Some New Anti Fungal Trivalent Transition Metal Ions Complexes: Synthesis and Characterization

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Abstract

Macrocyclic ligands and their metal complexes are being synthesized very fast as they are developing areas of research in bioinorganic and inorganic chemistry. A new series of trivalent chromium, cobalt and iron complexes has been prepared through template methods with 2, 2-dihydroxyindane- 1, 3-dione and isomeric diaminopyridines. The complexes have a tetra dentate ligand which coordinates to the metal ions through the nitrogen donor atoms. The structure of the complexes is mononuclear. Effectiveness towards anti fungal properties of these complexes is studied against cotton plant fungi: Alternaria alternata and Fusarium oxysporum. The complexes have been characterized by elemental analyses, molar conductance, electronic spectra, ESR, magnetic measurements and IR spectral data which points towards a distorted octahedral geometry. Conductivity measurements in dimethylsulphoxide indicated them to be 1:2 electrolytic in nature (130-170 $ohm^{-1}cm^2 mol^{-1}$). Their fungicidal properties have been compared with the standard indofil M-45 and bavistin. Some of the complexes have been found to be anti-fungal in nature.

Key words: *distorted octahedral geometry, Magnetic moments. Electronic spectra, template synthesis, ED_{50} values, Potato dextrose agar (PDA).*

I. INTRODUCTION

The chemistry of macrocycles has undergone tremendous growth in the recent years. Many "inorganic" elements are essential for life. Organisms make economic use of available resources, but also have developed mechanisms to accumulate certain elements. Despite the low amount of metal ions present in living systems, they are enormously important for virtually all life processes. Both deficiency and overload/excess lead to illness. These complexes have attracted increasing interest owing to their mixed soft-hard donor character and versatile coordination behavior. Their metal complexes with various metals have been extensively studied [1–5]. Transition metal macrocyclic complexes resemble with natural proteins

[6], hence have received much attention as an active part of metallo-enzymes [7, 8]. Catalysis is one field where these complexes are very useful [9]. Specific pthalocyanines have been shown to behave as catalyst in variety of chemical transformations and they also act like semiconductors. A class of macrocyclic antibiotic called as nonacetin, binds with potassium and acts as a carrier for K^+ to transfer it across the lipid bilayers in the cell membrane. Nitrogen containing macrocycles have a strong tendency to form stable complexes with transition metals. Synthetic tetraaza macrocycle (N_4) molecules are considered typically good models for oxygen carriers due to the presence of four nitrogen donor sites confined to a single four-fold or a slightly four-fold plane in a ring structure, appropriate for metal ligand binding. There has been an increased interest in the complexes of trivalent copper, nickel, iron and cobalt which are found to form five or six coordinated geometries in their macrocyclic complexes and are reported to be antimicrobial also [10–12]. In the present paper, the complexes of 2,2-dihydroxyindane-1,3-dione and isomeric diaminopyridines are synthesized and characterized with the help of various physico-chemical techniques like elemental analyses, molar conductance, magnetic measurements, electronic spectra, ESR and IR spectra. Effectiveness of these complexes as antifungal compounds has been studied against Alternaria alternata and Fusarium oxysporum and compared with the standard indofil M-45 (Mancozeb 75% WP $(C_4H_6MnN_2S_4)_x Zn_y$) and bavistin, (Carbendazole);. The fungus has been extracted from the leaves and roots of the cotton plant respectively.

II. MATERIALS AND METHODS:

A. Synthesis of Complexes:

All the metal complexes were synthesized by template method. To a stirring methanolic solution (~100 ml) of 2, 3-/2, 6-diaminopyridines (~10 mmol) was added trivalent chromium, iron and cobalt (cobaltous chloride was added to 50 ml of 20 % hydrogen peroxide in faintly acidic solution, the solution was heated for half an hour) salts (~5 mmol)

dissolved in minimum quantity of methanol. The resulting solution was refluxed for half an hour. After that, ninhydrin (10 mmol) was dissolved in methanol (~20 ml) added in the refluxing mixture and refluxing was continued for 8-10 h, depending upon the metal salts. The mixture was concentrated to half of its original volume and kept in desiccator for two days. The complexes were filtered, washed with methanol, acetone and ether and dried *in vacuum.* (Yield 40-65%). The purity of the complexes was checked by TLC. The complexes were found soluble in dimethylformamide and dimethylsulphoxide but were insoluble in common organic solvents and water. They were thermally stable up to ~250°C and then decomposed into a wet solid.

B. Efficacy Against Fungi: Alternaria Alternata, Fusarium Oxysporum

The transition metal complexes have been found to be anti microbial [13]. The antimicrobial activities of the ligand and its complexes, as growth inhibiting agents, have been screened *in vitro* against *Alternaria alternata*, *Fusarium oxysporum. Alternaria alternata*, affects the leaves of the cotton plants and *Fusarium oxysporum*, affects the roots of the cotton plants. *Fusarium oxysporum*, destroys the water-conducting vessels (xylem) of the plant. As a result of breakdown of xylem, leaf wilting, yellowing and eventually plant death is observed. *Alternaria alternata* is opportunistic pathogen on numerous hosts causing leaf spots, rots and blights on many plant parts. It also causes upper respiratory tract infections in AIDS patients and asthma in people with sensitivity. *Alternaria alternata* is a fairly common indoor mould also. It is regarded as the main cause of allergy and asthma in children aged 6–11 years.Compounds were screened for their antifungal activity by spore germination inhibition technique Nene and Thapliyal [13].

C. Isolation and maintenance

From experimental areas of Punjab Agricultural University, Ludhiana, diseased samples of cotton leaves and roots were collected and washed with running tap water for 5-10 minutes. The infected parts were cut into small pieces using a sterilized blade. These samples were then sterilized with mercuric chloride solution (0.1%) for one minute followed by three washings with the sterilized distilled water. Sterilized infected pieces were transferred to dextrose agar (PDA) medium (200 g peeled potato, 20 g dextrose and 20 g agar in 1 liter water) slants under aseptic conditions. In order to get good growth of the fungi, test tubes were incubated at 25±1°C.The culture so obtained were purified and maintained by further sub culturing on PDA slants and keeping them in refrigerator.

D. Preparation Of Stock Solution

The stock solution of each compound and two standard fungicide viz. **Indofil M-45** (75% manganese ethylene bis dithiocarbamate + 2% zinc ion) and **Bavistin 50WP** (methyl benzimidazol-2-yl carbamate) were prepared by dissolving each chemical (20 mg) in DMSO and volume was made to 10 ml with sterilized water. Tween-20 was added to get a clear solution. The stock solution of 2000 ppm of each chemical thus prepared on active ingredient basis was kept in refrigerator till use. The required dilution of 1000, 500, 250, 100, 50, 25 and 10 ppm were subsequently made from the stock solution by adding distilled water as and when required.

E. Spore germination and Inhibition technique

Ten-day old cultures of fungi were taken from PDA slants and sterilized distilled water was added to form the suspension of spores. After shaking the tube thoroughly, the suspension was filtered through three layers of sterilized cheese cloth under aseptic conditions to remove mycelial and agar bits. Standardized spore suspension (1×10^{6} spores/ml) was made with the help of haematocytometer. Double strength concentration of the compounds was prepared and used as desired. Small droplets (0.02 ml) of the spore suspension in equal quantity with solution of the test compound were seeded in the cavity of cavity slides. These slides were placed in petriplates lined with moist filter paper. The petriplates containing cavity slides were incubated at 25 ±1°C for 24 hours. The germination of the spores was calculated by the following formula:

$$\% \text{ spore germination inhibition} = \frac{\begin{array}{c}\text{spore germination} \\ \text{in control}\end{array} - \begin{array}{c}\text{spore germination} \\ \text{in treatment}\end{array}}{\begin{array}{c}\text{spore germination} \\ \text{in control}\end{array}} \times 100$$

F. Indofil M-45 and **Bavistin 50WP** were used as check to compare the activity of the compounds. The antifungal activity has been expressed in terms of ED$_{50}$ values *i.e.* effective dose to inhibit 50% spore germination.

III. RESULTS AND DISCUSSION:

The analytical data of trivalent macrocyclic complexes derived from 2,3-/2,6-diaminopyridines and ninhydrin has been given in Table-1-2 and complexes may be represented by the formulae: [M(C$_{30}$H$_{16}$N$_{4}$O$_{2}$)Cl]Cl$_{2}$ and [M(C$_{28}$H$_{14}$N$_{6}$O$_{2}$)Cl]Cl$_{2,}$ respectively; where M = Cr(III), Fe(III) and Co(III).

The test for anions was positive before and after decomposing the complexes indicating their presence inside as well as outside the coordination sphere. Conductivity measurements in dimethylsulphoxide indicated them to be 1:2 electrolytic in nature (130-170 ohm^{-1}cm^2 mol^{-1}) [14].

A. Infrared Spectra

In the infrared spectra of all the metal complexes, strong band appears at ~1720 cm^{-1} may be assigned due to carbonyl >C=O group which was formed by dehydration, due to heating, of the geminal hydroxyl groups, present at 2,2 position on indanone. A pair of bands at ~3200 and 3250 cm^{-1} corresponding to -NH$_2$ group was present in infrared spectra of diaminopyridines. These were found absent in the infrared spectra of all the metal complexes. Instead a strong absorption band in the region ~1595-1640 cm^{-1} was observed which is attributed to the ν(C=N) group [15-16]. The lower values of ν(C=N) stretching frequency may be explained on the basis of drift of lone pair density of azomethine nitrogen towards the metal atom. These indicate the formation of macrocyclic frame, probably due to the condensation of -NH$_2$ groups of diaminopyridines with >C=O group of ninhydrin. The bands present in the range ~1350-1000 cm^{-1} in all the complexes were assigned to ν(C-N) stretching vibrations. The presence of stretching bands at ~1462 and ~1500 cm^{-1} may be assigned to >C=C< skeleton of benzenoid rings. The unchanged pyridine ring vibrations occurring at ~1595-1610, ~1565-1585, ~1450-1485 and ~1435-1440 cm^{-1} of pyridine ring ruling out the possibility of coordination of the pyridine nitrogen towards metal atom. [17] The spectra exhibit a ring breathing mode at ~990 cm^{-1}, an out- of-plane ν(C-H) deformation at ~810 cm^{-1}, an in- plane ν(C-C) deformation at ~ 620 cm^{-1} and out- of- plane deformation at ~410 cm^{-1}, respectively[18]. These unchanged pyridine ring vibrations in the complexes also indicate non-coordination of the pyridine nitrogen atom. The far infrared spectra showed bands in the region ~ 420-470 cm^{-1} corresponding to ν(M-N) vibrations [19]. The presences of these bands in all complexes give an idea about the coordination of azomethine nitrogen to the central metal atom [19]. The bands present at ~290 -310 cm^{-1} may be assigned as being due to ν(M-Cl) vibrations [20]. However, the absence of various ν(M-Py) vibrations also supports the non-involvement of the pyridine nitrogen in coordination to the metal atom [20].

B. ^{1}H NMR spectra

The ^{1}H NMR spectrums could not be obtained because the compounds were not soluble in common solvents and don't form a clear solution.

C. Magnetic measurements and electronic spectral studies

Absorption spectra in most cases involve the transitions of the electrons in the d orbitals of the metal. Electronic transitions occur between split'd' levels of the central atom. These split'd' orbitals give rise to the micro states, which are represented by term symbols like ^{4}B$_1$, ^{4}E^a, ^{4}A$_2$. The term symbols are in the form of $^{2S+1}L_J$, where S represents the total spin angular momentum, L specifies the total orbital angular momentum, and J refers to the total angular momentum. Electrons of an atom may undergo certain transitions which may have strong or weak intensities. There are rules about which transitions should be strong and which should be weak. Usually an electronic transition is excited by heat or radiation. If the different excited vibrational levels (micro states) are represented as υ_1, υ_2, etc., and the ground state as υ_0, the fine structure in the main peak of the spectrum is assigned to $\upsilon_0 \to \upsilon_0$, $\upsilon_0 \to \upsilon_1$, $\upsilon_0 \to \upsilon_2$ etc., vibrational states. The $\upsilon_0 \to \upsilon_0$ transition is the lowest energy (longest wave length) transition [21]

1) Chromium (III) Complexes

Magnetic moments of the chromium complexes were found in the range of 4.12-4.46 B.M at room temperature which was close to the predicted values for three unpaired electrons in the metal ion [22]. The electronic spectra of chromium(III) complexes show bands at ~9100-9300 cm^{-1}, ~13000-13300 cm^{-1}, ~17550-18300 cm^{-1}, ~27,280cm^{-1} and ~34810 cm^{-1}. The spectral bands were consistent with that of five-coordinated square-pyramidal chromium (III) complexes, whose structure has been confirmed with the help of X-ray measurements [23]. Thus, on the basis of the analytical data and electrolytic nature of these complexes, a five coordinated square-pyramidal geometry may be assigned for these complexes. Thus, assuming the symmetry C$_{4V}$ for these complexes, [25] the various spectral bands may be assigned as: ^{4}B$_1$ $\to$ ^{4}E^a, ^{4}B$_1 \to$ ^{4}B$_2$, ^{4}B$_1 \to$ ^{4}A$_2$ and ^{4}B$_1 \to$ ^{4}E^b.

2) Iron(III) Complexes

The magnetic moments of iron complexes was found in the range of 5.7-5.9 B.M., corresponding to the five unpaired electrons and was close to predicted high spin values for these metal ions [22]. The electronic spectra of iron (III) complexes showed various bands at ~9830-9980 cm^{-1}, ~15500 -15580 cm^{-1}, ~27500-27,700 cm^{-1} and were consistent with the range of spectral bands reported for five coordinate square-pyramidal iron (III) complexes [24]. Assuming C$_{4V}$ symmetry for these complexes, the various bands may be assigned as: d$_{xy} \to$ d$_{xz}$, d$_{yz}$ and d$_{xy} \to$ d$_z^2$. Any attempt to make accurate assignment was difficult due to interactions of the metal-ligand л-bond systems lifting the degeneracy

of the d_{xz} and d_{yz} pair.

3) Cobalt (III) Complexes

The magnetic moment of the complexes is 5.7-5.9 B.M indicating the electronic configuration to be $3d^6 4s^0$ [22]. This value is in the range reported for high spin, square pyramidal geometry around the Co (III) ion. The values that appear for the absorption in the electronic spectrum (18,800-18,200 cm^{-1}, 22,900 cm^{-1} and 39'000 cm^{-1}) support high spin, square pyramidal geometry around Co (III) ion [24]. The strong absorption bands found at 18,000 cm^{-1} in the spectrum of the complexes may be due to a ligand field transition e"$\rightarrow$e' or e"$---\rightarrow$ a_1'.It may be an electron transfer band [24].

Table-1. Analytical data of trivalent chromium iron and cobalt derived from ninhydrin and diaminopyridines.

Complexes	Found (Calcd.) %				
	C	H	N	M	Mol.Wt
$[Cr(C_{28}H_{14}N_6O_2)Cl]Cl_2$[a]	53.5(53.8)	2.1(2.2)	13.2(13.4)	8.2(8.3)	624.5
$[Cr(C_{28}H_{14}N_6O_2)Cl]Cl_2$[b]	53.6(53.8)	2.0(2.2)	13.1(13.4)	8.1(8.3)	624.5
$[Fe(C_{28}H_{14}N_6O_2)Cl]Cl_2$[a]	53.1(53.5)	2.1(2.2)	13.0(13.4)	8.6(8.9)	628.5
$[Fe(C_{28}H_{14}N_6O_2)Cl]Cl_2$[b]	53.3(53.5)	2.0(2.2)	13.2(13.4)	8.5(8.9)	628.5
$[Co(C_{28}H_{14}N_6O_2)Cl]Cl_2$[a]	53.0(53.2)	2.1(2.2)	13.2(13.3)	9.1(9.3)	631.5
$[Co(C_{28}H_{14}N_6O_2)Cl]Cl_2$[b]	53.1(53.2)	2.0(2.2)	13.1(13.3)	9.2(9.3)	631.5

a - 2, 3-diaminopyridine, b -2, 6 - diaminopyridine

Table-2: Analytical data of the trivalent chromium, iron and cobalt complexes derived from diaminopyridines and ninhydrin.

Complexes	Color	Molar Conductance (ohm^{-1}cm^2 mol^{-1})	Yield (%)	μ_{eff}
$[Cr(C_{28}H_{14}N_6O_2)Cl]Cl_2$[a]	Shiny dark green	101	45%	4.17
$[Cr(C_{28}H_{14}N_6O_2)Cl]Cl_2$[b]	Black green powder	110	46%	4.20
$[Fe(C_{28}H_{14}N_6O_2)Cl]Cl_2$[a]	Shiny Brown	116	49%	5.70
$[Fe(C_{28}H_{14}N_6O_2)Cl]Cl_2$[b]	Brown powder	118	47%	5.81
$[Co(C_{28}H_{14}N_6O_2)Cl]Cl_2$[a]	Greenish blue	90	50%	5.70
$[Co(C_{28}H_{14}N_6O_2)Cl]Cl_2$[b]	Brownish blue	93	47%	5.60

a -2, 3-diaminopyridine, b -2, 6-diaminopyridine

D. Proposed Structure

Based on various physicochemical techniques such as elemental analyses, molar conductivity measurements, magnetic susceptibility measurements, electronic and infrared spectral studies, a square-pyramidal structure as shown in Fig. may be proposed for all the trivalent metal complexes.
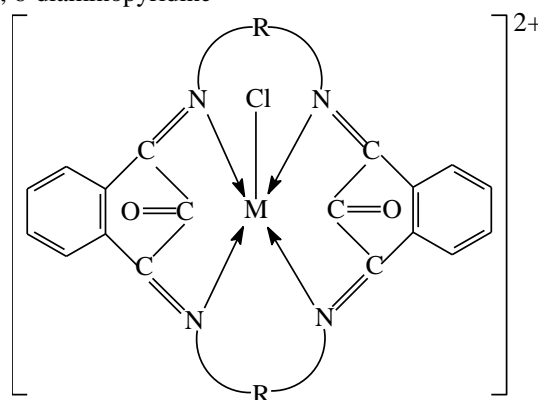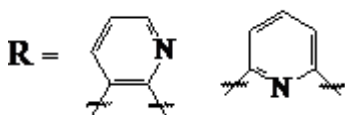
Fig. 1

M = Cr (III), Fe (III), Co (III)

R =

E. Results For Antifungal Activities

All the synthesized trivalent metal complexes were subjected to tests for antifungal activities. Their percentage inhibition in mg/l was determined in different dilutions from where their ED_{50} values were calculated.

1) *Alternaria alternata*: Table 3 showed the percentage inhibition in mg/ml against *Alternaria alternata* using the divalent metal complexes of 2,3-/2,6-daminopyridines and 2,2-dihydroxyindane-1,3-

dione. When compared with standard fungicide, **Indofil M-45** whose ED_{50} value was found to be 37, it was observed that the complexes of cobalt, nickel and copper of diaminopyridines have effective anti-fungal properties against *Alternaria alternate* but in the trivalent series (Tables 3), $[Co(C_{28}H_{14}N_6O_2)Cl]Cl_2{}^b$ has anti-alternaria properties against.

2) *Fusarium oxysporum*: *Bavistin 50WP* was used as standard fungicide to compare the efficacy of synthesized trivalent metal complexes of 2,3-/2,6-daminopyridines and 2,2-dihydroxyindane-1,3-dione against *Fusarium oxysporum*. Its ED_{50} value was found to be 7. Table 4 showed the percentage inhibition in mg/ml. Most of the compound inhibits growth to a very less extent. There ED_{50} values were very high but some complexes e.g. have low values. Trivalent series has $[Fe(C_{30}H_{16}N_4O_2)Cl]Cl_2$ complex as antifusarium complex only. But their effectiveness is not as of the standard.

Table-3 Efficacy of synthesized isomeric diaminopyridines complexes against Alternaria alternata

| Compound	Percent inhibition in mg/ml						ED_{50}
	1000	500	250	100	50	25	(mg/ml)
$[Cr(C_{28}H_{14}N_6O_2)Cl]Cl_2{}^a$	38	32	20	19	11	3	*
$[Cr(C_{28}H_{14}N_6O_2)Cl]Cl_2{}^b$	40	36	29	20	12	5	*
$[Fe(C_{28}H_{14}N_6O_2)Cl]Cl_2{}^a$	33	22	19	13	13	4	*
$[Fe(C_{28}H_{14}N_6O_2)Cl]Cl_2{}^b$	37	25	19	15	13	6	*
$[Co(C_{28}H_{14}N_6O_2)Cl]Cl_2{}^a$	46	38	22	15	10	8	*
$[Co(C_{28}H_{14}N_6O_2)Cl]Cl_2{}^b$	55	44	40	35	15	8	*
INDOFIL M-45	100	100	95	77	62	40	37

a - 2, 3-diaminopyridine, b - 2, 6-diaminopyridine

Table-4 Efficacy of synthesized isomeric diamino pyridines complexes against Fusarium Oxysporium

Compound	Percent inhibition in mg/ml								ED_{50}
	1000	500	250	100	50	25	10	5	(mg/ml)
$[Cr(C_{28}H_{14}N_6O_2)Cl]Cl_2{}^a$	36	19	17	13	10	4	0	0	*
$[Cr(C_{28}H_{14}N_6O_2)Cl]Cl_2{}^b$	35	18	18	12	10	7	0	0	*
$[Fe(C_{28}H_{14}N_6O_2)Cl]Cl_2{}^a$	80	62	52	36	25	11	10	3	280

$[Fe(C_{28}H_{14}N_6O_2)Cl]Cl_2$[b]	94	78	64	61	51	47	35	10	60
$[Co(C_{28}H_{14}N_6O_2)Cl]Cl_2$[a]	40	15	10	10	8	5	0	0	*
$[Co(C_{28}H_{14}N_6O_2)Cl]Cl_2$[b]	37	21	18	15	10	6	0	0	*
Bavisitin	100	100	100	100	92	75	60	42	7

a - 2,3-diaminopyridine, b - 2,6-diaminopyridine

Bar Graph representation of the data given in Table 3&4
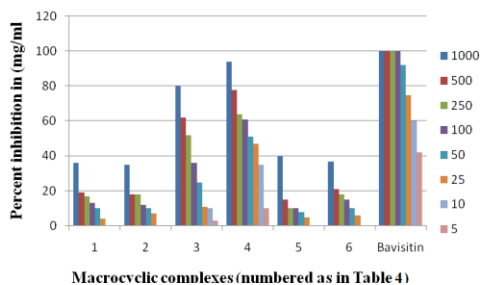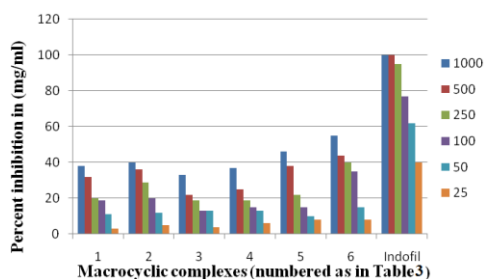
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