its usefulness . Thermal analysis technique is becoming a usefull tool in different fields of study such as chemical science, polymer science, biological science and medical science.

The present paper deals the solid state kinetics of Cd(II)complex with 5-amino-1,2,3,4-thiatriazole) and determine the kinetics parameters such as order of reaction, frequency factor, activation energy and entropy of activation using Freeman-Carroll method as well as Doyles method modified by Zsako.

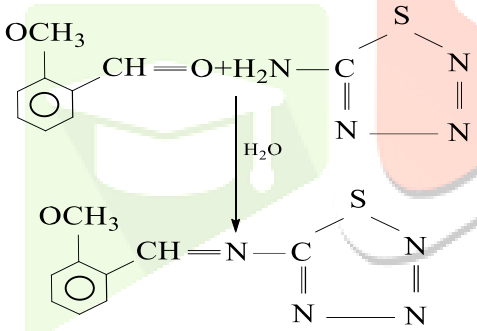
Material and methods

An ice cold solution of 20 grams of thiosemicarbazide in 95 cc of 2.2(N) HCl, was added from a burette, with stirring in a total of 14.7 gram of $NaNo_2$ in 150 ml water. After each 50 ml was added, the product was collected and washed with 10 ml of ice water. The filtrate being returned to the reaction vessel the crude product was vacuum dried and recrystallized from methanol yielded fine, colorless needle which decomposed with a slight explosion of 136^0 in a capillary tube.



5-amino-1,2,3,4-thiatriazole

Preparation of Schiff base: 1:1 molar solution of o-methoxy-benzaldehyde and 5-amino-1,2,3,4, thiatriazole in ethanol and condensed in acidic medium light yellow solid Schiff base is filtered and recrystallized with ethanol.



Preparation of complex of Cd(II)

0.002 M of ligand in ethanolic solution was mixed with 0.001M Cd(II) Chloride in ethanolic solution. The resulting solution was refluxed for half hour on steam bath. The precipitate was filtered off and washes with ethanol and dried in a desiccator over anhydrous $CaCl_2$

Results and discussion

The result obtained by the usual elemental analysis and estimation of metal content are suggestive of the molecular formula $[CdLCl_2]$ and the molecular weight 403.41mg to the complexes.

The basis of the calculation of kinetic parameter from a TG curve is based on the formal kinetic equation $-d\alpha/dt=k\alpha$

Where α is the fraction of the initial compound undergoing reaction, k is the specific rate constant.

The specific rate constant depends upon the temperature by the expression, $k = Ae^{-E/RT}$.

where A is the pre-exponential factor, E the activation energy and R is the gas constant.

The thermo-gram of the complex shows three stages of the decomposition. Second stage of the decomposition was selected for the determination of kinetic parameter, i.e. order of reaction, activation energy, entropy of activation and frequency factor firstly by graphical method of freeman-carroll and Doyle's method as modified by Zsako

The following table contains the data obtained by freeman-carroll method

Table-I: Data obtained by Freeman and carroll method:

S.No.	Temp(0C)	Weight (mg)	$\frac{\Delta \log dw/dt}{\Delta \log Wr}$	$\frac{\Delta T^{-1} \times 10^{-3}}{\Delta log\ Wr}$
1	180	4.153283	-124.51982	24.81801
2	190	4.129806	-66.69759	13.98417
3	200	4.089590	-39.62382	7.73522
4	210	4.029593	-19.40516	4.88607
5	220	3.938945	-12.90656	3.02233
6	230	3.807430	-7.70669	1.92178
7	240	3.614830	-5.07243	1.18577
8	250	3.335061	-3.10010	0.91221
9	260	2.842910	-2.21436	0.72365
10	270	2.379888	0.19107	0.24901
11	280	1.879694	-0.14806	0.14695
12	290	1.333416	-0.06400	0.05368
13	300	1.178640	0.68907	0.03898

Initial weight at 160^0C = 4.175021mg.
Final weight at 310^0C = 1.149076mg.
Order of reaction = 0.7M/Sec.
Activation energy = 22.518kcal/mol.

Table-II : Data of log f(α) values for complex [CdLCl$_2$] calculated at different temperatures:

S.No.	Temp(^{0}C)	Weight (mg)	$\alpha = \frac{W_o - W_t}{W_o - W_f}$	$log\ \alpha$	$log\left(ln\frac{1}{1-\alpha}\right)$	$log\left(\frac{\alpha}{1-\alpha}\right)$
1	170	4.167195	0.00258630	-2.587321	-2.586759	-2.586197
2	180	4.153283	0.00718387	-2.143641	-2.142077	-2.140510
3	190	4.129806	0.01494244	-1.825578	-1.822313	-1.819040
4	200	4.089590	0.02823283	-1.549246	-1.543041	-1.536808
5	210	4.029593	0.04806036	-1.318213	-1.307562	-1.296822
6	220	3.938945	0.07801728	-1.107809	-1.090290	-1.072532
7	230	3.807430	0.12147974	-0.915496	-0.887676	-0.859248
8	240	3.614830	0.18512927	-0.732525	-0.688827	-0.643614
9	250	3.335061	0.27758601	-0.556602	-0.487907	-0.415389

10	260	2.842910	0.44022975	-0.356321	-0.236401	-0.104330
11	270	2.379888	0.59324707	-0.226764	-0.045975	0.163905
12	280	1.879694	0.75854882	-0.120016	0.152621	0.497154
13	290	1.333416	0.939080	-0.027297	0.446878	1.187944
14	300	1.178640	0.990230	-0.004264	0.665433	2.005834

Initial weight at 160^0C = 4.175021mg.

Final weight at 310^0C = 1.149076mg.

The values obtained above have been utilized to calculate B_0&δ_0 , B_1& δ_1, B_2& δ_2, using standard deviation method.

Table – III: Calculation of B_0 for different activation energies and δ_0 value at different temperature for [CdLCl$_2$] complex.

S.No.	Temp(^{0}C)	18 kcal	20 kcal	22 kcal
1	170	8.954678814	10.027678814	11.093678814
2	180	9.184358554	10.236358554	11.279358554
3	190	9.292421505	10.327421505	11.349421505
4	200	9.373754460	10.385754460	11.390754460
5	210	9.412787002	10.408787002	11.390787002
6	220	9.441190808	10.415190808	11.385190808
7	230	9.461503840	10.417503840	11.365503840
8	240	9.475475097	10.414475097	11.344475097
9	250	9.487397575	10.408397575	11.326397575
10	260	9.528679385	10.437679385	11.336679385
11	270	9.508235601	10.404235601	11.346235601
12	280	9.469983535	10.344983535	11.216983535
13	290	9.422702678	10.286702678	11.138702678
14	300	9.308736005	10.155736005	10.999736005
	Average*(B_0)*	*9.380136061*	*10.333636061*	*11.283136061*

	Standard deviation(δ_0)	*0.149413946*	*0.115595917*	*0.119135988*

Table-IV: Calculation of B_1 for different activation energies and δ_1 value at different temperature for [$CdLCl_2$] complex.

S.No.	Temp(^{0}C)	24 kcal	26 kcal	28 kcal
1	170	12.153241028	13.205241028	14.258241028
2	180	12.318923202	13.348923202	14.375923202
3	190	12.367686599	13.381686599	14.386686599
4	200	12.390958507	13.382958507	14.369958507
5	210	12.383438398	13.353438398	14.318438398
6	220	12.360710027	13.314710027	14.262710027
7	230	12.334324446	13.271324446	14.201324446
8	240	12.312172569	13.230172569	14.149172569
9	250	12.301092990	13.207092990	14.103092990
10	260	12.350599312	13.238599312	14.121599312
11	270	12.342024982	13.253024982	14.084024982
12	280	12.352620962	13.211620962	14.062620962
13	290	12.462878262	13.306878262	14.146878262
14	300	12.506432885	13.332432885	14.159432885
	Average(B_1)	*12.352650298*	*13.288436012*	*14.214293155*
	Standard deviation(δ_1)	*0.077531967*	*0.062874061*	*0.10957466*

Table-V: Calculation of B_2 for different activation energies and $\delta_2$value at different temperature for [$CdLCl_2$] complex.

S.No.	Temp(^{0}C)	30 kcal	32 kcal	34 kcal
1	170	15.303803484	16.343803484	17.360803484
2	180	15.404489731	16.423489731	17.438489731
3	190	15.394959897	16.391959897	17.385959897
4	200	15.359192239	16.339192239	16.811192239
5	210	15.295177589	16.253177589	17.207177589
6	220	15.223468027	16.164468027	17.106468027
7	230	15.155752056	16.078752056	16.702752056
8	240	15.102386381	16.008386381	16.911386381
9	250	15.071611427	15.959611427	16.844611427
10	260	15.127669568	16.002669568	16.874669568
11	270	15.154904909	16.016904909	16.870904909
12	280	15.251154198	15.859154198	16.941154198
13	290	15.722944125	16.317944125	17.287944125
14	300	16.321833841	16.912833841	17.950833841
	Average (B_2)	*15.349239105*	*16.219453391*	*17.121024819*
	Standard deviation(δ_2)	*0.314367117*	*0.259880173*	*0.32726714*

Comparative value of δ along with their activation energies for the presumed order of reaction are given in Table as follows :-

Table-VI

b = 0		b = 1		b = 2	
Ea		Ea		Ea	
k cal /mol	δ0	kcal /mol	δ1	k cal /mol	δ2
18	*0.149413946*	24	*0.077531967*	30	*0.314367117*
20	*0.115595917*	26	*0.062874061*	32	*0.259880173*
22	*0.119135988*	28	*0.10957466*	34	*0.32726714*

The minimum value for B_1 is 0.062874067 and here order of reaction is 1M/sec and activation energy 26 kcal/mole.

The apparent frequency factor Z = 1.4944887 X $10^7 sec^{-1}$ and apparent entropy of activation. where calculated using the equation

$$\log z = \bar{B} + \log Rq - logEa$$

Where R is the gas constant and a is the heating rate. The frequency factor was calculated to be 1.4944887 X $10^7 sec^{-1}$ and the apparent activation entropy was also found to be -48.77981223 e.u. by the solving equation.

$$\Delta S^{\neq} = 8.3143 logzh/kT$$

Table – VII

SN.	Methods	Order of reaction	activation energy
1	Freeman and Carroll	0.7M/sec	22.518 kcal/mole
2	J. Zsako	1M/sec	26.000 kcal/mole

The value for absolute temperature T was taken as the temperature of which the weight loss was half of the total weight loss for the considered step i.e. 528 Kelvin.

The thermogram and plotted graph one shown in next page.

Freeman and carroll graph of [$CdLCl_2$]

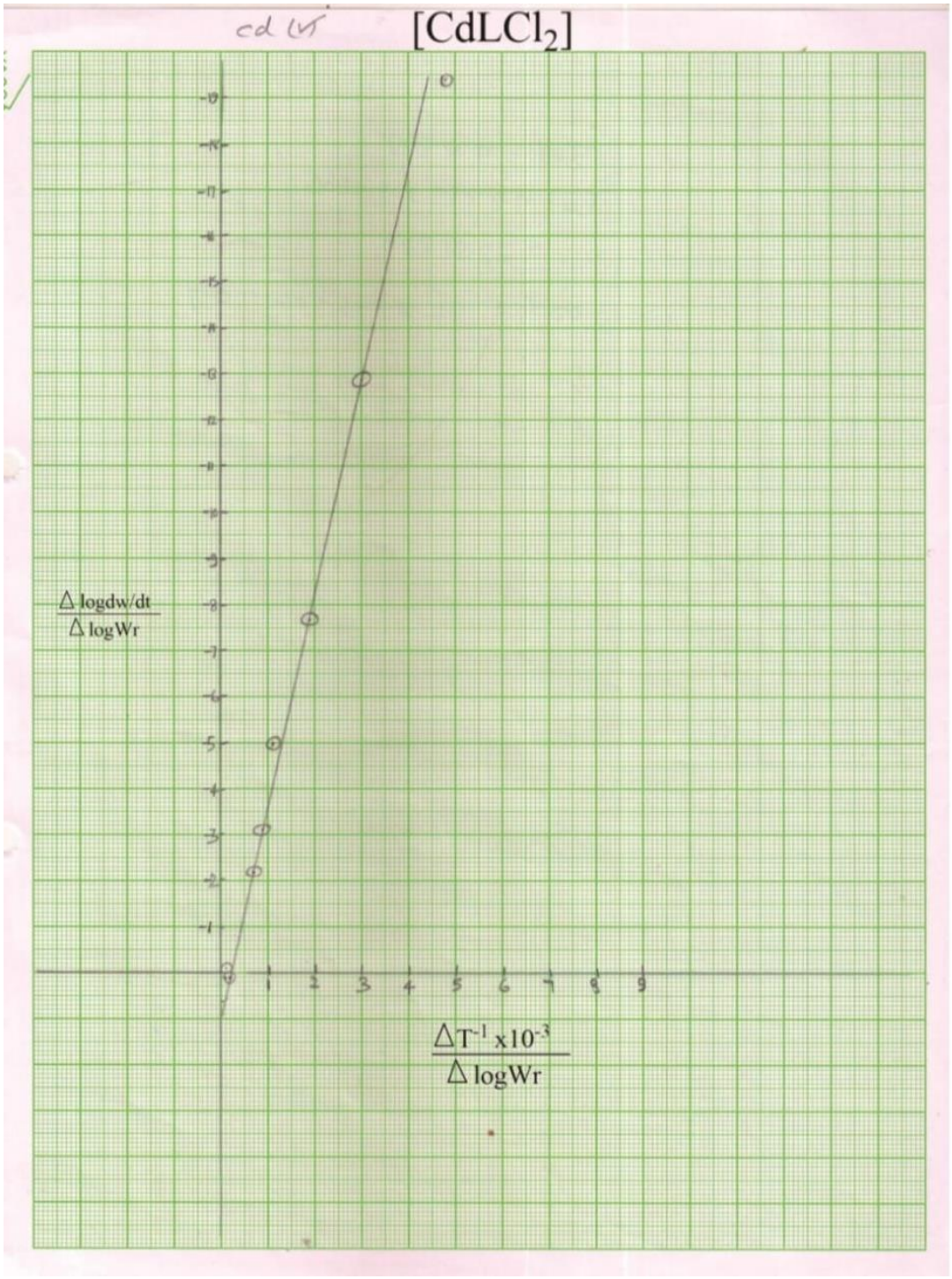
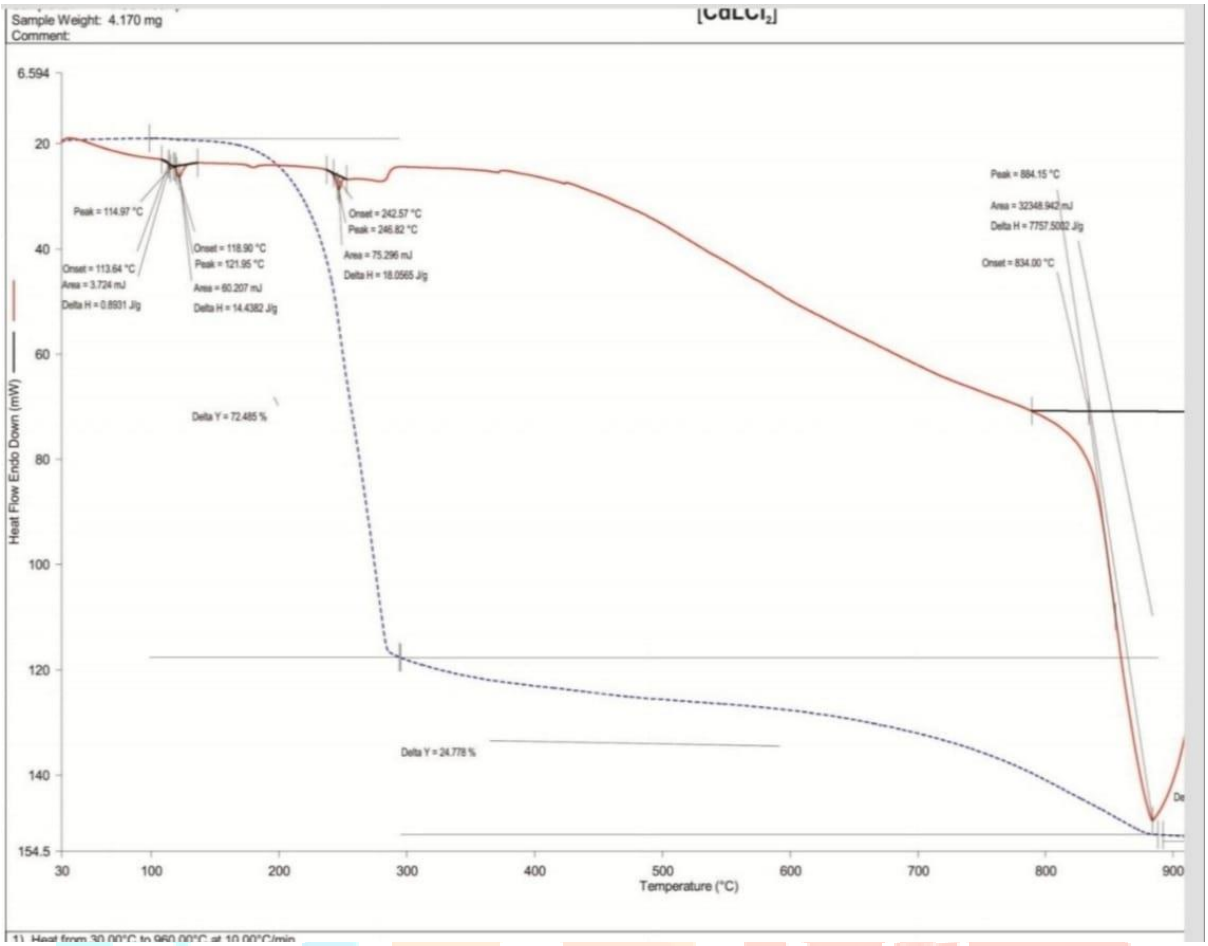


Figure 1. freeman-Carroll plot [$CdLCl_2$]

TG Curve of [$CdCL_2$]



Application

→This work may be used in the establishment of solid state mechanism of complex compounds.

→ Determination of kinetic parameters in non isothermal condition of complex compounds will help to determine the solid state reaction mechanism.

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