



SYNTHESIS, CHARACTERISATION AND BIOLOGICAL ASPECTS OF IRON(III) AND COBALT(III) COMPLEXES WITH SCHIFF BASES DERIVED FROM SUBSTITUTED MERCAPTOTRIAZOLE

Namrata Tripathi SHALINI and Vinod Kumar SHARMA*

Department of Chemistry, University of Lucknow, Lucknow 226007, India

Received September 24, 2007

A series of metal complexes of Fe(III) and Co(III) with Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole and pyridine-2-carboxaldehyde or thiophene-2-carboxaldehyde having composition $[M(L)_3]$ (where M = Fe(III) and Co(III); LH = Schiff bases) are reported and characterized based on elemental analyses, electrical conductance, magnetic moments, spectral (electronic, IR, ^1H NMR) and thermal analysis. Spectroscopic studies reveal that Schiff bases $L_1H-L_{10}H$ behave as monoanionic bidentate towards the metal ions. The magnetic moment data suggest an octahedral geometry around the central metal atom. The molar conductance of complexes is an indicative of their non-electrolytic nature. The thermal behavior of complexes $[\text{Fe}(\text{PTMT})_3]$ and $[\text{Co}(\text{PPMT})_3]$ has been studied by TG and agree with the complexes composition. The antifungal activity screening against *Aspergillus niger* and *Fusarium solani* show that complexes are more potent in comparison with free ligands.

INTRODUCTION

Among the five membered heterocyclic compounds triazoles are of great interest because of their action as pesticides, herbicides, insecticides, bactericides and anticonvulsants.¹⁻⁵ One family of derivatives are amine and thione substituted triazoles containing S=C-N-N structural unit similar to thiosemicarbazones.⁶⁻⁸ These compounds has been proved as effective anti-inflammatory and antimicrobial agents and were used as precursors for some biologically active and flexible Schiff bases synthesis.⁹⁻¹² The presence of an exocyclic thione group heterocyclic moiety make them more interesting because the combination of these two groups generate a species with a considerable coordination potential. Bonding through amine and thione group results in formation of stable metal complexes involving highly favoured five membered ring systems.^{13,14}

Literature survey reveals that a number of complexes with these ligands have been reported

for a variety of transition metals which have shown interesting biological and magnetic properties.¹⁵⁻¹⁸

To extend the knowledge with respect to the coordination and biological properties of the transition metal complexes of substituted 1,2,4-triazoles, we describe here the synthesis and characterization of a series of iron(III) and cobalt(III) complexes with Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazoles and pyridine-2-carboxaldehyde or thiophene-2-carboxaldehyde.

EXPERIMENTAL

Chemicals and methods

All chemicals used in this work were of analytical grade. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and carbon disulphide were obtained from SD Fine chemicals Ltd. (Mumbai, India) and were used as received. Solvents were purified and dried following standard procedures.¹⁹ The melting points were determined by placing finally powdered sample in a glass capillary and heating by using Ambassador melting point apparatus. Infrared spectra of KBr pellets were obtained using

* Corresponding author: vksharma21@hotmail.com

Perkin–Elmer PC–16F FTIR spectrometer in the range 4000–350 cm^{-1} . The conductivity measurements of 10^{-3} M solution in DMF at 25°C were carried out with a Beckman conductivity bridge model RC-18A. Magnetic measurements were performed by Gouy's method using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a calibrant. The electronic spectra were recorded on Perkin Elmer Lambda in DMF. Proton NMR spectra of the complexes were recorded in $\text{DMSO}-d_6$ on a Bruker DRX 300 spectrometer at a sweep width of 900 Hz. The elemental analysis (C, H, N and S) was carried out with a Carlo-Erba 1108 elemental analyzer. The metals were estimated gravimetrically by precipitating them as hydroxides and decomposing to respecting metal oxides at $\sim 698^\circ\text{C}$ while the chloride was estimated as silver chloride. The thermal behavior of Fe(III) and Co(III) complexes have been investigated using a Shimadzu TGA 50H analyzer in the temperature range 25–800°C at a heating rate of $10^\circ\text{C min}^{-1}$. Antifungal studies were done following the method described earlier.^{20,21} The solutions of metal complexes with different concentrations were mixed in DMF which were then mixed with the medium. The linear growth of the fungus was recorded by measuring the diameter of the colony after 96 h and the percentage inhibition was calculated as $100(\text{C}-\text{T})/\text{C}$, where C and T are the diameters of the fungal colony in control and test plates, respectively.

Synthesis of ligands

A series of 3-substituted-4-amino-5-mercapto-1,2,4-triazoles were prepared by the method reported in literature.²² Schiff bases were prepared by refluxing a mixture of appropriate mercaptotriazoles (0.01 mol) with pyridine-2-carboxaldehyde or thiophene-2-carboxaldehyde (0.01 mol) in ethanol (35 cm^3) for 6–8 h. The resulting solution was concentrated to half of its original volume and cooled at ambient temperature for 2 h. After cooling, the coloured solid products were filtered, washed with cold ethanol and *in vacuo* dried over CaCl_2 .

Synthesis of Fe(III) complexes

To a hot ethanolic alkaline ($\text{pH} = 8-9$) solution (40 cm^3) of appropriate mercaptotriazole derivative (Schiff base) (0.03

mol) was added an ethanolic solution (10 cm^3) of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.01 mol). The brown to black coloured complexes precipitated immediately but the mixture was gently warmed on water bath for 2–3 h in order to complete the reaction. The products were filtered, washed several times with distilled water and *in vacuo* dried over CaCl_2 .

Synthesis of Co(III) complexes

An ethanolic solution (10 cm^3) of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.01 mol) was added to a hot ethanolic solution (40 cm^3) of appropriate mercaptotriazole (0.03 mol). The reaction mixture was refluxed for $\frac{1}{2}$ h and after that 3 cm^3 of 30% H_2O_2 was added. A sudden change in colour was observed. The pH of the solution was raised by adding 2 cm^3 of saturated solution of KOH. The brown to grey coloured complexes precipitated was refluxed for further 2–3 h. After cooling, the solid complexes were filtered, washed several times with distilled water and *in vacuo* dried over CaCl_2 .

RESULTS AND DISCUSSION

All the ligands were prepared by refluxing 3-substituted-4-amino-5-mercapto-1,2,4-triazoles with two different aldehydes, namely pyridine-2-carboxaldehyde and thiophene-2-carboxaldehyde in ethanol. These ligands react with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in absolute ethanol in the presence of a base, such as KOH, to give the complexes with the formula $[\text{M}(\text{L})_3]$. All these complexes are coloured microcrystalline powders, quite stable in air and soluble in THF, DMF and DMSO. The molar conductivity values for the complexes lie in the range $10.8-15.6 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$. This is consistent with the non-electrolytic nature of these complexes.²³ The analytical data support the expected compositions of all the complexes (Table 1).

Table 1

Melting point, yield and analytical data for mercaptotriazole derivatives and complexes

Compound/ Empirical Formula	M.P. (°C)	Yield (%)	Analysis (found) Calcd. %					
			C	H	N	S	Cl	M
PPMTH	160	50	(59.6)	(3.6)	(24.8)	(11.0)	–	–
$\text{C}_{14}\text{H}_{11}\text{N}_5\text{S}$			59.7	3.9	25.0	11.3		
CPMTH	136	59	(53.0)	(2.8)	(22.0)	(10.0)	(11.0)	–
$\text{C}_{14}\text{H}_{10}\text{N}_5\text{SCl}$			53.2	3.1	22.2	10.1	11.2	
TPMTH	145	62	(60.7)	(4.2)	(23.6)	(10.6)	–	–
$\text{C}_{15}\text{H}_{13}\text{N}_5\text{S}$			60.9	4.4	23.8	10.8		
MPMTH	140	58	(57.5)	(4.0)	(22.3)	(10.0)	–	–
$\text{C}_{15}\text{H}_{13}\text{N}_5\text{SO}$			57.8	4.2	22.5	10.2		
SPMTH	260	65	(56.3)	(3.5)	(23.4)	(10.5)	–	–
$\text{C}_{14}\text{H}_{11}\text{N}_5\text{SO}$			56.5	3.7	23.6	10.7		
PTMTH	175	62	(54.2)	(3.2)	(19.4)	(22.0)	–	–
$\text{C}_{13}\text{H}_{10}\text{N}_4\text{S}_2$			54.4	3.5	19.6	22.3		
CTMTH	145	65	(53.8)	(3.0)	(19.2)	(11.0)	(12.0)	–
$\text{C}_{13}\text{H}_9\text{N}_4\text{SCl}$			54.0	3.1	19.4	11.1	12.2	
TTMTH	170	56	(55.7)	(3.8)	(18.5)	(21.0)	–	–
$\text{C}_{14}\text{H}_{12}\text{N}_4\text{S}_2$			55.9	4.0	18.7	21.3		

Table 1 (continued)

MTMTH	185	77	(53.0)	(3.6)	(17.4)	(20.0)	–	
C ₁₄ H ₁₂ N ₄ S ₂ O			53.1	3.8	17.7	20.2		
STMTH	240	87	(51.4)	(3.1)	(18.4)	(21.0)	–	
C ₁₃ H ₁₀ N ₄ S ₂ O			51.6	3.3	18.6	21.2		
[Fe(PPMT) ₃]	260 ^d	58	(56.1)	(3.1)	(23.2)	(10.5)	–	(6.0)
FeC ₄₂ H ₃₀ N ₁₅ S ₃			56.2	3.3	23.4	10.7		6.2
[Fe(CPMT) ₃]	280 ^d	56	(50.2)	(2.5)	(20.8)	(9.4)	(10.4)	(5.3)
FeC ₄₂ H ₂₇ N ₁₅ Cl ₃			50.4	2.7	21.0	9.6	10.6	5.5
[Fe(TPMT) ₃]	300	62	(57.4)	(3.6)	(22.1)	(10.1)	–	(5.7)
FeC ₄₅ H ₃₆ N ₁₅ S ₃			57.5	3.8	22.3	10.2		5.9
[Fe(MPMT) ₃]	285 ^d	64	(54.5)	(3.4)	(21.0)	(9.5)	–	(5.4)
FeC ₄₅ H ₃₆ N ₁₅ S ₃ O ₃			54.7	3.6	21.2	9.7		5.6
[Fe(SPMT) ₃]	270	76	(53.1)	(3.1)	(22.0)	(10.0)	–	(5.7)
FeC ₄₂ H ₃₀ N ₁₅ S ₃ O ₃			53.3	3.2	22.2	10.1		5.9
[Fe(PTMT) ₃]	275	51	(51.2)	(2.7)	(18.2)	(20.9)	–	(6.0)
FeC ₃₉ H ₂₇ N ₁₂ S ₆			51.3	2.9	18.4	21.0		6.1
[Fe(CTMT) ₃]	300 ^d	61	(46.0)	(2.1)	(16.4)	(18.6)	(10.4)	(5.3)
FeC ₃₉ H ₂₄ N ₁₂ Cl ₃ S ₃			46.1	2.3	16.6	18.9	10.2	5.5
[Fe(TTMT) ₃]	290 ^d	48	(52.6)	(3.2)	(17.5)	(20.0)	–	(5.5)
FeC ₄₂ H ₃₃ N ₁₂ S ₆			52.8	3.4	17.6	20.1		5.8
[Fe(MTMT) ₃]	200	68	(50.1)	(3.2)	(16.5)	(19.0)	–	(5.3)
FeC ₄₂ H ₃₃ N ₁₂ S ₆ O ₃			50.3	3.3	16.7	19.2		5.5
[Fe(STMT) ₃]	300 ^d	72	(48.5)	(2.6)	(17.4)	(20.0)	–	(5.6)
FeC ₃₉ H ₂₇ N ₁₂ S ₆ O ₃			48.7	2.8	17.5	20.0		5.8
[Co(PPMT) ₃]	280	63	(56.0)	(3.1)	(23.0)	(10.4)	–	(6.2)
CoC ₄₂ H ₃₀ N ₁₅ S ₃			56.0	3.3	23.3	10.6		6.5
[Co(CPMT) ₃]	320	60	(50.0)	(2.4)	(20.8)	(9.3)	(10.4)	(5.5)
CoC ₄₂ H ₂₇ N ₁₅ Cl ₃			50.2	2.7	20.9	9.5	10.6	5.8
[Co(TPMT) ₃]	310 ^d	59	(57.0)	(3.5)	(22.0)	(10.0)	–	(6.2)
CoC ₄₅ H ₃₆ N ₁₅ S ₃			57.3	3.8	22.3	10.2		6.2
[Co(MPMT) ₃]	300	69	(54.1)	(3.4)	(21.9)	(9.5)	–	(5.6)
CoC ₄₅ H ₃₆ N ₁₅ S ₃ O ₃			54.5	3.6	22.2	9.7		5.9
[Co(SPMT) ₃]	295 ^d	75	(53.1)	(2.8)	(21.9)	(9.8)	–	(6.0)
CoC ₄₂ H ₃₀ N ₁₅ S ₃ O ₃			53.2	3.1	22.1	10.1		6.2
[Co(PTMT) ₃]	290	56	(51.0)	(2.6)	(18.0)	(21.0)	–	(6.2)
CoC ₃₉ H ₂₇ N ₁₂ S ₆			51.1	2.9	18.3	21.0		6.4
[Co(CTMT) ₃]	300	62	(45.6)	(2.0)	(16.0)	(18.5)	(10.4)	(5.4)
CoC ₃₉ H ₂₄ N ₁₂ Cl ₃ S ₃			45.9	2.3	16.5	18.8	10.4	5.7
[Co(TTMT) ₃]	280 ^d	58	(52.5)	(3.1)	(17.2)	(20.0)	–	(6.0)
CoC ₄₂ H ₃₃ N ₁₂ S ₆			52.7	3.4	17.5	20.1		6.1
[Co(MTMT) ₃]	300 ^d	68	(50.0)	(3.0)	(16.4)	(19.0)	–	(5.4)
CoC ₄₂ H ₃₃ N ₁₂ S ₆ O ₃			50.1	3.1	16.7	19.1		5.8
[Co(STMT) ₃]	296	72	(48.4)	(2.4)	(17.2)	(19.6)	–	(5.8)
CoC ₃₉ H ₂₇ N ₁₂ S ₆ O ₃			48.6	2.8	17.4	19.9		6.1

d = decomposition temperature

IR spectra

The characteristic IR bands of the ligands and complexes are shown in Table 2. By comparing the infrared spectra of the complexes with those of free ligands one may conclude the following:

The ligand molecules exhibit thione \rightleftharpoons thiol tautomerism. In the spectra of the free ligands the presence of bands at 3050–3200 cm⁻¹ and 2450–2560 cm⁻¹ assigned to $\nu(\text{N-H})$ and $\nu(\text{S-H})$ vibrations respectively,²⁴ clearly give an evidence of establishment of this type of thione \rightleftharpoons thiol tautomeric system.

The deprotonation of thiol group and complexation through sulphur atom is indicated by the absence of the band in the range 2450–2560 cm⁻¹ (assigned to $\nu(\text{S-H})$) in the spectra of complexes. The appearance of a new band in the range 650–700 cm⁻¹, due to conversion of C=S into C-S further supported the coordination through sulphur atom. The $\nu(\text{M-S})$ vibration appear in the range 370–390 cm⁻¹ in the spectra of complexes.²⁵

The band in the range 1605–1625, 1560–1580 and 1480–1500 cm⁻¹ in the spectra of ligands may be assigned to $\nu(\text{C=N})$ (N=N=C-), $\nu(\text{C=N})$ (ring) and $\nu(\text{C=C})$ (phenyl) vibrations, respectively.

The strong band at 1605-1625 cm^{-1} corresponding to azomethine $\nu(\text{C}=\text{N})$ in the spectra of free ligands shifted to lower wave numbers on complex formation by (20-35 cm^{-1}) indicate that nitrogen atom of the azomethine group coordinate

to metal ion in all complexes.²⁶ This coordination mode is further confirmed by the presence of a band in the range 450-470 cm^{-1} in complexes spectra assigned to $\nu(\text{M}-\text{N})$ vibrations.²⁷

Table 2

Physical and spectral data of the ligands and complexes

Compound	Colour	μ_{eff} (B.M.)	IR (cm^{-1})	λ_{max} (cm^{-1})
PPMTH	Yellow	–	3106(NH), 2545(SH), 1617(C=N)	–
MPMTH	Yellowish green	–	3092(NH), 2500(SH) 1613(C=N)	–
SPMTH	Mud green	–	3109(NH), 2510(SH), 1617(C=N)	–
PTMTH	Light yellow	–	3142(NH), 2550(SH), 1615(C=N)	–
CTMTH	Cream	–	3095(NH), 2502(SH), 1605(C=N)	–
TTMTH	Cream	–	3188(NH), 2560(SH), 1625(C=N)	–
MTMTH	Yellow	–	3050(NH), 2450(SH), 1611(C=N)	–
STMTH	Pale yellow	–	3106(NH), 2530(SH), 1614(C=N)	–
[Fe(PPMT) ₃]	Coffee	5.74	1597(C=N), 464(M-N), 375(M-S)	16650, 23000
[Fe(CPMT) ₃]	Black	5.82	1586(C=N), 469(M-N), 372(M-S)	16300, 22429
[Fe(TPMT) ₃]	Brown	5.62	1600(C=N), 462(M-N), 381(M-S)	17210, 22120
[Fe(MPMT) ₃]	Coffee	5.58	1587(C=N), 465(M-N), 374(M-S)	17560, 22026
[Fe(SPMT) ₃]	Black	5.40	1592(C=N), 451(M-N), 384(M-S)	16915, 23095
[Fe(PTMT) ₃]	Dark brown	5.76	1594(C=N), 453(M-N), 389(M-S)	16825, 22642
[Fe(CTMT) ₃]	Light brown	5.65	1579(C=N), 456(M-N), 390(M-S)	17350, 22810
[Fe(TTMT) ₃]	Brown	5.79	1601(C=N), 463(M-N), 386(M-S)	17663, 23105
[Fe(MTMT) ₃]	Brown	5.48	1578(C=N), 454(M-N), 379(M-S)	17453, 22942
[Fe(STMT) ₃]	Black	5.80	1582(C=N), 462(M-N), 388(M-S)	16525, 22091
[Co(PPMT) ₃]	Brown	Dia.	1589(C=N), 459(M-N), 382(M-S)	15335, 21410, 23560
[Co(CPMT) ₃]	Brown	Dia.	1578(C=N), 468(M-N), 390(M-S)	15129, 21300, 23600
[Co(TPMT) ₃]	Dark brown	Dia.	1594(C=N), 470(M-N), 379(M-S)	15210, 21244, 23429
[Co(MPMT) ₃]	Black	Dia.	1593(C=N), 459(M-N), 378(M-S)	15100, 21383, 23500
[Co(SPMT) ₃]	Light brown	Dia.	1590(C=N), 454(M-N), 383(M-S)	15395, 21140, 23756
[Co(PTMT) ₃]	Brown	Dia.	1587(C=N), 466(M-N), 388(M-S)	15280, 21198, 23810
[Co(CTMT) ₃]	Black	Dia.	1583(C=N), 460(M-N), 370(M-S)	15142, 21456, 23540
[Co(TTMT) ₃]	Black	Dia.	1596(C=N), 461(M-N), 384(M-S)	15405, 21585, 23875
[Co(MTMT) ₃]	Brown	Dia.	1588(C=N), 450(M-N), 380(M-S)	15429, 21636, 23630
[Co(STMT) ₃]	Dark green	Dia.	1592(C=N), 457(M-N), 385(M-S)	15444, 21538, 23450

The spectra of the ligands SPMTH and STMTH show bands in the range 3360-3400 cm^{-1} assigned to $\nu(\text{O}-\text{H})$ vibration. In the corresponding complexes these bands persist indicating the non deprotonation.²⁷

values for iron(III) complexes (5.4-5.8 B.M.) are consistent with a high spin configuration.²⁸ The cobalt(III) complexes are diamagnetic as expected for a low spin d^6 system ($S=0$) corresponding to t_{2g}^6 configuration in octahedral environment.²⁹

Magnetic moment studies

The magnetic moments of the complexes were recorded at room temperature and the values are given in Table 2. The high magnetic moment

Electronic spectra

The electronic absorption spectra of complexes measured in DMF and bands obtained together with their assignments are given in Table 2. The

iron(III) complexes exhibit two bands in the ranges 16,300-17,663 and 22,026-23,105 cm^{-1} which can be attributed to the ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (G) and ${}^6A_{1g} \rightarrow {}^4T_{2g}$ (G) transitions, respectively.^{30,31} Being spin forbidden d-d transition the intensity of these bands was very low. The higher energy ligand field bands obscured by the intense charge transfer band³² observed in the ranges 24,390-25,505 cm^{-1} . The electronic spectra of cobalt(III) complexes show the presence of three bands in the ranges 15,100-15,444, 21,140-21,636 and 23,429-23,875 cm^{-1} corresponding to ${}^1A_{1g} \rightarrow {}^3T_{2g}$, ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively. These are similar to those observed for other six coordinated cobalt(III) complexes.³³

${}^1\text{H}$ NMR spectra

The ${}^1\text{H}$ NMR spectra of ligands and their cobalt(III) complexes have been recorded in DMSO(d_6). The following conclusions can be derived by comparing the spectra of ligands with their cobalt(III) complexes:

The ligands show a singlet at ca. δ 8.6 ppm due to $-\text{SH}$ proton. In solution the ligands mainly exist in thiol form. However, this signal disappear in corresponding cobalt(III) complexes indicating the coordination of sulphur to metal ion after deprotonation. The singlet at δ 8.0-8.3 ppm in the spectra of ligands ascribed to azomethine protons are shifted downfield in the complexes. This confirms deshielding as a result of the coordination of the ligand to the metal ion through the nitrogen atom of the azomethine group. In the spectra of ligands PPMTH, CPMTH, TPMTH, MPMTH and SPMTM a multiplet was observed at δ 7.3-7.5 ppm that probably includes both the aromatic protons of the phenyl and pyridine rings. No major shift for this multiplet was observed in the corresponding cobalt(III) complexes, indicating the non involvement of pyridine nitrogen in complexation. For ligands PTMTH, CTMTH, TTMTH, MTMTH and STMTH three multiplets were observed in the region δ 5.8-6.7 ppm along with multiplets of aromatic protons previously mentioned. This could be due to thiophene protons. Slight shift was found for these protons in the spectra of cobalt(III) complexes. This indicates that thiophene-S is not participating in coordination. Other signals appeared in the spectra of ligands and complexes are at ca. δ 2.2 ppm due to $-\text{CH}_3$ and at ca. δ 3.4

ppm due to $-\text{OCH}_3$. In addition, signals at ca. δ 9.4-9.6 ppm in the spectra of ligands SPMTM, STMTH and in their complexes may be assigned to phenolic protons.

Thermal studies

The thermal results of $[\text{Fe}(\text{PTMT})_3]$ and $[\text{Co}(\text{PPMT})_3]$ complexes lead to conclusions that both complexes are thermally stable up to 270°C as results of the fact that are anhydrous species. The first mass loss was observed in the temperature range 270-360°C. This could be correlated with the removal of one mole of the ligand, which was confirmed by mass loss of 31.15-31.50 % at this stage. Another mole of triazole moiety was lost between 370-500°C with a mass loss of 31.15-31.55 % on TG curve. In the third step the weight loss was observed in the temperature range 520-650 °C which corresponds to the loss of third molecule of ligand. Finally the formation of metal oxides ($\text{Co}_3\text{O}_4 + \text{Fe}_2\text{O}_3$) takes place at \sim 698°C.

Biological evaluation

All the ligands and their corresponding iron(III) and cobalt(III) complexes were screened *in vitro* for their antifungal activity against two fungal cultures *Aspergillus niger* and *Fusarium solani* by agar plate technique. The results of antifungal screening are presented in Table 3. The results show that the complexes exhibit antifungal properties and it is important to note that their activity is enhanced in comparison to the free ligands.^{34,35} These results may be rationalized on the basis that chelation reduces the polarity of the metal ion mainly because of the partial sharing of its positive charge with the donor groups and possibly the π - electron delocalization within the whole chelate ring system thus formed during coordination.³⁶ This process of chelation increases the lipophilic nature of the complex, which in turn favours its permeation through the lipid layer of the membrane. This increase in lipophilicity enhances the biological utilization ratio and activity of testing compound. It may be suggested that these complexes deactivate various cellular enzymes, which play a vital role in various metabolic pathways of these microorganisms.

Table 3
Antifungal activity of ligands and complexes

Compounds	Average inhibition % after 96h					
	<i>Aspergillus niger</i>			<i>Fusarium solani</i>		
	100 ppm	500 ppm	1000 ppm	100 ppm	500 ppm	1000 ppm
Ridomil	56.5	68.2	89.5	54.8	72.0	88.9
PPMTH	21.6	26.8	39.5	21.4	32.2	48.8
CPMTH	22.6	28.0	41.4	22.8	34.2	41.8
TPMTH	21.2	30.2	39.0	21.0	32.6	49.2
MPMTH	22.8	34.5	42.2	23.0	34.4	41.8
SPMTH	21.9	32.4	40.0	21.8	32.5	49.6
PTMTH	20.8	31.5	39.2	21.2	31.6	49.5
CTMTH	21.9	33.6	40.9	21.5	33.6	41.4
TTMTH	20.0	31.2	39.0	20.6	31.0	48.4
MTMTH	22.0	34.8	42.0	22.4	34.8	41.5
STMTH	21.0	32.1	39.8	20.8	32.0	40.2
[Fe(PPMT) ₃]	35.2	56.0	70.4	35.6	56.2	70.9
[Fe(CPMT) ₃]	36.8	57.4	72.6	36.4	58.2	73.4
[Fe(TPMT) ₃]	35.0	55.6	69.8	35.2	55.8	70.2
[Fe(MPMT) ₃]	37.2	57.9	74.5	38.2	59.2	75.6
[Fe(SPMT) ₃]	36.1	56.2	71.2	36.0	56.8	72.0
[Fe(PTMT) ₃]	34.8	55.5	70.2	35.0	55.8	70.6
[Fe(CTMT) ₃]	36.2	56.9	71.9	37.0	57.6	74.3
[Fe(TTMT) ₃]	35.4	55.0	70.0	35.6	55.7	71.2
[Fe(MTMT) ₃]	36.9	57.2	73.5	37.6	59.0	74.8
[Fe(STMT) ₃]	35.8	56.0	70.6	35.1	56.4	72.6
[Co(PPMT) ₃]	34.8	55.8	70.0	35.0	56.0	70.4
[Co(CPMT) ₃]	35.9	57.0	72.0	36.1	57.2	72.4
[Co(TPMT) ₃]	34.1	55.2	69.6	34.8	55.6	71.1
[Co(MPMT) ₃]	37.0	57.5	74.0	37.4	57.8	74.5
[Co(SPMT) ₃]	34.6	55.6	71.0	34.8	55.9	71.6
[Co(PTMT) ₃]	34.0	54.8	69.6	34.6	55.2	70.0
[Co(CTMT) ₃]	36.5	56.5	71.4	36.8	57.2	72.5
[Co(TTMT) ₃]	33.9	54.6	68.5	35.2	54.8	70.3
[Co(MTMT) ₃]	37.2	57.0	73.9	37.5	58.2	74.2
[Co(STMT) ₃]	36.0	55.3	70.0	35.8	55.5	70.5

CONCLUSIONS

The results show that Schiff bases have a tautomeric structure (Figure 1), which means that they exist in the solid state in thione-thiol forms. Upon coordination they probably exist only in the thiol form. The ligands behave as monoanionic bidentate and coordinate to iron(III) and cobalt(III)

ions generating complexes of general formula $[M(L)_3]$. According to results obtained, the geometry of all the complexes is octahedral. Based on foregoing arguments, the proposed structure of Schiff base ligands and their complexes are depicted in Figures 1 and 2, respectively.

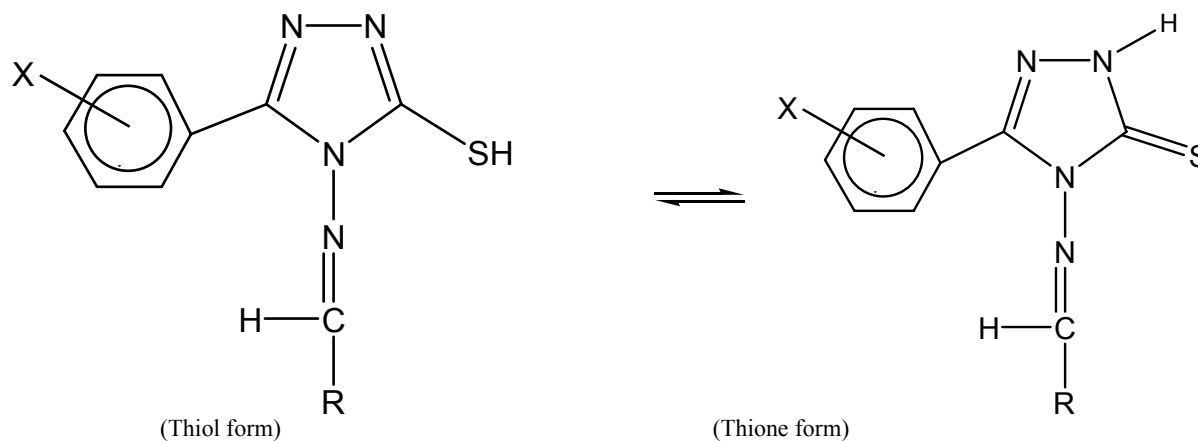
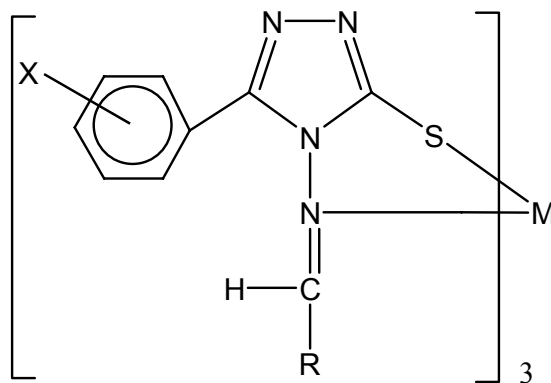


Fig. 1 – Structure of the ligands.



M = Fe(III), Co(III)

X	R	LH
H		PPMTH
2-Cl		CPMTH
4-CH ₃		TPMTH
4-OCH ₃		MPMTH
2-OH		SPMTH
H		PTMTH
2-Cl		CTMTH
4-CH ₃		TTMTH
4-OCH ₃		MTMTH
2-OH		STMTH

Fig. 2 – The coordination proposed for the complexes.

Acknowledgements: The authors are thankful to Head of Department, Department of Chemistry, University of Lucknow, Lucknow for providing laboratory facilities and to University Grants Commission, New Delhi, India for financial assistance.

REFERENCES

1. E. S. Raper, *Coord. Chem. Rev.*, **1996**, 153, 199.
2. W. Dietzsch, R. Kirmse and E. Hoyer, *Coord. Chem. Rev.*, **1992**, 99, 117.
3. T. W. Kajdan, P. J. Squattrito and S. N. Dubey, *Inorg. Chim. Acta*, **2000**, 300, 1082.
4. R. A. Nazareth and B. Narayana, *Indian J. Chem.*, **2003**, 42A, 564.
5. Z. A. Kaplancikli, G. Turan-Zitouni, A. Ozdemir and G. Revial, *Eur. J. Med. Chem.*, **2008**, 43, 155.
6. R. W. Clark, P. J. Squattrito, A. K. Sen and S. N. Dubey, *Inorg. Chim. Acta*, **1999**, 293, 61.
7. S. Goel, O. P. Pandey and S. K. Sengupta, *Bull. Soc. Chim. Fr.*, **1989**, 8, 771.
8. M. Amir, M. S. Y. Khan and M. S. Zaman, *Indian J. Chem.*, **2004**, 43B, 2189.
9. K. B. Gudasi, P. B. Maravalli and T. R. Goudar, *J. Serb. Chem. Soc.*, **2005**, 70, 643.
10. M. S. Yadawe and S. A. Patil, *Indian J. Heterocyclic Chem.*, **1992**, 2, 41.

11. K. Singh, M. S. Barwa and P. Tyagi, *Eur. J. Med. Chem.*, **2006**, *41*, 147.
12. X. P. Hui, C. H. Chu, Z. Y. Zang, Q. Wang and Q. Zhang, *Indian J. Chem.*, **2002**, *41B*, 2176.
13. D. H. Boschelli, D. T. Connor and D. A. Barnemeir, *J. Med. Chem.*, **1993**, *36*, 1802.
14. S. H. Gaikwad, T. N. Lokhande and M. A. Anuse, *Indian J. Chem.*, **2005**, *44A*, 1625.
15. S. Dubey, R. Handa and B. Vaid, *Monatsh. Chem.*, **1994**, *225*, 395.
16. A. Sen, G. Singh, K. Singh, R. Noren, R. Handa and S. Dubey, *Indian J. Chem.*, **1997**, *36A*, 891.
17. E.L. Chang, C. Simmers and D.A. Knight, *Pharmaceuticals*, **2010**, *3*, 1711.
18. W. Vieujdjenhil, S. Gorter, J. G. Haasnoot and J. Reddijk, *Polyhedron*, **1985**, *4*, 1969.
19. A. I. Vogel, "A Textbook of Practical Organic Chemistry", 4th edn., Longmans, London, 1978.
20. V. K. Sharma, S. Srivastava and A. Srivastava, *J. Coord. Chem.*, **2006**, *59*, 1321.
21. V. K. Sharma and S. Srivastava, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **2005**, *35*, 311.
22. R. El-Sayed, *Indian J. Chem.*, **2006**, *45B*, 738.
23. W. J. Geary, *Coord. Chem. Rev.*, **1971**, *7*, 81.
24. K. B. Gudasi, S. A. Patil, R. S. Vadavi, R. V. Shenoy and M. S. Patil, *Transition Met. Chem.*, **2005**, *30*, 1014.
25. S. Chandra and K. Gupta, *Transition Met. Chem.*, **2002**, *27*, 196.
26. P. Bera and N. C. Saha, *J. Indian Chem. Soc.*, **2010**, *87*, 919.
27. K. Nakamoto, "Infrared and Raman Spectra of Inorganic and Coordination Compounds", John Wiley & Sons, Inc, New York, 1997.
28. C. R. Bhattacharjee, P. Goswami and P. Mondal, *J. Coord. Chem.*, **2010**, *63*, 2002.
29. V. K. Sharma, S. Srivastava and A. Srivastava, *J. Appl. Biosci.*, **2005**, *31*, 114.
30. K. K. Narang and V. P. Singh, *Synth. React. Inorg. Met.-Org. Chem.*, **1993**, *23*, 971.
31. N. N. Greenwood and A. Earnshaw, "Chemistry of the Elements", 2nd edn., Butterworth-Heinemann, 2005.
32. A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, 1984.
33. N. C. Saha, R. J. Butcher, S. Chaudhuri and N. Saha, *Polyhedron*, **2002**, *21*, 779.
34. V. K. Sharma, S. Srivastava and A. Srivastava, *Rev. Roum. Chim.*, **2005**, *50*, 751.
35. N. Tripathi, Shalini and V. K. Sharma, *Polish J. Chem.*, **2008**, *82*, 523.
36. Z. H. Chohan, *Synth. React. Inorg. Met.-Org. Chem.*, **2004**, *34*, 833.