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Cr (III), Mn(III), Fe(III) And Co(III) Complexes of Schiff Bases Derived From 3-(Substituted Aryl)-4-Amino-5-Hydrazino-1,2,4-Triazole And 2-Hydroxynaphthaldehyde

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ABSTRACT

A series of trivalent chromium, manganese, iron and cobalt complexes with Schiff bases (LH_2), derived from 3-(substituted aryl)-4-amino-5-hydrazino-1,2,4-triazole and 2-hydroxy- naphthaldehyde, of the type $[M(L)X(H_2O)]$ [M= Cr, Mn, Fe, Co; X= Cl (for Cr and Fe) or CH_3COO (for Mn and Co)] have been synthesized in ethanol. The complexes were characterized by analyses, electrical conductance, magnetic moment and spectral (U.V.-vis., IR and ^1H NMR) data. The presence of coordinated water molecule in these complexes has been inferred from TG studies. Tentative structures of the complexes have been proposed. The antifungal activity of the ligands and complexes were evaluated against Aspergillus niger, Colletotrichum falcatum, and Curvularia pallescence. The complexes are found to be more potent against all species of fungi as compared to free ligands. The activity has been compared with the structural features of compounds.

Keywords: Schiff bases, Chromium, Manganese, Iron, Cobalt, UV-vis., IR, Antifungal activity.

INTRODUCTION

Schiff bases are an important class of ligands in coordination chemistry and their complexing ability containing different donor atoms is widely reported. In recent years, considerable interest has been shown in the study of Schiff base complexes of non-transition, transition and inner-transition elements due to their striking structural features and also on account of their varied utility particularly in analytical, pharmaceutical and industrial fields [1-10]. However, very few papers have appeared on Schiff bases containing heterocyclic ring [11,12]. One important class of Schiff bases is the ligand containing 1,2,4-triazole ring. 1,2,4-Triazoles and their derivatives are associated with various biological activities such as anticonvulsant, antifungal, anticancer, anti-inflammatory and antibacterial properties [13-16]. The coordination behaviour of such ligands depends upon the nature of metal ion, nature of substituent's on the ligands and pH of the medium [17]. The present paper describes the synthesis, characterization and antifungal activities of chromium (III), manganese(III), iron(III) and cobalt(III) complexes with Schiff bases derived from hydrazine 1,2,4-triazoles.

MATERIALS AND METHODS

All the chemicals used were of A.R. grade. Ethanol and other solvents were distilled before use. Metal chlorides or acetates were procured from Sigma-Aldrich. The ligands and manganese (III) acetate were prepared as reported in the literature [18,19].

Preparation of the complexes

Preparation of chromium (III), manganese(III) and iron(III) complexes with Schiff bases derived from 3-(Substituted aryl)-4-amino-5-hydrazino-1,2,4-triazole and 2-hydroxynaphthaldehyde: To a hot solution of appropriate ligand in methanol (25 mL), a solution of chromium(III) chloride, iron(III) chloride or manganese(III) acetate in methanol (20 mL) was added drop wise in equimolar ratio with the help of dropping funnel. The mixture was refluxed for *ca.* 10-18 h when coloured precipitate appeared. The precipitate was washed with methanol and ether, filtered and dried *in vacuo* . Yield = 58-70%

Preparation of cobalt(III) complexes Schiff bases derived from 3-(Substituted aryl)-4-amino-5-hydrazino-1,2,4-triazole and 2-hydroxynaphthaldehyde: To a hot solution of appropriate ligand in methanol (25 mL), a solution of cobalt(II) acetate in methanol (20 mL) was added drop wise in equimolar ratio with the help of dropping funnel. H_2O_2 (30%, 0.02 mol, 6 mL) was added and this mixture was refluxed and stirred for 10-15 h. This resulted in the formation of dark brown precipitate. The mixture was cooled on an ice bath and filtered. The precipitate was washed with methanol and ether, filtered and dried *in vacuo.* Yield 64-72%.The physical properties and analytical data of the complexes are given in Table 1.

Table 1: Analytical data and physical properties of chromium (III), manganese (III), iron (III) and cobalt (III) complexes with Schiff bases derived from 3-(substituted aryl)- 4-amino-5-hydrazino-1, 2, 4-triazole and 2-hydroxynaphthaldehyde

Complex	**Mol.formula**	**Colour**	**Yield (%)**	**Conduc tance**	**Analysis Found (Calcd) %**			
					C	H	N	M
$[Cr(SPTN)Cl(H_2O)]$	$Cr\ C_{30}H_{23}N_7O_3Cl$	Green	55	4.6	57.5 (58.4)	3.7 (3.8)	15.4 (15.9)	8.2 (8.4)
$[Cr(SCTN)Cl(H_2O)]$	$CrC_{30}H_{22}N_7O_3Cl_2$	Yellowish green	58	3.8	55.0 (55.3)	3.3 (3.4)	15.0 (15.1)	8.1 (8.0)
$[Cr(SPCTN)Cl(H_2O)]$	$CrC_{30}H_{22}N_7O_3Cl_2$	Green	62	3.5	55.1 (55.3)	3.4 (3.4)	15.0 (15.1)	7.9 (8.0)
$[Cr(SDTN)Cl(H_2O)]$	$Cr\ C_{30}H_{21}N_7O_3Cl_3$	Green	65	3.9	51.8 (52.5)	2.9 (3.1)	14.2 (14.3)	7.5 (7.6)
$[Cr(SNTN)\ Cl(H_2O)]$	$CrC_{30}H_{22}N_8O_5Cl$	Green	60	4.2	53.9 (54.4)	3.2 (3.3)	16.3 (16.9)	7.9 (7.9)
$[Mn(SPTN)(OAc)(H_2O)]$	$MnC_{32}H_{26}N_7O_5$	Brown	55	4.6	59.0 (59.7)	4.0 (4.1)	15.1 (15.2)	8.4 (8.5)
$[Mn(SCTN)(OAc)(H_2O)]$	$Mn\ C_{32}H_{25}N_7O_5Cl$	Light brown	52	5.2	56.4 (56.7)	3.5 (3.7)	14.5 (14.5)	8.0 (8.1)
$[Mn(SPCTN)(OAc)(H_2O)]$	$Mn\ C_{32}H_{25}N_7O_5Cl$	Brown	58	5.0	56.5 (56.7)	3.5 (3.7)	14.5 (14.5)	8.1 (8.1)
$[Mn(SDTNH)(OAc)(H_2O)]$	$Mn\ C_{32}H_{24}N_7O_5Cl_2$	Brown	55	4.5	53.4 (53.9)	3.3 (3.4)	13.5 (13.8)	7.7 (7.7)

[Mn(SNTN) (OAc) (H_2O)]	Mn $C_{32}H_{25}N_8O_7$	Brown	60	5.2	55.2 (55.8)	3.5 (3.7)	16.0 (16.3)	7.9 (8.0)
[Fe(SPTN) Cl(H_2O)]	$FeC_{30}H_{23}N_7O_3Cl$	Yellowish brown	64	6.7	57.8 (58.0)	3.5 (3.7)	15.6 (15.8)	9.0 (9.0)
[Fe(SCTN)Cl(H_2O)]	Fe $C_{30}H_{22}N_7O_3Cl_2$	Yellowish brown	66	5.8	55.0 (55.0)	3.3 (3.4)	15.0 (15.0)	8.2 (8.5)
[Fe(SPCTN)Cl(H_2O)]	$FeC_{30}H_{22}N_7O_3Cl_2$	Yellowish brown	62	6.0	54.7 (55.0)	3.3 (3.4)	15.0 (15.0)	8.4 (8.5)
[Fe(SDTN)Cl(H_2O)]	Fe $C_{30}H_{21}N_7O_3Cl_3$	Brown	65	6.2	51.9 (52.2)	3.0 (3.1)	14.1 (14.2)	8.0 (8.1)
[Fe(SNTN)Cl(H_2O)]	$FeC_{30}H_{30}N_8O_5Cl$	Brown	58	5.4	54.0 (54.1)	3.2 (3.3)	16.8 (16.8)	8.3 (8.4)
[Co(SPTN) (OAc) (H_2O)]	$CoC_{32}H_{26}N_7O_5$	Brown	60	4.2	59.1 (59.3)	3.9 (4.0)	15.2 (15.1)	9.0 (9.1)
[Co(SCTN) (OAc) (H_2O)]	$CoC_{32}H_{25}N_7O_5Cl$	Brown	58	4.8	56.1 (56.3)	3.5 (3.7)	14.2 (14.4)	8.5 (8.6)
[Co(SPCTN) (OAc) (H_2O)]	$CoC_{32}H_{25}N_7O_5Cl$	Brown	54	4.5	56.0 (56.3)	3.6 (3.7)	14.3 (14.4)	8.6+ (8.6)
[Co(SDTNH)(OAc)(H_2O)]	$CoC_{32}H_{24}N_7O_5Cl_2$	Brown	58	5.2	53.5 (53.6)	3.2 (3.4)	13.6 (13.7)	8.0 (8.2)
[Co(SNTN) (OAc) (H_2O)]	$CoC_{32}H_{25}N_8O_7$	Brown	58	5.0	55.3 (55.5)	3.5 (3.6)	16.0 (16.2)	8.3 (8.5)

Where,
$SPTNH_2$ = Schiff base derived from 3-phenyl- 4-amino-5-hydrazino-1, 2, 4-triazole and 2-hydroxynaphthaldehyde.
$SCTNH_2$= Schiff base derived from 3-(o-chlorophenyl)- 4-amino-5-hydrazino-1, 2, 4-triazole and 2-hydroxynaphthaldehyde.
$SPCTNH_2$ = Schiff base derived from 3-(p-chlorophenyl)- 4-amino-5-hydrazino-1, 2, 4-triazole and 2-hydroxynaphthaldehyde.
$SDTNH_2$ = Schiff base derived from 3-(2,4-dichlorophenyl)- 4-amino-5-hydrazino-1, 2, 4-triazole and 2-hydroxynaphthaldehyde.
$SNTNH_2$ = Schiff base derived from 3-(p-nitrophenyl)- 4-amino-5-hydrazino-1, 2, 4-triazole and 2-hydroxynaphthaldehyde.

Characterization of ligands and metal complexes: The melting points of ligands and their metal complexes were determined by open capillary method and are uncorrected. C,H and N analyses were carried out at B.H.U., Varanasi. Metals were estimated gravimetrically. The IR spectra of the ligands and the complexes were recorded in the range 4000-200 cm^{-1} in potassium bromide medium on Matson 1000 model FTIR spectrophotometer and Beckman Acculab-9 spectrometer. The electronic spectra were recorded on Perkin Elmer UV-VIS spectrophotometer model 2000. The ^1H NMR spectra of ligands and few complexes were recorded in DMSO-d_6 on JEOL Al 300 spectrometer at the sweep width of 900 Hz and a sweep time of 300 sec. Chemical shifts are expressed relative to an internal reference TMS (1% by volume). Magnetic susceptibility measurements were made by the Faraday method using ferrous ammonium sulphate as calibrant.

For antifungal activity, all compounds were tested against all test fungi by the food poison technique at three concentrations (10, 100 and 1000 mg L^{-1}). For this, the desired amount of chemical was dissolved in 0.5 mL of acetone and mixed with the culture medium on the basis of the volume of the medium in each

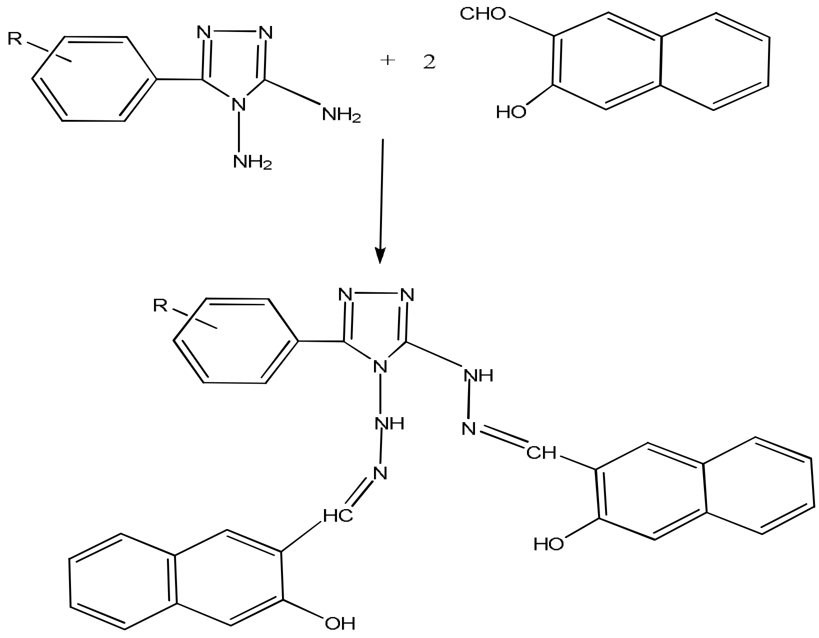
Petri plate (about 80 mm diameter). Oatmeal-agar medium were used for all test fungi. In controls, the same amount of medium containing the requisite amount of solvent was poured in place of test chemicals. A mycelial disk (5 mm diameter) obtained from the periphery of 2-week-old cultures was taken and transferred to the centre of each Petri plate. Plates were incubated for 7 days at 28 ± 2^0C. Each treatment was repeated three times, and the inhibition was recorded relative to percent mycelial inhibition calculated using the formula:

$dc-dt/dc \times 100$

where dc is the average diameter of the mycelial colony of the control and dt is the average diameter of the mycelial colony of the treatment.

RESULTS AND DISCUSSION

The condensation reactions of 3-(Substituted aryl)-4-amino-5-hydrazino-1,2,4-triazole and 2-hydroxynaphthaldehyde in ethanol give rise to Schiff base ligands (LH_2), as shown below:



[R= H ($SPTNH_2$), 2-Cl ($SCTNH_2$), 4-Cl ($SPCTNH_2$), 2,4-Cl_2 ($SDTNH_2$), 4-NO_2 ($SNTNH_2$)]

(LH_2)

A systematic study of the reactions of chromium (III) chloride, iron (III) chloride and manganese(III) acetate with Schiff bases have been studied in ethanol. The complexes of type $[M(L)X(H_2O)]$ are obtained according to the following reaction:

$$MX_3 + LH_2 \rightarrow [M(L)X(H_2O)]$$

(M= Cr, Mn or Fe)

Cobalt (II) acetate reacts with these ligands in ethanol on addition of H_2O_2 and complexes of type $[Co(L)CH_3COO(H_2O)\}]$ are obtained according to the following equation:

$Co\ (CH_3COO)_2 + LH_2 \rightarrow [Co(L)CH_3COO(H_2O)]$

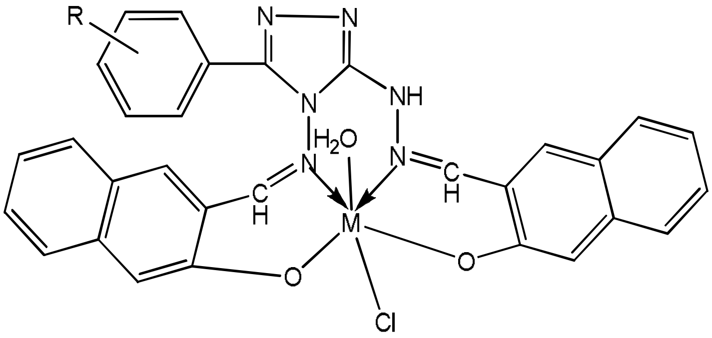
The analytical data of the complexes are given in table 1. The methods used for the preparation and isolation of these compounds give materials of good purity as supported by their analysis. All these complexes are coloured. They are thermally stable but decompose in the temperature range 225-282°C. They are quite stable in air. Conductance measurements in dimethylformamide reveal that they are essentially non-electrolytes. The presence of coordinated water molecule in all these complexes have been studied by TG which show weight loss at 165-180^{0}C, corresponding to one water molecule.

Magnetic Moments: The interaction between the motion of the electron and the external magnetic field *i.e.* the magnetic susceptibility of studied transition metals is measured. The chromium complexes (d^3), $t_{2g}{}^3$, without any expected orbital configuration, with ground term $^4A_{2g}$ (^4F) show the magnetic moments in the range 3.80-3.90 B.M. at room temperature which is in accord with the observed spin-only value having no TIP contribution, suggesting octahedral environment around chromium ion [20.21]. The complexes of manganese (III) have magnetic moments in the range 4.80-4.90 B.M. at room temperature. These values are in the range expected for spin-only value for four unpaired electrons, irrespective of whether the symmetry of the complexes are octahedral, tetragonal or lower and indicate the absence of exchange or super exchange interaction in these complexes [22]. The iron(III) complexes (d^5, $t_{2g}{}^3e_g{}^2$) for the $^6A_{1g}$ (^6S) ground term showed magnetic moment between 4.98-5.20 B.M., there is no T. I. P effect and no reduction of the moment below the spin-only value by spin-orbit coupling with higher ligand field terms [23]. The moments are indeed, found to be very close to the spin only value of 5.92 B.M. The cobalt (III) complexes (d^6, $t^4{}_{2g}e_g{}^2$) are spin paired complexes (diamagnetic) possessing the $^1A_{1g}$ (^5D) ground term; there is no first order Zeeman effect (J = S = 0) [24].

Electronic Spectra: UV-vis spectra have been recorded for 1-5 × 10^{-3} solution of complexes in DMSO or $CHCl_3$. The chromium complexes exhibit d-d transitions typically observed for octahedral chromium in the +3 oxidation state. The electronic spectra of chromium(III) complexes show bands at 16800-17200, 21200-22030 and 29000-29800 cm^{-1}. The positions of these bands are consistent with the six-coordinate stereochemistry. Six-coordinate complexes may either have octahedral or tetragonal stereochemistry. In the former case, the electronic spectra show three bands, while in the case of tetragonal complexes, four band spectra are obtained [25,26]. In the present complexes, the three bands can be assigned to the transitions ν_1, $^4A_{2g} \rightarrow {}^4T_{2g}$ (F) (16800 – 17200 cm^{-1}) ν_2, $^4A_{2g} \rightarrow {}^4T_{1g}$ (F) (21200 – 22030 cm^{-1}) ν_3, $^4A_{2g} \rightarrow {}^4T_{1g}$ (P) (29000 – 29800 cm^{-1}). The possibility of the complexes understudy being tetragonally distorted has been ruled out because no splitting of $^4T_{2g}$ is observed. The special interest in the spectra of manganese (III) compound is due to the ^5Eg ground state anticipated in octahedral symmetry which is subjected to Jahn-Teller forces. The electronic spectra of manganese(III) complexes show bands in the regions 15300-15600, 18600-19200 and 21500-22620 cm^{-1}. Despite elaborate studies on manganese (III) complexes, difficulties have arisen in the assignments of the bands. The ground term in the regular high-spin octahedral environment is ^5Eg but the degeneracy of the ^5Eg ground term will necessarily be lifted by the Jahn-Teller effect, so that regular octahedral d^4 complexes normally do not exist. The octahedral d^4 complexes would be expected to be tetragonally or rhombically distorted. In the present complexes, two bands near 18600-19200 and 21500-22620 cm^{-1} are observed with a separation of about 2500 cm^{-1} . Most probably the splitting arise from a Jahn-Teller distortion of the T_{2g} excited state. It is probably a reasonable approximation to assume that the mean frequency of the two bands corresponds to 10Dq. The three bands observed may be assigned[27] to $^5B_{1g} \rightarrow {}^5A_{1g}$, $^5B_{1g} \rightarrow {}^5B_{2g}$, $^5B_{1g} \rightarrow {}^5E_g$ transitions respectively. The electronic spectra of iron(III) complexes show three bands in the 14200–15100, 20400–21400 and 25100–25450 cm^{-1} regions. The spectra of high spin iron(III) complexes have not been adequately characterized. Perhaps the best resolved spectra of octahedral iron(III) is that of iron(III) in beryl but the band assignments are in doubt [25]. In view of the oxidizing nature of iron(III) species, charge transfer transitions from ligand to metal is quite common which render the interpretation of electronic spectra more difficult. The high spin octahedral complexes are generally characterized by presence of a broad band around 16000 cm^{-1}, which is infact the combination of several bands corresponding to $^4T_1(G)$, $^4T_2(G)$, $^4A_{1g}$ and $^4E_g(G)$ states [27]. However, in the present complexes, the three bands observed are well defined. The spectra of these complexes resemble those of octahedral, high-spin iron(III) complexes. Accordingly, these bands may be assigned [28,29] to $^6A_{1g} \rightarrow {}^4T_{1g}(G)$, $^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and $^6A_{1g} \rightarrow {}^4A_{1g}(G)$ transitions in the order of increasing energy., respectively. The electronic spectra of cobalt(III) complexes show bands in the regions 15600-16400, 21400-22600 and 23300-24650 cm^{-1} . The positions of these bands indicate the octahedral geometry for these complexes [30]. The octahedral complexes can either have pseudo-octahedral or tetragonally distorted octahedral stereochemistry. For an octahedral complex, two d-d bands corresponding to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions are expected and the separation between these two transitions is of the order of 7000-10000 cm^{-1}. In the present complexes, the three bands are observed of d-d transitions and the separation between the first and the second band is around 6000-7000 cm^{-1}. The appearance of three band spectra indicates the presence of low-symmetry ligand field in these complexes. The lowering of O_h symmetry to D_{4h} causes the splitting of first band into two bands. Accordingly, the three bands observed can be assigned [25.30] to the transitions $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions in increasing order of energy.

Infrared Spectra: The spectra of Schiff bases show a medium band at *ca*. 3150 cm^{-1} due to √(N-H) which remains almost at the same position in the complexes indicating the non-involvement of N-H group in bond formation. The ligands show one strong intensity band at *ca*. 1630 cm^{-1} assignable [31] to √(C=N) which shifts to lower frequency in the complexes. This shift indicates the coordination of azomethine nitrogens to metal ion. The band at *ca*. 430-450 cm^{-1} are assigned [32] to √(M-N). Schiff bases show a broad band at *ca*. 2620 cm^{-1} due to intramolecular H-bonded O-H group which disappears in their corresponding metal complexes suggesting the coordination of phenolic oxygens to metal ions through deprotonation [33]. This is further supported by shift of phenolic C-O band of ligands from 1280 cm^{-1} to 1340 cm^{-1} in the metal complexes. The coordination of phenolic oxygen atoms to metal ions is confirmed by the appearance of band at *ca*. 470-485 cm^{-1} assignable [32] to √(M-O). The presence of coordinated water molecule in these complexes is indicated by a broad band [33,34] in the region 3480-3380 cm^{-1} and two weaker bands in the regions 790-750 and 725-710 cm^{-1} due to √(O-H) rocking and wagging modes of vibrations, respectively. The IR spectra of manganese and cobalt complexes show strong band in the region 1760-1725 cm^{-1} which has been assigned to √(COO) of coordinated acetate group.

Proton Magnetic Resonance Spectra: The proton NMR spectra of cobalt (III) complexes were recorded in deuterated chloroform and dimethyl sulphoxide; the intensities of all the resonance lines were determined by planimetric integration. In general, a slight low field shift of the resonance signals of various protons (R) in these complexes, in comparison with the respective proton signals in free ligands, may be attributed to deshielding upon coordination. The spectra of Schiff bases exhibit signals at *ca.* 12.30 and 10.50 due to hydrazine NH and phenolic OH protons respectively. The signal due to OH proton disappears in cobalt(III) complexes while hydrazine proton remains almost at the same position. Multiplet is observed at 6.95-7.50 ppm due to aromatic protons in Schiff bases and their corresponding cobalt(III) complexes. The signal due to –HC=N appears at *ca*. 8.30. The complexes show new signal at ca. 5.5 ppm due to water protons. On the basis of elemental analysis, electrical conductance measurements and spectral features, the following structures are tentatively proposed for the [M (L)X(H_2O)] complexes.



M= Cr(III), Mn(III), Fe(III) or Co(III); X= Cl (for Cr or Fe); -OOCCH_3 (for Mn or Co)

APPLICATIONS

Antifungal activity: All the ligands and their corresponding complexes were screened *in-vitro* for their antifungal activity against *Aspergillus niger*, *Colletotrichum falcatum and Curvularia pallescence.* The results of antifungal screening are presented in table 2. The activities were compared with those of the standard drugs ciprofloxacin. Metal complexes are found to be more active than their corresponding ligands. In other words, chelation increases the fungicidal activity. For any particular species of fungus, manganese (III) derivatives show better activity than iron(III) derivatives which in turn show better activity than cobalt(III) derivatives. Chromium (III) complexes show least activity as compared to manganese (III), iron(III) and cobalt(III) derivatives. The activity of the ligands is affected by the nature of substituent, this in relation to the lipophilicity of the ligands and their membrane permeability, a key factor in determining their entry inside the cell. The presence of –2,4Cl_2 or –4-Cl group at the phenyl ring of the ligands increases the activity of the derivatives. The activity decreases on dilution.

Table 2: Fungicidal screening data of Cr(III), Mn(III), Fe(III) and Co(III) complexes of Schiff bases derived from 3-(substituted aryl)- 4-amino-5-hydrazino-1, 2, 4-triazole and 2-hydroxynaphthaldehyde

Compound	**% inhibition**								
	Aspergillus niger			***Colletotrichum falcatum***			***Curvularia pallescence***		
	10	**100**	**1000**	**10**	**100**	**1000**	**10**	**100**	**1000**
[Cr(SPTN)Cl(H_2O)]	42.6	54.7	60.3	40.7	51.3	62.7	43.2	47.8	52.4
[Cr(SCTN)Cl(H_2O)]	44.2	55.2	71.8	50.8	61.5	69.1	50.1	58.2	68.7
[Cr(SPCTN)Cl(H_2O)]	48.7	64.1	74.2	51.2	64.3	73.7	54.2	63.4	71.6
[Cr(SDTN)Cl(H_2O)]	50.2	68.7	77.5	53.2	68.7	77.4	58.7	68.7	76.5
[Cr(SNTN) Cl(H_2O)]	40.0	45.6	54.7	38.7	48.8	58.7	39.9	42.6	48.9
[Mn(SPTN)(OAc)(H_2O)]	58.7	70.4	78.9	51.5	65.8	77.8	52.8	57.8	69.8
[Mn(SCTN)(OAc)(H_2O)]	63.8	76.9	85.8	60.2	74.1	83.2	60.1	68.4	80.8
[Mn(SPCTN)(OAc)(H_2O)]	65.8	80.2	86.7	65.0	78.9	87.8	63.5	72.3	84.2
[Mn(SDTNH)(OAc)(H_2O)]	70.6	85.2	94.8	71.7	86.8	92.0	69.5	80.2	89.5
[Mn(SNTN) (OAc) (H_2O)]	59.8	72.1	80.7	55.8	67.4	80.1	54.2	62.0	74.3
[Fe(SPTN) Cl(H_2O)]	52.3	68.4	72.0	50.8	62.4	73.4	50.2	54.8	63.6
[Fe(SCTN)Cl(H_2O)]	60.6	70.8	83.2	56.7	70.2	79.8	57.8	64.3	76.8
[Fe(SPCTN)Cl(H_2O)]	63.2	74.2	84.8	58.9	73.4	83.2	60.0	66.8	79.9
[Fe(SDTN)Cl(H_2O)]	66.7	75.4	87.5	61.2	77.6	87.7	63.4	68.9	82.2

[Fe(SNTN)Cl(H_2O)]	50.7	63.5	68.9	48.7	58.7	70.0	48.8	52.3	60.9
[Co(SPTN) (OAc) (H_2O)]	48.7	60.8	67.9	46.7	58.7	68.5	46.7	49.8	57.6
[Co(SCTN) (OAc) (H_2O)]	55.8	58.8	79.8	54.7	68.7	74.6	53.7	60.8	74.3
[Co(SPCTN) (OAc)(H_2O)]	50.8	70.9	80.7	52.3	69.9	79.8	65.8	60.8	74.7
[Co(SDTNH)(OAc)(H_2O)]	64.5	72.3	84.2	52.1	73.2	84.2	59.9	63.7	78.6
[Co(SNTN) (OAc) (H_2O)]	45.7	58.7	61.8	44.2	52.4	64.5	42.3	49.7	57.6
ciprofloxacin	100	100	100	100	100	100	100	100	100

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