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# Synthesis, characterization of biologically active Schiff base 14-membered M (III) macrocyclic complexes derive from 1 H-indol and diethyl oxalate and thiocarbonohydrazide

**[1] Gajendra Kumar, [2] Vidhi Singh, [3] Preeti Sharma**
[1-3] Department of Chemistry, Bhagwant University, Ajmer, Rajasthan, India
[1] Department of Chemical Science, Bhagwant Institute of Technology, Muzaffarnagar, Uttar Pardesh, India

## Abstract

Biologically active Cr(III), Mn(III) and Fe(III) macrocyclic complexes [{$M(C_{38}H_{28}N_{12}S_2)X$}$X_2$] of Schiff base ligand ($C_{38}H_{28}N_{12}S_2$) obtained through the condensation of thiocarbonodihydrazide, 1 H-indol and diethyl oxalate with the molar ratio 2:2:4. The structure configurations of the newly synthesized compounds have been determined by various spectroscopic: Electronic, IR, $^1$H NMR, $^{13}$C NMR, GCMS techniques and characterized with the help of magnetic measurements, elemental analysis, and condensation measurements. The electronic spectra of the complexes indicate a five coordinate square pyramidal geometry of the center metal ion. These compounds were tested for their antimicrobial inhibition potential against the bacteria: *Staphylococcus aureus, Bacillus subtilis, Escherichiacoli, Salmonella typhi, Pseudomonasaeruginosa.*and fungi *Rizoctonia sp., Aspergillus sp., Penicillium sp*.

**Keywords:** schiff base, macrocyclic complexes, biological evaluation, spectroscopic study

## 1. Introduction

Schiff bases take part in a number of biochemical reactions involving interaction of the amino group of an enzyme [1]. Stereochemical investigations carried out with the aid of molecular models showed that Schiff bases formed between methylglyoxal [2]. Schiff bases are involved as intermediates in the processes of non-enzymatic glycosylations. These processes are normal during aging but they are remarkably accelerated in pathogeneses caused by stress, excess of metal ions or diseases such as diabetes, Alzheimer's disease, and atherosclerosis. Non-enzymatic glycosylation begins with an attack of sugar carbonyls or lipid peroxydation fragments on amino groups of proteins, amino phospholipids and nucleic acid, causing tissue damages by numerous oxidative rearrangements. One of the consequences is cataract of lens proteins [3]. Many biologically important Schiff bases have been reported in the literature possessing, antimicrobial, antibacterial, antifungal, anti-inflammatory, anticonvulsant, antitumor and anti HIV activities [4-9]. Transaminases are found in mitochondria and cytosal of eukaryotic cells catalyzed by a class of enzymes. Most of the work in the field of coordination chemistry describes mainly four, five, six or seven coordinate compounds of transition and inner transition metals ions mono, bi, tri, tetra and multidentate open chain organic ligands. Another class of synthetic and natural compounds is known for more than fifty years and is called macrocyclic ligands. Early examples were found in natural products e.g. porphyrins, phthalocyanine and coring ring derivatives. Majority of such polyether's show a limited tendency to form stable complexes with transition metal ions. However polyethers have received much attention because of their unusual behavior towards transition and non-transitional elements. Metal ligand and complexes have attracted increasing interest owing to their role in the understanding of molecular processes occurring in biochemistry, material science, catalysis, encapsulation, activation, transport and separation phenomena, hydrometallurgy, etc. [11-14]. In these studies Schiff bases have been extensively employed and a large variety of planar Schiff base ligands have been synthesized to ascertain correctly the role of the different donor atoms, their relative position, the number and size of the chelating rings formed, the flexibility and the shape of the coordinating moiety on the selective binding of charged or neutral species [15-17]. The evolution of these Schiff bases has produced macrobicyclic ligands obtained in one-step multiple condensation reactions [15, 16]; the cyclic [2+3] Schiff base condensation represents the extension of the [2+2] macrocyclic coordination systems into the third dimension. In addition to the use in the field of molecular recognition, catalysis and transport, these cage molecules are promising in the stabilization of particular species. The nature and disposition of donor atoms in the rigid cage may enhance the stability of unusual oxidation states in the coordinated transition metal ion, while encapsulation may protect normally labile substrate species. This combination of characteristics will eventually permit moisture sensitive chemistry to be carried out in the protected cavity under room temperature and atmospheric pressure. Pendant arm macrocyclic or macroacyclic ligands and their metal complexes have also attracted attention [18-20]. Arms bearing additional potential ligating groups have been introduced at both carbon and nitrogen atoms of macrocycles generally based on polyaza or polyoxa-donor sets in order to obtain modified complexation properties relative to the corresponding simple macrocyclic or macroacyclic precursors [21-22].

In the present paper we report the structure and biological activity synthesized compound by condensation of thiocarbonodihydrazide with 1,2-di(1H-indol-1-yl)ethane-1,2-dione and its Cr (III), Mn (III) and Fe (III) complexes. Results are reported on the bases of elemental analysis, conductance measurements, magnetic measurements and various spectroscopic studies.

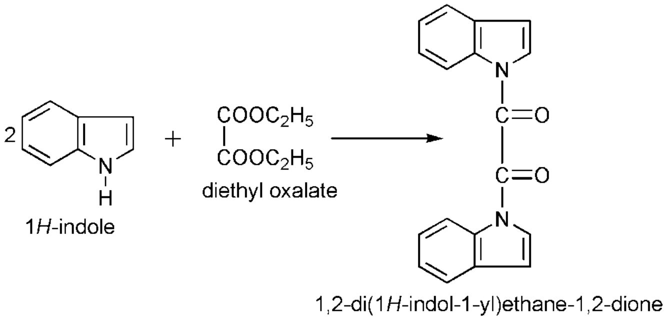
## 2. Experimental

### 2.1 Reagents

The entire chemicals used, were of the analytical grade, diethyl oxalate, Indole and thiocarbonodihydrazide procured from s.d.-fine. Metal salts were purchased from Merck.

### 2.2 Synthesis of 1,2-di(1H-indol-1-yl)ethane-1,2-dione

1 H-indol was dissolved in ethanol and this solution was added diethyl oxalate in a 2:1 molar ratio containing few drop of concentrated HCl. The solution was refluxed for 5h. The cream crystalline product which formed was filtered off under vacuum and recrystallized from ethanol (Scheme I) [23].

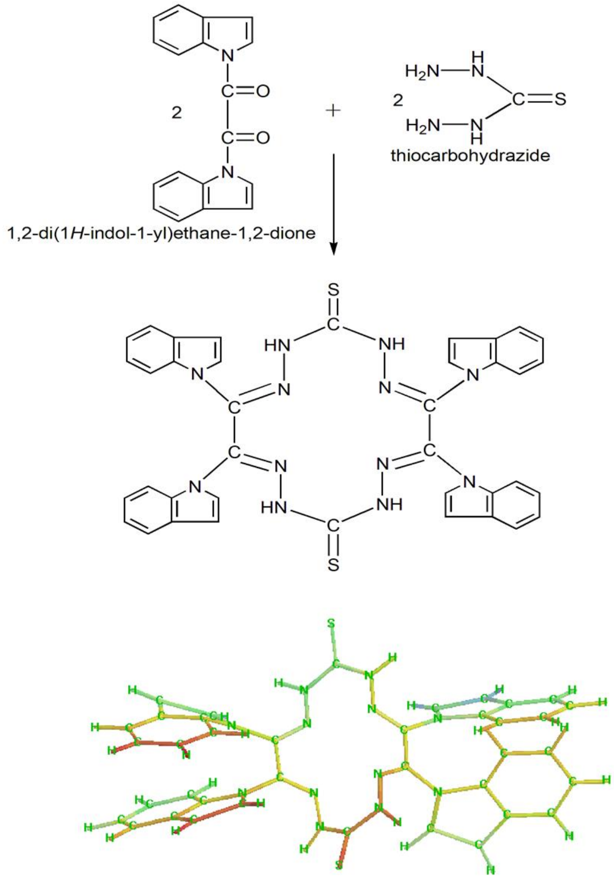


Scheme I. 1,2-di(1*H*-indol-1-yl)ethane-1,2-dione

### 2.3 Synthesis of macrocyclic ligand

1,2-di(1H-indol-1-yl) ethane-1, 2-dione in ethanol (20 mL) was added to an ethanolic solution of thiocarbonodihydrazide (30 mL) containing a few drops of concentrated HCl. The reaction mixture was refluxed for 5 h. The mixture was cooled to room temperature and the solvent removed under reduced pressure by rotavapour until a solid product was formed and it was washed with cold ethanol and dried under vacuum. $C_{38}H_{28}N_{12}S_2$ Melting point 151°C and Yield 70–75% (scheme II): calcd. C 63.67, H 3.94, N 23.45,; found C 63.66, H 3.98, N 23.44. $^1$ H NMR (300 MHz, DMSO-$d_6$) δ= 6.45-7.65 (m, 24H, Ar–H Indol), 8.13 (s, Ar–H, Carbonyl Phenyl), 10.15 (s, 4x1H, NH of Hydrazide). $^{13}$C NMR (300 MHz, DMSO-$d_6$) δ= 154.2 (C ═ N), 170.6 (C═O), 147.6, 145.9, 138.1, 135.5, 132.2, 130.1, 128.3, 112.4 (Ar–C). UV/vis (Nujolmul (nm)): λ = 370, 420, 480. UV/vis ($1\times 10^{-4}$mol, DMSO): λ = 360, 390, 445. IR (KBr): *v*(N$^2$H) 3240, *v*(C=O) 1710, *v*(C=N) 1620, ν(N–N) 1112, ν(C–C) 750, ν(C=C, aromatic) 1520, ν(C–H, aromatic) 3030, ν(NH, hydrazide) 3145 cm$^{-1}$.

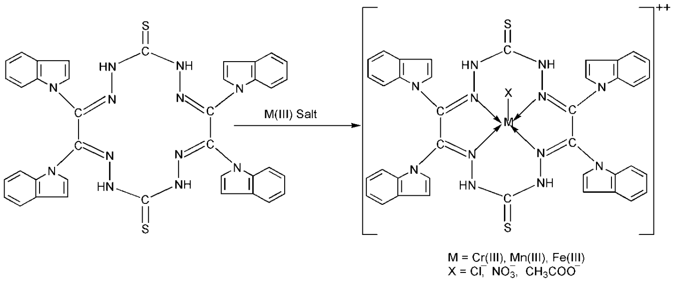
### *2.4 Synthesis of the Cr(III), Mn(III) and Fe(III) complexes*



Scheme II. Formation of Schiff base ligand

A solution of trivalent metal salt (1.0 mmol) in methanol (8 mL) was added to a hot solution (75 °C) of macrocyclic ligand (1.0 mmol) in ethanol (25 mL), and the reaction mixture was refluxed for 8 h. The solution was concentrated under vacuum. The precipitate was filtered off, washed with methanol and dried under vacuum over anhydrous $CaCl_2$ (68-75% yield) scheme III.

(2.0



Scheme III. Formation of Schiff base metal complex cation

### 2.4.1 Synthesis of the metal complex (1)

[Cr($C_{38}H_{28}N_{12}S_2$)Cl]$Cl_2$ yield 71% (873.03): calcd. C 52.15, H 3.22, N 19.20, Cr 5.94; found C 52.12, H 3.18, N 19.15, Cr 5.92. Conductance *Λ*m: 141Ω$^{-1}$ cm$^2$ mol$^{-1}$. UV/vis (Nujolmul (nm)): λ=355, 420, 525, 720 and 1155. IR (KBr): ν(N$^2$H) 3272, ν(C=N) 1640, *v*(C=S) 2140, ν(N–N) 1120, ν(C–C) 740, ν(C=C, aromatic) 1530, ν(C–H, aromatic) 3030, ν(NH, hydrazide) 3145, ν(M–N) 420, ν(M–Cl) 320 cm$^{-1}$.

### 2.4.2 Synthesis of the metal complex (2)

$[Cr(C_{38}H_{28}N_{12}S_2)NO_3](NO_3)_2$ yield 78% (954.09): calcd. C 47.80, H 2.96, N 22.00, Cr 5.45; found C 47.78, H 2.95, N 21.88, Cr 5.44. Conductance $\Lambda$m: 169 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. UV/vis (Nujolmul (nm)): λ=255, 525, 720 and 1155. IR (KBr): ν($H_2O$) 3420, ν($N^2H$) 3270, *ν*(C=S) 2144, ν(C=N) 1645, ν(C–C) 760, ν(C=C, aromatic) 1544, ν(C–H, aromatic) 3020, ν(NH, hydrazide) 3130, ν(N–N) 1110, ν(M–N) 420, ν(M–O) 480 $cm^{-1}$.

### 2.4.3 Synthesis of the metal complex (3)

$[Cr(C_{38}H_{28}N_{12}S_2)OAc](OAc)_2$yield 75% (945.18): calcd. C 55.87, H 3.94, N 17.77, Cr 5.50; found C 55.88, H 3.98, N 17.65, Cr 5.48. Conductance $\Lambda$m: 161 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. UV/vis (Nujolmul (nm)): λ=260, 520, 724 and 1150. IR (KBr): ν($H_2O$) 3330, ν($N^2H$) 3250, ν(C=S) 2138, ν(C=N) 1650, ν(N–N) 1120, ν(C–C) 760, ν(C=C, aromatic) 1544, ν(C–H, aromatic) 3030, ν(NH, hydrazide) 3140, ν(M–N) 420, ν(M–O) 510 $cm^{-1}$. $\nu_{sym}(OC(O)CH_3)$ 1549 (m), $\nu_{asym}(OC(O)CH_3)$ 1366 $cm^{-1}$,(Δν=190$cm^{-1}$).

### 2.4.4 Synthesis of the metal complex (4)

$[Mn(C_{38}H_{28}N_{12}S_2)Cl]Cl_2$ yield 73% (776.03): calcd. C 51.97, H 3.21, N 19.14 Mn 6.26; found C 51.92, H 3.18, N 19.15 Mn 6.22. Conductance $\Lambda$m: 141$\Omega^{-1}$ $cm^2$ $mol^{-1}$. UV/vis (Nujolmul (nm)): λ=260, 280, 320, 450, 700, 1150. IR (KBr): ν($H_2O$) 3370, ν($N^2H$) 3260, ν(C=S) 2147, ν(C=N) 1670, ν(N–N) 1145, ν(M–N) 440, ν(C–C) 755, ν(C=C, aromatic) 1540, ν(C–H, aromatic) 3040, ν(NH, hydrazide) 3145, ν(M–Cl) 320 $cm^{-1}$.

### 2.4.5 Synthesis of the metal complex (5)

$[Mn(C_{38}H_{28}N_{12}S_2)NO_3](NO_3)_2$ yield72%. (957.09): calcd. C 47.65, H 2.95, N 21.94, Mn 5.74; found C 47.62, H 2.90, N 21.85, Mn 5.71. Conductance $\Lambda$m: 158 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. UV/vis (Nujolmul (nm)): λ=255, 710 and 1151. IR (KBr): ν($H_2O$) 3420, ν($N^2H$) 3271, ν(C=S) 2145, ν(C=N) 1644, ν(N–N) 1112, ν(C–C) 754, ν(C=C, aromatic) 1540, ν(C–H, aromatic) 3040, ν(NH, hydrazide) 3145, ν(M–N) 420, ν(M–O) 495 $cm^{-1}$

### 2.4.6 Synthesis of the metal complex (6)

$[Mn(C_{38}H_{28}N_{12}S_2)OAc](OAc)_2$ yield 77% (948.17): calcd. C 55.69, H 3.93, N 17.71 Mn 5.79; found C 55.66, H 3.91, N 17.75, Mn 5.77, Conductance $\Lambda$m: 143 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. UV/vis (Nujolmul (nm)): λ= 255, 451, 680 and 1144. IR (KBr): ν($H_2O$) 3310, ν($N^2H$) 3250, ν(C=S) 2142, ν(C=N) 1655, ν(N–N) 1122, ν(C–C) 730, ν(C=C, aromatic) 1530, ν(C–H, aromatic) 3040, ν(NH, hydrazide) 3130, ν(M–N) 450, ν(M–O) 520 $cm^{-1}$, $\nu_{sym}(OC(O)CH_3)$ 1550, $\nu_{asym}(OC(O)CH_3)$ 1360 $cm^{-1}$, (Δν=188$cm^{-1}$).

### 2.4.7 Synthesis of the metal complex (7)

$[Fe(C_{38}H_{28}N_{12}S_2)Cl]Cl_2$ yield 75 % (877.03): calcd. C 51.92, H 3.21, N 19.12, Fe 6.35; found C 51.88, H 3.18, N 19.15, Fe 6.33.. Conductance $\Lambda$m: 130 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. UV/vis (Nujolmul (nm)): λ=260, 652 and 1060. IR (KBr): ν($H_2O$) 3407, ν($N^2H$) 3280, ν(C=S) 2142, ν(C=N) 1640, ν(N–N) 1144, ν(C–C) 744, ν(C=C, aromatic) 1530, ν(C–H, aromatic) 3045, ν(NH, hydrazide) 3140, ν(M–N) 450, ν(M–Cl) 330 $cm^{-1}$.

### 2.4.8 Synthesis of the metal complex (8)

$[Fe(C_{38}H_{28}N_{12}S_2)$ $NO_3](NO_3)_2$*Yield* 74%. (958.09): calcd. C 47.61, H 2.94, N 21.92, Fe 5.83; found C 47.59, H 2.91, N 21.88, Fe 5.82. Conductance $\Lambda$m: 145 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. UV/vis (Nujolmul (nm)): λ=255, 525, 720 and 1150. IR (KBr): ν($H_2O$) 3420 (br), ν($N^2H$) 3270, ν(C=S) 2141, ν(C=N) 1630, ν(N–N) 1130, ν(C–C) 755, ν(C=C, aromatic) 1530, ν(C–H, aromatic) 3050, ν(NH, hydrazide) 3135, ν(M–N) 420, ν(M–O) 480 $cm^{-1}$.

### 2.4.9 Synthesis of the metal complex (9)

$[Fe(C_{38}H_{28}N_{12}S_2)$ $OAc](OAc)_2$ yield 1.76% (949.17): calcd. C 55.64, H 3.94, N 17.70, Fe 5.88; found C 55.62, H 3.91, N 17.68, Fe 5.85. Conductance $\Lambda$m: 154 $\Omega^{-1}$ $cm^2$ $mol^{-1}$. UV/vis (Nujolmul (nm)): λ = 265, 636, 1051. IR (KBr): ν($H_2O$) 3410, ν($N^2H$) 3270, ν(C=S) 2146, ν(C=N) 1620, ν(N–N) 1122, ν(C–C) 751, ν(C=C, aromatic) 1530, ν(C–H, aromatic) 3040, ν(NH, hydrazide) 3140, ν(M–N) 450, ν(M–O) 520 $cm^{-1}$$\nu_{sym}(OC(O)CH_3)$ 1560 (m), $\nu_{asym}(OC(O)CH_3)$ 1360 $cm^{-1}$ (m) (Δν=191$cm^{-1}$).

### 2.4.10 Antimicrobial activity

Antimicrobial inhibition potential of the newly synthesized compound was screened using agar well diffusion method [24]. The biological activity of the free ligand, its metal complexes and standard drug (antibacterial lmipenem and antifungal miconazol) were studied against the *Staphylococcus aureus, Bacillus subtilis* (as gram positive bacteria) and *Pseudomonas aeruginosa*, *Escherichia coli*, *Salmonella typhi* (as gram negative bacteria) and fungi *Rizoctonia sp.*, *Aspergillus sp.*, *Penicillium sp*. The solution of different concentration of each compound and standard drug lmipenem and miconazol in DMSO was prepared for testing against spore germination. Centrifuged pellets of microorganism from a 24 h old culture containing approximately $10^4$ CFU (colony forming unit) per mL were spread on the surface of Muller Hinton Agar media plates. Wells with 6 mm diameter made, and then solution of test compound was filled to the wells. The plates were incubated at 30ºC for 24h. The activity of the compounds was determined by measuring diameter of the inhibition zone (in mm) each test was carried in triplicate [24, 25].

## 3. Results and discussion

### 3.1 FAB mass spectra

The mass spectra of newly synthesized Schiff base trivalent transition complexes have been recorded. The molecular ion ($M^+$) peaks obtained from various complexes are as follows (table 1): m/z = 716.20 (Ligand), m/z = 873.03 (complex 1), m/z = 954.09 (complex 2), m/z = 945.17 (complex 3), m/z = 876.03 (complex 4), m/z = 957.09 (complex 5), m/z = 948.17 (complex 6), m/z = 877.03 (complex 7), m/z = 958.09 (complex 8), m/z = 949.17 (complex 9). The spectra exhibit peaks assignable to various fragments arising from the thermal cleavage of the complexes.

### 3.2 IR Spectra

The IR spectral of the Schiff base ligand show a $_{ν}$(C=N) peak at 1610 $cm^{-1}$ and a medium intensity absorption band at 3180 $cm^{-1}$ which is attributed to the$_{ν}$(N−H) stretching vibration. The high intensity band at 1613-1632 $cm^{-1}$ which is attributed to the $\nu$(C=N) vibration. The various absorption band in the range ~1455-1570 cm$^{-1}$ may be assigned due to $_{\nu}$(C=C) aromatic stretching vibrations of the aromatic ring [26]. The presence of the absorption bands at 1400-1445, 1280-1315 and 1020-1045 cm$^{-1}$ in the IR spectra of the nitrato complexes suggests that the nitrate groups are coordinated to the central metal ion in a unidentate fashion [27]. The peak around 2140 cm$^{-1}$ may be assigned to $_{\nu}$(C=S ). In IR spectra of the acetate complexes the appearance of three characteristic bands in the ranges 1555 – 1575cm$^{-1}$, 1377 – 1395cm$^{-1}$ and 1795–1810 cm$^{-1}$ in the case of complexes was attributed to $\nu_{asym}(COO^{-})$,$\nu_{sym}(COO^{-})$ and uncoordinated $(COO^{-})$, respectively, indicating the participation of the carboxylate oxygen in the complexes formation. The IR spectra of nitrato complexes exhibits bands at 1290–1310 cm$^{-1}$, 1050–1065 cm$^{-1}$and 1435–1450 cm$^{-1}$ [28], IR absorption band ~1355–1360 cm$^{-1}$ assigned the uncoordinated nitro group. The far infrared spectra show bands in the region 420-450 cm$^{-1}$ corresponding to$_{\nu}$(M−N) vibration [29-31]. The presence of bands in all complexes in the region 420-450 cm$^{-1}$ indicates coordination of (M−N) azomethine nitrogen [32]. The band present in the range 310-330 cm$^{-1}$ may be assigned due to$_{\nu}$(M−Cl) vibration [29-31]. The bands present in the region 235-260 cm$^{-1}$ in all the nitrato complexes are assignable to $_{\nu}$(M−O) stretching vibration [29, 30].

### 3.3 $^{1}$H NMR

A survey of literature reveals that Schiff base have characterized by $^{1}$H NMR and $^{13}$C NMR spectra to ensure ligand structure and purity in d$_6$-dimethylsulfoxide (DMSO-d$_6$) solution using Me$_4$Si (TMS) as internal standard. The $^{1}$H NMR spectra of Schiff base ligand (HL) was recorded. The $^{1}$H NMR spectra of the ligand shows broad signal at 9.4-12.1 ppm due to the presence of –NH [33] and 2.1-2.8 ppm due to the –CH$_2$– (cyclic) [34]. The multiples in the region 6.54-8.76 ppm may be assigned to aromatic proton [35, 36]. $^{13}$C NMR of the Schiff base ligand, the signal appeared in the region 113-158 are assigned to aromatic carbon. The signal at 198.3-185.6, 182.8-171.2 and 165.4-150.7 due to C=S, C=N and C=O respectively.

### 3.4 Electronic spectral studies, magnetic measurements and molar conductance

The electronic spectra of Cr (III) complexes showed absorption band in the region 8970-9310, and 27530-27820 cm–$^{1}$ attributed to $^{4}B_{1g}\rightarrow{}^{4}E_{1g}$, $^{4}B_{1g}\rightarrow{}^{4}B_{2g}$, $^{4}B_{1g}\rightarrow{}^{4}A_{2g}$ and $^{4}B_{1g}\rightarrow{}^{4}E_{g}$. The spectral bands are consistent with that of five coordinated Cr (III) complexes [37, 38]. The magnetic moment values for these complexes were found to be 3.58-4.81 B.M. [39].

The absorption spectral bands of manganese (III) complexesshowed three spin allowed transitions: $^{5}B_{1g}\rightarrow{}^{5}A_{1g}$, $^{5}B_{1g}\rightarrow{}^{5}B_{2g}$, $^{5}B_{1g}\rightarrow{}^{5}E_{g}$ appearing in the ranges 12235–12640, and 35360–35520 cm–$^{1}$, The magnetic moment values for these complexes were found in the range 4.81-5.62 B.M [39].

The electronic spectra of the iron (III) complexes gave two bands at 9940-9990, and 27440-27650 cm$^{-1}$, which could be assigned to the transitions $^{6}A_{1g}\rightarrow{}^{4}T_{1g}$ and $^{6}A_{1g}\rightarrow{}^{4}T_{2g}$, respectively, suggesting a five coordinated square pyramidal geometry of Fe (III) complexes [40]. The complexesshow magnetic moment values in the range 5.10-5.40 B.M [41].

### 3.5 Thermogravimetric analysis (TGA).

TGA was performed at ambient temperature 900ºC on a Perkin Elmer TGA7 instrument. The sample was heated over the temperature range of 30-900ºC at the heating rate 10ºC min$^{-1}$. TGA was carried out for $[Cr(C_{38}H_{28}N_{12}S_2)NO_3](NO_3)_2$ complex, the complex was decomposed at 900ºC in three steps. The first step shows a steep slope between 90-110ºC indicating the removal of H$_2$O molecule, second step at 200-250ºC attributed to removal of non-coordinated part of the ligand and the third at 450-650ºC corresponding to decomposition of coordinated part of the ligand [42, 43].

**Table 1**: FAB mass spectral data of the trivalent chromium, manganese and iron complexes derived from macrocyclic ligand

| Complexes | Mol. wt. | Molecular ion peak [M]$^{+}$ | Important peak due to complex fragmentation |
|---|---|---|---|
| $C_{52}H_{36}N_{12}O_4$ | 716.20 | 715.20 | 31.0, 75.0, 105.0, 116.0, 232.0, 259.1, 361.1, 463.1, 482.1, 596.1, 711.21 |
| $[Cr(C_{38}H_{28}N_{12}S_2)Cl]Cl_2$ | 873.03 | 872.03 | 31.0, 75.0, 105.0, 116.0, 232.0, 259.1, 361.1, 463.1, 482.1, 596.1, 711.21, 715.2, 766.14, 802.1 |
| $[Cr(C_{38}H_{28}N_{12}S_2)NO_3](NO_3)_2$ | 954.09 | 953.09 | 31.0, 75.0, 105.0, 116.0, 232.0, 259.1, 361.1, 463.1, 482.1, 596.1, 711.21, 715.2, 766.14, 829.12 |
| $[Cr(C_{38}H_{28}N_{12}S_2)OAc](OAc)_2$ | 945.17 | 944.17 | 31.0, 75.0, 105.0, 116.0, 232.0, 259.1, 361.1, 463.1, 482.1, 596.1, 711.21, 715.2, 766.14, 826.15 |
| $[Mn(C_{38}H_{28}N_{12}S_2)Cl]Cl_2$ | 876.03 | 875.03 | 31.0, 75.0, 105.0, 116.0, 232.0, 259.1, 361.1, 463.1, 482.1, 596.1, 711.21, 715.2, 769.10, 805.10 |
| $[Mn(C_{38}H_{28}N_{12}S_2)NO_3](NO_3)_2$ | 957.09 | 956.09 | 31.0, 75.0, 105.0, 116.0, 232.0, 259.1, 361.1, 463.1, 482.1, 596.1, 711.21, 715.2, 769.10, 832.12 |
| $[Mn(C_{38}H_{28}N_{12}S_2)OAc](OAc)_2$ | 948.17 | 947.17 | 31.0, 75.0, 105.0, 116.0, 232.0, 259.1, 361.1, 463.1, 482.1, 596.1, 711.21, 715.2, 769.10, 829.10 |
| $[Fe(C_{38}H_{28}N_{12}S_2)Cl]Cl_2$ | 877.03 | 876.03 | 31.0, 75.0, 105.0, 116.0, 232.0, 259.1, 361.1, 463.1, 482.1, 596.1, 711.21, 715.2, 770.13, 806.10 |
| $[Fe(C_{38}H_{28}N_{12}S_2)NO_3](NO_3)_2$ | 958.09 | 957.09 | 31.0, 75.0, 105.0, 116.0, 232.0, 259.1, 361.1, 463.1, 482.1, 596.1, 711.21, 715.2, 770.13, 833.12 |
| $[Fe(C_{38}H_{28}N_{12}S_2)OAc](OAc)_2$ | 949.17 | 948.17 | 31.0, 75.0, 105.0, 116.0, 232.0, 259.1, 361.1, 463.1, 482.1, 596.1, 711.21, 715.2, 770.13, 830.14 |

### 3.6 Antibacterial activity

The Schiff base ligand, its metal complexes, standard drug Imipenem and DMSO solution control were screened for their antibacterial activity against the bacteria *Staphylococcus aureus* and *Bacillus subtilis* (as gram positive bacteria) and *Pseudomonas aeruginosa, Escherichia coli* and *Salmonella typhi* (as gram negative bacteria), The walls of gram negative cells are more complex than those of gram positive strain. The results of the study are displayed in table 2. The zones of inhibition (ZOI) values obtained indicate that all the complexes towards gram positive and gram negative bacteria are quite significant. Antibacterial study reveals that, metal complexes have more biological activity than free ligand. Complex $[Cr(C_{38}H_{28}N_{12}O_2)OAc](OAc)_2$ shows best antimicrobial activity against the given microorganism. Further to it, the ligand showed moderate, and the complexes moderate to high activities as compared to standard drug towards the all organism. The variation in the antimicrobial inhibition potential of each compound depends on their impermeability of the cell or the differences in ribosomes in microbial strain [44, 45].

**Table 2**. Bactericidal screening data of the ligand and their corresponding metal complexes (inhibition zone in mm)

| Microorganism | Ligand | Complexes | | | | | | | | | Imipenem |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | |
| Gram-positive | | | | | | | | | | | |
| *Staphylococcus aureus* | 34 | 59 | 68 | 89 | -- | 20 | 39 | 28 | 22 | 60 | 100 |
| *Bacillus subtilis* | 32 | 56 | 64 | 87 | 40 | 23 | 37 | 35 | 26 | 56 | 100 |
| Gram-negative | | | | | | | | | | | |
| *Escherichia coli* | -- | 19 | 42 | 66 | 08 | 16 | 33 | 38 | 19 | 29 | 100 |
| *Salmonella typhi* | 08 | 58 | 35 | 60 | 12 | 23 | 34 | 39 | 22 | 31 | 100 |
| *Pseudomonas aeruginosa* | 06 | 37 | 22 | 59 | 07 | 19 | 29 | 32 | 22 | 59 | 100 |

[a] Excellent activity (90-100% inhibition), Good activity (60-70% inhibition), Significant activity (30-50% inhibition), negligible activity (08-20% inhibition),

[b] Complex 1 = $[Cr(HL)Cl]Cl_2$, 2 = $[Cr(HL)NO_3](NO_3)_2$, 3 = $[Cr(HL)OAc](OAc)_2$, 4 = $[Mn(HL)Cl]Cl_2$, 5 = $[Mn(HL)NO_3](NO_3)_2$, 6 = $[Mn(HL)OAc](OAc)_2$, 7 = $[Fe(HL)Cl]Cl_2$, 8 = $[Fe(HL)NO_3](NO_3)_2$, 9 = $[Fe(HL)OAc](OAc)_2$,

[c] Imipenem = Standard drug.

### 3.7 Antifungal activity

The antifungal activity of newly synthesized compounds Schiff base ligand, its metal ion complexes screened a considerable enhancement against *Aspergillus sp*.,*Rizoctonia sp.* and *Penicillium sp*. at 1, 1.5 and 2 mg/ml concentration. DMSO (control) has showed a negligible activity as compare to ligand and M(III) Schiff base metal complexes. However, the metal complexes show better activity than the ligand [46, 47]. The antifungal experimental results of the compounds were compared with the standard antifungal drugs Miconazole. The activity is greatly enhanced at the higher concentration. From the data (table 3) it has been also observed that the activity depends upon the type of metal ion and varies in the following order of the metal ion: Cr > Fe>Mn. $[Cr(C_{38}H_{28}N_{12}S_2)OAc](OAc)_2$ is the only complex to show 96% activity against *Aspergillus sp.*

**Table 3**. Fungicidal screening data of the ligand and their corresponding metal complexes.

| Compound | % Inhibition of spore germination | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Aspergillus sp. (mg/ml) | | | Penicillium sp. (mg/ml) | | | Rizoctonia sp. (mg/ml) | | |
| | 1.0 | 1.5 | 2.0 | 1.0 | 1.5 | 2.0 | 1.0 | 1.5 | 2.0 |
| $C_{52}H_{36}N_{12}O_4$ | 48 | 56 | 61 | 29 | 37 | 42 | 50 | 56 | 59 |
| $[Cr(C_{38}H_{28}N_{12}S_2)Cl]Cl_2$ | 77 | 86 | 89 | 67 | 72 | 84 | 61 | 66 | 68 |
| $[Cr(C_{38}H_{28}N_{12}S_2)NO_3](NO_3)_2$ | 65 | 71 | 82 | 58 | 63 | 75 | 54 | 57 | 64 |
| $[Cr(C_{38}H_{28}N_{12}S_2)OAc](OAc)_2$ | 84 | 88 | 96 | 74 | 79 | 88 | 70 | 74 | 81 |
| $[Mn(C_{38}H_{28}N_{12}S_2)Cl]Cl_2$ | 75 | 80 | 84 | 68 | 70 | 76 | 61 | 65 | 68 |
| $[Mn(C_{38}H_{28}N_{12}S_2)NO_3](NO_3)_2$ | 64 | 68 | 73 | 57 | 61 | 69 | 58 | 60 | 62 |
| $[Mn(C_{38}H_{28}N_{12}S_2)OAc](OAc)_2$ | 81 | 83 | 91 | 68 | 72 | 76 | 60 | 50 | 67 |
| $[Fe(C_{38}H_{28}N_{12}S_2)Cl]Cl_2$ | 70 | 80 | 86 | 63 | 70 | 77 | 56 | 61 | 73 |
| $[Fe(C_{38}H_{28}N_{12}S_2)NO_3](NO_3)_2$ | 53 | 63 | 80 | 56 | 61 | 73 | 50 | 53 | 62 |
| $[Fe(C_{38}H_{28}N_{12}S_2)OAc](OAc)_2$ | 82 | 87 | 91 | 68 | 71 | 81 | 61 | 64 | 77 |
| Miconazole (standard) | 57 | 69 | 100 | 65 | 78 | 83 | 76 | 82 | 94 |

## 4. Conclusion

The electronic spectral data is in the favour of a five coordinate square pyramidal geometry of the complexes. New synthesized compounds were tested for antibacterial evaluation against some pathogenic strains and compared with standard drug. Antibacterial study reveals that, metal complexes have more biological activity than free ligand. Complex $[Cr(C_{38}H_{28}N_{12}O_2)OAc](OAc)_2$ shows best antimicrobial activity against the given microorganism.

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