



Chromium(III), Manganese(III), Iron(III), and Cobalt(III) Complexes of Schiff Bases Derived From 4-Amino-3-(Phenyl / Substituted Phenyl) -5-Mercapto-1, 2, 4-Triazole and β -Diketones

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ABSTRACT

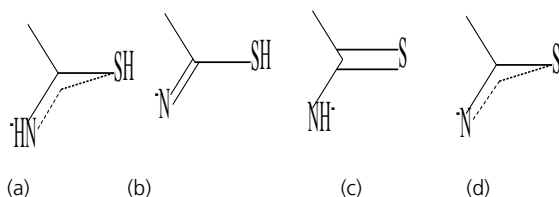
A series of trivalent chromium, manganese, iron and cobalt complexes with Schiff bases (LH_2), derived from 4-amino-3-(phenyl / substituted phenyl) -5-mercapto-1, 2, 4-triazole and β -diketones, of the type $[M(L)X(H_2O)]$ [$M = Cr, Mn, Fe, Co$; $X = Cl$ (for Cr and Fe) or CH_3COO (for Mn and Co)] have 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 pallescens*. 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

In recent years, there has been considerable interest in the chemistry of transition metal complexes with heterocyclic thione / thiol donors [1-26]. The combination of an exocyclic thione (thio-keto) group and heterocyclic molecule, which may contain nitrogen, oxygen, sulphur or a combination of these generates a group of molecules with considerable coordination potential. An important factor in realizing such potential is that of prototropic tautomerism [7] and in particular, which tautomer is present in solution immediately prior to the formation of metal-ligand bond. A common feature of all nitrogen containing heterocyclic thiones is 'thione' (c) 'thiol' (b) tautomerism



Structural evidence, Particularly from X-ray crystallographic studies indicates a tendency for the thione form to dominate in the solid state [6]. Determination of the proportion of π -character in the resultant carbon-sulphur bond, however points to a variable degree of delocalization of the π -electron density with in the heterocyclic 'thioamide'.

Tautomeric equilibria may be further modified in solution by changes in pH, in highly acid media, fully protonated species are likely and may appear to have all coordination sites blocked. Alternatively because imido (NH) protons are labile species such as are also potentially ambident with the pKa values varying from about 5-11, deprotonation is possible

over a wide pH range. The resultant thiolate anion is capable of monodentate, bidentate or bridging coordination behavior and of involving either or both, sulphur and nitrogen in the processes. Thus, the coordination behavior of heterocyclic thione / thiol molecules depends upon reaction conditions, nature of metal ion and pH of the medium. Extensive use has been made of heterocyclic thione/thiol molecules [25].

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 [14, 15].

Preparation of the complexes

Preparation of chromium(III), manganese(III), and iron(III) complexes with Schiff bases derived from 4-amino-3-phenyl-5-mercapto-1,2,4-triazole and acetylacetone (APMTH₂)

To a hot solution of ligand (APMTH₂) (0.01 mol) in methanol (25 cm³), a solution of chromium(III) chloride (0.01 mol) or manganese(III) acetate (0.01 mol) or ferric chloride (0.01 mol) in methanol (20 cm³) was added dropwise with the help of dropping funnel. The mixture was refluxed for 10-18h when colored precipitate appeared. The precipitate was filtered washed with methanol and ether, and dried *in vacuo*. The product was identified to be $[M(APMT)X(H_2O)]$ ($M = Cr, Mn, Fe$; $X = Cl$ or CH_3COO) Yield : 60-70 %

Preparation of cobalt(III) complexes with Schiff bases derived from 4-amino-3-phenyl-5-mercapto-1,2,4-triazole and acetylacetone (APMTH₂)

To a hot solution of ligand (0.01 mol) in methanol (25 cm³), a solution of cobalt(II) acetate (0.01 mol) in methanol (20 cm³) was added dropwise with the help of dropping funnel H_2O_2 (30% , 0.01 mol) was added and this mixture was re-

fluxed and stirred for 10 h which resulted in the formation of 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*. The product was identified

to be [Co(APMT)(OAc)(H₂O)] Yield 65%. The same synthetic procedure was adopted for the synthesis with other Schiff base ligands. The physical properties and analytical data of the complexes are given in table 1.

Table 1 : Analytical data of chromium(III), manganese(III), iron(III) and cobalt(III) complexes with Schiff bases derived from 4-amino-3-(phenyl / substituted phenyl) -5-mercapto-1,2,4-triazole and β -diketone

Complex	Mol. formula	Colour	Yield (%)	Conductance	Analysis Found (Calcd) %			
					C	H	N	M
[Cr(APMT) Cl(H ₂ O)]	[Cr(C ₂₁ H ₂₀ N ₈ S ₂ OCl)]	Green	65	9.2	45.5 (45.7)	3.5 (3.6)	20.1 (20.3)	9.2 (9.4)
[Cr(ACMT) Cl(H ₂ O)]	[Cr(C ₂₁ H ₁₈ N ₈ S ₂ OCl ₃)]	Green	70	8.7	40.3 (40.6)	2.8 (2.9)	18.0 (18.1)	8.2 (8.4)
[Cr(ANMT)Cl(H ₂ O)]	[Cr(C ₂₁ H ₁₈ N ₁₀ S ₂ O ₅ Cl)]	Green	68	8.0	39.2 (39.3)	2.7 (2.8)	21.7 (21.8)	8.0 (8.1)
[Cr(BPMT)Cl(H ₂ O)]	[Cr(C ₂₆ H ₂₂ N ₈ S ₂ OCl)]	Green	64	7.8	50.6 (50.8)	3.5 (3.6)	18.1 (18.3)	8.3 (8.5)
[Cr(BCMT)Cl(H ₂ O)]	[Cr(C ₂₆ H ₂₀ N ₈ S ₂ OCl ₃)]	Green	70	9.0	45.6 (45.7)	2.8 (2.9)	16.2 (16.4)	7.5 (7.6)
[Cr(BNMT) Cl(H ₂ O)]	[Cr(C ₂₆ H ₂₀ N ₁₀ S ₂ O ₅ Cl)]	Green	70	8.5	44.1 (44.3)	2.7 (2.9)	19.7 (19.9)	7.2 (7.4)
[Mn(APMT)(OAc)(H ₂ O)]	[Mn(C ₂₃ H ₂₃ N ₈ S ₂ O ₃)]	Brown	70	6.5	45.1 (45.2)	3.7 (3.8)	18.3 (18.4)	8.8 (9.0)
[Mn(ACMT)(OAc)(H ₂ O)]	[Mn(C ₂₃ H ₂₁ N ₈ S ₂ Cl ₂ O ₃)]	Brown	65	7.2	42.5 (42.6)	3.2 (3.3)	17.1 (17.3)	8.4 (8.5)
[Mn(ANMT)(OAc)(H ₂ O)]	[Mn(C ₂₃ H ₂₁ N ₁₀ S ₂ O ₇)]	Brown	70	6.0	41.0 (41.3)	3.1 (3.2)	20.9 (21.0)	8.1 (8.2)
[Mn(BPMT)(OAc)(H ₂ O)]	[Mn(C ₂₈ H ₂₅ N ₈ S ₂ O ₃)]	Brown	62	7.8	52.4 (52.5)	3.7 (3.9)	17.3 (17.5)	8.3 (8.6)
[Mn(BCMT)(OAc)(H ₂ O)]	[Mn(C ₂₈ H ₂₃ N ₈ S ₂ Cl ₂ O ₃)]	Brown	70	6.8	47.2 (47.4)	3.2 (3.3)	15.6 (15.8)	7.5 (7.7)
[Mn(BNMT) (OAc)(H ₂ O)]	[Mn(C ₂₈ H ₂₃ N ₁₀ S ₂ O ₇)]	Brown	70	6.7	45.7 (46.0)	3.1 (3.2)	19.1 (19.2)	7.4 (7.5)
[Fe(APMT) Cl(H ₂ O)]	[Fe(C ₂₁ H ₂₀ N ₈ S ₂ OCl)]	Brown	60	9.2	45.1 (45.3)	3.5 (3.6)	20.1 (20.2)	9.7 (10.0)
[Fe(ACMT) Cl(H ₂ O)]	[Fe(C ₂₁ H ₁₈ N ₈ S ₂ OCl ₃)]	Brown	60	10.0	40.0 (40.3)	2.7 (2.9)	17.7 (17.9)	8.7 (8.9)
[Fe(ANMT) Cl(H ₂ O)]	[Fe(C ₂₁ H ₁₈ N ₁₀ S ₂ O ₅ Cl)]	Brown	64	8.9	38.8 (39.0)	2.7 (2.8)	21.5 (21.7)	8.5 (8.6)
[Fe(BPMT) Cl(H ₂ O)]	[Fe(C ₂₆ H ₂₂ N ₈ S ₂ OCl)]	Brown	70	8.6	50.3 (50.5)	3.5 (3.6)	18.0 (18.1)	8.8 (9.0)
[Fe(BCMT) Cl(H ₂ O)]	[Fe(C ₂₆ H ₂₀ N ₈ S ₂ OCl ₃)]	Brown	65	7.5	45.2 (45.5)	2.8 (2.9)	16.0 (16.3)	8.0 (8.1)
[Fe(BNMT) Cl(H ₂ O)]	[Fe(C ₂₆ H ₂₀ N ₁₀ S ₂ O ₅ Cl)]	Brown	65	9.8	44.0 (44.1)	2.7 (2.8)	19.7 (19.8)	7.7 (7.9)
[Co(APMT) (OAc)(H ₂ O)]	[Co(C ₂₃ H ₂₃ N ₈ S ₂ O ₃)]	Brown	65	7.2	44.7 (44.9)	3.7 (3.8)	18.1 (18.2)	9.5 (9.6)
[Co(ACMT) (OAc)(H ₂ O)]	[Co (C ₂₃ H ₂₁ N ₈ S ₂ Cl ₂ O ₃)]	Brown	70	7.6	42.3 (42.4)	3.1 (3.2)	17.1 (17.2)	8.8 (9.0)
[Co(ANMT) (OAc)(H ₂ O)]	[Co (C ₂₃ H ₂₁ N ₁₀ S ₂ O ₇)]	Brown	70	8.0	40.9 (41.0)	3.0 (3.1)	20.6 (20.8)	8.7 (8.8)
[Co(BPMT) (OAc)(H ₂ O)]	[Co (C ₂₈ H ₂₅ N ₈ S ₂ O ₃)]	Brown	70	7.0	52.0 (52.1)	3.8 (3.9)	17.3 (17.4)	9.0 (9.1)
[Co(BCMT) (OAc)(H ₂ O)]	[Co (C ₂₈ H ₂₃ N ₈ S ₂ Cl ₂ O ₃)]	Brown	62	6.8	47.0 (47.1)	3.1 (3.2)	15.5 (15.7)	8.1 (8.3)
[Co(BNMT) (OAc)(H ₂ O)]	[Co (C ₂₈ H ₂₃ N ₁₀ S ₂ O ₇)]	Brown	60	6.5	45.5 (45.7)	3.1 (3.2)	19.0 (19.1)	7.9 (8.0)

Where,

APMT₂ = Schiff bases derived from 4-amino-3-phenyl-5-mercapto-1,2,4-triazole and acetylacetone

ACMT₂ = Schiff bases derived from 4-amino-3-(*o*-chlorophenyl)-5-mercapto-1,2,4-triazole and acetylacetone

ANMT₂ = Schiff bases derived from 4-amino-3-(*p*-nitrophenyl)- 5-mercapto-1,2,4-triazole and acetylacetone

BPMT₂ = Schiff bases derived from 4-amino-3-phenyl-5-mercapto-1,2,4-triazole and benzoylacetone

BCMT₂ = Schiff bases derived from 4-amino-3-(*o*-chlorophenyl)-5-mercapto-1,2,4-triazole and benzoylacetone

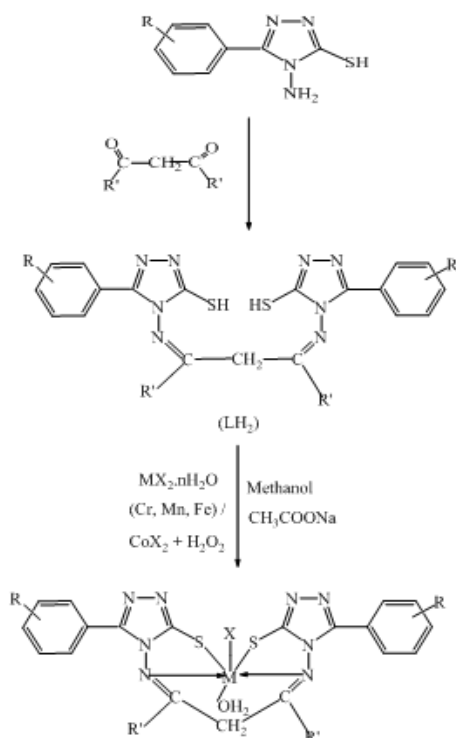
BNMT₂ = Schiff bases derived from 4-amino-3-(*p*-nitrophenyl)- 5-mercapto-1,2,4-triazole and benzoylacetone

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 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 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 the test fungi by the food poison technique at three concentration (10, 100 and 1000 mg/L). 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 100 mm diameter). Oatmeal-agar medium were used for all the test fungi. In controls, the same amount of medium containing the requisite amount of solvent was poured in place of the test chemicals. A mycelia disk (5 mm diameter) obtained from the periphery of 2-week-old cultures was taken and transferred to the center of each petriplate. Plated were incubated for 7 days at $28 \pm 2^\circ\text{C}$. 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 mycelia I colony of the control and dt is the average diameter of the mycelia colony of the treatment

RESULTS AND DISCUSSION

The reactions of chromium(III) chloride, manganese(III) acetate, iron(III) chloride and cobalt(III) acetate with Schiff bases derived from 4-amino-3-(phenyl / substituted phenyl)-5-mercapto-1,2,4-triazoles and β -diketones ligands have been carried out in ethanol, which leads to the formation of $[\text{M}(\text{L})\text{X}(\text{H}_2\text{O})]$ [$\text{M} = \text{Cr}(\text{III}), \text{Mn}(\text{III}), \text{Fe}(\text{III})$ or $\text{Co}(\text{III})$; $\text{LH}_2 =$ Schiff bases derived from 4-amino-3-(phenyl / substituted phenyl)-5-mercapto-1,2,4-triazole and β -diketones] type complexes as shown in Scheme-1.



$\text{R}' = \text{CH}_3$ or C_6H_5

[$\text{M} = \text{Cr}(\text{III})$ or $\text{Fe}(\text{III})$, $\text{X} = \text{Cl}$; $\text{M} = \text{Mn}(\text{III})$ or $\text{Co}(\text{III})$, $\text{X} = \text{CH}_3\text{COO}$]

Scheme-1

The complexes are colored solids, amorphous in nature and soluble in DMSO, DMF and pyridine. The molar conductance values are found to be in the range of $6\text{-}10 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ which indicate that the complexes are non electrolytes in DMSO solution.

Magnetic moment

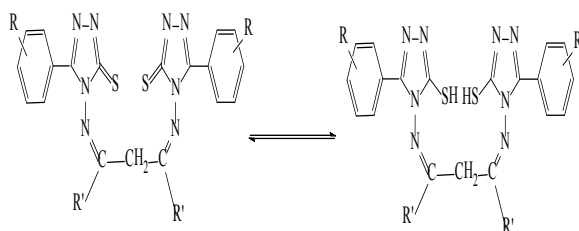
Magnetic susceptibility data for polycrystalline samples of chromium(III) complexes were collected at room temperature. Chromium(III) complexes have a magnetic moment of $3.88\text{-}3.95 \mu_B$, suggestive of a normal moment for octahedral stereochemistry[29]. The magnetic moment of manganese(III) complexes is around $4.80\text{-}4.92 \mu_B$ at room temperature revealing the high spin nature of complexes having four unpaired electrons[30,31]. The iron(III) complexes have magnetic moment values of $4.92\text{-}5.20 \mu_B$ [31]. The cobalt(III) complexes show diamagnetic behavior, which indicates octahedral surroundings of the donor atoms around the metal ion producing a strong field.

Electronic spectra

The electronic spectra of chromium(III) complexes show three absorption bands at $16500\text{-}17500$ (ν_1), $21,200\text{-}23500$ (ν_2) and $30800\text{-}32500$ (ν_3) cm^{-1} . The spin allowed transition for chromium(III) in an octahedral field are : ${}^4\text{A}_{1g} \longrightarrow {}^4\text{T}_{1g}(\text{F})$ (ν_1), ${}^4\text{A}_{1g} \longrightarrow {}^4\text{T}_{1g}(\text{F})$ (ν_2), and ${}^4\text{A}_{1g} \longrightarrow {}^2\text{T}_{1g}(\text{P})$ (ν_3). The ν_2 / ν_1 ratio is in the range $0.70\text{-}1.35$ which is close to the value obtained for octahedral chromium(III) complexes[32,33]. The manganese(III) complexes show bands around $14800\text{-}14950$, $16800\text{-}16900$ and $18350\text{-}18800 \text{cm}^{-1}$ assigned to ${}^5\text{B}_{1g} \longrightarrow {}^5\text{A}_{1g}$, ${}^5\text{B}_{1g} \longrightarrow {}^5\text{B}_{2g}$, and ${}^5\text{B}_{1g} \longrightarrow {}^5\text{E}_g$ transitions, respectively, suggesting spin free manganese(III) complexes with octahedral geometry[30, 31]. The electronic spectra of iron(III) complexes show several bands at $14500\text{-}16800$, $19350\text{-}20000$, and $25000\text{-}26500 \text{cm}^{-1}$ which may be assigned to : ${}^6\text{A}_{1g} \longrightarrow {}^4\text{T}_{1g}$, ${}^6\text{A}_{1g} \longrightarrow {}^4\text{T}_{2g}$, and ${}^6\text{A}_{1g} \longrightarrow {}^4\text{A}_{1g}$, E_g transitions, respectively. The positions of these spectral bands are found to correspond well to earlier reports for high-spin octahedral stereochemistry around iron(III) ion[35, 37]. The electronic spectra of cobalt(III) complexes show bands in the regions $6500\text{-}6580$ (ν_1), $16500\text{-}17000$ (ν_2), $20,000\text{-}22800$ (ν_3) and $24000\text{-}25500$ (ν_4) cm^{-1} which may be assigned[21-26] to transitions ${}^1\text{A}_{1g} \longrightarrow {}^3\text{T}_{1g}$, ${}^1\text{A}_{1g} \longrightarrow {}^3\text{T}_{2g}$, ${}^1\text{A}_{1g} \longrightarrow {}^1\text{T}_{1g}$ and ${}^1\text{A}_{1g} \longrightarrow {}^1\text{T}_{2g}$, respectively.

Infrared spectra

The IR spectra provide valuable informations regarding the nature of the functional group attached to the metal atom. Schiff bases appear to exist in both thiol and thione tautomeric forms as suggested by a broad band at ca. $2700\text{-}2600 \text{cm}^{-1}$ assignable to $\nu(\text{SH})$. In complexes $\nu(\text{SH})$ band disappears indication[40] the deprotonation of thiol group and formation of bond between metal and sulphur. This is further confirmed[41] by appearance of the new band in complexes at ca. $415\text{-}380 \text{cm}^{-1}$, assignable to $\nu(\text{M-S})$.



Schiff bases exhibit strong band at ca. 1620cm^{-1} assigned [44] to $\nu(\text{C}=\text{N})$ in complexes this band shifts to lower frequency (ca. $10\text{-}15 \text{cm}^{-1}$) indicating the participation of azomethine nitro-

gen in bond formation with metal ion. New bands appear in metal complexes at ca. 475-430 cm^{-1} due to $\nu(\text{M-N})$ vibrations[41]. The band due to $\nu(\text{C=N})$ (triazole ring) appears at ca. 1570 cm^{-1} in the ligands which remains almost at the same position in the complexes indicating non- coordination to ring azomethine nitrogen in bond formation[42,43]. All Schiff bases and their metal complexes show bands ca. 3130-3055 cm^{-1} due to $\nu(\text{Ar-H})$. The presence of coordinated water molecules in complexes is indicated[44] by a broad band at 3400 cm^{-1} due to $\nu(\text{-OH})$ and weak bands in the region 820-780 and 720-680 cm^{-1} due to $\nu(\text{-OH})$ rocking and wagging modes of vibration.

On the basis of IR data, we conclude that the metal ion is bonded with ligands through azomethine nitrogens, thiol sulphur and coordinated water oxygen. All these data indicate that ligands are dibasic, tetradentate chelating agents.

¹H NMR Spectra

Schiff bases (BPMTH₂, BCMTH₂, BNMTH₂) exhibit singlet at ca. 3.4 and multiplet at ca. 6.20-8.15 due to $-\text{CH}_2$ and aromatic ring protons, respectively. In corresponding cobalt(III) complexes, methylene proton shows slight downfield while signal due

$-\text{OCH}_3$ group at the phenyl rings 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 4-amino-3-(phenyl / substituted phenyl)-5-mercapto-1,2,4-triazoles and β -diketones

S.No	Compound	Fungicidal Inhibition (%)								
		Aspergillus niger			Colletotrichum falcatum			Curvularia pallescens		
		10	100	1000	10	100	1000	10	100	1000
1	APMTH ₂	19.5	21.4	23.7	20.0	22.2	24.5	19.0	21.0	23.2
2	ACMTH ₂	27.5	29.5	31.7	28.5	30.5	32.7	27.0	29.5	31.5
3	ANMTH ₂	24.5	23.4	25.5	22.0	24.3	26.0	21.0	22.1	25.2
4	BPMTH ₂	18.5	20.4	22.4	19.0	21.3	23.5	18.0	20.1	22.2
5	BCMTH ₂	26.5	28.4	30.5	27.5	29.4	31.5	26.0	28.2	30.2
6	BNMTH ₂	20.5	22.4	24.3	21.0	23.2	25.4	20.0	22.0	24.2
7	[Cr(APMT) Cl(H ₂ O)]	50.8	60.8	70.4	48.9	58.4	72.4	51.4	58.5	68.8
8	[Cr(ACMT) Cl(H ₂ O)]	53.8	62.4	74.4	54.7	62.4	76.5	55.0	62.5	70.4
9	[Cr(ANMT)Cl(H ₂ O)]	52.7	61.5	72.5	51.4	64.5	73.0	53.8	65.0	69.2
10	[Cr(BPMT)Cl(H ₂ O)]	49.7	58.2	62.8	48.6	59.2	64.5	50.4	58.4	62.5
11	[Cr(BCMT)Cl(H ₂ O)]	52.5	60.6	65.8	53.5	59.4	66.4	55.5	62.3	65.4
12	[Cr(BNMT) Cl(H ₂ O)]	51.5	59.5	64.2	53.4	61.5	65.3	55.7	59.4	64.8
13	[Mn(APMT)(OAc)(H ₂ O)]	59.8	64.8	74.5	57.4	63.8	73.7	60.5	64.2	74.5
14	[Mn(ACMT)(OAc)(H ₂ O)]	65.8	70.9	76.8	67.4	70.5	75.5	69.4	70.3	77.0
15	[Mn(ANMT)(OAc)(H ₂ O)]	63.8	68.9	75.4	65.4	69.0	74.2	66.7	68.7	75.0
16	[Mn(BPMT)(OAc)(H ₂ O)]	58.2	63.4	70.4	57.4	63.2	69.4	59.4	63.5	69.8
17	[Mn(BCMT)(OAc)(H ₂ O)]	64.5	69.8	75.4	66.5	69.0	74.8	68.7	69.8	75.0
18	[Mn(BNMT) (OAc)(H ₂ O)]	62.1	67.4	73.2	63.4	65.6	71.4	65.6	67.2	73.4
19	[Fe(APMT) Cl(H ₂ O)]	55.8	63.4	72.3	54.4	62.8	71.4	56.5	63.2	72.2
20	[Fe(ACMT) Cl(H ₂ O)]	63.4	68.4	75.4	65.2	67.2	73.2	67.3	67.9	74.5
21	[Fe(ANMT) Cl(H ₂ O)]	58.8	67.4	74.9	69.4	66.5	73.4	60.1	67.2	74.2
22	[Fe(BPMT) Cl(H ₂ O)]	54.7	62.1	69.4	53.5	60.2	68.2	55.7	62.0	69.2
23	[Fe(BCMT) Cl(H ₂ O)]	62.4	68.2	74.8	63.4	66.5	73.2	65.4	67.8	74.8
24	[Fe(BNMT) Cl(H ₂ O)]	57.8	66.2	73.2	59.2	65.4	73.2	60.1	66.0	73.4

to aromatic ring protons appear almost at the same position . Schiff bases show signal at ca. 3.8 ppm due to $-\text{SH}$ proton. The presence of $-\text{SH}$ signal indicates that ligands exist in thiol form in solution. In metal complexes $-\text{SH}$ disappears indicating the bond formation between Co(III) and sulphur. New signals are observed at ca. 5.4 ppm due to water protons.

APPLICATIONS

All the ligands and their corresponding complexes were screened *in-vitro* for their antifungal activity against *Aspergillus niger*, *Colletotrichum falcatum* and *Curvularia pallescens*. The results of antifungal screening are present in Table 2. The activity was compared with those of the standard drugs fluconazole. 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 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 the substituents, 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 $-\text{Cl}$ or

25	[Co(APMT) (OAc)(H ₂ O)]	53.8	62.1	71.9	52.9	60.2	70.4	54.2	62.0	71.8
26	[Co(ACMT) (OAc)(H ₂ O)]	58.8	65.4	74.6	59.4	64.2	74.0	60.5	65.0	74.2
27	[Co(ANMT) (OAc)(H ₂ O)]	55.8	66.2	73.7	56.4	65.4	73.0	58.4	66.2	73.4
28	[Co(BPMT) (OAc)(H ₂ O)]	52.7	62.0	70.6	51.4	59.5	70.0	53.5	62.0	70.1
29	[Co(BCMT) (OAc)(H ₂ O)]	57.3	64.4	71.4	58.4	64.0	71.0	59.6	64.2	71.2
30	[Co(BNMT) (OAc)(H ₂ O)]	54.7	63.9	72.4	56.5	63.8	72.0	58.5	64.0	72.2

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