CHAPTER - V

5.1 Antimicrobial Activities (Antibacterial and Antifungal)

5.2 Thermogravimetric Analysis

5.3 X-ray Powder Diffraction Study

5.3 Conclusion
5.1 GENERAL INTRODUCTION (ANTIMICROBIAL ACTIVITIES)

Antibiotics are vital medicinally important molecules used for the treatment of bacterial infections in both human and animals. Antibiotics are the name given to drugs, which either selectively kill bacteria or at least inhibit their growth. The discovery and development of antibiotics are among the most powerful and successful achievements of modern science and technology for the control of infectious diseases. The concept of antibiotics includes now also, chemically or biochemically synthesized derivatives as well as substances from plant or animal origin. The antimicrobial drugs occupy a unique niche in the history of medicine. These drugs have been used for decades to effectively treat a variety of bacterial infection. Although the mechanism of antibiotics action were not scientifically understood until the late 20th century. The principle of using organic compounds to fight infections has been known since ancient times. Penicillin is the most well known antibiotic and has been used to fight many infectious disease, including syphilis, gonorrhea, tetanus and scarlet fever. Penicillin was discovered accidentally in 1928 by Fleming. They were used at very low concentrations. At low concentration, they are either bactericidal by killing other microorganisms or bacteriostatic by reversibly inhibiting growth.

In the beginning of 20th century, tremendous studies were made in the systemic treatment of certain microzoal infections. Nevertheless, these advances did not affect directly the overall practice of medicine. The advent of sulphanilamides in 1935, marked the beginning of a major revolution in the practice of medicine. The subsequent profusion of antibacterial agents overwhelmed the physician
with golden tools. The realization that certain microorganisms are successfully resisting the "wonder drugs," not only impels a ceaseless search for new systemic antimicrobial agents but also forces a sober return to certain ancillary art of medical and surgical management of infectious diseases.

Fungitoxicity of an active organic molecule may increase its chelation with metal ions. Acid hydrazide, furfural, chloro, bromo, amides, nitro derivatives of certain organic compounds are well known for their fungicidal, bactericidal and pharmacological activities. The toxic effect of an organic molecule will be diminished by the chelation of metal ions at least in some cases.

**EXPERIMENTAL**

The experimental\(^1-7\) part has been divided into two heads.

1. Evaluation to antibacterial activity and
2. Evaluation of antifungal activity

For present studies, three bacteria have been selected viz. Escherichia coli, Staphylococcus aureus and Streptococcus fecalis and two fungi viz. Aspergillus niger and Trichoderma polysporum. The bacteria E. coli is a leading cause of food born illness. Infection with E.coli, often leads to bloody diarrhea and occasionally to kidney failure while S. aureus can cause a range of illness from minor skin infection (as pimples, boils etc.) to life threatening disease such as pneumonia, meningitis and septicemia.

The fungi A niger is animal pathogen causes pulmonary tuberculosis but Trichoderma infections are opportunistic and develop in immuno compromised patients.
A. EVALUATION OF ANTIBACTERIAL ACTIVITY

In the present work, activities of the some synthesized compounds have been evaluated by the Agar well diffusion method using Agar nutrient as the medium. The aim of these investigation was, to study the changes in the activity with the variation in the structures of the molecule, and there by draw some inferences whether the structure of the compound may have some correlation with antibacterial activity. All the synthesized compounds have been screened in vitro against to following three bacteria. Here Norfloxacine and Gentamycine have been used as a standard.

a. Escherichia coli
b. Staphylococcus aureus
c. Streptococcus fecalis

Its methodology follows the following Steps

1. Preparation of the medium and its sterilization,
2. Treatment of the glass apparatus and it's sterilization,
3. Pouring of needed medium into sterilized petridishes,
4. Preparation of required concentration of the compounds,
5. Incubation at particular temperature and
6. Measurements of the zone of inhibition,

Some of the factors, which influence in vitro test are:

1. The kind and condition of the organism,
2. The concentration of the drug solution and the dilution of the bioactive compound at the site of action (incubation period).
3. Environmental factors which may argument or counteract the interaction of compounds and the parasite.

4. pH of the medium (usually range 7.2-7.6).

5. Temperature of the incubation for each bacteria. There is an optimum temperature; however for most of the pathogenic bacteria; this temperature is kept at 37°C for 24 hours.

In the present work the medium has the following composition.

**NUTRIENT AGAR MEDIA**

<table>
<thead>
<tr>
<th>Component</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agar</td>
<td>20 gm.</td>
</tr>
<tr>
<td>Peptone</td>
<td>10 gm.</td>
</tr>
<tr>
<td>Beef extract</td>
<td>3 gm.</td>
</tr>
<tr>
<td>NaCl</td>
<td>1 gm.</td>
</tr>
<tr>
<td>Distilled water</td>
<td>1000 ml.</td>
</tr>
</tbody>
</table>

All the ingredients-peptone (10 gm), Agar (20 gm), Beef extract (3 gm) were dissolved in 1000 ml. of distilled water and shaken well. The media so obtained was poured into the, sterile flasks and plugged with sterile cotton plug which was then sterilized in an autoclave 15 lb pressure for 2-3 hours, (pH adjusted at 7.4). Finally, it was transferred into the sterilized petridishes.

Agar is a complex carbohydrate, obtained from certain marine algae and is used as a solidifying agent for media; it is not used as a source of a nutrition for the bacteria.
INOCULATION OF THE TEST PLATES

Inoculation of the test strain was done by the pour plate technique. 0.2 ml of the activated strain was inoculated into the media when it reached a temperature of 40-45°C. Proper homogenization of the strain was realized by gently pouring into a petriplate. Formation of air bubbles during this procedure of inoculation was strictly avoided. The complete procedure of the preparation of the plate was performed in a laminar airflow to maintain strictly sterile and aseptic conditions. The media was allowed to solidify. After solidification of the media holes/wells were made in each plate with the help of a cork-borer and then 0.1 ml of the synthesized compound (dissolved in DMSO) was added into these wells. The controls were maintained (for each bacteria strain), where 0.1 ml of the pure solvent was inoculated into the well.

INCUBATION OF TEST PLATES

The individual plates were evenly dispersed on the incubator self (at 37°C) so as to make each plate reached approximately to incubator temperature for some time. During this period, the test solution diffused and the growth of the inoculated microorganism was affected.

READING AND INTERPRETATION

After 24 hours of incubation, the plates were examined and the diameter of the zone of complete inhibition was measured by using zone recorder.
B. EVALUATION OF ANTIFUNGAL ACTIVITY

There are several methods available for recording the antifungal activity. We describe here the Well Diffusion method using Agar nutrient as medium.

Some of the synthesized compounds have been screened for their in vitro antifungal activity against the following two fungi using Nystetine/streptomycine as a control.

1. Aspergillus niger
2. Trichoderma polysporum

STERILIZATION OF THE APPARATUS

All the glass apparatus were cleaned with chromic acid followed by distilled water and were sterilized by heating at 150°C in a hot air oven.

PREPARATION OF THE MEDIUM

Sabourauds dextrose agar medium was used for antifungal screening which consists of:

Dextrose - 20 gm.
Potato - 200gm.
Agar - 20 gm.
Distilled water - 1000ml.
Nystetine/ Streptomycine - 0.2 mg.

Nystetine was used to check the growth of undesirable bacteria. The above mentioned ingredients were weighted and dissolved in a 500 ml. of distilled water. When the ingredients were dissolved
completely more distilled water was added to make the solution up to one liter and pH of the medium was kept at 7.4. The medium so obtained was poured into the sterile flask and plugged with sterile cotton plug, which was then sterilized in an autoclave15 lb, pressure for 2-3 hours. Finally, it was transferred into sterilized petridishes.

INOCULATION OF THE TEST PLATES

The petridishes were inoculated in the same manner as described earlier for antibacterial screening.

INCUBATION OF TEST PLATES

These petridishes were incubated at 28°C for 3-4 days. The zone of inhibition was considered as an indication for the antifungal activity.

RESULTS

<table>
<thead>
<tr>
<th>Comp. No. (Schiff bases)</th>
<th>Schiff bases (Ligands)</th>
<th>Complex No. Cu(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>HINH</td>
<td>9</td>
</tr>
<tr>
<td>10</td>
<td>MAP</td>
<td>12</td>
</tr>
</tbody>
</table>

HINH- 2-Hydroxyacetophenone isonicotinic acid hydrazide

MAP- Methyl isobutyl ketone-2-amino-4-chloro phenol
# TABLE - 1

**ANTIBACTERIAL ACTIVITY OF THE SYNTHESIZED COMPOUNDS**

<table>
<thead>
<tr>
<th>Compound (No.)</th>
<th>Staphylococcus aureus</th>
<th>Streptococcus fecalis</th>
<th>Escherichia coli</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25*</td>
<td>50*</td>
<td>100*</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>9</td>
<td>13</td>
<td>14</td>
<td>15</td>
</tr>
<tr>
<td>10</td>
<td>12</td>
<td>12</td>
<td>14</td>
</tr>
<tr>
<td>12</td>
<td>10</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Gentamycin</td>
<td>20</td>
<td>21</td>
<td>23</td>
</tr>
<tr>
<td>(Standard)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Diameter of Inhibition Zone (mm)

*Concentration in ppm

(-) Inactive/ Not Measurable)
### TABLE - 2

**ANTIFUNGAL ACTIVITY OF THE SYNTHESIZED COMPOUNDS**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Trichoderma polysporum</th>
<th>Aspergillus niger</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25*</td>
<td>50*</td>
</tr>
<tr>
<td>No. 7</td>
<td>-</td>
<td>19</td>
</tr>
<tr>
<td>No. 9</td>
<td>12</td>
<td>12</td>
</tr>
<tr>
<td>No. 10</td>
<td>10</td>
<td>19</td>
</tr>
<tr>
<td>No. 12</td>
<td>19</td>
<td>22</td>
</tr>
<tr>
<td>Nystatine</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>(Standard)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMSO</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Diameter of Inhibition Zone (mm)

*Concentration in ppm

(-) Inactive/ Not Measurable)
DISCUSSION ANTIBACTERIAL

Generally all the synthesized compounds show good activity against all three selected bacteria.

Compound 7 exhibit better antibacterial activity than compound 10 against E-coli (compound 7 and 10 are Schiff Bases) but compound 10 exhibited better activity than compound 7 against Staphylococcus aureus and Streptococcus fecalis bacteria. compound 9 exhibit better antibacterial activity in comparison to compound 12 against all the three bacteria. Compound 9 exhibit better activity than its' Schiff base (compound 7) against S. aureus and S. fecalis while compound 7 (Schiff base) show good activity than their metal complexes against E.coli. Compound 12 is more active than it's Schiff base (compound 10) against S. aureus and S. fecalis, while compound 10 (Schiff base) showed better antibacterial activity than their metal complex against E.coli.

This makes to draw the conclusion that on chelation, in majority of the cases, the antibacterial activity enhances.

ANTIFUNGAL

Compound 10 did not exhibit any remarkable antifungal activity against A. niger. Compound 9 and compound 12 give better activity in comparison to it's Schiff base(compound 7 & 10) against A. niger. Compound 9 and 12 show good activity against A. niger. But compound 9 exhibit more antifungal activity in comperision to compound 12 against A. niger.

Generally all the synthesized compounds are more active against Trichoderma. Compound 10 (ligand) so more activity in
comparison to compound 7 (ligand) against fungi Trichoderma. compound 9 and compound 12 show good activity against Trichoderma but compound 12 exhibit more antifungal activity in comparison to compound 9 (complexes) against Trichoderma.

CONCLUSIONS

These observations show that the majority of the complexes show more active than their respective Schiff base (ligands). In some cases, Schiff base are more active than their metal complexes against bacteria and fungi. The chelation either give a positive or negative contribution to the antimicrobial activity or remains neutral. Thus, metal chelation either enhances of suppress the therapeutic value of organic compound drug or keeps the property entact by further stabilizing or reducing the biodegradability of the organic ligand and the chemical structure through chelation.

CHEMOTHERAPEUTIC VALUE

Chelation may enhance or suppress the biochemical potential of bioactive organic species. The higher activity of complexes may be owing to the effect of metal ion on the normal cell processes. Lipids and polysaccharides are important constituents of cell membrane. Metal - chelate bears polar and non polar properties together, this property make them suitable for permeation to the cells and tissues. Changing hydrophilicity and lipophilicity probably leads to bring down the solubility and permeability barriers of cells, which in turn enhance the bioavailability of chemotherapeutics on one hand and potentiality at another. Besides, in course of ligand competition, within the biosystems changing co-ordination number and oxidation states, ligand replacement, some associative and dissociative processes, add more to the
chemotherapeutic value of metal-chelate.\textsuperscript{8,10} In the light of above observation/findings, it may be concluded that the metal chelates may work as a good alternative to combat and cope with the problem of drug resistance, since more than 50\% disease are being caused by microbes. Besides this, the coordinatively bonded life essential metal ions suppress the rate of metabolic decay of the bioactive molecules/drugs thus reducing the amount of the thus reducing the amount of the dose. This may be viewed as an emerging thrust area in the field of biocoordination chemistry, which is the core of Bio-inorganic chemistry and some new research area like medicinal inorganic chemistry may emerge up futher and prosper.\textsuperscript{19-23}
Antibacterial Screening Data of Schiff base [Comp. No. 7 (HINH)] and its Metal Complex [Comp. No. 9 Cu(II)] for S. aureus

- **Schiff base**
- **Cu (II) Complex**
- **Standard**

Antibacterial Screening Data of Schiff base [Comp. No. 10 (MAP)] and its Metal Complex [Comp. No. 12 Cu(II)] for S. aureus

- **Schiff base**
- **Cu (II) Complex**
- **Standard**
Antibacterial Screening Data of Schiff base
[Comp. No. 7 (HINH)] and its Metal Complex [Comp. No. 9 Cu(II)]
for S. fecalis

![Graph 1]

Schiff base | Cu (II) Complex | Standard

Antibacterial Screening Data of Schiff base
[Comp. No. 10 (MAP)] and its Metal Complex [Comp. No. 12 Cu(II)] for S. fecalis

![Graph 2]

Schiff base | Cu (II) Complex | Standard
Antibacterial Screening Data of Schiff base [Comp. No. 7 (HINH)] and its Metal Complex [Comp. No. 9 Cu(II)] for E. coli

- Schiff base
- Cu (II) Complex
- Standard

Antibacterial Screening Data of Schiff base [Comp. No. 10 (MAP)] and its Metal Complex [Comp. No. 12 Cu(II)] for E. coli

- Schiff base
- Cu (II) Complex
- Standard
Antifungal Screening Data of Schiff base
[Comp. No. 7 (HINH)] and it Metal Complex [Comp. No. 9 Cu(II)]
for T. polysporum

Antifungal Screening Data of Schiff base
[Comp. No. 10 (MAP)] and it Metal Complex [Comp. No. 12 Cu(II)]
for T. polysporum
Antifungal Screening Data of Schiff base
[Comp. No. 7 (HINH)] and its Metal Complex [Comp. No. 9 Cu(II)]
for A. niger

- Schiff base
- Cu (II) Complex
- Standard

Antifungal Screening Data of Schiff base
[Comp. No. 10 (MAP)] and its Metal Complex [Comp. No. 12 Cu(II)]
for A. niger

- Schiff base
- Cu (II) Complex
- Standard
ANTIBACTERIAL ACTIVITY OF SCHIFF BASE METAL COMPLEX [COMP. NO. 9 CU(II)] HINH
ANTIBACTERIAL ACTIVITY OF SCHIFF BASE

[COMP. NO. 10 (MAP)]
5.2 GENERAL INTRODUCTION (THERMOGRAVIMETRIC ANALYSIS)

Thermal analysis includes a group of methods by which the physical and chemical properties of a substance, a mixture or reaction mixture are determined as a function of temperature or time. In the early years of the twentieth century the TGA technique first came into practice in its primitive form.\textsuperscript{24-25} Duval et. al.\textsuperscript{26-27} described the historical aspects of TGA.

The change in weight of a sample followed during continuous increase in temperature is, TGA. It provides to the analyst, a quantitative measurement of any weight change associated with thermally induced transition. The curve are characteristics for a given compound or system because of the unique sequence of physico-chemical reaction occurring at definite temperature range and rate.

TGA involves the measurement of the weight of a sample either as a function of time at constant temperature or as function of some parametric temperature as the system temperature change. The sample may either loss weight to the atmosphere or gain weight by the reaction with atmosphere. Thus, a rate differential curve $dw/dt$ is obtained between absolute weight ($W$) as the Y-axis and time(t) or temperature(T) on the X-axis.\textsuperscript{28}

KINETICS

Chemical kinetics deal with a more chemical aspect of chemical phenomenon, namely the rate of change from initial to final state under non-equilibrium conditions, which depends upon the path followed by the reactants while getting converted in to the products. The
activated complex theory, which postulates the existence of an activated complex at the top of an energy barrier with height $E$, the activation energy, deals with a quasi equilibrium involving the reactants, activated complex and the product. The rate of the reaction at temperature $T$ is proportional to:

1. The probability $p$, of the activated complex getting converted into products;

2. The frequency of collisions $u$, between the reactant molecules;

3. The number of particles with energy $E$ required to surmount the energy barrier and

4. A function of concentration $f(c)$.

According to Maxwell-Boltzmann distribution law, the number of particles with energy $E$ in excess of the average energy, at temperature $T$, is given by $\exp \left( -\frac{E}{kT} \right)$.

where $k$ is the Boltzmann constant and hence the rate of a homogenous reaction at concentration $C$ is given by:

$$-\frac{dc}{dt} = p_0 \cdot \exp \left[ -\frac{E}{kT} \right] f(c) = Z \cdot \exp \left[ -\frac{E}{RT} \right] C^n = KC^n$$

where $n$ is the order of reaction, $Z$ is the pre-exponential factor and $K$ is the rate constant at time $t$.

The parameters $n$, $E$, $Z$ and $k$ constitute the kinetics parameters.$^{29-30}$ The above arguments are valid for homogenous reaction where as for heterogeneous reaction (involving more than one phase), several factors like the rate of diffusion of the components to or away from the reaction interphase, rate of nucleation of product in the
reactants, rate of growth of nuclei, geometry of the reaction interphase, effect the chemical reaction etc. Hence, the space co-ordinates, beside time co-ordinate, will have to be introduced in the rate equation.

In solids, the atoms of the reactants are not free to mix with each other but are constrained to oscillate about fixed sites in the lattice and the thermal energy inducing activation, which has vibrational character only. The essential difference between solid-state reaction and solution reaction can be ascribed to the fact, the solid-state reaction occur within the constraining environment of the crystal lattice. In many solid phase reactions, the separation distances and mutual orientations of the reactions in the solid determine the product. Such reactions are said to be topochemically controlled.27,29,31-33

A large number of thermal reactions of coordination compounds have been studied in solid phase, but very few systematic studies were performed prior to the 1960. At first, these studies were focussed mainly on the thermal stability and reaction stoichiometry. Now the kinetic and thermodynamic studies are also being reported. The difficulty in solid state reaction is the identification, description and control of experimental parameters such as particle surface area, defect structures and sample atmosphere. To find an appropriate kinetic model for a reaction is also a significant thing.26,29,31-33

Solid phase reaction include ligand exchanges, isomerization of various types, redox reactions and reactions of coordinated ligands. Unfortunately, investigators often consider kinetic models appropriate to solids and instead uncritically apply procedures for solution kinetics. As a result, many kinetic studies of questionable reliability have appeared. Equations with the thermogravimetric data can
be derived for non-reversible reactions, so that rate dependent parameters like the rate of reaction, activation energy and order of reaction may be calculated from a single experimental curve. An excellent discussion of dynamic and isothermal methods has been given by Doyle. All methods suggested to date suffer more or less seriously from procedural and experimental errors. However, in many cases, TG data are the only experimental facts available and must be used. To facilitate such calculations, the following method are being given. When the reactant is considered in the solid state where one of the product is volatile and other being in the condensed state.

\[ A(s) = B(g) + C(s) \]

Weight loss at any given temperature may be defined as- Fraction of reaction \( \alpha = [W_0 - W_t] / [W_0 - W_\infty] \), where \( W_t \) is the indicated weight at time \( t \), \( W_0 \) is the initial weight and \( W_\infty \) is the weight at the end of the process under study.

In practice, a plot of \( \ln \left( \frac{1}{\alpha} \right) \) versus \( 1000/T \) (where \( T \) is the temperature in Kelvin) is made. This must yield a straight line if the data are accurate and the reaction is of first order. The method is very sensitive to weighing errors. Proof has been offered that if the plot is linear over the total range of decomposition, the reaction must be first order.

In isothermal studies (\( \alpha \) vs \( t \)) curves are plotted at a number of temperature by the measurement of pressure, volume or weight change. The \( \alpha \) vs \( t \) plot is then converted to \( g(\alpha) \) vs \( t \) plots using several of the probable mechanism. These plots may be compared with one another by least square method. The plot giving least variance represent the correct mechanism. The value of \( K \) is obtained from the
slope of this plot. A plot of log K vs 1/T is constructed using the values obtained from the different isotherms, it has a slope of -E / 2.303 R and an intercept of log Z. The disadvantage is that one has to carry out a number of experiments to obtain the Arrhenius plot. It is possible to obtain the kinetic parameters from a single non-isothermal experiment but the interpretation of the results is more difficult, since both time and temperature are varied simultaneously. The usual practice is to increase the temperature linearly with time. Changing the variable from time to temperature the rate equation can be written as.

\[ \frac{d\alpha}{dT} = \frac{Z}{\beta} \exp \left( \frac{-E}{RT} \right) f(\alpha) \]

where \( \beta = \frac{dT}{dt} \) is the heating rate. On rearranging and integration the above equation.

\[ \int \frac{d\alpha}{f(\alpha)} = \frac{Z}{\beta} \int \exp \left( \frac{-E}{RT} \right) dT \]

On solving the equation.

\[ g(\alpha) = \frac{ZE [p(x)]}{\beta R} \]

The equation can be rewritten in logarithms as:

\[ \log g(\alpha) - \log p(x) = \log \left( \frac{ZE}{\beta R} \right) \]

The right hand side being a constant, \( \log p(x) \) varies with temperature in the same manner as \( \log g(\alpha) \).

The following equations may be employed for determining the kinetic parameters in non-isothermal decomposition (integral method) of solids.

I. Method of Coats and Redfern (C-R);\(^{38}\)

\[ \log g(\alpha) / T^2 = \log \left[ -\ln(1-\alpha)/T^2 \right] = E/2.303RT + \log \left[ \frac{Z}{\beta E} (1-2RT/E) \right] \text{ for } n=1 \]
This is one of the most widely used method for determining E and Z. The model for which the plot of log \([g(\alpha) / T^2]\) vs \(1/T\) gives the straight line, representing the correct mechanism and E as well as Z can be calculated from such a plot:

**II. Method of Piloyan and Novikova (P-N)**\(^{41}\)

Piloyan and Novikova suggested a further simplification whereby.

\[
g(\alpha) = \alpha, \text{ for } 0.05 < \alpha < 0.4 \text{ to } 0.5 \text{ and hence}
\]

\[
\log [\alpha/T^2] = \log [ZR/\beta E] - E/2.303 RT
\]

This method does not give an insight into the mechanism of reaction but is one of the simplest methods available for the determination of E and Z from TG curves.

The linear fits for different models\(^{33,39-41}\) were investigated. The best fit linear plot with minimum least square error was selected. The values of slope, intercept and energy of activation were obtained from plots i.e. \(
\log g(\alpha) / T^2 \text{ vs } 1/T\) for C-R and P-N methods. The values of intercept and energy of activation were substituted in equation (1) for evaluating the values of Z in case of C-R and P-N methods the entropy of activation (\(\Delta S^*\)) was calculated by employing equation (2).

\[
\text{Intercept} = \log ZR / \beta E \quad (1)
\]

\[
Z = k T_m / h \exp. (\Delta S^*/R) \quad (2)
\]

Or \(\Delta S^* = 2.303 \cdot R \cdot \log = Zh/kT.\)

Where \(k\) is the Boltzmann constant and \(h\) the plank constant. In the analysis of the TG curves, the linearity criterion of log
\( g(\alpha) / T^2 \) vs \( 1/T \) is taken as sufficient proof for the correct form of \( g(\alpha) \). However, some workers based on their theoretical analysis, have concluded that this linearity of \( \log g(\alpha) / T^2 \) vs \( 1/T \) is necessary but not a sufficient criterion to assigning an unequivocal \( g(\alpha) \) function. They have shown that the \( g(\alpha) = - \log (1-\alpha)^{1/n} \) (where order of reaction \( n=1, 2 \) or \( 3 \)) yielded about the same linear correlation.

Different models or mechanism\(^{33,39-40}\) have been proposed for solid state reaction depending upon the type of processes leading to the reaction. Some of the important models together with the final form of the equations are being given.
## MODELS APPLICABLE TO SOLID STATE REACTIONS

### WITH RATE OF REACTION

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>$f(\alpha)$</th>
<th>$g(\alpha) = kt = \int dx/(f(\alpha))$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Power law ($P_i$)</td>
<td>$(1/r) \alpha^{1-r}$</td>
<td>$\alpha'(r=1/4, 1/3, 1/2, 1, 3/2, \text{or} 2)$</td>
</tr>
<tr>
<td>2. Exponential law ($E_i$)</td>
<td>$(1/r)\alpha$</td>
<td>$\ln \alpha'$, $(r=1 \text{ or } 2)$</td>
</tr>
<tr>
<td>3. Nucleation and Nuclei growth</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Random nucleation ($F_t$)</td>
<td>$(1- \alpha)$</td>
<td>$-\ln(1-\alpha)$</td>
</tr>
<tr>
<td>b. Avarami-Erofeev nuclei growth ($A_t$)</td>
<td>$1/(1-\alpha) [-\ln(1-\alpha)^{1+r}]$</td>
<td>$[-\ln(1-\alpha^r)]$</td>
</tr>
<tr>
<td>c. Prout Tompkins branching nuclei ($B_t$)</td>
<td>$\alpha(1-\alpha)$</td>
<td>$\ln[\alpha/(1-\alpha)]$</td>
</tr>
<tr>
<td>4. Diffusion controlled</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Jander, 3-dimensional diffusion ($D_{3}$)</td>
<td>$(1-\alpha)^{1/3} [(1-\alpha)^{1/3}-1]^{-1}$</td>
<td>$3/2[1-(1-\alpha)^{1/3}]^2$</td>
</tr>
<tr>
<td>b. Anti jander -3 dimensional counter diffusion</td>
<td>$(1+\alpha)^{1/3} [1-(1+\alpha)^{1/3}]^{-1}$</td>
<td>$3/2[(1+\alpha)^{1/3}-1]^2$</td>
</tr>
<tr>
<td>c. Bronstein-Ginstling, 3-dimensional diffusion</td>
<td>$[1-\alpha^{-1/3}-1]^{-1}$</td>
<td>$3/2[1-(2/3)\alpha-(1-\alpha)^{2/3}]$</td>
</tr>
<tr>
<td>d. One dimensional diffusion ($D_1$)</td>
<td>$1/\alpha$</td>
<td>$(1/2)\alpha^2$</td>
</tr>
<tr>
<td>e. Valency two dimensional diffusion ($D_{2v}$)</td>
<td>$[-\ln(1-\alpha)^{-1}]$</td>
<td>$(1-\alpha) \ln (1-\alpha) + \alpha$</td>
</tr>
<tr>
<td>5. Phase boundary</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a. Contracting sphere ($R_3$)</td>
<td>$(1-\alpha)^{2/3}$</td>
<td>$3[1-(1-\alpha)^{1/3}]$</td>
</tr>
<tr>
<td>b. Contracting cylinder ($R_2$)</td>
<td>$(1-\alpha)^{1/3}$</td>
<td>$2[1-(1-\alpha)^{1/3}]$</td>
</tr>
<tr>
<td>6. Constant rate (Fix)</td>
<td>$1$</td>
<td>$\alpha$</td>
</tr>
<tr>
<td>7. Reaction order</td>
<td>$1/(1-\alpha)^{1-\alpha}$</td>
<td>$1-(1-\alpha)^r$ $(r=2, 3 \text{ or } 4)$</td>
</tr>
</tbody>
</table>
TG and DTA are widely applicable for obtaining the maximum usable temperature and the rate determination of materials in high temperature environment. TG measurements provide data on solid-gas reaction like adsorption, desorption, volatilization, oxidation-reduction and decomposition as well as solid-solid reactions involving gaseous products. Information on the loss of constituent water molecules and volatile ligands as well as pyrolytic degradation, are valuable in the investigation of the nature and structure of inorganic compounds.43-44

Thermogravimetric studies can also be supported by X-ray crystallographic, IR and DTA studies, so that, possible modes of dehydration and decomposition can be established. Crystalline rearrangements eg. crystallization from an amorphous structure at high, temperature are characterized by energy changes and hence give DTA peaks. Preparation of inorganic compounds by pyro-synthesis is another area of interest to thermal analysis as well as to these investigation of the thermodynamics and kinetics, of the reactions and transition that result from the application of heat materials. TGA and DSC are widely used in the pharmaceutical, industry in support of drug substance purity assessment, polymer characterization, polymorphism, screening lyophilization process, optimization, residual solvent quantification etc.

**THERMAL DECOMPOSITION OF SCHIFF BASE METAL COMPLEXES**

1. Cu (II) MKN Complex; [Cu (C_{11}H_{14}N_{2}O)_{2} (H_{2}O)_{2}]Cl_{2}

The Thermogram of [Cu (C_{11}H_{14}N_{2}O)_{2} (H_{2}O)_{2}]Cl_{2} complex show the loss corresponding to two coordinated water molecules, has been observed between 180-240°C (Remaining wt% obs / cal. 93/
On increasing the temperature above 240°C, a weight loss at fast rate occurs up to 350°C, which corresponded with the decomposition of the ligand moiety. A horizontal zone beyond 350°C suggest the formation of ultimate pyrolysis product. (Remanining wt% obs/cal. 34/29.89).

2. Ni (II) HAN complex [Ni (C_{14}H_{12}N_{2}O_{2})_{2}]

The thermogram of [Ni (C_{14}H_{12}N_{2}O_{2})_{2}] complex show no loss in weight up to 270°C. After 270°C, a weight loss has been observed in general up to 550°C, indicating decomposition of the ligand in two steps. The weight loss observed between 280-410°C may be due to partially decomposed ligand part in complex (Remaining wt. % obs/cal. 39/36.89) Above 410°C, an inflection occurs in the curve and loss in weight progresses up to 510°C. Above this temperature, no further loss in weight occurs. thus metal oxide has been inferred to be the final product. (Remaining wt.% obs/cal. 21/18.33)

3. Ni (II)- HINH Complex [Ni(C_{14}H_{13}N_{3}O_{2})(H_{2}O)] Cl. 3H_{2}O

The Thermogram of [Ni(C_{14}H_{13}N_{3}O_{2})(H_{2}O)] Cl. 3H_{2}O complex show weight loss between 60°-150°C which corresponds to three lattice water molecules. The complex does not show any loss in weight between 150-230°C. An elimination of one coordinated water molecule has been observed between the temperature 240-260°C. (Remaining wt.% obs/cal. 82./82.91). Above this temperature, a weight loss has been observed in general up to 360°C indicating the loss of major part of the ligand in this step. (Remaining wt.% obs/cal. 49/42.5). The decomposition of remaining intermediate moiety occurs between 360-500°C. After 500°C a horizontal curve has been obtained.
Suggesting an ultimate pyrolysis product of metal oxide. (Remaining wt.% obs/cal. 21/19.9).

4. Cu (II) FCA Complex [Cu (C_{11}H_{7}NOCl_{2})_2Cl_2]

The thermogram of [Cu (C_{11}H_{7}NOCl_{2})_2Cl_2] complex show no loss in weight up to 140°C, indicating the absence of any water in the complex. On increasing the temperature above 140°C, a weight loss at faster rate occurs up to 370°C, which corresponded with the decomposition of the ligand moiety. A horizontal zone beyond 370°C suggest the formation of ultimate pyrolysis product as metal oxide (Remaining wt.% loss % obs/cal. 29/26.77)

5. Cu (II) - PINH Complex [Cu (C_{12}H_{10}N_4O)Cl] Cl. 2H_2O

The nonisothermal heating of the complex [Cu (C_{12}H_{10}N_4O)Cl] Cl. 2H_2O show that its thermal degradation starts at 60°C. Pyrolysis curve shows that two water molecule from the lattice comes out between 60-130°C temperature. (Remaining wt.% obs/cal. 96/90.93).

The complex does not show any loss in weight between 130-210°C. After 220°C, a loss in weight has been observed in general up to 330°C corresponding to the loss of partially decomposed ligand part from the complex. (Remaining wt.% obs/cal. 41/37.96). Above 330°C, an inflection occurs in the curve and loss in weight progresses up to 470°C. This indicates the elimination of the remaining thermally degradable part of the complex. After this temperature the curve shows a constant weight region which may be due to metal oxide ultimate pyrolysis product (Remaining wt.% obs/cal. 29/25.35).
RESULTS

**TABLE - 1**

**THERMAL DECOMPOSITION OF THE LIGAND-METAL COMPLEXES**

<table>
<thead>
<tr>
<th>S.NO.</th>
<th>COMPLEXES</th>
<th>TEMPERATURE RANGE (°C)</th>
<th>WEIGHT LOSS (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Obs.</td>
</tr>
<tr>
<td>1.</td>
<td>Cu (II) MKN Complex</td>
<td>180-240</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>240-350</td>
<td>66</td>
</tr>
<tr>
<td>2.</td>
<td>Ni (II) HAN Complex</td>
<td>280-410</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>420-510</td>
<td>79</td>
</tr>
<tr>
<td>3.</td>
<td>Ni (II) HINH Complex</td>
<td>240-260</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>270-360</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>360-370</td>
<td>79</td>
</tr>
<tr>
<td>4.</td>
<td>Cu (II) FCA Complex</td>
<td>150-370</td>
<td>71</td>
</tr>
<tr>
<td>5.</td>
<td>Cu (II) PINH Complex</td>
<td>60-130</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>230-330</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>340-470</td>
<td>71</td>
</tr>
<tr>
<td>S. No.</td>
<td>COMPLEXES</td>
<td>METHODS</td>
<td>DECOM-POSITION STAGE/ TEMP. (K.)</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------------------</td>
<td>---------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>Methyl isobutyl ketone nicotinamide Cu(II) complex (T₁)</td>
<td>P-N</td>
<td>I₁</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-R</td>
<td>523</td>
</tr>
<tr>
<td>2</td>
<td>2-Hydroxy acetophenone nicotinamide Ni(II) Complex (T₂)</td>
<td>P-N</td>
<td>I₁</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-R</td>
<td>573</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P-N</td>
<td>II₁</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-R</td>
<td>693</td>
</tr>
<tr>
<td>3</td>
<td>2-hydroxy acetonenone isonicotinic acid hydrazied Ni(II) Complex (T₃)</td>
<td>P-N</td>
<td>I₁</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-R</td>
<td>543</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P-N</td>
<td>II₁</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-R</td>
<td>643</td>
</tr>
<tr>
<td>4</td>
<td>Furfurlidene 3-4 dichloro aniline Cu(II) Complex (T₄)</td>
<td>P-N</td>
<td>I₁</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-R</td>
<td>513</td>
</tr>
<tr>
<td>5</td>
<td>2-Pyridine carboxylidene isonicotinic acid hydrazide Cu(II)</td>
<td>P-N</td>
<td>I₁</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-R</td>
<td>503</td>
</tr>
<tr>
<td></td>
<td></td>
<td>P-N</td>
<td>II₁</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C-R</td>
<td>613</td>
</tr>
</tbody>
</table>
DISCUSSION (Thermal Kinetic Parameters)

The value of kinetic parameters $E, Z$ and $\Delta S^*$ have been calculated by C-R and P-N methods. The value of kinetic parameters are given in Table. In general, high value of $\Delta E$ (activation energy) and lower values of $Z$ (frequency factor) favors the reaction to proceed slower than normal.\textsuperscript{35,40,46,50-54}

In present studies, the numerical values of activation energy $E$, frequency factor ($Z$) and entropy of activation ($\Delta S^*$) altogether indicate about the smoothness of the feasibility and reaction rate of the initial reactants and intermediate stage compounds. The negative value of entropy of activation ($\Delta S^*$) indicate that the activated complexes have a more ordered or more rigid structure than the reactant or intermediate (activated complex) resulting the reaction to go slower than normal.\textsuperscript{34,40,45,47,50-52}

Quantitatively slight change in the entropies $\Delta S^*$ of the compounds (than $E^*$) can not be set as a reaction governing factor.\textsuperscript{43-44,46,51-52,55,59} Kinetic parameters of these compounds have been determined individually for first and second decomposition stages.

Usually the first decomposition temperature lie in the range 503-573 K and the second decomposing temperature falls at the higher temperature region i.e. 613-693 K. The order of the thermal stability of compounds come to be $T_5 > T_4 > T_1 > T_3 > T_2$ on the basis of first (decomposition temperature) and $T_5 > T_3 > T_2$ on the basis of second step (decomposition temperature).

The variation in the trend might be interpreted on account of some intermolecular interaction (structural as well as electronic) occurring there in, besides several experimental factors.\textsuperscript{40,4650-52,60}
The kinetic model which have been used for the calculating, the $g(\alpha)$ for the complexes in present studies, is phase boundary (contracting cylinder) $R_2$ for all the five complexes.

Such kinetic parameter can necessarily be treated as reaction course governing under particular set of conditions but their specific physical significance and intrinsic behaviour become generalized with the change in conditions. $^{33,43-44,48,55-59}$
FIRST STEP

PILOYAN-NOVIKOVA (P-N) AND COATS - REDFERN (C-R)
PLOTS OF Cu(II) - MKN Complex
(First Decomposition Stage)
FIRST STEP

PILOYAN-NOVIKOVA (P-N) AND COATS - REDFERN (C-R)
PLOTS OF Ni(II) - HAN Complex
(First Decomposition Stage)
PILOYAN-NOVIKOVA (P-N) AND COATS - REDFERN (C-R)

PLOTS OF Ni(II) - HAN Complex

(Second Decomposition Stage)
PILOYAN-NOVIKOVA (P-N) AND COATS - REDFERN (C-R)

PLOTS OF Ni(II) - HINH Complex

(First Decomposition Stage)
SECOND STEP

PILOYAN-NOVIKOVA (P-N) AND COATS - REDFERN (C-R)

PLOTS OF Ni(II) - HINH Complex

(Second Decomposition Stage)
FIRST STEP

PILOYAN-NOVIKOVA (P-N) AND COATS - REDFERN (C-R)

PLOTS OF Cu(II) - FCA Complex

(First Decomposition Stage)
FIRST STEP

PILOYAN-NOVIKOVA (P-N) AND COATS - REDFERN (C-R)

PLOTS OF Cu(II) - PINH Complex

(First Decomposition Stage)
PILOYAN-NOVIKOVA (P-N) AND COATS - REDFERN (C-R)

PLOTS OF Cu(II) - PINH Complex

(Second Decomposition Stage)
5.3 GENERAL INTRODUCTION (X-RAY DIFFRACTION)

X-ray in essence permits one to look inside the crystal and this provide a patent tool for this purpose.

The scattering power of an atom for X-rays depends upon the number of electrons, it possesses. Thus, the position of the diffraction beams from a crystal depends only upon the size and shape of the repetitive unit of a crystal and wave length of the incident X-ray beam. The intensities of the diffracted beams depend also upon the type of atoms in the crystal and the location of the atoms in the fundamental repetitive unit i.e the unit cell\textsuperscript{71}. The infinite variety in the properties of the solid materials show that the world is really an expression of infinite variety of the ways in which the atoms and molecules can be tied together (W. Bragg)\textsuperscript{70}.

In the method of X-ray diffraction analysis, the diffraction of X-ray from the planes of a crystal is studied. This method depends upon the wave character of X-rays and the regular spacing of planes in a crystal. In X-ray powder diffraction method, the crystal is replaced by a large and a continuous cone of diffracted rays. The cone obtained with a single crystal are not continuous because the diffracted beams occur only at certain points along the cone; where as cone with the powder method are continuous because of the random orientation of the crystallites. The reciprocal lattice points generate a sphere of radius $\sigma_{hkl}$ about the origin of the reciprocal lattice. A number of these spheres intersect the sphere of reflection.

Every atom in a crystal scatters an X-ray beam incident upon it in all direction. Atoms located exactly on the crystal planes contribute maximally to the intensity of the diffracted beam, atoms
exactly half way between the planes exert maximum destructive influence and those at some intermediate location interfere constructively or destructively depending on their exact location but with less than their maximum effect.

Several basic concept are essential to understand for Bragg's equation. These include the following :-

1. Space lattice
2. Unit cell
3. Crystal system
4. Elements of symmetry
5. Point groups
6. Space groups
7. Miller indices

These details are available in standard text books.\textsuperscript{63-67} Their diffraction pattern is thus a "fingerprint" of a crystalline compound and the crystalline components of a mixture can be identified individually. X-ray wavelengths are roughly of same magnitude as the separation of atoms in matter. This is a necessary condition for the diffraction phenomenon. Most solids are constructed from some elementary spatial unit duplicate over and over at regular intervals. This is equivalent to saying that most solids are crystalline. A diffracted ray represents the integrated effect of many scattering centers and hence, a reasonable perfection in structure is required.

In present investigation, the crystal system, lattice parameters, cell volume and density have been determined by powder method and crystalloid size have been determined by Scherrer equation.
Scherrer equation $B = 0.9\lambda / t \cos \theta$

where $B =$ broadening of diffraction line measured at half of its maximum intensity (radians)

$t =$ diameter of crystal particle

$\lambda =$ 1.54056 Å

$\theta =$ half of 2θ of maximum intense peak (radians)

Diffraction phenomena can be interpreted most conveniently with the aid of the reciprocal lattice constant when a normal is drawn to each plane in a crystal and the normals are drawn from a common origin, the terminal points of these normals constitute a lattice array. This is called the reciprocal lattice. Near the origin, the traces of several planes in a unit cell of a crystal may be written (100), (001), (101) planes. The normal to these plane are called the reciprocal lattice vectors $\sigma_{hkl}$ and is defined by

$\sigma_{hkl} = \lambda / d_{hkl}$

In three dimensions, the lattice array is described by these reciprocal lattice vectors whose magnitudes are given by -

$a^* = \sigma_{100} = \lambda / d_{100}$

$b^* = \sigma_{010} = \lambda / d_{010}$

$c^* = \sigma_{001} = \lambda / d_{001}$

And whose directions are defined by three interaxial angles $a^*, b^*, c^*$ writing the Bragg's equation in a form that relates the glancing angle $\theta$ most clearly to the other parameters is an.

$\sin \theta_{hkl} [\lambda / d_{hkl}] / 2$
There are seven different crystal systems which differ from one another in terms of the parameters of the space lattices. These parameters are the three repeating distances $a$, $b$ and $c$ and the three angles between the crystal axes. The angle between the $x$ and $y$ axis is $\gamma$, that between the $Y$ and $Z$ axis is $\alpha$ and that between the $x$ and $z$ axis is $\beta$.77-81.

<table>
<thead>
<tr>
<th>No.</th>
<th>System</th>
<th>Axis</th>
<th>Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Triclinic</td>
<td>$a\neq b\neq c$</td>
<td>$\alpha\neq \beta\neq 90^0$</td>
</tr>
<tr>
<td>2.</td>
<td>Monoclinic</td>
<td>$a\neq b\neq c$</td>
<td>$\alpha = \gamma = 90^0$, $90^0 &lt; \beta &lt; 180^0$</td>
</tr>
<tr>
<td>3.</td>
<td>Orthorhombic</td>
<td>$a\neq b\neq c$</td>
<td>$\alpha = \beta = \gamma = 90^0$</td>
</tr>
<tr>
<td>4.</td>
<td>Tetragonal</td>
<td>$a=b\neq c$</td>
<td>$\alpha = \beta = \gamma = 90^0$</td>
</tr>
<tr>
<td>5.</td>
<td>Hexagonal</td>
<td>$a=b\neq c$</td>
<td>$\alpha = \beta = 90^0$, $\gamma = 120^0$</td>
</tr>
<tr>
<td>6.</td>
<td>Rhombohedral</td>
<td>$a=b=c$</td>
<td>$90^0 \neq \alpha = \beta = \gamma &lt; 120^0$</td>
</tr>
<tr>
<td>7.</td>
<td>Cubic</td>
<td>$a=b=c$</td>
<td>$\alpha = \beta = \gamma = 90^0$</td>
</tr>
</tbody>
</table>

In a crystal the atoms are arranged in a regular three-dimensional pattern, the repeating units of which may be found at regular intervals in many different directions. One has to choose three directions ($X$, $Y$, and $Z$) corresponding to the three shortest repeating distances ($a$, $b$, and $c$) as the crystal axes. The repeating units may be atoms, molecules or even groups of atoms or molecules. The repeating unit may be replaced by points which results space lattice. Each family of planes is characterized by three integers $h$, $k$ and $l$ called miller indices. A miller index of a family of planes is the number of such planes that are crossed on moving a distance of one lattice spacing along one
of the axes of the lattice. The indices h, k and l, refer to the axes x, y, z, and the lattice spacing a, b and c respectively.

The (100), (010), (001) planes from the boundaries of a set of parallelepipeds with side dimensions of a, b, and c. Each parallelepiped called a unit cell, contains an integral number of structural units.

**CRYSTAL SYSTEM IDENTIFICATION AND UNIT CELL DETERMINATION**

When the unit cell is unknown, assigning indices to the lines on a powder photographs or peaks in a diffractogram is much more complicated, in general the substance should first be assumed cubic and if this does not work then successively more complicated system should be tried. There are three types of cubic lattice, primitive cubic, face-centred cubic and body centred cubic. The characteristic of the cubic system is that the values of \( \sin^2 \theta \) have a common factor. The \( \sin^2 \theta \) values for first few lines of photograph are listed to be given a common factor, when we divide all values of \( \sin^2 \theta \) by this common factor, one get number close to integer. The forbidden number 7, 15, 23, 28, 31 are not observed. The distinction between the face centered, body centered and primitive cube can be done on the basis of integers. The primitive cube gives natural numbers except for the forbidden numbers. In a face centered cube, these numbers are 3, 4, 8, 11, 12, 16, 19, 20, 24, 27, 32, where as the body centred cube gives only the even numbers.

In a primitive cubic lattice, X-ray reflections can be obtained from all planes. In a face centered cubic lattice, reflections are obtained
only from planes for which \( h,k,l \) are all even or all odd. In a body centered cubic lattice, reflection are obtained only from planes for which the sum \( h+k+l \) is even. There are certained values of \( N(7,15,23) \) etc. for which reflections are not obtained in any of the cubic lattices.

For the space lattice lattice belongs to the cubic system, the expression for \( d_{hk} \) (interplaner spacing) is very simple.

\[
d_{hk} = \frac{a}{(h^2+k^2+l^2)^{1/4}} \quad \text{where} \ a = \text{lattice constant}
\]

\[
\sin^2 \theta = \frac{\lambda^2}{4} \left( \frac{h^2+k^2+l^2}{4a^2} \right) = \frac{\lambda^2}{4} \frac{N}{a^2} \quad \text{(cubic)}
\]

where \( N=h^2+k^2+l^2 \)

A more complicated expression / pattern are required for non-cubic or for space lattices of lower symmetry. The simplest procedure is to see the relationship between the value of \( \sin^2 \theta \) which will give an indication of the symmetry for a tetragonal substance.

\[
\sin^2 \theta_{hk} = A (h^2+k^2) + c^2
\]

where \( A = \frac{\lambda}{4a^2} \) and \( C=\frac{\lambda}{4c^2} \)

The problem is, therefore, to find values of \( A \) and \( C \) which gives the observed value of \( \sin^2 \theta \) integral values of \( h, k, l \).

Consider a spectra with \( l=0 \);

\[
\sin^2 \theta_{100} = A, \quad \sin^2 \theta_{110} = 2A, \quad \sin^2 \theta_{200} = 4A,
\]

\[
\sin^2 \theta_{210} = 5A, \quad \sin^2 \theta_{220} = 8A.
\]

The ratio 2 occurs frequently, except by chance, the only other system in which this ratio is found, is cubic one. If the substance is not cubic and \( \sin^2 \theta \) of two low angle lines are in the ratio on 2; it is probable that the substance is tetragonal and that the two lines are 100
or 110 and 200. The quantity 'A' can be derived and the presence of other hk0 lines can be tested. If other lines do fit in, the original guess is probably correct. Now the problem is to find the value of C. This is achieved by subtracting the multiplets of A from all the value of \( \sin^2 \theta \).

In case the substance is neither cubic nor tetragonal, the next system to be tried is hexagonal and trigonal.

For hexagonal axis, the equation is

\[ \sin^2 \theta_{hk0} = A \left( h^2 +hk+k^2 \right) + C \]

Where \( A = \lambda/3a^2 \) and \( C = \lambda/4c^2 \)

For hk0 spectra, \( \sin^2 \theta_{100} = A \)

\( \sin^2 \theta_{110} = 3A, \sin^2 \theta_{200} = 4A, \sin^2 \theta_{210} = 7A, \)

\( \sin^2 \theta_{300} = 9A, \sin^2 \theta_{220} = 12A \)

It will be seen that the most frequently occurring ratio is 3.

If the unknown system has trigonal symmetry then it may be based on either a hexagonal or a rhombohedral lattice. If the lattice is hexagonal, then the procedure is as described for a hexagonal system, but if the underlying lattice is rhombohedral then the hexagonal cell will be determined by this method. The particular absences depend on the relative orientation of the true rhombohedral cell and the selected hexagonal cell. They fall into one of the two categories for one possible orientation, the only lines present on hexagonal indexing are those for which:

\[-h + K + l = 3n, \quad n = 0, 1, 2 \]

for the other orientations, the condition for a reflection to occur is:

\[ h - k + l = 3n, \quad n = 0, 1, 2 \]
If the substance is orthorhombic, the problem is more difficult. Three constants have to be found and these are related to the \( \sin^2 \theta \)'s by the equation:

\[
\sin^2 \theta_{hkd} = Ah^2 + Bk^2 + Cl^2
\]

where \( A = \lambda^2/4a^2 \), \( B = \lambda^2/4b^2 \) and \( C = \lambda^2/4c^2 \)

Some idea of the probable magnitudes of \( A \), \( B \) and \( C \) may be obtained from the number of lines on photographs. The smaller these constants are, the greater the number of lines that can appear, if \( M \), is the number of observed lines then;

\[
M = \frac{2\pi \sin^2 \theta}{m/24} \frac{m}{24} (ABC)^{1/2} = (ABC)^{1/2} = \sin^2 \theta \frac{m}{4M}
\]

If \( A, B, C \), are of the same order of magnitude the \( (ABC)^{1/2} \) may be replaced by \( A^{3/2} \) (or \( B^{3/2} \) and \( C^{3/2} \)) the approximate value of \( A \) is given by \( (\sin^2 \theta m/4M)^{2/3} \) that is

\[
A = 0.4 \sin^2 \theta / M^{2/3}
\]

The problem is still formidable but not insoluble. For example:

\[
\sin^2 \theta_{100} = A; \sin^2 \theta_{010} = B, \sin^2 \theta_{001} = C
\]

\[
\sin^2 \theta_{011} = B + C = \sin^2 \theta_{010} + \sin^2 \theta_{001}
\]

\[
\sin^2 \theta_{101} = A + C, \sin^2 \theta_{100} = \sin^2 \theta_{001}
\]

\[
\sin^2 \theta_{110} = A + B = \sin^2 \theta_{100} + \sin^2 \theta_{010}
\]

\[
\sin^2 \theta_{111} = A + B + C = \sin^2 \theta_{100} + \sin^2 \theta_{010} + \sin^2 \theta_{001}
\]

It might be possible to find lines whose values of \( \sin^2 \theta \) had this type of relation. This, however, is unlikely because the chance that
100,010 and 001 will be absent for one or more reasons are high. We therefore, may alternatively rewrite the equations as follows.

\[ C = \sin^2 \theta_{001} = \sin^2 \theta_{101} - \sin^2 \theta_{100} \]

\[ = \sin^2 \theta_{011} - \sin^2 \theta_{010} \]

\[ = \sin^2 \theta_{hkd} - \sin^2 \theta_{hk0} \]

That is, \( C \) should often occur as the difference between the \( \sin^2 \theta \) for two lines and so conversely, any difference that occurs often may be tried as A,B, or C. In case, the compound does not belong to cubic, tetragonal, hexagonal or orthorhombic symmetry; the monoclinic and triclinic systems be tried.

**NUMBER OF ATOMS OR MOLECULES PER UNIT CELL**

Unit cell values should always be checked by calculating the number of atoms or molecules per unit cell. A face centred cubic crystal contains four equivalent points, a body centred crystal has two points and hexagonal crystal possesses one point per unit cell. The number of atoms for elements or molecules (for compound) will be equal to this or be some multiple of these numbers. If calculations show this to be true, one may feel assured that unit cell constants are probably correct. The number of molecules per unit cell is determined as follows:

\[ \text{Density of the body } D = n M / V \cdot N \]

Where \( n \) = number of molecules per unit cell

\( M = \) Molecular weight

\( V = \) Volume of cell

\( N = \) Avogadro's number
After indexing a cubic powder pattern, the lattice parameters, 
a may be calculated from the relation \( a = dN^x \) for each \( d \) value.

X-ray diffraction furnishes a rapid, accurate method for the 
identification of the crystalline phases content in many minerals and 
matterials. Some times it is only method available for determining, that 
which of the possible polymorphic forms of substance are present eg. 
differentiation among various oxides such as \( \text{FeO, Fe}_2\text{O}_3 \) and \( \text{Fe}_3\text{O}_4 \) 
or between materials present in such mixtures as \( \text{KBr + NaCl + KCl + NaBr} \) easily accomplished with X-ray diffraction. X-ray diffraction is 
adaptable for qualitative and quantitative applications because the 
intensities of the diffraction peaks of a given compound in a mixture are 
proportional to the fraction of the material in the mixture\(^{15} \).

XRD is used as an adjunct to chemical analysis in the 
identification of the constituents of mixture of crystalline phase e.g. in 
minerals cements and alloys for measurement of the lattice parameters 
of artificially produced structures such as the epitaxially grown 
materials in modern electronic materials, used by the pharmaceutical 
industry to identify change in raw material or method that might alter 
drugs efficary.

In some cases a "powder pattern" can give information 
about symmetry or the size of the molecules unit. It is very characteristic 
of the substance and can be used for identification. For a powder 
sample it's diffraction pattern be compared with diagrams of known 
substance (X-ray powder data file) until a match is obtained.
DISCUSSION

Three of the present complexes have been investigated for their powder-microcrystalline structure. These compounds were subjected to X-ray powder diffraction analysis. The crystal system, lattice parameters, cell volume and density have been determined in present studies for selected complex compounds.\textsuperscript{77-78, 81}

X-ray powder diffraction data and diffractograms were recorded at SAIF, R.T.M. Nagpur university Sin$^2\theta$ and hkl value of different lattice planes have been presented in table -3x, 4x & 8x

X-ray crystal system has been worked out by trial and error method for finding the best fit between observed and calculated Sin$^2\theta$ value. The calculated and experimental value of density of complexes show good agreement and are with in the experimental error limits. All the complexes have been crystallized in tetragonal and orthorhombic crystal system. All the three compounds have been found crystalline giving number of peaks in their diffractogram. The (2-Pyridine carboxylidene-isonicotinic acid hydrazide)-Nickel (II) complex, shows maximum number of peaks 31 while minimum number of peaks 12 have been observed for (2-hydroxy-acetophenone - isonicotinic acid hydrazied) Nickel (II), complex.

The system to which the crystal of complexes belong, have been determined, taking in view the angle $\alpha$, $\beta$ and $\gamma$ on their axes and relative length of the primitive translations $a$, $b$ and $c$.

The X-ray diffraction data of (2-hydroxyacetophenone isonicotinic acid hydrazide) Nickel (II) complex give 12 reflections
between $5^\circ-99^\circ$ ($2\theta$), which corresponds to $d=6.2167$ Å. The maxima reflection was observed at $2\theta = 14.235$. The observed value fit well in the orthorhombic system to give a unit cell with lattice constant $a=b=13.9338$ Å $c=34.7975$ Å and the cell volume =6755.96 Å$^3$. The number of molecules per unit cell are 12. The observed and calculated density of the complex compound comes to be 1.2421 and 1.2847 gm/cm$^3$ respectively.

The diffractogram of (Methyl isobutyl ketone-2- amino-4-chlorophenol) Nickel(II) complex, show 19 refractions between $5^\circ-99^\circ$ ($2\theta$) with maximum of reflection at $2\theta=6.090$ which corresponds to $d=14.5007$ Å. A comparison of the values reveals that there is a good agreement between calculated and observed value of $\sin^2\theta$. The observed values fit well in the tetragonal system and gives a unit cell with lattice constant $a=20.5097$ Å $c=34.4477$ Å and cell volume 14490.34 Å$^3$ and $n=26$ (number of molecules per unit cell). The cell volume gives the observed value of density which is 1.4886 gm/cm$^3$ while the calculated value of density has been found to be 1.5176 gm/cm$^3$.

The diffraction of (2-Pyridine carboxylidene-isonicotinic acid hydrazide) Nickel(II) complex consist 31 reflection between $5^\circ-99^\circ$ ($2\theta$) with reflection maxima $2\theta=12.930$ Å which corresponds to $d=6.8411$ Å. A comparison of the value reveal that there is a good agreement between calculated and observed values of $\sin^2\theta$. The observed values fit in the tetragonal system and gives a unit cell with lattice constant $a=13.3103$ Å $c=35.6441$ Å and cell volume 6314.88
A\textsuperscript{03}. The number of molecules per unit cell are 13. The observed and calculated density of the complex compound comes to be 1.4003 and 1.4315 gm/cm\textsuperscript{3}, respectively. The density of complex have been determined experimentally which show good agreement with the calculated values.
5.4 CONCLUSION

Studies made in present context are focussed mainly on structure elucidation of Ni(II) and Cu(II) complexes. The applications of Ni (II) and Cu (II) complexes are extremely varied and of great importance and can be used in heterogeneous catalysis. The ligand undertaken for present studies are of specific nature having their importance in medicinal, analytical, biological, catalytical and industrial field. Ni(II) and Cu(II) -ONO, N₂, NO donor complexes have been synthesized and characterized by elemental analysis, molar conductance, magnetic measurement, thermal, UV-VIS, ESR, IR spectroscopic and XRD powder method. The proposed geometry for the Ni (II) and Cu (II) complexes are square planar or octahedral. The reactivity and substitution behaviour of the synthesized complexes against aquo, amine, chloro, hydroxo and thiocynato ligands have been studied. Polarimetric studies reflect optical behaviour of the Schiff bases and their metal complexes. Some of the Schiff bases and their Cu(II) complexes act as antimicrobial agents. The Schiff base transition metal complexes may be of attractive oxidation catalyst for a variety of organic substrates because of their cheap and easy synthesis and their chemical and thermal stability; thus, may be of great academic and commercial interest.
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