Synthesis and Characterization of Some new Cr(III), Mn(III), Fe(III) and Co(III) Complexes with 2-Hydroxy-1-Naphthaldehyde Thiosemicarbazones Derived Ligands

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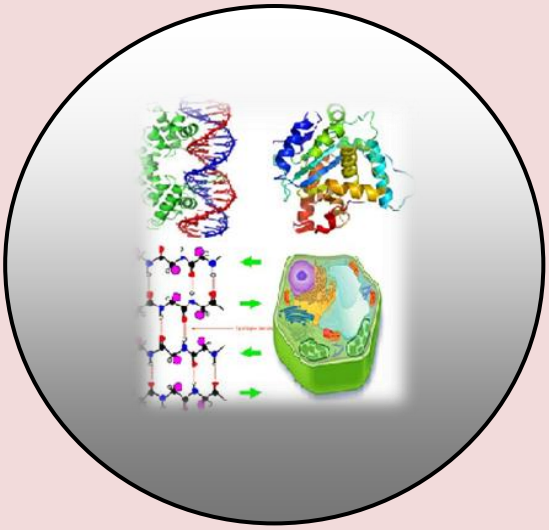

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RESEARCH PAPER

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Synthesis and Characterization of Some new Cr(III), Mn(III), Fe(III) and Co(III) Complexes with 2-Hydroxy-1-Naphthaldehyde Thiosemicarbazones Derived Ligands

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ABSTRACT

A Series of Schiff bases derived Cr(III), Mn(III), Fe(III) and Co(III) complexes with thiosemicarbazones of general formula $[M(TSC)_2]Cl$ were synthesized. Thiosemicarbazones were formed by condensation of 2-hydroxy-1-naphthaldehyde and various thiosemicarbazideslike N-methyl thiosemicarbazide, N-phenyl thiosemicarbazide, 4-chloro-N-phenyl thiosemicarbazide and 4-methoxy-N-phenyl thiosemicarbazide. Physicochemical characterization of compounds has been carried out by elemental analysis, spectroscopic (IR, electronic, ^1H NMR) and magnetic studies. On the basis of above studies complexes have octahedral nature with phenolic oxygen, azomethine nitrogen andthione sulphur group as coordinating sites and exhibited monomeric nature of complexes. Co(III) complexes were diamagnetic and show high absorption while Cr(III), Mn(III) and Fe(III) complexes show paramagnetic nature. In addition, antifungal and antibacterial studies have been carried out in vitro for investigated compounds against fungus (A. nigerand C. albicans) and bacteria (Baccilluspumilus, Escherichia coli and Staphylococcus aureus). Number of metals chelate show high biocidal activity for the above micro-organisms than that of their ligands.
Key words: Thiosemicarbazone, 3d-Transition Metals, Spectral Analysis and Biological Activity.

INTRODUCTION

The centre of attention of synthesis and structural investigations of thiosemicarbazones and their metal complexes because of it have pharmacological and chemotherapeutic properties such as anticancer, antitumour, antibacterial, antifungal, antiulcer, antiviral, antiplasmodial, cytotoxic and enzymatic inhibition (Candido-BacaniPde M. et al., 2011; Siddiqui, N. et al., 2011; G. Krishnegowda et al., 2011; N. Karali et al., 2010; Chang et al., 2010; Shrivastava et al., 2010; Agarwal et al., 2006; Shaabani, B. et al., 2017). Thiosemicarbazone ligands have ability to form chelate with transition metals with N, S and O as a donor atom (El-Gammal, O. A. et al., 2014; Mishra, D., et al., 2006; Jayabalakrishnan, C., et al., 2002; Afrasiabi, Z., et al., 2004). Most of the transition metals have medicinally important, coordinating with different ligands. Cr, Mn, Fe and Co metals are very essential for biological system and small amount performing enzymatic functions such as urease (Raza, K., et al., 2014; Sharma et al., 2006; Sharma et al; 2005).

With the growing interest of thiosemicarbazones of chromium(III), manganese(III), iron(III) and cobalt(III) metal ions with different thiosemicarbazone ligands like N-methyl thiosemicarbazone, N-phenyl thiosemicarbazone, 4-bromo-N-phenyl thiosemicarbazone, 4-chloro-N-phenyl thiosemicarbazone and 4-methoxy-N-phenyl thiosemicarbazone (Bhaskar, G. et al., 2012).

Experimental materials

$CrCl_3 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ (Figgis, B. N., et al; 1960) and other chemical and solvents used were analytical grade and $Mn(OAc)_3 \cdot 2H_2O$ was prepared by oxidation of $Mn(OAc)_2 \cdot 4H_2O$ as reported in the literature (Vogel, 1989, Patel and Thakar, 1999). The electronic spectra of the complexes were taken on Hitachi Perkin Elmer Lambda Spectrometer range of 800-200 nm in DMSO solvent. The IR spectra were recorded in KBr pellets on Shimadzu FT-IR spectrophotometer range of 4000-400 cm^{-1}. ^{1}HNMR spectra of ligands and complexes were recorded in DMSO-d_6 using Bruker-300 spectrometer. Melting points were recorded with an Ambassador melting point apparatus by using thin capillaries. Magnetic measurements were carried out by Gouy's balance using calibrant $Hg[Co(SCN)_4]$.

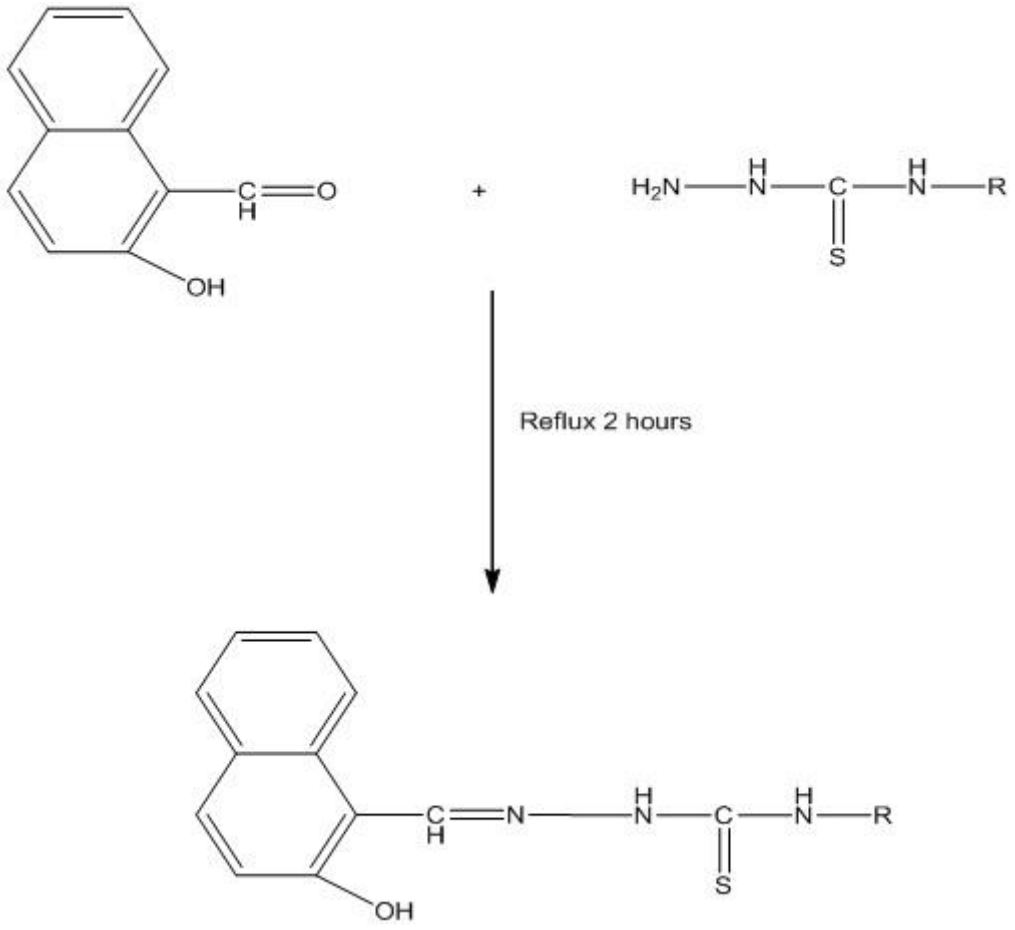


Figure 1

Synthesis of the ligands

Substituted aryl thiosemicarbazides have been prepared by the method of Kazakov and Vostouskii. Equimolar amount of 2-hydroxy-1-naphthaldehyde was dissolved in methanol and treated with substituted thiosemicarbazide like 4-methyl thiosemicarbazide, N-phenyl thiosemicarbazide, 4-bromo-N-phenyl thiosemicarbazide, 4-chloro-N-phenyl thiosemicarbazide, 4-methoxy-N-phenyl thiosemicarbazide. The reaction mixture was stirred well reflux for half an hour on a water bath.

On cooling the mixture a coloured crystals separate out. The precipitate was recrystallized from alcohol and dried in vaccuo (Ali, A. Q., et al; 2017; Ali, A. Q., et al; 2014). Ligand (TSC1) 4-methyl thiosemicarbazone, (TSC2) N-phenyl thiosemicarbazone, (TSC3) 4-bromo-N-phenyl thiosemicarbazone, (TSC4) 4-chloro-N-phenyl thiosemicarbazone, (TSC5) 4-methoxy-N-phenyl thiosemicarbazone obtained. The synthesis route of ligands in **figure (1)**.

S.NO	R	Abbreviation
1	CH_3	TSC_1
2	C_6H_5	TSC_2
3	C_6H_4Br	TSC_3
4	C_6H_4Cl	TSC_4
5	$C_6H_4OCH_3$	TSC_5

Synthesis of the complexes

Hydrated salts of $CrCl_3 \cdot 6H_2O$, $Mn(OAc)_3 \cdot 2H_2O$, $FeCl_3 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ in ethanol were added in 1:2 (M:L) molar ratio. The reactions with $CoCl_2 \cdot 6H_2O$ were followed by the addition of H_2O_2 (6 ml of a 30% aqueous solution, 0.05 mol). The reaction mixture was stirred on steam bath 1 hr the complexes get precipitated; the coloured solid compounds were collected by filtration, washed the complexes with ethanol then dried *in vacuo* (Ali, A. Q., et al; 2017; Ali, A. Q., et al; 2014).

RESULTS AND DISCUSSION

The complexes were synthesized by reacting ligands with metal ions in 3:1 molar ratio in methanolic medium, formula of complexes is $[M(TSC)_2]^+ Cl^{\cdot\cdot} nH_2O$. The analytical data, colour and formula weights of the compounds supported the formulations presented in **table-1**. All the complexes are soluble in DMSO, DMF. The complex compounds have been characterised by elemental analysis, infrared, electronic and ^1H NMR spectra and all the synthesised complexes were tested for their biological activity.

Infrared spectra

The tentative infrared absorption of the significant IR spectral bands of thiosemicarbazones in their metal complexes are presented in **table-2**.

The complexes of substituted thiosemicarbazones contain mono deprotonated tridentate ligands which are coordinated to the central metal ion through deprotonated phenolic oxygen atom forming five membered metalocycles. The IR spectra of phenolic group δ(OH) in range of 3100-3190 cm.$^{-1}$ A broad band of υ(NH) observed in complexes in the region 3400-3430cm.$^{-1}$ Theazomethine nitrogen υ(C=N) in the ligand at 1602 cm^{-1} shifted to lower frequencies by 5-20 cm^{-1} upon metal coordination (Bera and Saha, 2010). The υ(C-O) stretching vibration bands observed in the range of 1312-1290 cm^{-1} in the spectra of the ligands to lower frequency at around 10-20 cm.$^{-1}$ A strong band at 1160 cm^{-1} in the spectrum of thiosemicarbazones υ (C=S) and shifted by ca 5-25 cm^{-1} in the spectra of metal complexes (Chen, L. M. et al., 2008). The υ(N-N) in ligand range of 1050-1030 cm^{-1}shifted to higher frequency in the spectra of all complexes (Ummathur, M. B., et al., 2014; Silverstein & Webster., 1997). Some band also appear of metal hetero atoms are υ(M-N), υ(M-O) and υ(M-S) in the region 550-525 cm,$^{-1}$ 495-475 cm,$^{-1}$ and 390-370 cm^{-1} respectively (Sharma et al., 2007;Takjoo et al., 2014; Sharma & Chandra, 2011).

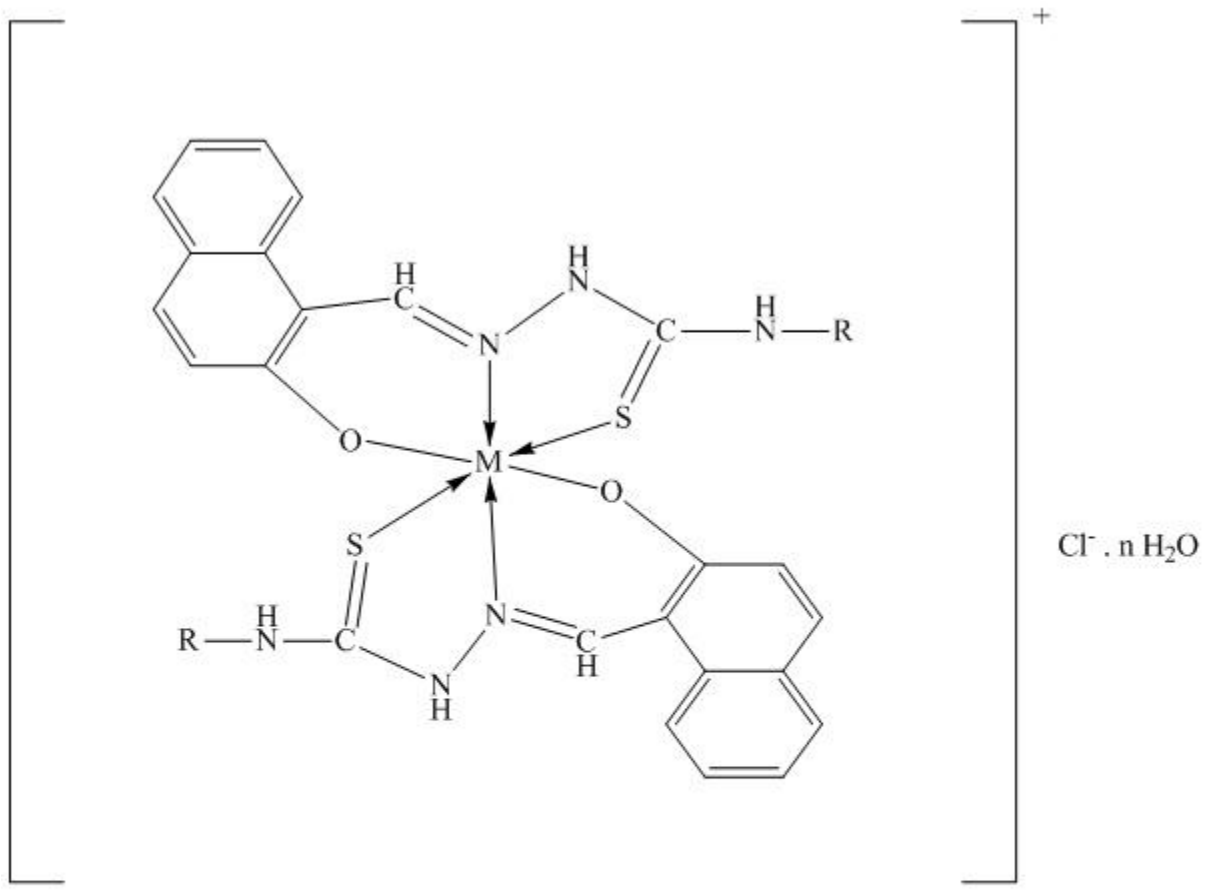
Electronic spectra

The electronic spectra recorded in DMSO and with the help of band position and magnetic measurements suggest assignments and probable geometries of all metal complexes in **table-3**. The Co(III) complexes diamagnetic in nature bands observed in electronic spectra 16700-17800 cm^{-1}, 21580-21900 cm^{-1}, 23450-24700 cm^{-1} respectively. These are reported six coordination of Cr(III) complex and it assigned to $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{2g}$, transition respectively. These observations show octahedral geometry of complex. The Cr(III) complexes paramagnetic in nature the magnetic moment ranges 3.68-3.88 B.M, this shows d^3 ions. In Cr(III) observe three bands ranges of 16520-17600 cm^{-1}, 21220-23825 cm^{-1}, 30330-32390 cm^{-1} and bands assignments to $^4A_{2g} \rightarrow {}^4T_{2g}$, $^4A_{2g} \rightarrow {}^4T_{1g}$,$^4A_{2g} \rightarrow {}^4T_{1g}$ respectively. This results show octahedral geometry with Cr(III) ion.

The Mn(III) complexes 4.81-4.97 B.M magnetic moment this reveals the complexes which in high spin (Sharma & Srivastava, 2006; Gajendra et al., 2012). The electronic spectra bands ranges 18100-18450 cm^{-1}, 19490-19800 cm^{-1} , 25000-25600 cm^{-1} and assignments of bands $^5B_{1g} \rightarrow {}^5A_{1g}$, $^5B_{1g} \rightarrow {}^5B_{2g}$, $^5B_{1g} \rightarrow {}^5E_g$ respectively. The Fe(III) complexes also in high spin with sharp bands in regions 16450-16640 cm^{-1}, 24100-24800 cm^{-1}, 26000-26430 cm^{-1} and assignment of bands $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$, $^6A_{1g} \rightarrow {}^4A_{1g}$ respectively. In this type of electronic transition represent octahedral geometry (Aslan et al., 2011; Alex et al., 2009; Lever, 1968; Radanovic, D. J., Djuran, M. I., 1993).

^{1}HNMR spectra

^{1}HNMR spectra recorded for diamagnetic Co(III) complexes at 90 MHz in DMSO-d_6(Table-4). The spectra of the ligand exhibit singlet at δ 11.70 ppm and δ 9.65-9.87 ppm due to phenolic –OH and –NH protons. The signal at δ 11.70 ppm disappears in all complexes indicating deprotonation of the enolic group. The chemical shift due to aromatic ring protons appears at δ 7.30-8.13 ppm in the spectra of thiosemicarbazone ligand and their complexes. Thiosemicarbazone ligand exhibit signals at δ 8.15-8.55 ppm due to azomtehine protons which shift downfield in the spectra of complexes due to the coordination of azomethine nitrogen to the central metal ion. The methoxy proton shows chemical shift at δ 3.55 ppm.



Proposed Structure of Complex

Figure 2

R= CH_3 , Ph , 4-Br C_6H_4 , 4-Cl C_6H_4 , 4-OCH_3 C_6H_4

M = Cr , Mn , Fe , Co

Table 1. Physical data of the thiosemicarbazones and their complexes.

Compound	F.W.	colour	Yield (%)	Analysis found (calcd.)								Decom. Temp.
				C	H	N	S	O	Cl	Br	M	
TSC_1 ($C_{18}H_{13}N_3OS$)	259.34	Creamy White	75	60.2 (59.1)	5.0 (4.8)	16.2 (16.1)	12.3 (12.1)	6.1 (6.0)	-	-	-	200
TSC_2 ($C_{18}H_{15}N_3OS$)	321.41	Dark yellow	70	67.2 (67.1)	4.7 (4.6)	13.0 (13.1)	9.9 (9.7)	4.9 (4.8)	-	-	-	210
TSC_3 ($C_{18}H_{14}N_3SBrO$)	400.26	Yellow	68	54.0 (53.8)	3.5 (3.3)	10.4 (10.2)	8.0 (8.1)	3.9 (3.7)	-	19.9 (19.7)	-	205
TSC_4 ($C_{18}H_{14}N_3SClO$)	355.81	Brown	73	60.7 (60.5)	3.9 (3.8)	11.8 (11.6)	9.0 (9.1)	4.4 (4.3)	9.9 (9.7)	-	-	210
TSC_5 ($C_{19}H_{17}N_3SO_2$)	351.39	Dark yellow	72	64.9 (64.7)	4.8 (4.7)	11.9 (11.8)	9.1 (9.0)	9.1 (9.0)	-	-	-	210
$Cr(TSC_1)$ ($C_{26}H_{24}N_6S_2O_2CrCl$)	604.05	White	65	51.6 (51.5)	4.0 (3.9)	13.9 (13.8)	10.6 (10.5)	5.2 (5.1)	5.8 (5.7)	-	8.8 (8.7)	240
$Cr(TSC_2)$ ($C_{36}H_{28}N_6S_2O_2CrCl$)	728.18	Dark brown	68	59.3 (59.2)	3.8 (3.7)	11.5 (11.4)	8.8 (8.7)	4.3 (4.1)	4.8 (4.6)	-	7.1 (7.0)	240
$Cr(TSC_3)$ ($C_{24}H_{18}N_6S_2O_2BrCrCl$)	653.89	Light yellow	63	44.4 (44.1)	2.7 (2.5)	12.8 (12.6)	9.8 (9.6)	4.8 (4.7)	5.4 (5.3)	12.2 (12.1)	7.9 (7.8)	240
$Cr(TSC_4)$ ($C_{24}H_{18}N_6S_2O_2CrCl_3$)	644.89	Light yellow	65	44.6 (44.5)	2.8 (2.7)	13.0 (13.1)	9.9 (9.7)	4.9 (4.7)	16.4 (16.3)	-	8.0 (8.1)	240
$Cr(TSC_5)$ ($C_{26}H_{24}N_6S_2O_4CrCl$)	363.05	Yellow	67	49.0 (49.2)	3.8 (3.7)	13.2 (13.1)	10.0 (9.9)	10.0 (10.1)	5.5 (5.4)	-	8.1 (8.0)	240
$Mn(TSC_1)$ ($C_{26}H_{24}N_6S_2O_2MnCl$)	606.99	Dark brown	68	51.4 (51.3)	3.9 (3.7)	13.8 (13.7)	10.5 (10.4)	5.2 (5.1)	5.8 (5.6)	-	9.0 (8.9)	260
$Mn(TSC_2)$ ($C_{36}H_{28}N_6S_2O_2MnCl$)	731.12	Dark brown	63	59.1 (59.0)	3.8 (3.7)	11.4 (11.3)	8.7 (8.6)	4.3 (4.1)	4.8 (4.6)	-	7.5 (7.4)	250
$Mn(TSC_3)$ ($C_{24}H_{18}N_6S_2O_2BrMnCl$)	656.83	Light yellow	60	43.8 (43.7)	2.7 (2.6)	12.7 (12.5)	9.7 (9.5)	4.8 (4.7)	5.3 (5.1)	12.1 (12.0)	8.3 (8.1)	250
$Mn(TSC_4)$ ($C_{24}H_{18}N_6S_2O_2MnCl_3$)	647.83	Yellow	62	44.4 (44.1)	2.8 (2.7)	12.9 (12.7)	9.8 (9.7)	4.9 (4.8)	16.4 (16.2)	-	8.4 (8.2)	240
$Mn(TSC_5)$ ($C_{26}H_{24}N_6S_2O_4MnCl$)	638.99	Dark yellow	60	48.8 (48.6)	3.7 (3.5)	13.1 (13.0)	10.0 (9.9)	10.0 (10.1)	5.5 (5.3)	-	8.5 (8.3)	240
$Fe(TSC_1)$ ($C_{26}H_{24}N_6S_2O_2FeCl$)	607.90	Dark brown	65	51.3 (51.2)	3.9 (3.7)	13.8(13.7)	10.5 (10.3)	5.2 (5.1)	5.8 (5.7)	-	9.1 (9.0)	250
$Fe(TSC_2)$ ($C_{36}H_{28}N_6S_2O_2FeCl$)	732.03	Bown	60	59.0 (58.9)	3.8 (3.7)	11.4 (11.3)	8.7 (8.6)	4.3 (4.2)	4.8 (4.6)	-	7.6 (7.5)	250
$Fe(TSC_3)$ ($C_{24}H_{18}N_6S_2O_2BrFeCl$)	657.74	Greenish yellow	67	43.8 (43.6)	2.7 (2.5)	12.7 (12.5)	9.7 (9.6)	4.8 (4.7)	5.3 (5.2)	12.4 (12.0)	8.4 (8.3)	250
$Fe(TSC_4)$ ($C_{24}H_{18}N_6S_2O_2FeCl_3$)	648.74	Dark brown	63	44.4 (44.3)	2.7 (2.5)	12.9 (12.7)	9.8 (9.7)	4.9 (4.7)	16.3 (16.2)	-	8.6 (8.5)	250
$Fe(TSC_5)$ ($C_{26}H_{24}N_6S_2O_4FeCl$)	639.90	Dark yellow	65	48.7 (48.5)	3.7 (3.5)	13.1 (13.0)	10.0 (10.1)	10.0 (10.2)	5.5 (5.3)	-	8.7 (8.6)	250
$Co(TSC_1)$ ($C_{26}H_{24}N_6S_2O_2CoCl$)	610.99	Dark brown	67	51.1 (51.0)	3.9 (3.8)	13.7 (13.5)	10.4 (10.3)	5.2 (5.1)	5.8 (5.7)	-	9.6 (9.5)	250
$Co(TSC_2)$ ($C_{36}H_{28}N_6S_2O_2CoCl$)	735.11	Brown	70	58.8 (58.7)	3.8 (3.7)	11.4 (11.3)	8.7 (8.6)	4.3 (4.2)	4.8 (4.6)	-	8.0 (8.1)	250
$Co(TSC_3)$ ($C_{24}H_{18}N_6S_2O_2BrCoCl$)	660.82	Light yellow	72	43.6 (43.5)	2.7 (2.5)	12.7 (12.6)	9.7 (9.6)	4.8 (4.6)	5.3 (5.2)	12.0 (11.9)	8.9 (8.7)	250
$Co(TSC_4)$ ($C_{24}H_{18}N_6S_2O_2CoCl_3$)	651.83	Dark yellow	68	44.2 (44.1)	2.7 (2.5)	12.8 (12.7)	9.8 (9.7)	4.9 (4.7)	16.3 (16.1)	-	9.0 (9.1)	250
$Co(TSC_5)$ ($C_{26}H_{24}N_6S_2O_4CoCl$)	642.99	Brownish yellow	70	48.5 (48.4)	3.7 (3.5)	13.0 (13.2)	9.9 (9.6)	9.9 (9.7)	5.5 (5.4)	-	9.1 (9.0)	250

In *vitro* antibacterial and antifungal activity

The synthesized Schiff bases and complexes were screened in ***vitro***for their antimicrobial activity against three bacteria, namely *Bacillus pumilus, Escherichia coli* and *Staphylococcus* and two fungi, namely *A. niger*and *C. albicans* using reported method (Sharma & Srivastava, 2005; Tweedy, 1964). A stock solution (1 mg ml^{-1}) of the test chemical was prepared by dissolving 10 mg of the test compound in 10 ml of DMF solvent. The stock solution was suitably dilution with sterilized distilled water to get dilutions of 500 and 1000 μgml^{-1}. Control for each dilution was prepared by diluting 10 ml of solvent instead of stock solution with sterilized distilled water.

The bacteria were subcultured in agar medium (Sharma & Srivastava, 2005). Petri dishes were incubated for 24 h at 37^{0}C (Thornberry, H. H., 1950). Standard antibacterial drug (gentamicin) was also screened under similar conditions for comparison. The fungi were subcultured in potato dextrose agar medium. Standard antifungal drug (fluconazole) was used for comparison. Petri dishes were incubated for 48 h at 37^{0}C. Wells were dug in the agar media using a sterile metallic borer. Activity was determined by measuring the diameter (mm) of the zone showing complete inhibition (Table 5). Growth inhibition was compared with that of the standard drugs. The percentage inhibition of the growth of the test organism was calculated using the following formula:

Inhibition (%) = $100\times C_d\text{-}T_d/C_d$

Where C_d is the colony diameter of the control and T_d the colony diameter of the treated set. Each set was kept in triplicate.

Table 2. IR spectral data (cm^{-1}) of thethiosemicarbazones and their metal complexes..

Complexes	-NH	-OH$_{(ass)}$	C=N	C-O (phe)	C=S	N-N	M-N	M-O	M-S
TSC_1	3400	3100	1602	1300	1150	1030	-	-	-
TSC_2	3400	3148	1594	1290	1150	1030	-	-	-
TSC_3	3400	3110	1602	1290	1160	1040	-	-	-
TSC_4	3410	3190	1590	1295	1150	1050	-	-	-
TSC_5	3400	3100	1602	1312	1160	1040	-	-	-
$Cr(TSC_1)$	3419	-	1595	1290	1170	1040	550	480	390
$Cr(TSC_2)$	3430	-	1590	1280	1175	1035	530	475	380
$Cr(TSC_3)$	3410	-	1595	1275	1170	1050	535	480	380
$Cr(TSC_4)$	3415	-	1585	1280	1170	1055	535	480	370
$Cr(TSC_5)$	3415	-	1595	1300	1170	1045	525	495	390
$Mn(TSC_1)$	3410	-	1595	1285	1160	1060	530	485	384
$Mn(TSC_2)$	3405	-	1590	1275	1160	1050	525	490	384
$Mn(TSC_3)$	3415	-	1595	1270	1170	1050	530	495	384
$Mn(TSC_4)$	3415	-	1590	1280	1161	1060	530	490	384
$Mn(TSC_5)$	3415	-	1585	1305	1165	1050	530	495	384
$Fe(TSC_1)$	3420	-	1595	1285	1160	1045	530	490	380
$Fe(TSC_2)$	3420	-	1580	1285	1155	1040	525	485	380
$Fe(TSC_3)$	3410	-	1590	1280	1165	1045	530	490	380
$Fe(TSC_4)$	3415	-	1580	1290	1155	1055	530	480	384
$Fe(TSC_5)$	3420	-	1595	1300	1165	1045	531	477	384
$Co(TSC_1)$	3415	-	1598	1285	1155	1035	525	490	380
$Co\ (TSC_2)$	3420	-	1585	1275	1155	1040	525	485	380
$Co\ (TSC_3)$	3415	-	1595	1270	1152	1050	530	495	380
$Co\ (TSC_4)$	3420	-	1575	1285	1160	1055	525	490	384
$Co\ (TSC_5)$	3420	-	1580	1310	1170	1050	535	490	385

Table 3. Magnetic moment (B.M.) and electronic spectral data (cm^{-1}) for chromium(III), manganese(III), iron(III) and cobalt(III) complexes with thiosemicarbazones derived from 2-hydroxy-1-naphthaldehyde and substituted hydrazides.

Complexes	μ_{eff} (B.M)	Band Observed	Assignments
$Cr(TSC_1)$	3.83	16520 21220 31000	$^4A_{2g} \rightarrow {}^4T_{2g}$ $^4A_{2g} \rightarrow {}^4T_{1g}$ $^4A_{2g} \rightarrow {}^4T_{1g}$
$Cr(TSC_2)$	3.86	17105 22000 30330	-do-
$Cr(TSC_3)$	3.92	17500 23830 31210	-do-
$Cr(TSC_4)$	3.96	16880 23825 32400	-do-
$Cr(TSC_5)$	3.94	17600 23529 32390	-do-
$Mn(TSC_1)$	4.81	18360 19780 25000	$^5B_{1g} \rightarrow {}^5A_{1g}$ $^5B_{1g} \rightarrow {}^5B_{2g}$ $^5B_{1g} \rightarrow {}^5Eg$
$Mn(TSC_2)$	4.85	18100 19800 25450	-do-
$Mn(TSC_3)$	4.89	18400 19580 25500	-do-
$Mn(TSC_4)$	4.97	18350 19600 25460	-do-
$Mn(TSC_5)$	4.93	18450 19490 25600	-do-
$Fe(TSC_1)$	5.27	16640 24100 26200	$^6A_{1g} \rightarrow {}^4T_{1g}$ $^6A_{1g} \rightarrow {}^4T_{2g}$ $^6A_{1g} \rightarrow {}^4A_{1g}$
$Fe(TSC_2)$	5.20	16450 24800 26100	-do-
$Fe(TSC_3)$	5.33	16560 24600 26430	-do-
$Fe(TSC_4)$	5.21	16500 24580 26230	-do-
$Fe(TSC_5)$	5.30	16490 24680 26290	-do-
$Co(TSC_1)$	Dia.	17800 21580 24700	$^1A_{1g} \rightarrow {}^3T_{2g}$ $^1A_{1g} \rightarrow {}^1T_{2g}$ $^1A_{1g} \rightarrow {}^1T_{2g}$

Table continued

$Co(TSC_2)$	Dia.	17600 21800 24500	-do-
$Co(TSC_3)$	Dia.	17400 21760 24470	-do-
$Co(TSC_4)$	Dia.	16700 21750 24650	-do-
$Co(TSC_5)$	Dia.	16900 21900 24450	-do-

Table 4.^{1}HNMR spectral data (δ, ppm) of thiosemicarbazones and their Cobalt(III) complexes.

Compounds	δ(HC=N)	δ(N-H)	δ(Phenyl Ring)	$\delta(OCH_3)$
TSC_1	8.49	9.70	7.30	-
TSC_2	8.35	9.65	8.13	-
TSC_3	8.15	9.73	7.35	-
TSC_4	8.45	9.61	7.50	-
TSC_5	8.40	9.80	7.62	3.43
$Co(TSC_{1)}$	8.55	9.72	7.33	-
$Co(TSC_{2)}$	8.53	9.70	8.02	-
$Co(TSC_3)$	8.21	9.75	7.44	-
$Co(TSC_4)$	8.51	9.66	7.52	-
$Co(TSC_5)$	8.45	9.87	7.65	3.55

Table 5. Antibacterial and Antifungal screening data of thiosemicarbazone and their Cr(III), Mn(III), Fe(III) and Co(III) complexes.

Compounds	Antibacterial activity						Antifungal activity			
	Inhibition zone (μgmL^{-1})						Inhibition zone (μgmL^{-1})			
	Bacillus Pumilus		Escherichia Coli		Staphylococus Aureus		A. niger		C. albicans	
	500	1000	500	1000	500	1000	500	1000	500	1000
TSC_1	24	28	19	31	20	32	22	26	21	30
TSC_2	25	31	23	30	28	32	19	34	28	35
TSC_3	24	30	23	26	22	31	21	28	17	25
TSC_4	23	30	24	31	21	28	20	24	25	28
TSC_5	26	30	23	33	26	32	18	26	20	26
$Cr(TSC_1)$	27	32	21	35	24	38	25	29	24	32
$Cr(TSC_2)$	28	35	27	38	33	37	23	38	33	38
$Cr(TSC_3)$	29	40	30	38	30	43	26	32	20	27
$Cr(TSC_4)$	30	45	29	40	29	38	24	27	27	30
$Cr(TSC_5)$	35	38	30	45	32	45	26	30	24	29
$Mn(TSC_1)$	30	32	24	34	27	36	23	32	25	34
$Mn(TSC_2)$	29	35	26	35	35	40	21	36	30	37
$Mn(TSC_3)$	28	33	27	30	28	35	28	32	21	28

Table continued

Mn (TSC_4)	30	38	30	40	29	37	25	26	32	32
Mn (TSC_5)	35	40	28	39	31	42	27	29	23	30
Fe(TSC_1)	32	37	25	36	26	35	24	30	27	33
Fe (TSC_2)	30	37	26	34	32	37	27	37	32	37
Fe (TSC_3)	28	34	28	29	26	35	29	32	26	32
Fe (TSC_4)	28	37	29	32	29	38	28	30	33	31
Fe (TSC_5)	34	38	31	40	32	41	26	28	25	35
Co(TSC_1)	29	32	23	35	26	34	25	32	27	35
Co(TSC_2)	28	36	29	34	32	38	23	39	34	39
Co(TSC_3)	29	38	30	32	28	37	27	35	19	33
Co(TSC_4)	26	33	31	40	28	35	22	29	30	36
Co(TSC_5)	32	34	29	42	29	41	24	31	26	31

CONCLUSION

Various tridentate thiosemicarbazone ligands like (TSC_1) 4-methyl thiosemicarbazone, (TSC_2) N-phenyl thiosemicarbazone, (TSC_3) 4-bromo-N-phenyl thiosemicarzone, (TSC_4) 4-chloro-N-phenyl thiosemicarbazone, (TSC_5) 4-methoxy-N-phenyl thiosemicarba zone coordinated to Cr(III), Mn(III), Fe(III), Co(III) metals ions. Thiosemicarbazone complexes were synthesized. These compounds are isolated and characterised by various physicochemical data. On the basis of elemental analysis, infrared, electronic and ^{1}HNMR spectral studies six coordinated octahedral geometry may be proposed for all the synthesized complexes [Figure-2].

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