

“A COMPARATIVE STUDY OF COPPER(II) AND NICKEL(II) COMPLEXES”

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Abstract:

Many chemical and biological processes depend on coordination complexes made of transition and main group elements. Coordinate covalent bonds hold ligands to a central metal atom or ion in these complexes. The ligands can form chelates with tetrahedral, square planar, or octahedral geometries, depending on how many donor atoms they include. Also, some compounds display optical or cis-trans isomerism. Coordination compounds are very helpful in fields like oxygen transport, water purification and medicine because of these special qualities.

Historically, kinetic parameters, such activation energy, have proven difficult to determine from thermograms because they involve regulating parameters, which can main to mistakes. Because of this, the results are questionable and better techniques are needed for calculations that are more responsible.

In particular, metal complexes combining Schiff bases and bidentate ligands are examined in this work along with their synthesis, characterisation, thermal stability and biological activity. The metal content of copper and nickel complexes was ascertained by means of exact breakdown and snow processes, supported by classy analytical techniques. By improving our comprehension of coordination complexes' temperature behavior and stability, these discoveries hope to advance their usefulness in a variety of industries.

Keywords:

Copper (II) complexes and Nickel (II) complexes.

Introduction:

The transition elements and main group elements can form coordination compounds, or complexes, in which a central metal atom or ion is bonded to one or more ligands by

coordinate covalent bonds. Ligands with more than one donor atom are called polydentate ligands and form chelates. The common geometries found in complexes are tetrahedral and square planar (both with a coordination. number of four) and octahedral (with a coordination number of six). C is and trans configurations are possible in some octahedral and square planar complexes. In addition to these geometrical isomers, optical isomers (molecules or ions that are mirror images but not superimposable) are possible in certain octahedral complexes. Coordination complexes have a wide variety of uses including oxygen transport in blood, water purification and pharmaceutical use.

The earlier efforts to determine the kinetics constant from the thermograms have been tedious to carry but besides being susceptible to so many errors, thereby necessitating an arbitrary choice of variable constant. It was therefore, possible to change the value of the experimental activation energy by varying "adjustable" parameters within permissible limits. Such conditions provide lack of confidence in the determination of apparent activation energy. For this reason; many careful workers preface such results by the onward "procedural" meaning that the results could contain variable not expected by the treatment of the data.

Review of literature:

Dynamic air atmosphere using thermogravimetric analysis of CO (II) and Ni (II) complexes of some Schiff's base were studied (1) and (2).

Biological activity studied on some transition metal complexes containing thiazole moiety. Microwave synthesis, spectral, thermal characterization and computational modelling were studied (3).

Thermal stability and kinetic studies of new binuclear copper (ii) complexes with octaazamacrocyclic and multidonor bidentate ligands were studied (4).

Studies on mononuclear chelates derived from substituted Schiff base ligands (Part-10), synthesis and characterization of a new 4-hydroxysalicylinden - p – aminoacetophenone oxime and its complexes with Co (II), Ni (II) were studied (5)

Method:

The Carbon, Hydrogen and Nitrogen contents of the ligand and the metal complexes were carried out in Micro Analytical Laboratory of P.G. Department of Chemistry Magadh

University Bodh-Gaya and Central Drug Research Laboratory Lucknow using Coleman U.S.A. Carbon Hydrogen and Nitrogen. The complexes were decomposed and their metal and sulphur, contents were determined by the standard procedures⁴⁶, the details of the methods are described below: -

Copper: -

The complex was decomposed by nitric acid and evaporated to dryness and was precipitated to dryness from its solution as copper salicydoximate, $\text{Cu}(\text{C}_7\text{H}_6\text{NO}_2)$ in dilute acidic medium (at pH 2.6). The chemical factor for copper is 0.18980.

Nickel: -

A weighted amount of nickel complex was taken and decomposed by repeated evaporation with perchloric acid and concentrated nitric acid mixture. The decomposed

product was treated with concentrated Hydrochloric acid and evaporated almost to dryness. It was diluted with water and the Nickel content was precipitated as Nickel dimethylglyoximate in ammoniacal medium. The bright red precipitate was filtered, washed with Water, dried at 105°C - 110°C in air oven and weighted as $\text{Ni}(\text{C}_4\text{H}_7\text{N}_2\text{O}_2)_2$. The amount of Nickel was calculated by multiplying the weight of the precipitate with the chemical factor 0.20314.

Comparative Analysis:

1. Co (II) complex with Schiff base of 5-anilino 1,2,3,4 – thiatriazole (5-ATT): -

The result obtained by the usual elemental analysis and estimation of metal content are suggestive of the molecular formula $[\text{Co}(\text{5-ATT})_2\text{Br}_2]$.

Thermal degradation pattern of this complex is as shown in Table-I

Table-1: Thermoanalytical data and decomposition temperature for $[\text{CoL}_2\text{Br}_2]$ Complex: -

S. No.	Temp. range ($^\circ\text{C}$)	Species Degraded	% Weight loss	
			Found	Cal
1.	100-270	Loss of	14.10	14.80

		moisture and 2 Br – ion		
2.	250-390	Loss of whole ligand moiety	71.20	71.81
3.	320	CoO formation	12.23	12.00

The second stage of decomposition was selected to study the chemical kinetics. The kinetic parameters, such as order of reaction, activation energy, entropy of activation and frequency factor were primarily evaluated by Freeman and carroll method and were compared by the values obtained by Doyle's method as modified by Zsako.

The following Table - II contained the data obtained by Freeman and Carroll method.

Table- II: Data obtained by Freeman and Carroll method.

S. No.	Temp.	Weight	$\frac{\Delta \log \left(\frac{dw}{dt} \right)}{\Delta \log W_r}$	$\frac{\Delta T^{-1} \times 10^{-3}}{\Delta \log W_r}$
1.	285	9.61473	-21.10397	3.67356
2.	295	9.39083	-11.35103	2.01356
3.	305	9.06139	-46.10797	1.57348
4.	315	8.5559	18.16408	0.97481
5.	325	7.85782	-2.53709	0.65727
6.	335	6.94174	-1.3467	0.45643
7.	345	5.88081	-0.43063	0.34086
8.	355	4.86864	0.24452	0.28216
9.	365	4.03628	0.56933	0.24785
10.	375	3.41992	0.71074	0.22394
11.	385	2.96615	0.58099	0.19514
12.	395	2.6495	-1.7829	0.16292

Initial weight at 260°C = 8.75760 mg.

Final weight at 400°C = 1.36115 mg.

The plot of $[\Delta \log dw / dt / \Delta \log wr]$ versus $[\Delta T-1] / [\Delta \log Wr]$ gave straight line with an intercept at 1.17 suggesting the order of reaction as 1.0 and applying $E_a = 2.303 R$ slop, gave the value of activation energy to be equal to 28.99 Kcal/mol. The same values for different weights taken at different temperature were further the subjected to the Zsako method to evaluate the data given in Table -III.

Table- III: Data of log F(α) values for the complex [CoL2Br2] at different temperatures.

S. No.	Temp.	Weight	$a = \frac{W_0 - W_t}{W_0 - W_f}$	Log a	$\text{Log} \left(\ln \frac{1}{1-a} \right)$	$\text{Log} \left(\frac{1}{1-a} \right)$
1.	275	9.77016	0.1243	0.18435	-1.76224	-1.75933
2.	285	9.61473	0.14532	-1.35345	-1.34589	-1.44923
3.	295	9.39083	0.17559	-1.07883	-1.06441	-1.04983
4.	305	9.06139	0.22013	-0.85105	-0.8262	-0.80087
5.	315	8.5559	0.28847	-0.63987	-0.59814	0.77702
6.	325	7.85782	0.38285	-0.45467	-0.3876	-0.31689
7.	335	6.94174	0.50671	-0.29162	-0.18682	-0.07286
8.	345	5.88.81	0.65014	-0.15729	0.00012	0.17913
9.	355	4.86864	0.78699	-0.05905	0.16291	0.43018
10.	365	4.03628	0.89952	0.00782	0.30234	0.68254
11.	375	3.41992	0.98286	0.05145	0.42373	0.94376
12.	385	2.96615	1.04421	0.08098	0.54336	1.25626
13.	395	2.6495	1.08702	0.10046	0.68277	1.7206

Initial weight at 260°C = 8.75760 mg.

Final weight at 400°C = 1.36115 mg.

The value of $\log F(\alpha)$ were used to evaluate the values of β_0 ,

β_1 and β_2 at different activation energies at all temperatures.

2. NiBr₂ complex with Schiff base of 5-anilino 1,2,3,4- thiatriazole (5-ATT): -

The value obtained by the elemental analysis and by the conventional gravimetric estimation for the metal content in the complex compound are suggestive of the molecular Formula [Ni(L₂)Cl₂] and molecular weight 487.11 mg. Thermal degradation pattern of this complex is as shown in Table-I

Table-1: Thermoanalytical data and decomposition temperature for [NiL₂Br₂]: -

S. No.	Temp. range (°C)	Species Degraded	% Weight loss	
			Found	Cal
1.	100 - 120	Loss of moisture and 2 Br – ion		11.78
2.	250 - 310	Loss of whole ligand moiety	74.17	71.56
3.	320	NiO formation	12.05	12.20

Freeman and Carroll graphical method was primarily employed to evaluate the order of reaction and activation energy for the first stage of decomposition. In the selected stage of thermal decomposition, the existing weights of the complex at equal temperature interval 10°C were noted as well as

$$\frac{\Delta T^{-1} \times 10^{-3}}{\Delta \log W_r}$$

were calculated and tabulated in Table-II.

Where $W_r = W_c - W$

W_c = Weight loss at completion of reaction

W = Total weight loss up to time T.

Table- II: Data obtained by Freeman and Carroll method.

S. No.	Temp.	Weight	$\frac{\Delta \log \left(\frac{dw}{dt} \right)}{\Delta \log W_r}$	$\frac{\Delta T^{-1} \times 10^{-3}}{\Delta \log W_r}$
1.	150	3.67197	3.42925	1.79492
2.	160	3.64645	4.29935	2.07683
3.	170	3.60597	-2.99586	1.43727
4.	180	3.53758	-2.81142	0.94889
5.	190	3.42591	-1.08142	0.35171
6.	200	3.26904	-0.42427	0.13124
7.	210	3.14530	0.06858	0.03999

Initial weight at 130°C = 3.77142 mg.

Final weight at 220°C = 3.14128 mg.

The plot $\frac{\Delta \log \left(\frac{dw}{dt} \right)}{\Delta \log W_r}$ Versus $\frac{\Delta T^{-1} \times 10^{-3}}{\Delta \log W_r}$ gave straight line with an intercept at 0.2 and applying $E_a = 2.303 R \times \text{Slope}$ gave the values of activation energy to be equal to 12.81 Kcal / mole.

The same values for different weights taken at different temperature were subjected to the Zsako method. The weight of the compound at different temperatures as noted

from the TG curves in the earlier procedure were used for the calculation with the help of following relations.

$$a = \frac{W_0 - W_f}{W_0 - W_i}$$

Where W_0 = Initial weight

W_f = final weight

W =Actual Weight

The log F(a) values are tabulated in Table – III

Table- III: Data of log F(α) values for the complex [Ni2L2Br2] at different temperatures.

S. No.	Temp.	Weight	$a = \frac{W_0 - W_t}{W_0 - W_f}$	Log a	$\text{Log} \left(\ln \frac{1}{1-a} \right)$	$\text{Log} \left(\frac{1}{1-a} \right)$
1.	140	3.71886	0.08340	-1.07870	-1.06000	-1.04095
2.	150	3.67797	0.14830	-0.82885	-0.79446	-0.75914
3.	160	3.64645	0.19832	-0.70263	-0.65551	-0.60663
4.	170	3.60597	0.26256	-0.58077	-0.51631	-0.44849
5.	180	3.53758	0.37109	-0.43052	-0.33370	-0.22910
6.	190	3.42591	0.54830	-0.26098	-0.09977	0.08416
7.	200	3.26904	0.79725	-0.09840	0.20297	0.59463
8.	210	3.14530	0.99362	-0.00277	0.70368	2.1923

The β_0 values for different order of reaction were calculated by the following equation.

$$\beta_0 = \log a - \log p(x)$$

$$\beta_1 = \log \left(\ln \frac{1}{1-\alpha} \right) - \log p(x)$$

$$\beta_2 = \log \left(\frac{\alpha}{1-\alpha} \right) - \log p(x)$$

The value of $-\log p(x)$ was noted from Zsako table for temperature from 100-430°C for energy of activation from 10-66 kcal / mole.

The value of $\log f(a)$ was used to evaluate the value of β_0 , β_1 and β_2 for different activation energies at all the temperatures.

Results:

Copper (II) and Nickle (II) ions are studied their thermal stabilities and have noted a large difference in the nature of the thermograms of ligand and it chelates. The ligand is reported to decompose in two steps, while the chelates are reported to decompose in one narrow step.

The comparison of decomposition range of the ligand and it the nature of the thermograms of ligand and it chelates.

The ligand is reported to decompose in two steps, while the chelates are reported to decompose in one narrow step. The comparison of decomposition range of the ligand and it chelates show that, the chelates are thermally less stable

than the unchelated ligand. Fluorenone anthranilic acid complexes of Co (II) and Ni (II) were synthesized by Thomas et al (14) and the thermal decomposition of these reported that CO (II) and Ni (II) chelates give a three-stage decomposition pattern.

Conclusion:

This study we have to achieve thermal stability study of Copper (II) and Nickel (II) chelates shows important differences compared to the ligand. The ligand breaks down in two distinct stages, show a larger stability range. But the chelates decompose in a single, narrow step, representative they are less constant than the free ligand.

This discrepancy demonstrates how the ligand's thermal behavior is impacted by interaction with metal ions, giving the chelates reduced stability. These results are consistent with previous work by Thomas et al., who found that fluorenone anthranilic acid complexes of Co (II) and Ni (II) show a three-stage breakdown pattern.

Overall, the research proposals important new information about the behavior of these complexes by demonstrating that metal-ligand interactions are active in changing heat stability and decomposition pattern.

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