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# SYNTHESIS &CHARACTERISATION OF CU (II) CHELATES OF DIETHYLMESOXALATE PHENYLHYDRAZONE AND THEIR DERIVATES IN AMMONIACAL MEDIUM

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# Synthesis &Characterisation of Cu (II) Chelates of Diethylmesoxalate Phenylhydrazone and Their Derivates in Ammoniacal Medium

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***Abstract – The presents work describes the synthesis and characterization of derivatives of diethylmesoxalate phenylhydrazone and their complexes with divalent copper ion in ammoniacal medium. The metal- ligand bonding and geometries of the complexes have been studies from the IR, magnetic and electronic spectral data. It has been observed that donor behavior of various hydrazones towards Cu (II) is abit different. In some cases their difference leads to isolation of different products.***

***Keywords: diethylmesoxalate phenylhydrazones/ spectral studies/ magnetic studies/ thermal studies/ metal chelates.***

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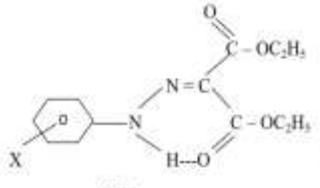
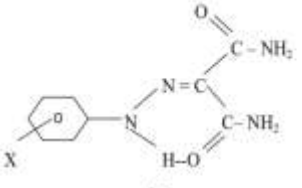
## INTRODUCATION

Complex arylhydrazones and their metal complexes assume considerable significance and importance due to their numerous applications e.g. Chemotherapeutic[1-4], insecticides[5], Chromogenic reagent[6], Photoreceptor in electro photography as also in analytical Chemistry[7-9] etc. the coupling product of benzyldiazonium chloride with diethlmesoxalate ($HL_1$), acetylacetone and diethylmalonate as ligand have been utilized by several workers and isolated complexes of different stoichiometry.

Complex formation of Cu (II) with ligand HL (X= 0-Carboxy) was studied spectrophotometrically at 0.1 M ionic strength (NaoAC) at $30^0$ by AL-Atrasch et. al. [10], but other substituted derivate of (HL) have not been reported till today. The above ligand can behave as polydentate ligand due to presence of several donor sites. In addition, one oxygen is involved in H-bonding. These hydrazones are interesting donor substance and it is quite interesting the mode bonding of these hydrazones to metal atoms.

This prompted us to study the preparation and characterization of complexes of Cu (II) with different substituted electron releasing as well as electron with drawing substituent in phenyl nucleus of ligand (HL)


[HL]


[A]

$HL_1 \Rightarrow X = H$
$HL_2 \Rightarrow X = O\text{-nitro } [NO_2]$
$HL_3 \Rightarrow X = m\text{-nitro } [NO_2]$
$HL_4 \Rightarrow X = p\text{-nitro } [NO_2]$
$HL_5 \Rightarrow X = O\text{-}CH_3$
$HL_6 \Rightarrow X = p\text{-}CH_3$

## MATERIALS AND METHODS

Diethylmesoxalate phenylhydrazone and their electron releasing & electron withdrawing substituent in phenyl nucleus were synthesized by coupling benzendiazonium chloride with diethylmalonate in sodium acetate medium.[11-12]

An ethanolic solution of copper acetate (1 gm, 0.005 mol) was prepared and to this an ethanolic solution of ligand (0.005 mol) was refluxed on small flame for 6 hours [10hours in case of ligand $HL_5$ & $HL_6$] after raising the pH of the mixture to 8 with ammonium hydroxide. It was found that no precipitate occurs in ammoniacal medium. The reaction mixture after reflux was diluted with water to precipitate the complex. The coloured complex was filtered and washed with water and then with benzene for complete removal of complex was ascertained by TLC.

## DISCUSSION

The analytical data (Table – 1) show that the isolated complexes have the general composition [ML(OH)$H_2$O)] for ligands $HL_1$to $HL_4$ and [M$L_2$.2$H_2$O] (in amidic form A) for ligands $HL_5$to $HL_6$. According to the data of element analysis (Table – 1) in case of ligand $HL_1$to $HL_4$, it is apparent that the hydrazone form mono ligated hydroxo complex [CuL(OH)$(H_2$O)] on refluxing in ammoniacal medium for about 4 to 6 hours. In case of ligand $HL_5$to $HL_6$ the product could not be isolated in six hours. When the reactant were refluxed for longer time interval an insoluble products was separated whose chemical analysis corresponds to $CuL_2$.2$H_2$O. where L is the amidic form of ligand (Structure A). The formation of amide of hydrazone has further been supported by the fact that on keeping ethanolic solution of hydrazone for 3-4 days in ammoniacal medium yielded amide form of ligand.

The magnetic data 1.8-2.1 B.M (Table-1) indicate that mono nuclear Cu(II) complexes are formed in all cases. The above data indicate that all the above complexes are magnetically dilute complexes.[13] The slight rise from spin only value for $Cu^{+2}$ (1.73 B.M) in all cases are due to spin orbit coupling and tip contribution.

In the uv-spectra, the characteristic absorption band of phenyl azo group in the region 270-280 nm not observed which is sufficient enough to rule out any possibility of azo form of the ligand.[14] The solid reflectance spectra (200-1100 nm)of $Cu^{+2}$ complex with ligand $HL_1$(ignoring the peak due to ligand) display two weak and broad ligand field transitions in the vicinity of 480 nm and 635 nm which are similar to planar $Cu^{+2}$ complexes. The two bands are probably due to$^2B_{1g} \rightarrow {}_2E_g$ and ${}_2B_{1g} \rightarrow A_{1g}$ transitions rspectively.[15-16]

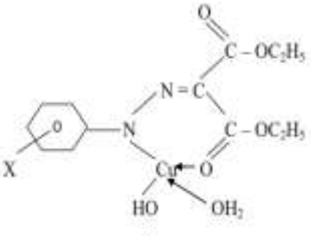
In IR spectra of $Cu^{+2}$ complexes with ligand $HL_1$to $HL_4$, the ligand display$^{\upsilon}$N – H around 3100 -3150 cm$^{-1}$ which disappear in all complexes indicating deprotonation of N – H proton. The $^{\upsilon}$C = O of ester part ( which is not involved in H-bonding) observed at 1690 -1730 cm$^{-1}$ in ligand is shifted to lower frequency to 20 – 30 cm$^{1}$. It is attributed to weak H-bonding from coordinated $H_2$O or OH group. The $^{\upsilon}$C = O of ester part (H-bonded) are localized around 1630 cm$^{-1}$ indicating that O atom of –COOEt group is involving in H-bonding. This $^{\upsilon}$C = O vibration is further shifted to lower frequency and usually complex with $^{\upsilon}$C = N vibration and observed at 1600 – 1620 cm$^{-1}$. The red shift of $^{\upsilon}$C = O indicates the coordination of ester O to metal ion. The aquo complexes display a broad band at 3300 – 3420cm$^{-1}$ attributed from $^{\upsilon}$O – H of water molecule.[17] In the region 3190 – 3280 cm$^{-1}$ the complexes display a medium band which is due to $^{\upsilon}$O – H of coordinated hydroxy group[18] in the complex.

The presence of $H_2$O/OH group might have been confirmed by the comparison of IR spectra in low frequency region of the sample. Due to our limited resources, this study could not be undertaken. However, in the absence of above study, we can assign the O-H stretching unambiguously. The O-H bond stretching mode observed at around 3200 – 3600 cm$^{-1}$ is sharp and usually can be seen even in the presence of water absorption.[19] In for IR region the complex display two to three new bands located around 480 cm$^{-1}$ and 420 cm$^{-1}$ attributed to $^{\upsilon}$Cu – O and $^{\upsilon}$Cu – N stretches respectively.

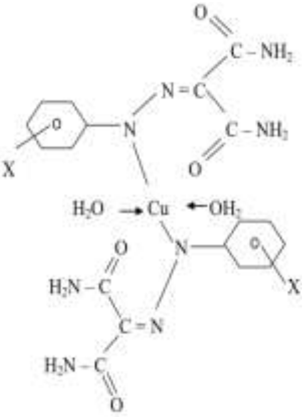
In IR spectra of $Cu^{+2}$ complexes with ligand $HL_5$ & $HL_6$ (in amidic form displays a sharp and broad band at around 3300 – 3380 cm$^{-1}$ attributed from $^{\upsilon}$O – H of water.[17,19] These complexes display two $^{\upsilon}$N – H as sharp and shoulder bands near 3065 – 3070 cm$^{-1}$ and 3140 – 3185 cm$^{-1}$. The presence of two $^{\upsilon}$N – H stretches band suggests the presence of amino group in metal complexes, which may be possible due to convertion of ester part of ligand into amide. Since ammoniacal medium has been used for reflux and the time required in complexation are comparative larger in these cases than in other cases.

The $^{\upsilon}$C = O of amide part in both cases observed as sharp band at 1665 – 1670 cm$^{-1}$. Another $^{\upsilon}$C = O of amide part in both complexes are further shifted to lower frequency and observed as strong bond around 1630 – 1640 cm$^{-1}$. The red shift of $^{\upsilon}$C = O indicates the involvement of carbonyl oxygen of amide in H-bonding. In for IR-region around 500 – 525 cm$^{-1}$ and 410 – 430 cm$^{-1}$ attributed to $^{\upsilon}$Cu – O and $^{\upsilon}$Cu – N stretches.

All the above complexes are stable at room temperature and do not lose weight below 140$^0$C, indicating that $H_2$O and OH group is in coordination sphere.[20] After heating above 140$^0$c the gradual loss of weight was observed with change in colour indicating the loss of coordinated molecule from complex. In this way structure (I) can be assigned for $Cu^{+2}$ complex with ligand $HL_1$ – $HL_4$ and structure (II) fir the $Cu^{+2}$ complexes with ligand $HL_5$ and $HL_6$.



(I)



(II)

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### Table

### Physical Constants, Magnetic moment and Analytical data

| Name of Complexes | $\mu_{eff}$(at 298K) in B.M | Decomposition Temp. | % Yield | Colour | % of N | % of Cu |
|---|---|---|---|---|---|---|
| $[CuL_1(OH)(H_2O)]$ | 1.96 | >$280^0$c | 41% | Bluish Green | 7.361<br>(7.745) | 17.31<br>(17.563) |
| $[CuL_2(OH)(H_2O)]$ | 2.01 | $262^0$c | 35% | Yellowish Grey | 10.42<br>(10.33) | 15.09<br>(15.62) |
| $[CuL_3(OH)(H_2O)]$ | 1.99 | $258^0$c | 38% | Greenish Grey | 10.19<br>(10.33) | 15.13<br>(15.62) |
| $[CuL_4(OH)(H_2O)]$ | 1.98 | $251^0$c | 38% | Greenish Grey | 10.09<br>(10.33) | 15.37<br>(15.62) |
| $[Cu(L_5)_2 .2H_2O]$ | 1.89 | $240^0$c | 40% | Yellowish Grey | 21.05<br>(20.83) | 11.46<br>(11.81) |
| $[Cu(L_6)_2 .2H_2O]$ | 1.87 | $246^0$c | 41% | Yellowish Grey | 20.35<br>(20.83) | 11.57<br>(11.81) |

Figure within the parentheses are calculated / theoretical values.

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