Pseudotetrahedral Co(II), Ni(II) and Cu(II) Complexes of N^1-(O-Chlorophenyl)-2-(2',4'-Dihydroxyphenyl)-2-Benzylazomethine their Fungicidal and Herbicidal Activity

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Introduction

It has been suggested that the fungicidal activity of the compound like 8-hydroxyquinoline and similar others is due to their ability to chelate the essential metals which the fungus needs in its metabolism [1, 2]. On the basis of chelation theory, the fungicidal activity of 1-hydroxyacridine, hydroxypyroline and similar other heterocycles containing -OH or -SH groups adjacent to nitrogen have been well explained [3, 4]. It has already been suggested by various authors that the metal chelates are more potent than the chelating agents themselves [5, 6].

An azomethine of the type (I) may be viewed as a suitable ligand capable of forming chelates with metals as shown in structure (II) and as such it may be anticipated to display fungicidal and herbicidal activities. Speculating this possibility the title compounds were synthesised.

In the present work metal chelates of N^1-(O-chlorophenyl)-2-(2',4'-dihydroxyphenyl)-2-benzylazomethine have been prepared and investigated for their geometry and fungicidal and herbicidal activities.

(I)   (II)
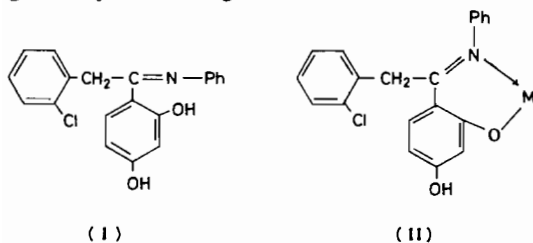
Experimental

All the chemicals used were of analytical grade or of equivalent quality. N^1-(O-chlorophenyl)-2-(2',4'-dihydroxyphenyl)-2-benzylazomethine (MP 151 °C) was synthesized by the method of Jadhav and Usgaonker [7] which involves the condensation of imidochloride with resorcinol in the presence of anhydrous AlCl$_3$. The complexes were all prepared by the following method.

A solution of the metal salt in methanol was added to the stirring ligand in methanol. The whole mixture was refluxed for 5–6 hours. This was cooled, filtered off, washed with water followed by methanol and dried in a vacuum desiccator. The analytical results are given in Table I.

TABLE I. Analytical Data[a], Melting Points and Magnetic Moments of the Complexes.

Complex	M.P. °C	Metal %	Nitrogen %	μ_{eff} B.M.
CoL$_2$	250	8.84 (8.88)	4.20 (4.21)	4.40
NiL$_2$	250	8.91 (8.88)	4.19 (4.21)	3.46
CuL$_2$	210	9.58 (9.56)	4.16 (4.18)	1.68

[a]Calculated values are given in parentheses. Satisfactory carbon and hydrogen analyses have been obtained from all the complexes.

The water content of the complexes was determined by heating them in the range of 150–300 °C and determining the loss in weight.

Conductivity titration and molar conductance were measured with the help of a Toshniwal's conductivity bridge (type CL 01/01), using a dip type cell at room temperature (293 K).

Magnetic susceptibility measurements were carried out by the Gouy method using cobalt, mercury tetrathiocyanate as standard. Diamagnetic corrections were also made by using Pascal's constants.

The electronic spectra of the chelating agent and the complexes was recorded on a Unicam SP 8000 UV Spectrophotometer in DMF.

Infrared spectra (200–4000 cm^{-1}) of ligand and complexes were recorded on a Perkin-Elmer model 337 Spectrophotometer in KBr.

Antifungal activity was evaluated against *A. niger* and *A. flavous* by the agar-plate technique [8] at three concentrations *viz.* 10 ppm, 100 ppm and 1000 ppm. The number of replications in each case was three. The percentage inhibition by various compounds are recorded in Table II.

$$\text{Percentage Inhibition} = \frac{(C-T) \times 100}{C}$$

where, C = diameter of the fungus colony in the control plate after 96 hour and T = diameter of the fungus colony in treated plates after 96 hour.

TABLE II. Fungicidal Screening Data.

| Compound serial as in Table I | Average percentage inhibition after 96 hours | | | | | |
| | Organism-*A. niger* concentration used (ppm) | | | Organism-*A. flavous* concentration used (ppm) | | |
	10	100	1000	10	100	1000
1	42.3	58.6	80.0	37.8	52.2	78.6
2	50.6	67.7	88.2	42.4	59.5	80.4
3	60.6	87.5	100.0	58.6	79.6	98.8
Ligand	30.4	46.5	75.5	30.2	45.8	70.6

TABLE III. Herbicidal Screening Results of Various Compounds.

| Compounds serial as in Table II | Average percentage inhibition against | | | | | |
| | *A. maxicana* concentration used (ppm) | | | *C. rotundus* concentration used (ppm) | | |
	10	100	1000	10	100	1000
1	50.0	62.2	70.0	58.6	68.0	72.4
2	55.7	60.5	76.6	59.5	70.2	80.4
3	64.0	85.8	100.0	70.0	80.6	99.8
4	40.6	45.8	64.9	30.9	45.5	58.6
2,4-D (Sodium salt)	58.5	88.4	100.0	54.4	70.4	96.6

Herbicidal activity of the ligand and the complexes were evaluated by pre-emergence test at 10, 100 and 1000 ppm concentrations against *Argemone maxicana* and *cyperus rotendus*. The number of replications in each case was three. Seeds/tubers of the test weeds were soaked for 24 hours in the test solutions/suspensions and then planted. A commercial herbicide 2,4-D (sodium salt) was also tested under similar conditions with view to comparing the results. The percentage inhibition of germination by various compounds are listed in Table III.

Results and Discussion

The elemental analyses (Table I) lead to the stoichiometry of ML_2 for all the complexes. The molar conductivities ranges in between 1.8–7.6 cm^2 Ω^{-1} $mole^{-1}$. The conductance measurements indicated that these are essentially non-electrolytes in acetone. This confirms coordination of azomethine anion.

From the corrected values of the magnetic moments (Table I) one would foresee a pseudotetra-

hedral geometry for all the complexes under investigation.

The reported ligand has two potential donor sites *viz.* nitrogen and oxygen as shown in structure I and II. In the IR the -N = C frequency in the ligand appears at 1600 cm^{-1} instead of 1660 cm^{-1} [9]. This band shift towards a lower frequency is most probably due to intramolecular hydrogen bonding between nitrogen of -N = C group and hydrogen of -OH group *ortho* to each other. The hydrogen bonding completely disappears on complexation due to the labile hydrogen and covalent bonding of the oxygen with the metal ion concerned. Further a negative shift of ∼30–40 cm^{-1} in -N = C band in the complexes indicate coordination through the nitrogen with the metal ion. The involvement of both nitrogen and oxygen in coordination indicates a bidentate behaviour of the ligand. Another band, appearing at ∼3500 cm^{-1}, in the ligand and the complexes may be assigned to the -OH group at *para* position. This -OH group does not enter into bonding with the metal ion, probably due to steric factors. Thus a six membered chelate ring is obtained having N_2O_2 isomer.

In the UV spectra the d—d transition peaks are confined to the region below 20500 cm^{-1} by the more intense parity allowed bands at higher energy. However, on the consideration of the band maxima, their characteristic splitting and calculations of the Dq, B' and β^0 value lead to the conclusion that in all the complexes metals are in pseudotetrahedral environment.

Thus the spectrum of Co(II) complex is characteristic of pseudotetrahedral species [10, 11] giving three multiplet bands at 6000, 15380 and 20000 cm^{-1} assigned to $^4A_{2g} \rightarrow {}^4T_{2g}$ (ν_1), $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) (ν_2) and $^4A_{2g} \rightarrow {}^4T_{1g}$ (P) (ν_3) transitions respectively. We have calculated the values of Dq, B' and β^0 which comes to 600 cm^{-1}, 933 cm^{-1} and 16.7% respectively. The magnetic moment of Co(II) complex is considerably in excess of the spin only value (3.89 BM). This might be due to the spin—orbit coupling caused by the $^4T_2$ state. In the case of Ni(II) complex the transitions are: $^3T_{2g} \rightarrow {}^3A_{2g}$ (ν_1) (9800 cm^{-1}); $^3T_{1g}(F) \rightarrow {}^3A_{2g}(\nu_2)$ (16450 cm^{-1}) and $^3T_{1g}(F) \rightarrow {}^3A_{2g}(P)$ (ν_3) (18000 cm^{-1}). In this case the values of Dq, B' and β^0 are 980 cm^{-1}, 546 cm^{-1} and 49.4% respectively. This is characteristic feature of distorted tetrahedral structure of Ni(II) complexes. The Cu(II) complex shows a very broad band with a maximum near 9800 cm^{-1}. This is indicative of distorted tetrahedral configuration and is assigned to the $^2T_2 \rightarrow {}^2E$ transition [12]. The broadness of this band is attributed to Jahn-Teller effect. The weaker band at $\sim$5300 cm^{-1} is probably due to $^2B_2 \rightarrow {}^2E$ transition [10].

Antifungal activity (Table II) was evaluated against *A. niger* and *A. flavous*. It was observed that the complexes are more fungitoxic than the ligand. Further, the toxicities of the complexes increases with decrease in the radii of the metals. Cu(II) complex completely inhibits the growth of the test fungi at 1000 ppm level after 96 hour compared to 50% by the ligand. All the compounds screened for herbicidal activities were significantly active against both the test weeds at 1000 ppm but their toxicity decreased considerably on dilution.

A possible mode of toxicity may be speculated in the light of chelation theory. Chelation reduces considerably polarity of the metal ion mainly because of partial sharing of its positive charge with the donor groups and possible π-electron delocalisation over the whole chelate ring. This increases the lipophilic character of the metal chelate which favours its permeation through lipoid layers of fungus and weed membranes. Furthermore, the mode of action of the compounds may involve the formation of hydrogen bond through the -N = C group and/or hydroxyl group with the active centres of the cell constituents resulting in interference with the normal cell process.

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