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# SPECTROSCOPIC AND ANTIMICROBIAL STUDIES ON SOME DIH YDRAZONE-COPPER COMPLEXES

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## Abstract

Some dihydrazones and their copper complexes were synthesized in order to study their molecular structures and antimicrobial activities. The dihydrazones were prepared by refluxing malonyldihydrazide with some aldehydes in absolute ethyl alcohol. The complexes were prepared by indirect method where copper acetate was refluex with the aldehydes and the solution was treated with malonyldihydrazides. All the complexes are characterized by elemental analysis, magnetic, electronic and IR data. Biological activities and their statistical analysis were also determined.

## Introduction

Metal complexes of acyl- and aroyl- Dihydrazone have a great attention because of their structural[1-3], biological[4,5], electrochemical[6], catalytic[7] and analytical[8] applications. Dihydrazone ligands can form different types of mono and binuclear complexes with different degrees of deprotonation[1-3,8-11] depending upon the experimental conditions as the solvent, the pH of medium and the ratio of the metal and ligand used. As the uranyl ion forms a large number of geometrical structures and also, it has some applications in solar energy conversion system[12]. Lal et a1.[3,13] presented an extensive study on the synthesis, characterization and structural assessment of dihydrazone uranyl complexes. The aim of the present work is to synthesize and characterize some copper complexes of benzaldehyde(benz), o-chlorobenzalc1ehyde-(o-Cl Benz), p-Chlorobenz-aldehyde-(p-Cl Benz), cinnamaldehyde-(Cin), salicylaldehyde-(Sal), o-hydroxynaphthaldehyde-(Naph) and furfuraylaldehyde malonyldihydrazone (Fur). This study can throw some light on the nature of coordination sites as well as the molecular and electronic structure. Furthermore, we amied to investigate the biological activity of the ligands and their copper chelate in order to improve their biological properties.

## Experimental

Copper acetate, diethyl malonate, hydrazine hydrate, benzaldehyde, o-cholorobenzaldehyde, p-chlorobenzaldellyde, salicylaldehyde, o-hydroxynaphthaldehyde, cinnamaldehyde and furfuraylaldehyde were of pure grade.

Malonyldihydrazide were prepared by reacting diethyl malonate (1 mole) with hydrazine hydrate (2 mole). The dihydrazones were prepared by refluxing malonyldihydrazide (1 mole) with the above aldehydes (2 mole) in absolute ethyl alcohol. All the dihydrazone ligands were filtered, washed with ethanol, recrystallized from ethanol and dried in vacuo.

The complexes were prepared by indirect method[1,3], due to the poor solubility of ligands in ethanol. Λ. solution of copper acetate (0.01 mole) in ethanol (100 ml) was refluxed with the aldehyde (0.01 mole) for 15 minutes. This solution was treated with the dihydrazide (0.005 mole) in ethanol (100 ml). The whole mixture was refluxed for 2 hour, the volume of the reaction mixture is reduced to about 100 ml, complexes were separated, washed with ethanol and dried in vacuo. The complexes were chemically analysed and proved to be in a pure form (Table 1). Electronic spectra of the complexes were recorded using Perkin - Elmer λ35 UV/Vis. Spcctrometcr and IR spectra were measured using Perk in - Elmer Spectrum RXl FT-IR. Magnetic susceptibility measurements was obtained at room temperature using Gouy method[14].

The antimicrobial activities were assessed using the classical diffusion methods culture of bacteria or yeast were inoculated in the form of a 100 ml each test organisms into 20ml of nutrient agar medium for bacteria and sobaroud agar medium for yeast at 45°C tilted and poured into sterile plates and left to solidify. In case of fungi Doxagar medium was used spore suspension tec1mique. The tested compounds were dissolved in (DMF) to get a solution of 1% concentration. Analytical paper disks (12 mm in diameter) were saturated with former solution and aseplically placed into the surface of the different inoculated plates with test organisms.

The petri dishes were kept in a refrigrator for diffusion for two hour just before incubated at 37°C for 24 hours for bacteria, at 30°C for 24 hours for yeast and 72 hours at 25°C for fungi according to (Mackie and McCartney[l5]. The minimal inhibitory concentration (MrCs) of the most potent compounds was measured by paper disc diffusion method[l6].

The results were analyzed statistically using the analysis of variance (ANOYA) procedure in the statistical analysis system[17].

**Results and Discussion**

The elemental analysis of the complexes (Table 1) indicates that the

stoichiometry of these complexes is 2: 1 (M/L).

The IR spectra of ligands Tables (2, 3) indicate that all the ligands show a band around 3200 $cm^{-1}$ assigned to νNH. The bands occurning at about 1670, 1650 and 1610 $cm^{-1}$ may be assigned to amide I(νC=O), νC=N and amide II(δNH) respectively.

The main IR bands of the ligands and their complexes have been compared in order to identify the coordination sites of the ligands. The IR spectra of complexes indicate that νNH, amide I and amide II are absent in all complexes, except for Cu-Naph complex.

Thus it is concluded that these complexes are in the enol form and the strong band around 1615 $cm^{-1}$ in these complexes is assigned to ν(C=N–N=C)[1]. Thus, one can suggest that the coordination sites of Cu-Benz, Cu-oCl Benz, Cu-p-Cl Benz and Cu-Cin are the enolic oxygen and C=N groups. As, the ligands Sal, and Fur contain additional coordination sites, phenolic OH in Sal or oxygen atom in Fur. Thus, it is expected that these ligands are hexadentate ligands. Beside the absence of νNH, amide I and amide II, there is a significant shin in νCO band upon colllplexation in the spectra of Cu-Sal and Cu-Fur. This indicates the participation of phenolic OH or furan oxygen in complexation.

In Cu-Naph complex, it is observed that amide 1 (νC=O) does not display any remarkable shift upon complexation. Furthennore νNH and δNH bands are shifted to lower frequency. Also, δOH band, present in the ligand disappears in the complexes. All of these arguments may be taken as a direct evidence for coordination through the phenolic oxygen and the amide nitrogen.

The presence of broad absorption features at about 3400 $cm^{-1}$ in addition to weak absorptions at about 850 and 520 $cm^{-1}$ in the IR spectra of these complexes indicates the presence of coordinated water molecules'8 in al1 complexes.

Absorption peaks attributed to acetate group were observed. It was reported by Nakamato et a1[19] that the free acetate ion has two strong absorption peaks locate at 1578 and 1425 $cm^{-1}$ attributed to asymmetric and symmetric C=O stretching vibrations, if the acetate ion coordinate to metal ion, a remarkable frequency shift caused by complex formation was clearly observed. Since there is significant frequency shift observed in the position of these bands, thus one can suggest that the acetate ion is involved in complex formation.

Magnetic susceptibility measurements showed the effective magnetic moment ($\mu_{eff}$) values for $Cu^{2+}$ complexes indicate the presence of one unpaired electron. The values are near the spin value (Table 3) and metal metal interaction is absent in these complexes may be due to the presence of bulky groups[9].

The electronic spectra of complexes were recorded in DMF solution and the peak positions are listed in table (3). The ligands do not have any absorption features in the studied range. The spectra of Cu (II) complexes reveal broad overlapped bands centered at about 16,000 cm $cm^{-1}$, which indicates tetragonal distortion in six-coordinate complexes. Such distortion can be assigned in terms of Jahn-Teller effect[20]. These overlapped peaks can be assigned as $^2E_g \longrightarrow {}^2T_{2g}$. The order of the ligand field strength (Table 3) is found as follows:

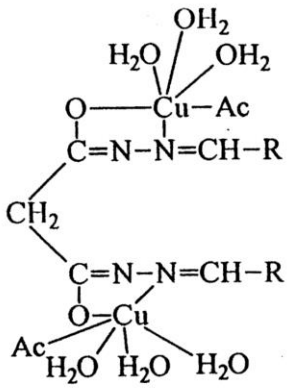
Cin < Benz < o-CI Benz < p-CI Benz < Naph < Sal

The results indicate that the presence of long chain or bulky groups in the ortho position reduce the ligand field strength as in case of Cin and this reduction may be attributed to steric hinderance. Also the data reveal that the presence of chlorine atom in the ligand increase the ligand field strength and this increment is clearly observed in case of p-CI Benz. Furthermore the results indicate that Sal have the greatest ligand field strength because the addition of the new coordination site, OH group of the ligand.

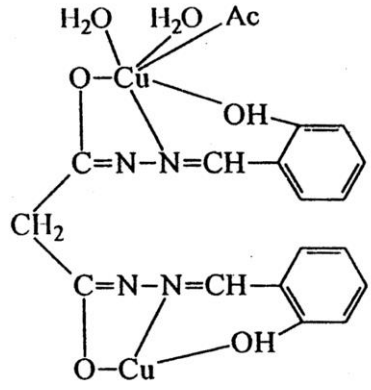
The newly synthesized compounds were screened for their antimicrobial activity against five bacterial species, Table (4) Gram-positive namely Bacillus subilis (NCTC 10400), S'laphylococcus aureus (NCTC 7447), Gram-negative Escherichia coLi (NCTC 10416), Pseudomonas aeruginosa (ATCC 10415), KLebsiella pneumonia (NCTC 9111), yeast Candida aLbicans (IMRU 3669) and fungi *Aspergillus niger* (ATCC 16404) using ciprofloxacin (30 μg) as reference.

The results of the statistical analysis of anitimicribiobial activity table (4) showed that the compounds Cu-o-Cl-Benz, Cu-Cin and Cu-Naph are the most active against bacteria, while the compounds Cu-Cin, Cu-Naph and Cu-fur are active against yeast and only the compound Cu-p-CI-8enz is active against fungi. The data of statistical analysis of the minimum inhibation concentration of the effective compounds (Table 5) indicate that Cu-p-Cl-Benz had superior effect compared with the other studied compounds.

The experimental data suggest the structures shown in Fig. (1) for the metal chelates under investigation.

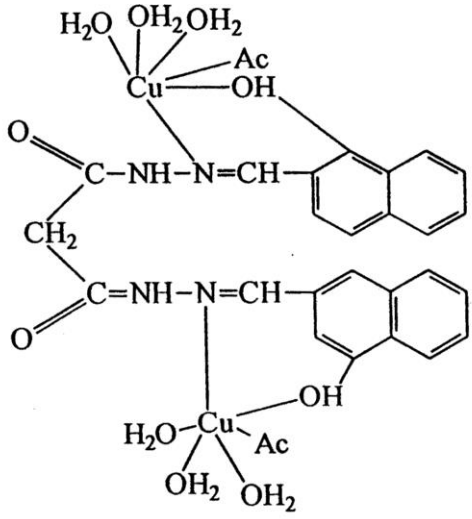


Structure (a)



Structure (b)

R = Phenyl, O-Cl-Phenyl, P-Cl-Phenyl and Cinnamyl



Structure (c)

Fig. (1): Proposed structure for complexes.

Table (1): Physical and Analytical data of ligands and their metal complexes.

| Compound No. | m.p (°C) | Molecular Formula | Mol. Wt. | Chemical Analysis Calculated /found % | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | C | H | N | Cl | M |
| Benz | 238 | $C_{17}H_{16}N_4O_2$ | 308 | 66.23 | 5.19 | 18.18 | --- | --- |
| | | | | 66.15 | 5.11 | 18.02 | --- | --- |
| Cu-Benz | <300 | $C_{17}H_{16}N_4O_2$ $Cu_2(Ac)_2.6H_2O$ | 658 | 38.29 | 4.86 | 8.51 | --- | 19.14 |
| | | | | 37.90 | 4.51 | 8.29 | --- | 18.95 |
| O-Cl Benz | 240 | $C_{17}H_{14}N_4Cl_2O_2$ | 376 | 54.25 | 3.72 | 14.89 | 18.61 | --- |
| | | | | 54.11 | 3.51 | 14.62 | 18.46 | --- |
| Cu-O-Cl Benz | <300 | $C_{17}H_{12}N_4Cl_2O_2$ $Cu_2(Ac)_2.6H_2O$ | 726 | 34.71 | 4.13 | 7.71 | 9.64 | 17.35 |
| | | | | 34.56 | 4.02 | 7.56 | 9.31 | 17.12 |
| P--Cl Benz | 242 | $C_{17}H_{14}N_4Cl_2O_2$ | 376 | 54.25 | 3.72 | 14.89 | 18.61 | --- |
| | | | | 53.96 | 3.59 | 14.68 | 18.32 | --- |
| Cu-P--Cl Benz | <300 | $C_{17}H_{12}N_4Cl_2O_2$ $Cu_2(Ac)_2.6H_2O$ | 726 | 34.71 | 4.12 | 7.71 | 9.64 | 17.35 |
| | | | | 34.39 | 4.06 | 7.52 | 9.39 | 17.18 |
| Cin | 182 | $C_{21}H_{20}N_4O_2$ | 360 | 79.00 | 5.55 | 15.55 | --- | --- |
| | | | | 70.30 | 5.29 | 15.42 | --- | --- |
| Cu-Cin | 240 | $C_{21}H_{18}N_4O_2$ $Cu_2(Ac)_2.6H_2O$ | 710 | 42.25 | 5.07 | 7.88 | --- | 17.74 |
| | | | | 42.13 | 5.12 | 7.57 | --- | 17.62 |
| Sal | 230 | $C_{17}H_{16}N_4O_4$ | 340 | 60.00 | 4.70 | 16.47 | --- | --- |
| | | | | 59.50 | 4.51 | 16.12 | --- | --- |
| Cu-Sal | <300 | $C_{17}H_{14}N_4O_2$ $Cu_2(Ac)_2.4H_2O$ | 654 | 38.53 | 4.28 | 8.56 | --- | 19.26 |
| | | | | 38.29 | 4.15 | 8.32 | --- | 18.99 |
| Naph | 261 | $C_{25}H_{20}N_4O_4$ | 440 | 68.18 | 4.54 | 12.72 | --- | --- |
| | | | | 67.80 | 4.36 | 12.49 | --- | --- |
| Cu-Naph | <300 | $C_{25}H_{18}N_4O_2$ $Cu_2(Ac)_2.6H_2O$ | 790 | 44.05 | 4.55 | 7.08 | --- | 15.94 |
| | | | | 44.60 | 4.35 | 6.98 | --- | 15.69 |
| Fur | 237 | $C_{13}H_{12}N_4O_2$ | 288 | 54.16 | 4.16 | 19.44 | --- | --- |
| | | | | 53.95 | 4.02 | 19.29 | --- | --- |
| Cu-Fur | <300 | $C_{13}H_8N_4O_4$ $Cu_2(Ac)_2.4H_2O$ | 603 | 33.83 | 4.14 | 9.28 | --- | 20.89 |
| | | | | 33.59 | 4.01 | 9.13 | --- | 20.67 |

Table (2): Infrared Characteristic Frequency Vibrations.

| Benz | Cu-Benz | O-Cl Benz | Cu-O-Cl Benz | P-Cl Benz | Cu-P-Cl Benz | Cin | Cu-Cin | Sal | Cu-Sal | Naph | Cu-Naph | Fur | Cu-Fur | Assignment |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| --- | 3412 br | --- | 3412 br | --- | 3414 br | 3212 br | 3400 br | 3280 m | 3390 br | 3250 sh | 3416 br | --- | 3412 br | νOH |
| 3216 vs | --- | 3194 m | --- | 3204 vs | --- | 3185 m | --- | 3200 w | --- | 3184 m | --- | 3206 vs | --- | νNH |
| 1668 m | --- | 1684 vs | --- | 1668 s | --- | 1682 m | --- | 1684 vs | --- | 1747 vs | 1674 vs | 1680 vs | --- | amide I (νC=O) |
| 1656 vs | --- | 1658 vs | --- | 1652 vs | --- | 1652 vs | --- | 1672 vs | --- | 1624 m | 1620 m | 1648 vs | --- | νC=N |
| --- | 1612 vs | --- | 1615 vs | --- | 1610 vs | --- | 1616 s | --- | 1618 vs | --- | --- | --- | 1630 vs | νC=N-N=C |
| --- | 1602 vs | --- | 1604 s | --- | 1596 vs | --- | 1584 s | --- | --- | --- | --- | --- | --- | νC=O acetate |
| 1608 | --- | 1604 m | --- | 1608 m | --- | 1624 m | --- | 1610 m | --- | 1594 m | 1570 w | 1624 vs | --- | amide II (δNH) |
| --- | 1560 vs | --- | 1570 w | --- | 1576 w | --- | 1554 s | --- | 1534 vs | --- | 1540 vs | --- | 1550 vs | νC=O (acetate) |
| --- | 1396 vs | --- | 1396 vs | --- | 1406 vs | --- | 1394 m | --- | 1390 s | --- | 1410 m | --- | --- | $CH_3$ (acetate) |
| --- | --- | --- | --- | --- | --- | --- | 1314 m | 1300 w | 1312 w | --- | --- | --- | --- | δOH |
| --- | --- | --- | --- | --- | --- | --- | --- | 1152 m | 1150 m | 1184 s | 1188 s | 1156 s | 1150 s | δC-O |
| --- | 852 w | --- | 872 w | --- | 840 m | --- | 882 m | --- | 852 w | --- | 880 w | --- | 855 w | $\rho_w(H_2O)$ |
| --- | 550 w | --- | 515 w | --- | 516 vw | | 508 m | --- | 520 w | --- | 500 w | --- | 520 v.w | $\rho_r(H_2O)$ |
| --- | 590 w | --- | 492 w | --- | 475 w | --- | 450 v.w | --- | 492 m | --- | 450 w | --- | 480 v.w | M-O |

Table (3): Colour magnetic and Electronic Spectral data of complexes.

| Compound | Colour | $\mu_{eff}$ | $\lambda_{max}$ |
|---|---|---|---|
| Cu-Cin | Blue | 1.71 | 14,245 |
| Cu-Benz | Blue | 1.75 | 15,625 |
| Cu-O-Cl Benz | Blue | 1.74 | 15,673 |
| Cu-P-Cl Benz | Blue | 1.79 | 16,000 |
| Cu- Naph | Green | 1.81 | 16,666 |
| Cu- Sal | Green | 1.87 | 17,241 |
| Cu- Fur | Blue | 1.79 | * |

* Insoluble in DMF

Table (4): Antimicrobial activity of the synthesized compounds.

| Compound | *Bacillus subtilis NCTC 10400* | | *Staphylococcus aureus* NCTC 7447 | | *Escherichia coli NCTC 10416* | | *Pseudomonas aeruginosa ATCC 10415* | | *Kelbsiella pneumonia NCTC 9111* | | *Candida albicans DMRU 3669* | | *Aspergillus niger ATCC 16404* | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Benz | -ve | F | -ve | F | -ve | F | -ve | D | -ve | E | -ve | B | -ve | B |
| Cu-Benz | ++ve | D | ++ve | D | ++ve | D | ++ve | C | ++ve | D | -ve | B | -ve | B |
| O-Cl-Benz | -ve | F | -ve | F | -ve | F | -ve | D | -ve | E | -ve | B | -ve | B |
| Cu-O-Cl-Benz | ++ve | D | ++ve | D | ++ve | D | ++ve | C | ++ve | D | -ve | B | -ve | B |
| P-Cl-Benz | -ve | F | -ve | F | -ve | F | -ve | D | -ve | E | -ve | B | -ve | B |
| Cu-P-Cl-Benz | +++ve | BC | +++ve | BC | ++ve | BC | ++ve | B | ++ve | C | -ve | B | ++ve | A |
| Cin | -ve | F | -ve | F | -ve | F | -ve | D | -ve | E | -ve | B | -ve | B |
| Cu-Cin | ++ve | B | +++ve | B | +++ve | B | +++ve | B | +++ve | B | +++ve | A | -ve | B |
| Sal | -ve | F | -ve | F | -ve | F | -ve | D | -ve | E | -ve | B | -ve | B |
| Cu-Sal | ++ve | D | ++ve | D | ++ve | D | ++ve | C | ++ve | D | -ve | B | -ve | B |
| Naph | -ve | F | -ve | F | -ve | F | -ve | D | -ve | E | -ve | B | -ve | B |
| Cu-Naph | +++ve | BC | +++ve | BC | +++ve | BC | +++ve | B | +++ve | BC | +++ve | A | -ve | B |
| Fur | +ve | E | +ve | E | +ve | E | -ve | D | -ve | E | -ve | B | -ve | B |
| Cu-Fur | +++ve | C | +++ve | C | +++ve | C | +++ve | B | +++ve | BC | +++ve | A | -ve | B |
| Ciprofloxcin 30 µg | +++ve | A | +++ve | D | +++ve | A | +++ve | A | +++ve | A | -ve | B | -ve | B |
| L.S.D | 1.376 | | 0.996 | | 1.163 | | 1.310 | | 1.238 | | 0.996 | | 0.351 | |

Means with dissimilar letters in vertical column ($P < 0.0.5$) indicate significant difference.

-ve (no activity)

+ve (when inhibition zone was up 10 mm).

++ve (when inhibition zone was between 10-15 mm)

+++ve (when inhibition zone was over 15 mm)

Table (5): Minimum inhibition concentration of the most effective compounds.

| Test organisms | MIC$_s$ (µg/ml) concentration | | | | | | | | L.S.D |
|---|---|---|---|---|---|---|---|---|---|
| | Cu-PCl-Benz | | Cu-Cin | | Cu-Fur | | Cu-Naph | | |
| *Bacillus subtilis* NCTC 10400 | 5.73 | C | 10.45 | B | 12.0 | A | 11.0 | AB | 1.317 |
| *Staphylococcus aureus NCTC 7447* | 7.12 | C | 10.0 | B | 12.75 | A | 11.0 | B | 1.215 |
| *Micrococcus luteus* ATCC 9341 | 6.51 | C | 10.0 | B | 13.0 | A | 10.25 | B | 1.198 |
| *Escherichia coli* NCTC 10416 | 14.25 | C | 21.30 | A | 20.0 | A | 18.25 | B | 1.500 |
| *Kelbsiella pneumonia NCTC 9111* | 15.75 | D | 25.20 | A | 22.0 | B | 18.0 | C | 1.610 |
| *Pseudomonas aeruginosa ATCC 10415* | 16.20 | C | 25.45 | A | 22.0 | B | 18.0 | C | 2.110 |
| *Proteus mirobilis* ATCC 2100 | 15.40 | D | 25.0 | A | 21.75 | B | 19.0 | C | 1.183 |
| *Candida albicans IMRU 3669* | 18.25 | B | 30.0 | A | 32.0 | A | 29.0 | A | 4.094 |
| *Aspergillus niger ATCC 16404* | 30.20 | | --- | | --- | | --- | | |

Means with dissimilar letters in row indicate indicate significant difference ($P < 0.0.5$).

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