Complexes of 3-Diphenylaminomethyl-5-o-hydroxyphenyl-1,3,4-oxadiazole-2-thione with Cu(I), Ag(I), Zn(II), Fe(III), Co(II) & Ni(II)

R. A. RAI, U. AGARWAL† & LAKSHMI*  
Department of Chemistry, University of Gorakhpur, Gorakhpur 273001  
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Complexes of Cu(I), Ag(I), Zn(II), Fe(III), Co(II) and Ni(II) with 3-diphenylaminomethyl-5-o-hydroxyphenyl-1,3,4-oxadiazole-2-thione have been prepared and characterized on the basis of IR and electronic spectral, magnetic susceptibility and analytical data. All the complexes have been screened for fungicidal activity against Helminthosporium oryzae by the poisoned food and modified paper disc technique.

The 3-substituted aminomethyl-5-substituted-1,3,4-oxadiazole-2-thiones have been reported to be biologically active1. In continuation of our work2 on the complexing behaviour of the biologically active ligands having NCS groups, we are reporting here, the preparation of the complexes of Cu(I), Ag(I), Zn(II), Fe(III), Co(II) and Ni(II) with 3-diphenylaminomethyl-5-o-hydroxyphenyl-1,3,4-oxadiazole-2-thione (I). These complexes have been characterized on the basis of spectral (visible, IR), analytical and magnetic susceptibility data. The crystal field parameters ($Dq$, $B$ and $g$), have also been calculated.

**Materials and Methods**

All the reagents used were of AR or CP grade. The ligand was prepared by the reported method3.  

**Preparation of metal complexes:** Monoacetato (3-diphenylaminomethyl-5-o-hydroxyphenyl-1, 3, 4-oxadiazole-2-thionato) copper (I) monohydrate — An aq. solution (25 ml) of copper acetate (0.5 g, 2.5 m mole) was mixed with a hot ethanolic solution (40 ml) of ligand (0.5 g, 1.3 m mole) with continuous stirring. A dark-green solid was obtained which was washed several times with water and hot ethanol. It was then dried in a desiccator at room temperature.  

[Found : C, 54.1; H, 4.3; N, 8.5; S, 6.4; Cu, 12.5. Calc. for $[Cu(C_{21}H_{17}N_{3}O_{2}S)(CH_{3}COO)]_2H_2O$: C, 53.5; H, 4.2; N, 8.1; S, 6.2; Cu, 12.3%]

Monoformato (3-diphenylaminomethyl-5-o-hydroxyphenyl-1, 3, 4-oxadiazole-2-thionato) silver (I) dihydrate — It was prepared by a method similar to that used for Cu(I) complex except that AgNO$_3$ solution was used in place of copper acetate.  

[Found : C, 43.2; H, 3.5; N, 9.9; S, 5.8; Ag, 18.9. Calc. for $[Ag(C_{21}H_{17}N_{3}O_{2}S)(NO_3)]_2H_2O$: C, 43.4; H, 3.6; N, 9.9; S, 5.5; Ag, 18.6%]

Biacetatobis (3-diphenylaminomethyl-5-o-hydroxyphenyl-1, 3, 4-oxadiazole-2-thionato) zinc (II) trihydrate — An ethanolic solution (50 ml) of zinc acetate (0.5 g, 2.8 m mole) was mixed with an ethanolic solution (30 ml) of the ligand (0.5 g, 1.3 m mole). It was stirred for about 1 hr when a white solid was obtained which was filtered, washed several times with water and hot ethanol and dried in a desiccator at room temperature.  

[Found : C, 53.9; H, 4.2; N, 8.3; S, 6.6; Zn, 6.3. Calc. for $[Zn(C_{21}H_{17}N_{3}O_{2}S)_{2}(CH_3COO)_{2}]_3H_2O$: C, 53.5; H, 4.4; N, 8.5; S, 6.5; Zn, 6.6%]

Trichlorotris (3-diphenylaminomethyl-5-o-hydroxyphenyl-1, 3, 4-oxadiazole-2-thionato) iron (III) tetrahydrate — A mixture of ferric chloride (0.6 g, 3.7 m mole) and ligand (0.6 g, 1.6 m mole) containing sodium acetate (0.8 g) was refluxed in 70 ml of ethanol for 4 hr on a water-bath. Violet-black solid, thus obtained was filtered, washed several times with water and hot alcohol and dried in a desiccator at room temperature.  

[Found : C, 56.2; H, 4.3; N, 9.2; S, 7.2; Fe, 4.2. Calc. for $[Fe(C_{21}H_{17}N_{3}O_{2}S)Cl_3]_2H_2O$: C, 55.6; H, 4.3; N, 9.3; S, 7.1; Fe, 4.1; Cl, 7.8%]

Dichlorobis (3-diphenylaminomethyl-5-o-hydroxyphenyl-1, 3, 4-oxadiazole-2-thionato) cobalt (II) pentahydrate — Cobalt chloride (0.7 g, 2.9 m mole) and the ligand (0.7 g, 1.8 m mole) containing sodium acetate (0.9 g) was refluxed in ethanol (60 ml) for 5 hr on a water-bath. A dark-blue solid, thus obtained, was filtered and washed with several times with
water and alcohol and dried in a desiccator at room temperature.

[Found : C, 52.6; H, 4.6; N, 8.4; S, 6.3; Co, 6.3; CI, 7.5. Calcul. for [Co(C2H7N2O4S)Cl]2.6H2O : C, 52.0; H, 4.5; N, 8.7; S, 6.6; Co, 6.1; CI, 7.3%].

Dichlorobis(3-diphenylamino-5-(o-hydroxyphenyl)-1, 3,4-oxadiazole-2-thionato) nickel (II) nonahydrate — The procedure for the preparation of the complex was the same as that for the Co(II) complex, except that NiCl2, 6H2O (0.7g, 2.9 mole) was used in place of CoCl2.6H2O. A green complex was formed.

[Found : C, 47.9; H, 4.8; N, 8.0; S, 6.3; Ni, 5.9; CI, 6.6. Calcul. for [Ni(C21H17N3O2S)2Cl]2.9H2O : C, 48.4; H, 5.0; N, 8.1; S, 6.1; Ni, 5.6; Cl, 6.8%].

The metal ions, chloride and sulphur were analysed by the methods described. Carbon, hydrogen and nitrogen analyses were performed at the Micro-Analytical Section of Banaras Hindu University, Varanasi. The water molecules in the complexes were analysed by isothermal TG analysis at 125 ± 5°C and no colour change was observed. All the complexes were insoluble in common organic solvents.

Infrared spectra of the ligand and the complexes were recorded using nujol mulls in the range 4000-200 cm⁻¹ on a Perkin Elmer spectrophotometer model 621. Magnetic susceptibilities were determined with the help of a Faraday balance at room temperature using ferrous ammonium sulphate as the standard. Electronic spectra of the complexes were obtained in nujol in the range 200-1400 nm on a Cary 14 recording spectrophotometer.

All the complexes were screened for fungicial activity against Helminthosporium oryzae by the poisoned food and modified paper disc technique.

Results and Discussion

The analytical data of the complexes indicate that the complexes have one or more molecules of water. The TGA data show that these water molecules can be easily removed by heating around 150° without decomposition of the complex. Thus, the water molecules are the water of crystallization. Further, it has been found that the directions of the shifts in the positions of all the bands in the spectra of Zn(II), Cu(I), Co(II), Ni(II) and Ag(I) complexes are the same, while that in silver complex is different. The bands arising due to normal coordination of the anions present in the complexes were present in all the complexes at their characteristic positions.

The position of the IR bands due to phenyl and oxadiazole groups do not change (maximum shift ± 5 cm⁻¹) in the Ag(I) complex. The bands due to ν OH group of water molecules were present at 3400 cm⁻¹ in the spectrum of the complex. The characteristic bands due to NO3 group were also present at 1375 cm⁻¹ and 1310 cm⁻¹ in its spectrum. The band due to ν C=S at 855 cm⁻¹ in the ligand shifted to lower wave number (840 cm⁻¹) in the complexes.

The above observations indicate that possibly the bonding in silver complex is through thiol sulphur only. In such a bonding scheme, the positions of the bands due to phenyl and OH groups should not change and further, no major shifts in the positions of the bands due to oxadiazole ring are expected.

The characteristic IR band due to water molecules and OH groups were present at 3400-3600 cm⁻¹ in the spectra of Cu(I), Co(II), Ni(II), Fe(III) and Zn(II) complexes. All the bands arising from the various modes of vibrations of the phenyl and oxadiazole rings were shifted, some towards higher and some towards lower wave numbers. The band due to ν C=N at 835 cm⁻¹ in the ligand is shifted towards higher wave number (850 cm⁻¹) in the complex. The band due to ν C=S at 855 cm⁻¹ does not shift (maximum shift ~ 5cm⁻¹). The characteristic band of CH3COO⁻ group is present at 1739 cm⁻¹ in the spectra of Cu(I) and Zn(II) complexes.

The above shifts indicate that the bonding in the complexes is through either of the two nitrogen atoms. It is quite possible that both the nitrogen atoms of —N(CH2)N (99) may participate in the bond formation, but the magnetic and electronic spectral data as discussed later in the paper, suggest that only one of the two nitrogen atoms is participating in the bond formation. Since the nitrogen attached to one phenyl group should be much less basic compared to that in the ring attached to CH3 group, it is assumed that N of —NCH2— group is participating in the bond formation. However this conclusion is only tentative.

The complexes of Cu(I), Zn(II) and Ag(I) are diamagnetic. The diamagnetism of copper complex confirms its oxidation state. It appears that the copper ion has been reduced to +1 state during the course of reaction possibly by the ligand.

The magnetic moment of Ni(II) complex is 3.53 B.M. indicating the presence of two unpaired electrons. A large orbital contribution to the magnetic moment of this complex indicates its structure to be tetrahedral (ground state S²). The possibility of its being octahedral is ruled out since generally the magnetic moments of Ni(II) octahedral complexes lie in the range 2.84-3.3 B.M.

The magnetic moments of Fe(III) and Co(II) complexes are 5.82 and 4.05 B.M. respectively indicating the presence of five and three unpaired electrons respectively. These values are very close to the spin-only values suggesting non-degenerate or doubly degenerate ground states of the metal ions in the complexes. This could be possible only if
the geometries of these complexes are tetrahedral\(^{12,13}\). Furthermore, these values lie well within the range of tetrahedral complexes of Co(II) and Fe(III)\(^{14,12}\). The dark blue colour of cobalt complex also indicates its tetrahedral geometry.

The electronic spectrum of the ligand shows two bands at 270 and 320 nm. These are present in the spectra of all the complexes but are slightly shifted. These bands have, therefore, been assigned as intraligand bands.

The electronic spectrum of Ni(II) complex shows two bands at 640 (15625 cm\(^{-1}\)) and 1200 nm (8333 cm\(^{-1}\)). The presence of these bands cannot distinguish between tetrahedral and octahedral geometries. However, the absence of any band around 400 nm suggests the tetrahedral geometry\(^{12,13}\). These bands have therefore, been assigned to the transitions \(4T_1 \rightarrow 3T_1\) (\(p\)) and \(4T_2 \rightarrow 3T_2\) respectively\(^{12,13}\). Assuming \(T_4\) symmetry around Ni(II) ion in the complex with no configuration interaction, the values of \(D_q\) (tetrahedral) \(B\) and \(\beta\) have been calculated to be 463 cm\(^{-1}\), 672 cm\(^{-1}\) and 0.66 respectively. The value of \(\beta\) (0.66) signifies a fair amount of covalent character in metal to nitrogen bond\(^{12,13}\). Taking the value of \(D_q\) (tetrahedral) to be 463 cm\(^{-1}\), one should expect a band due to the transition \(3T_1 \rightarrow 2T_2\) in the infrared region at 3704 cm\(^{-1}\) which could not be observed in the spectrum of the Ni(II) complex.

Similar to nickel complex the electronic spectrum of Co(II) complex also shows a band at 640 nm (16625 cm\(^{-1}\)), but no band appears around 400 nm. The absence of the band around 400 nm indicates the tetrahedral geometry of the complex and therefore, the band at 640 nm has been assigned to the transition \(4A_1 \rightarrow 3T_1\) (\(p\)).

The spectrum of Fe(III) complex shows a broad and very weak band around 675 nm (14815 cm\(^{-1}\)). The very weak intensity of the band suggests that this may be a spin-forbidden band. In the spectra of tetrahedral Fe(III) complexes a number of weak bands (spin-forbidden) exist around 500 nm\(^{12,13,18}\). The band at 675 nm may be assigned to these characteristic spin-forbidden bands of tetrahedral Fe(III) complex.

Cu(I), Zn(II) and Ag(I) do not show any \(d-d\) band as expected.

All the complexes and ligand were screened for fungicidal activity against Helminthosporium oryzae by poisoned food and modified paper disc technique\(^{3}\). The biological activity of the ligand and the complexes indicated that dilute solution of the complex ions of Co(II), Ni(II), Cu(I) and Zn(II) metal ions are more active than ligand (Table 1).

Thus, on the basis of analytical, magnetic, spectral (UV, visible, IR) data; Ni(II), Co(II), Fe(III) and Zn(II) have been assigned tetrahedral geometry while Ag(I) and Cu(II) seem to be linear.

Further, the ligand behaves as monodentate towards one metal ion with M-N bonding in Ni(II), Co(II), Fe(III), Cu(I) and Zn(II) complexes and with M-S bonding in Ag(I) complex.

In all the complexes bonds between the metal ions and the ligand molecules are formed through thiocarbonyl sulphur and N of the NH group after deprotonation.

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### References


### Table 1 — Biological Activity of Metal Complexes and Ligand Against H. oryzae

<table>
<thead>
<tr>
<th>Complex/ligand</th>
<th>Average percentage inhibition after 6 days at dilution</th>
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<tr>
<td></td>
<td>1:100</td>
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<tr>
<td>Ligand</td>
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<tr>
<td>[Fe(L)Cl]_2 \cdot 4H_2O</td>
<td>36.5</td>
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<tr>
<td>[CO(L)Cl]_2 \cdot 5H_2O</td>
<td>100</td>
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<tr>
<td>[Ni(L)Cl]_2 \cdot 9H_2O</td>
<td>100</td>
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<tr>
<td>[Cu(L)(CH_3COO)]_2 \cdot H_2O</td>
<td>100</td>
</tr>
<tr>
<td>[Ag(NO_3)]_2 \cdot 2H_2O</td>
<td>33</td>
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<tr>
<td>[Zn(L)(CH_3COO)]_2 \cdot 3H_2O</td>
<td>85</td>
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