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# SYNTHESIS AND STRUCTURAL INVESTIGATION OF TRANSITION METAL COMPLEXES OF THE LIGAND 2- AMINO -4- (P- DIHYDROXY PHENYL) OXAZOLE

Dinkar Malik, Sandeep Kumar, Punam Yadav

Department of Chemistry, M. S. College, Saharanpur U.P., India

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**For Correspondence:**

**Dr. Punam Yadav**

Department of Chemistry,
M. S. College, Saharanpur
U.P., India

**E-mail:**

yadavpunam200670@gmail.com

## ABSTRACT

Transition metal complexes of 2 - amino -4- (p- dihydroxy phenyl) oxazole derived from 2, 4 di hydroxy acetophenone have been prepared. From the analytical and spectral data the stoichiometry of these complexes have been found to be of the type $ML_2X_2$ (where M = Cu (II), Co (II) and Ni (II)}. The infrared studies suggest that the oxazole behaves as a bidentate ligand with nitrogen of the $–NH_2$ group and ring oxygen as two coordinating sites. The ligand complexes of Ni(II), Co(II) and Cu(II) with 2 - amino -4- (p- dihydroxy phenyl) oxazole were characterized by elemental analysis, electronic and magnetic susceptibility, IR and NMR spectra. In the complexes, the central metal displays a co-ordination number six. The fungicidal activities of ligands and metal complexes were screened by growth method against various fungi i.e. *Drechslere setramera*, *Fusarium oxyporum*, *Macrophomera phaseoli* at different concentrations. It is found that the activity decreases with decrease of concentration and the metal complexes are less toxic than the parent ligand.

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## INTRODUCTION

Complexes of the ligand 2 - amino -4- (p- dihydroxy phenyl) oxazole with paramagnetic transition metal ions have attracted close attention. A number of transition metal complexes of oxazole have gained wide interest because they show a broad spectrum of biological and pharmaceutical activities, such as anti-microbial, anti-tumor, anti- fungal, anti-tuberculostatic and anti-cancer action. In the transition metal complexes with various types of multi-dentate oxazole ligands, the metal can achieve high co-ordination number giving structural differences responsible for their important properties. In connection of our work on complexes of oxazole, we here in report the synthesis of new ligand 2 - amino -4- (p- dihydroxy phenyl) oxazole. Complexes of this ligand with transition metal ions of Ni(II), Co(II) and Cu(II) were prepared and their elemental analysis, IR, electronic and magnetic susceptibility have been studied. The fungicidal activities of ligands and metal complexes were screened by growth method against various fungi i.e. *Drechslere setramera, Fusarium oxyporum, Macrophomera phaseoli* at different concentrations. It is found that the activity decreases with decrease of concentration and the metal complexes are less toxic than the parent ligand. The Schiff's base derived metal complexes were synthesized from divalent transition metals[1]. Schiff's base derived complexes of derivatives of DHA were also studied by many workers[2]. Several transition metal complexes of thiazole and oxazole ligands were synthesized and screened for their fungicidal activities.[3-4]. Similar experiments on fungicidal and antimicrobial activities of Cu (II), Co (II) and Ni (II) Complexes with O, N, and S donor, their EPR and electronic spectral studies were also conducted by many workers[5-9]. Schiff's base derived complexes of derivatives of DHA, their spectra and synthesis under microwave irradiation were also studied by many workers[10-11]. The present paper deals with the preparation and characterization of Cu(II), Co(II) and Ni(II) complexes with 2-amino-4-(p-dihydroxy phenyl) oxazole. Metal complexes play an important role in biological activity. In many cases metal complexes are more potent than free ligands. The newly prepared complexes were also screened for their antifungal activity against different fungi at different concentrations[12].

## EXPERIMENTAL

### Materials and methods:

a) **Chemicals and Reagents:** All the chemicals and reagents used were of analytical grade; otherwise they were purified before use. Organic solvents viz. absolute alcohol, diethyl ether, benzene etc. were purified by distillation. The fungicidal activity of ligands as well as complexes was determined by using the Growth method.

b) **Preparation of Ligand:** The ligand 2 - amino -4- (p- dihydroxy phenyl) oxazole was prepared from 2, 4 di hydroxy acetophenone using the procedure reported in literature of oxazole.

**c)** **Preparation of Metal Complexes:** In general all these complexes were synthesized by refluxing the respective metal salts with ligand 2-amino-4-(p-dihydroxy phenyl) oxazole in 1:2 molar ratio in ethanolic medium on water bath for one hour. The solution was concentrated to half of its volume then it was kept for some time. The crystals of complexes separated out which were filtered, washed with alcohol and dried in vacuum. Similarily some complexes of oxazole were also synthesized by many workers[13-15].

d) **Elemental Analysis:** The complexes were analysed for their metal content by standard procedures after destroying the organic matter by heating with conc. $HNO_3$ and then treating with dil. HCl[16-18]. The estimation of carbon, hydrogen and nitrogen were carried out at BHU, Varanasi and CDRI, Lucknow and results are given in Table 1.

e) **Physical and Spectral Measurements:** Magnetic measurements were carried out at IIT Roorkee at room temperature using $Co[Hg(CNS)_4]$ as a calibrant. IR spectra of the ligand and complexes are recorded in nujolmull. The electronic spectra were recorded in MgO at room temperature on VSU-22 spectrophotometer. The measurements were carried out Guru Nanak Dev University, Amristar.

## Table 1 Elemental Analysis Data

| Complexes | % Calc./ Obs. | | | | |
|---|---|---|---|---|---|
| | C | H | N | O | M |
| $C_9H_8N_2O_3$ | 56.92<br>56.70 | 4.15<br>4.11 | 14.46<br>14.41 | 25.08<br>25.03 | ----- |
| $[Cu(C_9H_8N_2O_3)_2Cl_2]$ | 41.60<br>41.52 | 3.07<br>3.02 | 10.80<br>10.75 | 18.55<br>18.49 | 12.21<br>12.19 |
| $[Ni(C_9H_8N_2O_3)_2Cl_2]$ | 42.01<br>41.96 | 3.08<br>3.01 | 10.87<br>10.81 | 18.66<br>18.60 | 10.79<br>10.73 |
| $[Co(C_9H_8N_2O_3)_2Cl_2]$ | 41.99<br>41.93 | 3.09<br>3.03 | 10.82<br>10.77 | 18.68<br>18.61 | 10.77<br>10.74 |
| $[Cu(C_9H_8N_2O_3)_2(CH_3COO^-)_2]$ | 46.66<br>46.60 | 3.86<br>3.82 | 9.85<br>9.80 | 28.30<br>28.26 | 11.21<br>11.18 |
| $[Ni(C_9H_8N_2O_3)_2(CH_3COO^-)_2]$ | 47.00<br>46.98 | 3.88<br>3.82 | 9.91<br>9.86 | 28.57<br>28.51 | 10.51<br>10.48 |
| $[Co(C_9H_8N_2O_3)_2(CH_3COO^-)_2]$ | 46.98<br>46.93 | 3.86<br>3.81 | 9.87<br>9.85 | 28.54<br>28.51 | 10.49<br>10.41 |
| $[Cu(C_9H_8N_2O_3)_2Br_2]$ | 35.58<br>35.52 | 2.68<br>2.61 | 9.19<br>9.12 | 15.76<br>15.71 | 10.41<br>10.38 |
| $[Ni(C_9H_8N_2O_3)_2Br_2]$ | 35.80<br>35.72 | 2.65<br>2.61 | 9.30<br>9.25 | 15.88<br>15.83 | 9.79<br>9.75 |
| $[Co(C_9H_8N_2O_3)_2Br_2]$ | 35.76<br>35.72 | 2.67<br>2.59 | 9.32<br>9.29 | 15.84<br>15.81 | 9.74<br>9.70 |

The ligand 2-amino-4-(p-dihydroxy phenyl) oxazole was prepared using the procedure reported in the literature[19] .

## Table 2 Characteristic IR bands of ligands and complexes

| Complexes | IR Bands ($cm^{-1}$) | | | | | |
|---|---|---|---|---|---|---|
| | νN-H | νC-O-C | νC-H | νC=C | νC=N | νM-O |
| $C_9H_8N_2O_3$ | 3335-3300 | 1155-1103 | 3065-3005 | 1620-1580 | 1475-1455 | -- |
| $[Cu(C_9H_8N_2O_3)_2Cl_2]$ | 3228-3182 | 1035-999 | 3055-3008 | 1624-1571 | 1473-1450 | 375-275 |
| $[Ni(C_9H_8N_2O_3)_2Cl_2]$ | 3231-3168 | 1037-1001 | 3058-3007 | 1625-1573 | 1470-1449 | 372-275 |
| $[Co(C_9H_8N_2O_3)_2Cl_2]$ | 3230-3172 | 1040-1002 | 3059-3009 | 1623-1569 | 1477-1451 | 374-280 |
| $[Cu(C_9H_8N_2O_3)_2(CH_3COO^-)_2]$ | 3244-3185 | 1039-1010 | 3060-3002 | 1630-1578 | 1468-1446 | 368-282 |
| $[Ni(C_9H_8N_2O_3)_2(CH_3COO^-)_2]$ | 3241-3183 | 1043-1005 | 3068-3010 | 1628-1579 | 1469-1446 | 372-281 |
| $[Co(C_9H_8N_2O_3)_2(CH_3COO^-)_2]$ | 3239-3189 | 1044-1012 | 3064-3004 | 1626-1574 | 1475-1454 | 366-277 |
| $[Cu(C_9H_8N_2O_3)_2Br_2]$ | 3240-3181 | 1048-1006 | 3060-3007 | 1632-1580 | 1470-1449 | 373-280 |
| $[Ni(C_9H_8N_2O_3)_2Br_2]$ | 3242-3184 | 1043-1011 | 3062-3007 | 1631-1577 | 1478-1450 | 370-279 |
| $[Co(C_9H_8N_2O_3)_2Br_2]$ | 3239-3185 | 1049-1008 | 3059-3007 | 1629-1571 | 1469-1448 | 367-282 |

A shift in the ν C-O-C and ν N-H band frequencies is observed in all the complexes. This shows that the lone pair of electron presents on the oxygen atom of oxazole ring and nitrogen atom of free amino group is taking part in co-ordination (Table 2).

**Table 3 (a) Electronic reflectance spectral data and their assignments of Ni(II) complex**

| Complexes | $\nu_1$ | $\nu_2$ | $\nu_3$ | Dq | B | $\nu_2/\nu_1$ | $\nu_3$(Calc.) |
|---|---|---|---|---|---|---|---|
| $[Ni(C_9H_8N_2O_3)_2Cl_2]$ | 9100 | 15000 | 24200 | 910 | 912 | 1.64 | 27020 |
| $[Ni(C_9H_8N_2O_3)_2(CH_3COO^-)_2]$ | 9115 | 15140 | 24188 | 912 | 979 | 1.66 | 26910 |
| $[Ni(C_9H_8N_2O_3)_2Br_2]$ | 9097 | 15090 | 24195 | 910 | 965 | 1.65 | 26681 |

$\nu_1 = {}^3A_{2g}$ (F) → ${}^3T_{2g}$ (F), $\nu_2 = {}^3A_{2g}$ (F) → ${}^3T_{1g}$ (F) and $\nu_3 = {}^3A_{2g}$ (F) → ${}^3T_{1g}$ (P).

**(b) Electronic reflectance spectral data and their assignments of Co(II) complex**

| Complexes | $\nu_1$ | $\nu_2$ | $\nu_3$ | Dq | B | $\nu_2/\nu_1$ | $\nu_2$(Calc.) |
|---|---|---|---|---|---|---|---|
| $[Co(C_9H_8N_2O_3)_2Cl_2]$ | 8500 | 15115 | 18080 | 1010.1 | 745 | 1.77 | 18600 |
| $[Co(C_9H_8N_2O_3)_2(CH_3COO^-)_2]$ | 8510 | 15054 | 18070 | 1009.6 | 743 | 1.76 | 18606 |
| $[Co(C_9H_8N_2O_3)_2Br_2]$ | 8518 | 15040 | 18085 | 1010.5 | 744 | 1.76 | 18623 |

$\nu_1 = {}^4T_{1g}$ (F) → ${}^4T_{2g}$(F), $\nu_2 = {}^4T_{1g}$ (F) → ${}^4A_{2g}$ (F) and $\nu_3 = {}^4T_{1g}$ (F) → ${}^4T_{1g}$ (P).

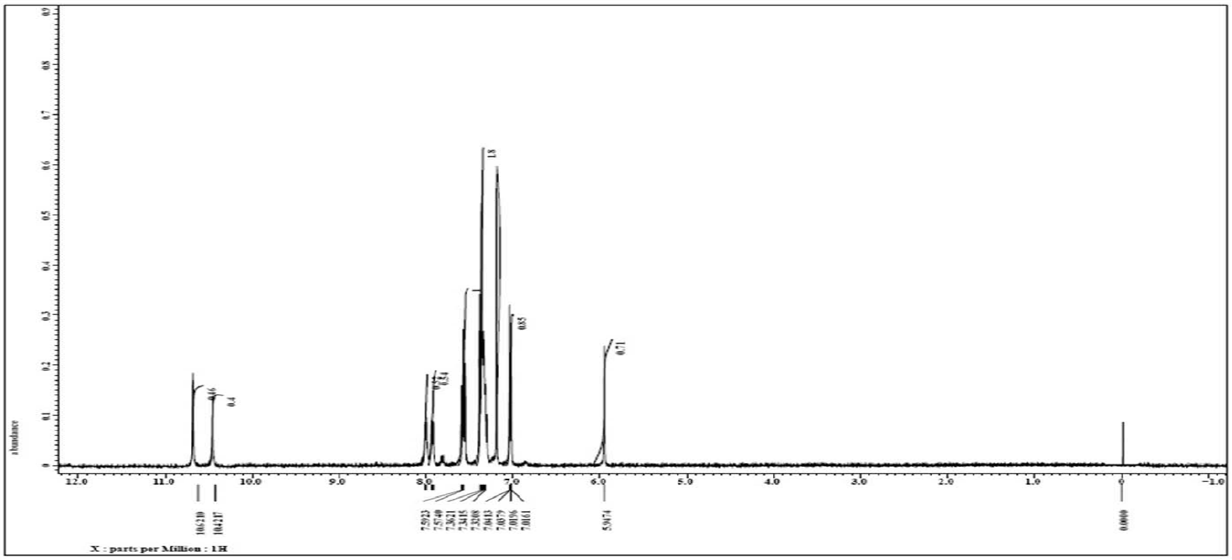
**(c) Electronic reflectance spectral data and their assignments of Cu(II) complex**

| Complexes | $\nu_1$ | $\nu_2$ | $\nu_3$ | Dq | B | $\nu_2/\nu_1$ | $\nu_2$(Calc.) |
|---|---|---|---|---|---|---|---|
| $[Cu(C_9H_8N_2O_3)_2Cl_2]$ | 15200 | -- | -- | 1520 | -- | -- | -- |
| $[Cu(C_9H_8N_2O_3)_2(CH_3COO)_2]$ | 15185 | -- | -- | 1518 | -- | -- | -- |
| $[Cu(C_9H_8N_2O_3)_2Br_2]$ | 15190 | -- | -- | 1519 | -- | -- | -- |

$\nu_1 = {}^2T_{2g} \rightarrow {}^2E_g$ .

CZ-record UV-Viz. spectrometer provided with an automatic recorder was used to record the electronic spectra of the complexes in ethanol at room temperature (Table 3).

**Figure 1 NMR Spectra of the Ligand**



## RESULTS AND DISCUSSION

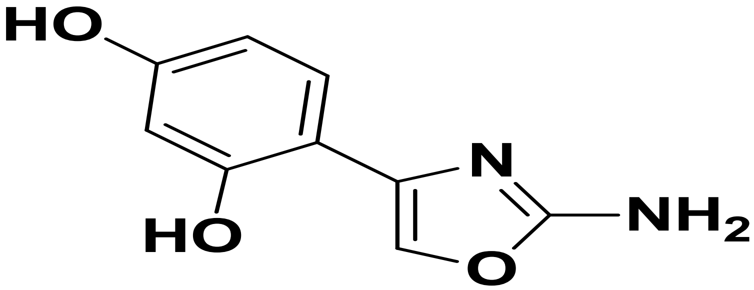
Adducts of all the complexes were prepared by refluxing the respective metal salts with ligands in 1:2 molar ratio in ethanolic medium. The crystals of complexes separated out which were filtered, washed with alcohol and dried in vacuum.

### IR Studies:

The characteristic bands of oxazole system appeared at 1640-1615, 1600-1590 and 1545-1530 cm$^{-1}$. The symmetric □ (C-O-C) frequency obtained at 1155-1103 cm$^{-1}$ is reduced after complexation. It confirms that the ring oxygen is taking part in complex formation. The □ (N-H) asymmetric and symmetric stretching frequencies appearing in the region 3335 and 3265 cm$^{-1}$ respectively, also decreases in the complex. This shows that the lone pair of electron available on nitrogen atom took part in coordination. The □ (C=N) band frequencies in the free ligand are completely unaffected on complexation. The unchanged position of the band indicates that the ring nitrogen does not take any part in the coordination. From the above observation it is clear that the nitrogen of the $-NH_2$ group and ring oxygen take part in coordination.

### NMR Studies $^1$H NMR ($CDCl_3$-d, 400 MHz):

The $^1$H NMR spectra showed a singlet at $\delta$ 7.59-7.57 (m, 1H, Aromatic proton), 7.36-7.32 (m, 1H, Aromatic proton) and 7.04-7.01 (m, 1H, Aromatic proton) which were assigned to benzene ring protons. The singlet at $\delta$ 5.94 (s, 1H, methylene proton) corresponds to protons of methylene group in heterocyclic ring. The peaks at $\delta$ 10.62 (s, 1H, -OH, $D_2O$ exchangeable) and 10.42 (s, 1H, -OH, $D_2O$ exchangeable) which were exchangeable with $D_2O$ corresponds to O-H protons. Another two proton singlet at $\delta$ 8.01 (s, 1H, $-NH_2$, $D_2O$ exchangeable) and 7.99 (s, 1H, $-NH_2$, $D_2O$ exchangeable) which were exchangeable with $D_2O$ corresponds to N-H protons of amino group[20](Figure 1). These observations from IR and NMR spectra confirmed the structure of ligand as:



**Electronic Reflectance Spectral Studies:**

The observed electronic reflectance spectra of Ni (II) complexes are similar to those reported in the adducts of Ni complexes. The bands around 9115 – 9097 $cm^{-1}$, 15140-15090 $cm^{-1}$ and 24200- 24188 $cm^{-1}$ are assigned to the $^3A_{2g}$ (F) → $^3T_{2g}$(F) ($\square_1$) , $^3A_{2g}$(F) → $^3T_{1g}$ (F) ($\square_2$) and $^3A_{2g}$(F) → $^3T_{1g}$ (P) ($\square_3$) transitions respectively (Table 3a). The ratio $\square_{2/}$ $\square_1$ which lies around 1.8 for perfectly octahedral Ni(II) complexes is found to lie at 1.65. The ratio was expected to lie still lower because of the large value of Dq but this is not so because the environment is tetragonal which splits the two $T_{2g}$(F) and $T_{1g}$(F) terms into E + $B_2$ and $A_2$ + E terms. The repulsion between the two E terms is expected to raise the value of $\square_{2/}$ $\square_1$ The value is however is raised only to a small extent suggesting that the splitting is weak and that the environment is quite close to an octahedral one[21].

The electronic reflectance spectra observed for Co (II) complexes are similar to spectra of those complexes in which Co (II) ion has been reported to be in an octahedral environment. Various band positions, their assignments and some of the evaluated parameters are given in table 3b. Observed bands around 8518 – 8500 $cm^{-1}$and 15115-15040 $cm^{-1}$ have been assigned to $^4T_{1g}$ (F) → $^4T_{2g}$(F)($\square_1$) and $^4T_{1g}$(F) → $^4A_{2g}$ (F)($\square_2$) transitions respectively. The band due to the third transition $^4T_{1g}$ (F) → $^4T_{1g}$ (P) ($\square_3$) is partially hidden under the strong band due to π-π* transition. The theoretically calculated value of $\square_2$ lie higher than the values assigned from the spectra. The ratio $\square_{2/}$ $\square_1$ which lies around 1.8 for perfectly octahedral Co(II) complexes is found to lie at 1.67.

The magnetic moment values of Cu (II) complexes are in the range of 1.87-2.05 B.M. These values supported the distorted octahedral and square planar configuration respectively. The electronic spectra of 15200-15180 $cm^{-1}$ assignable to $^2T_{2g}$ → $^2E_g$ transition supporting octahedral configuration.

The fungicidal activities of the ligand as well as of metal complexes were screened against different fungi at different concentrations 100, 50 and 20 ppm in Czapek's dox agar medium. It has been observed that the fungicidal activity of the metal complexes is lesser than the free ligand. This might be due to the fact that the group which is responsible for toxicity is not free in complexes due to co-ordination however it is free in ligand. The ligand as well as the metal complexes is most toxic at higher concentration i.e. the fungicidal activity decreases with the decrease of concentration.

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