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# SYNTHESIS, CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF SOME2,6-DICHLORO-3-(1,5-DISUBSTITUTED ARYL PYRAZOLIN-2YL) QUINOLINE DERIVATIVES AND ITS METALCOMPLEXES WITH COPPER AND COBALT

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**ABSTRACT**

*Synthesis of some heterocyclic compounds containing quinoline moiety were synthesized. They were characterized by elemental analyses as well as IR and $H^1$MR spectroscopic analyses. These compounds were treated with metal Co(II) and Cu(II) salts to produce complexes. The complexes were identified and characterized by elemental analyses, IR and electronic spectral studies. All heterocyclic compounds and metal complexes were screened for antimicrobial activity against Staphylococcus aureus and Bacillus megaterium, Aspergillus niger and Aspergillus parasiticus using DMF as a solvent. The activity was compared with known antibiotics like Penicillin,Ampicillin, Tetracycline, Chloramphenicol and Norfloxacin. The chloro- and nitro-substituted synthesized compounds have exhibited good activity against selected bacteria and fungi.*

***Keywords: Synthesis of 6-methoxy-2-Chloroquinoline-3-carbaldehyde, Schiff bases, preparation of complexes and Antimicrobial activity.***

## I. INTRODUCTION

Twenty first century has been regarded as on era of chemical, biochemical solid states and material science. Organic and inorganic chemistry have widened their scope in past two decades due to the emergence of sub-disciplines-molecular biology and nanotechnology. Transition metal plays a central role in the formation of coordination compounds. The coordination compounds have applications in diverse fields. The most important among them are heterogeneous/ homogenous catalysis in industry and biochemical processes occurring in plant, animals and mankinds.It is remarkable that the certain physical and chemical properties of quinoline and their derivatives have around interest with respect to the biochemistry and pharmacology. Several derivatives of these compounds after suitable structure modification are being used as drugs. A number of metal complexes have

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been documented which are biologically active as bacteriocidal,fungicidal,antiviral and antitumor agents and also used in dyes and agriculture industries[1-4].

## II. MATERIAL AND METHODS

Melting points were determined in an open capillary tube with a Buchi melting point apparatus and are uncorrected. Elemental analysis was obtained using Perkin-Elmer 240C CNH analyzer, I.R. spectra were recorded on FT-IR 8400S Simandzu spectrophotometer, $^1$HNMR spectra in $CDCl_3$ at 300MHz on a BrukerDRX 300 spectrometer. The purity of the compounds has been checked by TLC.

### 1. Synthesis of 4-chloro acetanilide:

*p*-chloroaniline (0.1 mol) was cooled at 15 to 20ºC in 50 ml water. Acetic anhydride (0.1 mol) was added with stirring and the reaction mixture was refluxed for two and half hours. The reaction mixture was poured into ice water. The product was isolated and recrystallized from methanol.

### 2. Synthesis of 2,6-dichloro quinoline-3-carboxaldehyde :

Dimethylformamide (0.125 mol.) was cooled at 5ºC in a flask equipped with drying tube and phosphorusoxochloride (0.35 mol.) was added dropwise with stirring. This solution was refluxed for 6 hours. The reaction mixture was poured into ice water and stirred for 30 min. at 0-10ºC. The product was isolated and recrystallized from ethyl acetate.

### 3.Synthesis of 1-substituted aryl 3-(2,6-dichloroquinolin-3yl)-2-propen-1-ones :

A solution of substituted acetophenone (0.02 mol.) in minimum quantity of ethanol (5 ml) was added to a mixture of 2,6-dichloroquinoline-3-carboxaldehyde (0.02 mol.) in 20 ml ethanol and 40% NaOH was added to make it slightly alkaline. The reaction mixture was then stirred for 20 hours at room temperature. The product was isolated and recrystallized from ethanol.

### 4. 2,6-dichloro-3-(1,5-disubstituted aryl pyrazolin-2yl) quinoline :

A mixture of compound **3** (0.01 mol.) in 20 ml acetic acid and hydrazine hydrate (0.01 mol.) was refluxed for 10 hours. The contents were poured into ice and product was isolated and recrystallized from ethanol.

## III. PREPARATION OF THE METAL COMPLEXES:

Metal complexes have been synthesized by the addition of the ethanoic solution of metallic salt $MCl_2.XH_2O$ (0.01 mol.) to aethanoic solution of synthesized compounds (0.01 mol.) in 1:2 ratio and mixture was refluxed on water bath for about 6 hours. The refluxate was kept overnight. The resulting coloured precipitate complex, washed with ethanol followed by petroleum, ether and dried under reduced pressure over anhydrous $CaCl_2$ in a desiccator.

The complexes are air stable and soluble in ethanol and methanol. The color of complexes, melting point, elemental analysis, and spectral data are given in table.

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**Table 1-Physical data of synthesized metal complexes.**

| Comp. Code | *Molecular Formula* | M. Wt. | *Color* | M. P. $^0$C | C% | | N% | | H% | | M% | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Found | *Calculated* | *Found* | *Calculated* | Found | *Calculated* | Found | Calculated |
| 1 | $[Co(C_{22}H_{22}N_2O_4)Cl_2]$ $6H_2O$ | 614.23 | ,, | 352 | 43.00 | 43.01 | 4.53 | 4.55 | 5.56 | 5.57 | 9.58 | 9.59 |
| 2 | $[Co(C_{22}H_{22}N_2O_2)Cl_2]$ $6H_2O$ | 582.25 | Greenish yellow | 310 | 45.36 | 45.37 | 4.79 | 4.80 | 5.86 | 5.88 | 10.11 | 10.12 |
| 3 | $[Co(C_{22}H_{22}N_2O_2)Cl_2]$ $6H_2O$ | 582.25 | ,, | 306 | 45.36 | 45.37 | 4.78 | 4.80 | 5.87 | 5.88 | 10.10 | 10.12 |
| 4 | $[Co(C_{20}H_{16}N_2O_2)Cl_2]$ $6H_2O$ | 552.06 | Green | 298 | 43.50 | 43.51 | 5.05 | 5.07 | 5.09 | 5.10 | 10.67 | 10.67 |
| 5 | $[Co(C_{20}H_{16}N_2O_2Cl_2)Cl_2]$ $6H_2O$ | 552.06 | ,, | 245 | 43.49 | 43.51 | 5.06 | 5.07 | 5.07 | 5.10 | 10.63 | 10.67 |
| 6 | $[Co(C_{20}H_{16}N_4O_6)Cl_2]$ $6H_2O$ | 644.19 | ,, | 245 | 37.27 | 37.28 | 8.67 | 8.69 | 4.32 | 4.34 | 9.13 | 9.15 |
| 7 | $[Cu(C_{22}H_{22}N_2O_4)Cl_2]$ | 512.94 | ,, | 217 | 51.46 | 51.51 | 5.42 | 5.46 | 4.29 | 4.32 | 12.34 | 12.38 |
| 8 | $[Cu(C_{22}H_{22}N_2O_2)Cl_2]$ | 480.96 | ,, | 300 | 54.92 | 54.93 | 5.80 | 5.82 | 4.56 | 4.61 | 13.19 | 13.21 |
| 9 | $[Cu(C_{22}H_{22}N_2O_2)Cl_2]$ | 480.96 | Light green | 252 | 54.89 | 54.93 | 5.78 | 5.82 | 4.54 | 4.61 | 13.18 | 13.21 |
| 10 | $[Cu(C_{20}H_{16}N_2O_2)Cl_2]$ | 521.17 | ,, | 247 | 46.00 | 46.08 | 5.34 | 5.37 | 3.00 | 3.09 | 12.15 | 12.17 |
| 11 | $[Cu(C_{20}H_{16}N_2O_2Cl_2)Cl_2]$ | 521.17 | Red | 242 | 46.02 | 46.08 | 5.32 | 5.37 | 3.04 | 3.09 | 12.14 | 12.17 |
| 12 | $[Cu(C_{20}H_{16}N_2O_6N_4)Cl_2]$ | 542.9 | Orange | 250 | 44.22 | 44.24 | 10.30 | 10.32 | 6.65 | 6.68 | 11.69 | 11.70 |

**Table N0 - 2 The CommonIR Spectral data of synthesized metal complexes with cobalt and copper metals. Intensity affected I.R. bands due to complexesation**

| S.No. | Compound (ligand) | | Complex compound Frequency ($cm^{-1}$) |
|---|---|---|---|
| | Vibrations | Frequency ($cm^{-1}$) | |
| 1 | Ar-$NO_2$Str | 1674.27 | 1647.26 |
| 2 | N = O Str | 1525 | 1496.81 |
| 3 | C = N Str | 1656.7 | 1604.83 |
| 4 | C - N Str | 1174.6 | 1166.97 |

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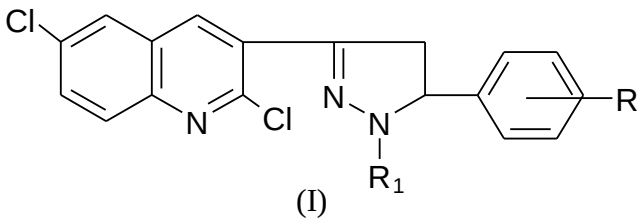
**Structure of ligands**

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## IV. ANTIMICROBIAL ACTIVITY OF THE SYNTHESIZED COMPOUNDS[5]:-

In the present study, the filter paper disc diffusion plate method has been employed to evaluate the antimicrobial activity *in vitro.*

**Table 2 : Antimicrobial activity of synthesized complexes with cobalt metal.**

| Comp. Code | Bacteria | | | | Fungi | | | |
|---|---|---|---|---|---|---|---|---|
| | Staphylococcusaureus | | Bacillus megaterium | | Aspergillus niger | | Aspergillus parasiticus | |
| | 2% | 4% | 2% | 4% | 2% | 4% | 2% | 4% |
| **1** | 15 | 17 | 15 | 17 | 11 | 13 | 16 | 18 |
| **2** | 12 | 13 | 10 | 12 | 6 | 8 | 10 | 13 |
| **3** | 15 | 17 | 19 | 22 | 14 | 16 | 11 | 14 |
| **4** | - | 7 | 10 | 12 | 8 | 10 | 10.5 | 12 |
| **5** | 16 | 22 | 15 | 17 | 10 | 13 | 15 | 16 |
| **6** | 18 | 23 | 16 | 18 | 12 | 14 | 16 | 18 |
| **7** | 18 | 21 | 14 | 18 | 19 | 24 | 19 | 22 |
| **8** | 20 | 22 | 15 | 20 | 20.5 | 21 | 20.5 | 21 |
| **9** | 17 | 19 | 16.5 | 18 | 17 | 22 | 19 | 22 |
| **10** | 15.5 | 20 | 17 | 19 | 18 | 19 | 19.5 | 22 |
| **11** | 20 | 22 | 15 | 20 | 20.5 | 21 | 20.5 | 21 |
| **12** | 18.5 | 20 | 17.5 | 19 | 20 | 19 | 21.5 | 23 |
| Standard | 16 | 20 | 15 | 19 | 21 | 23 | 15 | 20 |

Zone of inhibition in mm. (- ) not shown activity

## V. RESULT AND DISCUSSION

A careful comparison of ligands and complexes spectra follows by information regarding co-ordination through various groups.

The I.R. spectra of the ligands exhibits a band at 1656-1602 $cm^{-1}$ due to the azomethine [C = N] group in ligands. This band shifts to lower frequency by 20-25 $cm^{-1}$ and the ligands exhibits a bands at 1734-1674 $cm^{-1}$ due to C = O groups in ligands. This bands shifts to lower frequency by 20-30 $cm^{-1}$ in the complexation. The complex showing its participation in chelation through the azomethine nitrogen and carbonyl oxygen. The lowering is due to the reduction of electron density in both the groups.

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The shielding if the frequency in the spectra due to complexesation. This represented the participation of C = N, C = O and groups in co-ordination.

However, the appearance of bands at 743-723 $cm^{-1}$ [In cobalt] complexes suggest the coordinated water molecule.[6,7]

The synthesized compounds were complexes with two metals CO(II) and Cu(II) and characterized in present research work.

These complexes were prepared by using derivatives of synthesized compounds like quinolines and chloride ions of metals. In some complexes chloride ion is inside the coordination sphere and act as ligand while in other cases chloride ion is out of side of coordination sphere.

The water molecules in prepared complex compounds are either in lattice or in coordination sphere or in both. In general, the main donor atoms of the coordination ligands are nitrogen and oxygen.

The results of antimicrobial activity of synthesized compounds and metal complexes, so that the chloro- and nitro- substituted synthesized compounds have exhibited good activity against selected bacteria and fungi. The synthesized compounds are more effective against *S. aureus*and *A. niger*.

The complex compounds prepared with cobalt and copper metals are named as 3,6,7,8 and 12. All complexes have shown good activity in comparison with over all synthesized ligands. The copper containing complexes possess more activity over all the synthesized compounds and even their cobalt complexes.

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