

Synthesis, Spectral Studies and Antimicrobial Screening of 18-Membered Macrocyclic Complexes of Mn(III) and Fe(III)

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Abstract: A novel series of macrocycles of the type $[MLX]X_2$ (where $M = Mn(III)$ and $Fe(III)$; $L=18$ - membered trioxa-diazamacrocycle; $X = Cl, CH_3COO^-$) have been synthesized by (1+1) cyclocondensation of 4,7,10- trioxatridecane-1,13-diamine with β -diketones such as pentane-2,4-dione, 1-phenylbutane-1,3-dione and 1,3-diphenylpropane-1,3-dione in the presence of trivalent metal salts. The complexes have been characterized with the help of elemental analyses, molar conductances, magnetic measurement, electronic, 1H NMR, IR and mass spectral studies. On the basis of these studies, a six coordinate distorted octahedral geometry for all these complexes has been proposed. These macrocycles were also tested for their in vitro antimicrobial activities on some pathogenic bacterial strain *Streptomyces griseus* (gram-positive, MTCC 706), *Escherichia coli* (gram-negative, MTCC 1652), *Staphylococcus aureus* (gram-positive, MTCC 737), *Pseudomonas aeruginosa* (gram-negative, MTCC 1688) and antifungal activities against *Trichoderma Reesei* (MTCC 164), *Aspergillus niger* (MTCC 282), *Penicillium funiculosum* (MTCC 1013) and *Fusarium oxysporium* (MTCC 2480).

Keywords: Trioxa-diazamacrocycles, IR, magnetic measurement, mass spectral studies, antimicrobial activity

1. Introduction

In recent years coordination chemistry of macrocyclic complexes has been a fascinating area of research in inorganic chemistry all over the world due to its applications in analytical, biomedical and environmental field [1-5]. Macrocycles are the cyclic compounds comprising a ring of at least nine atoms including at least three donor atoms oriented so as to bind to a metal ion [6]. These are thermodynamically, kinetically more stable and more selective metal ion binders than their open chain analogues [7-9]. Some macrocyclic derivatives are fundamental unit in biological functions such as photosynthesis, transport of oxygen in mammalian [10-12]. Synthetic macrocyclic complexes have received much attention due to fact that they mimic important biological ligands in their structure and functions like metalloproteins, hemerythrin and enzymes [13]. There is a continued interest in synthesizing transition metal macrocyclic complexes because of their antibacterial, antifungal and antiviral activities [14]. Macrocyclic ligands containing a heteroatom are important complexing agent for cations, anions and molecules [15]. Condensation reactions between carbonyl compounds and primary amines are the most common reactions in the synthesis of new macrocyclic complexes [16-18].

A large number of reported papers are available on synthesis and characterization of macrocyclic complexes using transition metals as central metal ion. Martinez *et al.* [19] have been reported macrocyclic chiral manganese(III) salen complexes which were used as a catalyst for asymmetric epoxidation. Sharma *et al.* [20] have been synthesized tetraaza macrocyclic complexes of transition metals of Ni(II), Cu(II), Cr(III), Fe(III), Mn(III). Prasad *et al.* [21] have been synthesized macrocyclic complexes of Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) of the type $[ML(NO_3)_2]NO_3$ where $L=$ tetraazamacrocycles having 26- or 28-membered ring.

In the present work, we have synthesized a new series of macrocyclic complexes of the type $[MLX]X_2$ (where $M = Mn(III)$ and $Fe(III)$; $L = 18$ - membered trioxa-diazamacrocycle; $X = Cl, CH_3COO^-$) by (1+1) cyclocondensation of 4,7,10- trioxatridecane-1,13-diamine with β -diketones such as pentane-2,4-dione, 1-phenylbutane-1,3-dione and 1,3-diphenylpropane-1,3-dione in the presence of trivalent metal salts in butanolic medium. These complexes are characterized by molar conductances, magnetic measurement, electronic, 1H NMR, IR, mass spectral studies and in vitro antibacterial and antifungal activities.

2. Experimental

Material

All the chemicals used were of AR grade. 4,7,10-trioxatridecane-1,13-diamine (Merck), pentane-2,4-dione (Aldrich), 1-phenylbutane-1,3-dione (Merck) and 1,3-diphenylpropane-1,3-dione (Merck) were used as supplied and n-butanol (Merck) was distilled before use. $FeCl_3$ (Merck) was of AR grade and $Mn(CH_3COO)_3 \cdot 2H_2O$ was prepared from $Mn(CH_3COO)_2 \cdot 4H_2O$ (Aldrich) [22].

Analytical methods and measurements

Manganese and Iron were determined volumetrically by EDTA using eriochrome black T as indicator. C, H, and N were carried out using an elemental analyzer FLASH 2000. Molar conductances were measured at room temperature in DMF by a Systronic Direct Reading Conductivity Meter-304 using a glass cell having cell constant 1.0 cm^{-1} . Magnetic measurements were carried out on Gouy balance calibrated with $Hg[Co(NCS)_4]$. The IR spectra were recorded as KBr pellets in the region $4000-400 \text{ cm}^{-1}$ on Shimadzu-8400 S FTIR spectrophotometer. 1H NMR spectra were recorded in $DMSO-d_6$ on JEOL FX 90 QFT NMR spectrometer at 90 MHz using TMS as a reference. Electronic spectra (DMSO)

were recorded in the region 200-800 nm on a Hitachi U-2000 spectrophotometer. The mass spectra were recorded on WATERS, Q-TOF MICROMASS (LC-MS).

Pharmacology

Test microorganisms

Eight microbial strains (four bacterial and four fungi) were selected on the basis of their clinical importance in causing disease in humans. Clinical laboratory bacterial isolates of *Streptomyces griseus* (gram-positive, MTCC 706), *Escherichia coli* (gram-negative, MTCC 1652), *Staphylococcus aureus* (gram-positive, MTCC 737) and *Pseudomonas aeruginosa* (gram-negative, MTCC 1688) and fungal isolates of *Trichoderma Reesei* (MTCC 164), *Aspergillus niger* (MTCC 282), *Penicillium funicolusum* (MTCC 1013) and *Fusarium oxysporium* (MTCC 2480) were screened for evaluation of antibacterial and antifungal activities of the synthesized macrocyclic complexes.

Medium

Mueller Hinton Agar (for bacteria) and Sabouraud's dextrose agar, SDA (Merck) (for fungi) were used for the biological assay.

Determination of Antibacterial Assay

In vitro antibacterial activity of the samples gram positive and gram negative bacterial strains by the agar well diffusion method [23]. The Mueller Hinton agar was melted and cooled to 48 - 50°C and a standardized inoculum (1.5×10^8 CFU/mL, 0.5 McFarland) was then added aseptically to the molten agar and poured into sterile petri dishes to give a solid plate. Wells were prepared in the seeded agar plates. The test compound (100 µl) was introduced in the well (6 mm). The plates were incubated overnight at 37°C. The antimicrobial spectrum of the chemical compounds was determined for the bacterial species in terms of zone sizes around each well. The diameters of zone of inhibition produced by the agent were compared with those produced by the commercial control antibiotics, streptomycin. The control zones were subtracted from the test zones and the resulting zone diameter was measured with antibiotic zone reader to nearest mm. The experiment was performed three times to minimize the error and the mean values are presented.

Determination of Antifungal Assay

Anti fungal activity of the experimental sample was investigated by agar well diffusion method [23]. The yeasts and saprophytic fungi were subcultured onto Sabouraud's dextrose agar, SDA (Merck, Germany) and respectively incubated at 37°C for 24 h and 25°C for 2 - 5 days. Suspensions of fungal spores were prepared in sterile PBS and adjusted to a concentration of 10^6 cells/ml. The plates were dried at room temperature for 15 min. Wells of 10 mm in diameter and about 7 mm apart were punctured in the culture media using sterile glass tube. 0.1 ml of several dilutions of fresh chemical compounds was administered to fullness for each well. Plates were incubated at 37°C. After incubation of 24 h bioactivities were determined by measuring the diameter of inhibition zone (in mm). All

experiments were made in triplicate and means were calculated.

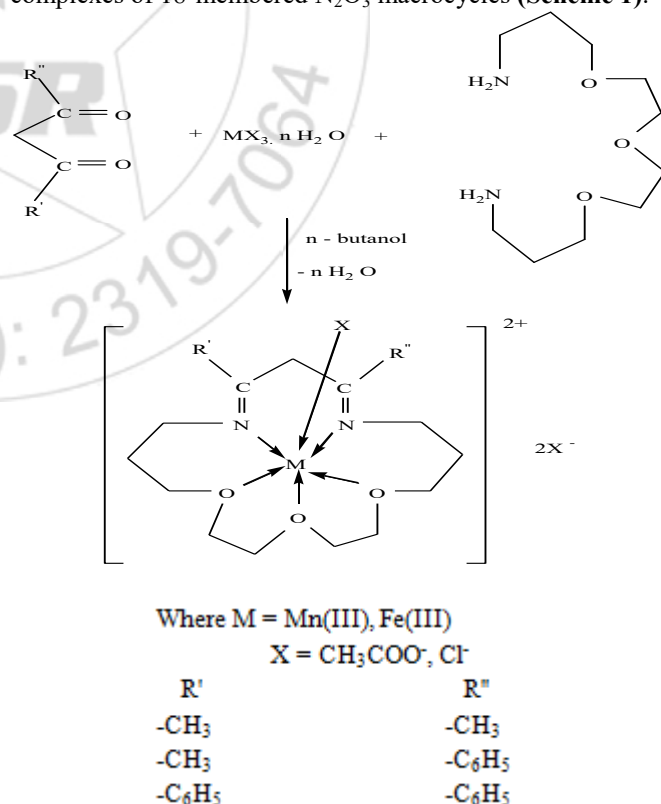
Synthesis of macrocyclic complexes

All the macrocyclic complexes were synthesized by template method. $Mn(CH_3COO)_3 \cdot 2H_2O$ (3.2 mmol, 0.882 g) was dissolved in 20 ml of n-butanol. To this, a solution of pentane-2,4-dione (3.2 mmol, 0.329 g) in ~15 ml n-butanol was added drop wise with constant stirring. It was followed by the addition of a butanolic solution of 4,7,10-trioxatridecane-1,13-diamine (3.2 mmol, 0.724g) drop wise with constant stirring which was continued for ~ 6 h. A brown solid appeared which was filtered, washed with petroleum ether and dried under reduced pressure.

Similarly, Mn(III) complexes of other oxazamacrocycles derived from 4,7,10- trioxatridecane-1,13-diamine and 1-phenylbutane-1,3-dione, 1,3-diphenylpropane-1,3-dione were synthesized. The Fe(III) complexes of oxazamacrocycles with 4,7,10- trioxatridecane-1,13-diamine and pentane-2,4-dione, 1-phenylbutane-1,3-dione, 1,3-diphenylpropane-1,3-dione were also synthesized by similar procedure.

3. Result and Discussion

The reaction of $Mn(CH_3COO)_3 \cdot 2H_2O$ and $FeCl_3$ with 4,7,10- trioxatridecane-1,13-diamine and different β -diketones such as pentane-2,4-dione, 1-phenylbutane-1,3-dione and 1,3-diphenylpropane-1,3-dione in 1:1:1 molar ratios have resulted in the formation of Mn(III) and Fe(III) complexes of 18-membered N_2O_3 macrocycles (**Scheme 1**).



Scheme 1: Synthesis of macrocyclic complexes of Mn(III) and Fe(III)

The complexes of Mn(III) and Fe(III) are red and brown respectively. These complexes are stable at room

temperature and decompose at higher temperature and insoluble in most of the organic solvents such as methanol and chloroform etc. but are soluble in DMSO and DMF. The characteristics and analyses of the complexes are given in **Table 1**.

Molar conductances

The molar conductance values for all the macrocycles of Mn(III) and Fe(III) (10^{-3} M) were determined in DMSO. These values were found in the range of 145-160 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ indicating 1:2 electrolytic nature. Singh *et al.* [24] reported molar conductances of Cr(III), Mn(III) and Fe(III)

complexes of the type $[\text{M}(\text{TML})\text{X}]_2\text{X}_2$ derived from dibenzoyl and thiocarbohydrazide in the range of 150-180 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. Same kind of results of macrocyclic complexes of Mn(III) also reported by Ravinder *et al.* [25].

Magnetic Moments

The magnetic moments of the manganese(III) complexes lay in the range 4.82 to 4.94 μ_B ; which indicates the high spin d^4 system [26]. The magnetic moment values for iron(III) complexes lay in the range 5.83 to 5.95 μ_B ; which corresponds to five unpaired electrons [27].

Table 1: Analytical data of macrocyclic complexes of Mn(III) and Fe(III)

Complex Formula Weight(g)	Color and Decomp. Temp.(°C)	Yield (%)	Found (Cal.) %				μ_B	A_m ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)
			M	C	H	N		
$[\text{Mn}(\text{C}_{15}\text{H}_{28}\text{O}_3\text{N}_2)(\text{OAc})](\text{OAc})_2$ 516.42	Brown 234	48	10.70 (10.64)	44.75 (48.83)	7.35 (7.22)	5.40 (5.42)	4.85	148
$[\text{Mn}(\text{C}_{20}\text{H}_{30}\text{O}_3\text{N}_2)(\text{OAc})](\text{OAc})_2$ 578.49	Brown 240	36	9.55 (9.50)	54.15 (53.98)	6.66 (6.79)	4.80 (4.84)	4.91	155
$[\text{Mn}(\text{C}_{25}\text{H}_{32}\text{O}_3\text{N}_2)(\text{OAc})](\text{OAc})_2$ 640.28	Brown 255	46	8.50 (8.53)	58.00 (58.15)	6.55 (6.45)	4.37 (4.37)	4.85	152
$[\text{Fe}(\text{C}_{15}\text{H}_{28}\text{O}_3\text{N}_2\text{Cl})\text{Cl}]_2$ 446.60	Red 225	54	12.55 (12.50)	40.30 (40.34)	6.40 (6.31)	6.40 (6.27)	5.92	150
$[\text{Fe}(\text{C}_{20}\text{H}_{30}\text{O}_3\text{N}_2\text{Cl})\text{Cl}]_2$ 508.67	Red 236	63	10.90 (10.98)	47.30 (47.23)	6.10 (5.94)	5.65 (5.51)	5.84	145
$[\text{Fe}(\text{C}_{25}\text{H}_{32}\text{O}_3\text{N}_2\text{Cl})\text{Cl}]_2$ 570.74	Red 242	62	9.86 (9.78)	52.75 (52.61)	5.55 (5.65)	5.10 (4.90)	5.88	157

Infra-red spectra

In free pentane-2,4-dione, 1-phenylbutane-1,3-dione and 1,3-diphenylpropane-1,3-dione, bands at 1720, 1724 and 1724 cm^{-1} respectively have been assigned due to $\nu(\text{C}=\text{O})$. A band observed in 3330-3380 cm^{-1} region in the spectra of 4,7,10-trioxatridecane-1,13-diamine, assigned to $\nu(\text{NH}_2)$. In the infra-red spectrum of metal complexes, these bands $\{\nu(\text{C}=\text{O})$ and $\nu(\text{NH}_2)\}$ are disappear and a new medium intensity band in 1580-1610 cm^{-1} confirm the condensation of $>\text{C}=\text{O}$ group of β -diketones and $-\text{NH}_2$ group of oxazadiamine and formation of macrocyclic schiff's base. These bands may be assigned due to $\nu(\text{C}=\text{N})$ stretching vibrations. Similar kind of bands in the region 1590-1620 cm^{-1} also reported by Prasad *et al.* correspond to $\nu(\text{C}=\text{N})$ [28]. A weak to medium intensity absorption bands in the region 420-500 cm^{-1} , which are absent in free ligands, may be assigned as $\nu(\text{M}-\text{O})$ vibrations [29]. In the IR spectra of macrocyclic complexes derived from 1-phenylbutane-1,3-dione or 1,3-diphenylpropane-1,3-dione, a medium intensity absorption band in the region 1400-1500 cm^{-1} may be assigned for phenyl ring absorption [30-31].

Electronic spectra

Manganese(III) has a d^4 ($t_{2g}^3 e_g^1$) high spin configuration. The electronic spectra of Mn(III) complexes of oxazamacrocycles show three transitions: ${}^5B_{1g} \rightarrow {}^5A_{1g}$, ${}^5B_{1g} \rightarrow {}^5B_{2g}$ and ${}^5B_{1g} \rightarrow {}^5E_g$ appearing in the range 12260-12500, 16250-18900 and 35350-35650 cm^{-1} respectively, suggesting an octahedral geometry around Mn(III) ion [32].

Iron(III) has a d^5 ($t_{2g}^3 e_g^2$) high spin configuration. The electronic spectra of Fe(III) complexes of oxazamacrocycles show three absorption bands. The absorption band in the region 13580-13650 cm^{-1} may be due

to ${}^6A_{1g} \rightarrow {}^4T_{2g}$ transition. Absorption band in the region 16400-16950 cm^{-1} may be assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transition. An intense ligand to metal charge transfer band appear in the region 29300- 30150 cm^{-1} [9].

${}^1\text{H-NMR}$ Spectrum

A peak in the region δ 2.48-2.59 ppm is observed in the macrocyclic complexes due to the residual methyl protons of the solvent DMSO. The spectral datas for free diamine are as follows: $-\text{NH}_2$ (4H) singlet at δ 1.48 ppm, $-\text{NH}_2-\text{CH}_2-$ (4H) multiplet at δ 2.85 ppm, $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ (4H) multiplet at δ 2.77 ppm, $-\text{CH}_2-\text{O}$ (4H) triplet at δ 3.15 ppm. A peak in free diamine due to the $-\text{NH}_2$ at δ 1.48 ppm disappears in the spectra of complexes confirm the condensation of $-\text{NH}_2$ group of diamine with $>\text{C}=\text{O}$ group of ketone. In the metal complexes $\text{N}-\text{CH}_2$ (δ 2.35 ppm) and $-\text{CH}_2-\text{O}$ (δ 2.64 ppm) peaks appeared at high field support the coordination of donor atoms to the metal ion. In free pentane-2,4-dione the $-\text{CH}_3$ protons appears at δ 2.17 ppm and $-\text{CH}_2-$ protons at δ 3.54 ppm. In 1-phenylbutane-1,3-dione $-\text{CH}_3$ at δ 2.21 ppm, $-\text{CH}_2-$ at δ at 3.62 ppm and phenyl protons as a multiplate at δ 7.18 ppm. In 1,3-diphenylpropane-1,3-dione peaks at δ 7.22 ppm due to $-\text{ph}$ protons and peaks at δ ppm due to $-\text{CH}_2$ protons reported. In complex methyl proton, methylene proton and phenyl proton shift toward high field.

Mass spectra

LC-MS spectra of Mn(III) and Fe(III) complexes were recorded and spectra of $[\text{Mn}(\text{C}_{20}\text{H}_{30}\text{O}_3\text{N}_2)(\text{OAc})](\text{OAc})_2$ and $[\text{Fe}(\text{C}_{15}\text{H}_{28}\text{O}_3\text{N}_2\text{Cl})\text{Cl}]_2$ complexes are represented in **Fig. 1 and 2**.

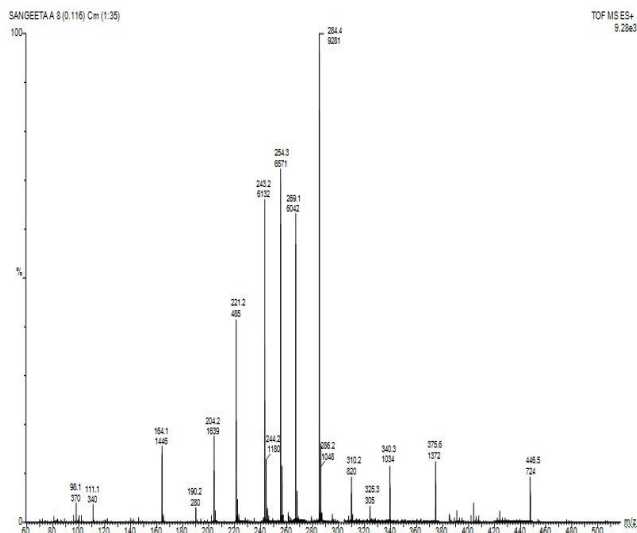


Figure 1: Mass spectrum of $Mn(C_{20}H_{30}O_3N_2)(OAc)(OAc)_2$

In the spectrum of $[Mn(C_{20}H_{30}O_3N_2)(OAc)(OAc)_2]$ complex a low abundance molecular ion peak (M^+) observed at m/z 578.5. A peak with highest abundance observed at m/z 346.3 (base peak) due to the macrocyclic ring which is formed by the condensation of β -diketone and diamine. Similarly many other peaks observed at m/z 460.5, 401.2, 324.6, 309.5, 254.2, 269.5, 331.4 due to different fragments of the complex. $[Fe(C_{15}H_{28}O_3N_2)Cl]Cl_2$ complex show a low abundance molecular ion peak (M^+) at m/z 446.5. A peak with highest abundance known as base peak is due to macrocyclic ring observed at m/z 284.4. Other peaks observed at m/z 375.6, 340.3, 284.4, 269.1, 254.3, 325.3, 310.2 due to different fragments of the complex. These data suggests the 1+1 cyclocondensation of β -diketone and 4,7,10- trioxatridecane-1,13-diamine.

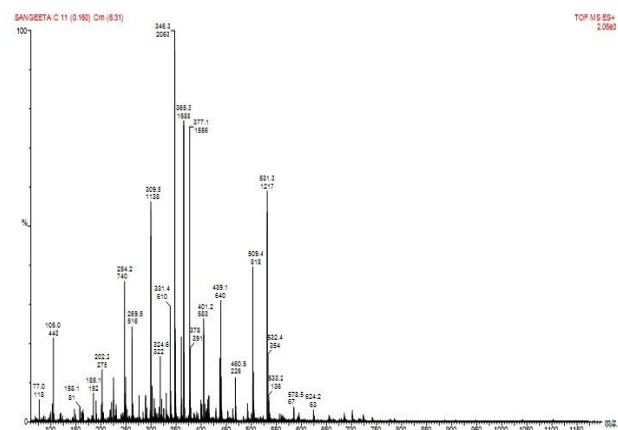


Figure 2: Mass spectrum of $[Fe(C_{15}H_{28}O_3N_2)Cl]Cl_2$

Antibacterial and antifungal activity

Antibacterial and antifungal activities of Fe(III) and Mn(III) macrocyclic complexes have been screened and reported in Table 2 & 3. The antibacterial behaviour of $[Fe(C_{15}H_{28}O_3N_2)Cl]Cl_2$ and $[Mn(C_{15}H_{28}O_3N_2)(OAc)(OAc)_2]$ against *E. coli* were shown in Fig. 3. All these synthesized macrocyclic complexes showed good antimicrobial activity. The datas in table 2 showed that the macrocyclic complexes did not show antibacterial activity against *P. aeruginosa*. On increasing the concentration inhibitory activity of complexes also increased. It is observed that Fe(III) complexes show more inhibitory activity as compared to Mn(III) complexes. All the complexes showed higher activities against *S. griseus* and *E. coli*. The activity of metal complexes was found to be similar to standard antibiotics which indicate that it has better antibacterial activity. The antimicrobial activity can be explained on the basis of chelation theory. Chelation may enhance the biochemical potency of bioactive species. It enhances the penetration of complex in to lipid membrane and blocking of the metal binding sites in the enzymes of microorganisms.

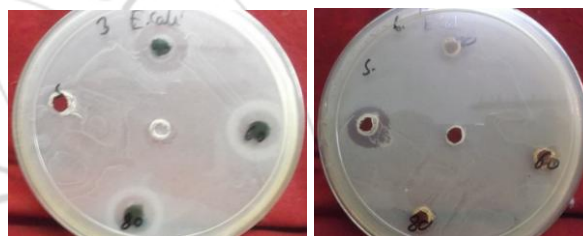


Figure 3: Photograph showing antibacterial studies of $[Fe(C_{15}H_{28}O_3N_2)Cl]Cl_2$ and $[Mn(C_{15}H_{28}O_3N_2)(OAc)(OAc)_2]$ against *E. coli*

Table 2: Antibacterial screening data of macrocyclic complexes (conc. in mg/ml)

Complexes	Diameter of zone of inhibition (mm)											
	<i>S. griseus</i> (+ve)			<i>E. coli</i> (-)			<i>S. aureus</i> (+)			<i>P. aeruginosa</i> (-ve)		
	40	80	100	40	80	100	40	80	100	40	80	100
$[Mn(C_{15}H_{28}O_3N_2)(OAc)(OAc)_2]$	4	--	14	4	5	8	4	8	10	--	--	--
$[Mn(C_{20}H_{30}O_3N_2)(OAc)(OAc)_2]$	--	9	12	--	8	10	7	10	12	--	--	--
$[Mn(C_{25}H_{32}O_3N_2)(OAc)(OAc)_2]$	10	11	14	--	11	12	--	11	12	--	--	--
$[Fe(C_{15}H_{28}O_3N_2)Cl]Cl_2$	14	22	28	14	10	14	--	8	--	--	--	--
$[Fe(C_{20}H_{30}O_3N_2)Cl]Cl_2$	6	10	11	--	12	14	--	6	10	--	--	--
$[Fe(C_{25}H_{32}O_3N_2)Cl]Cl_2$	--	7	8	4	10	13	4	8	14	--	--	--
Streptomycin	15	17	18	16	18	22	12	15	18	13	15	17

Table 3: Antifungal screening data of macrocyclic complexes (conc. in mg/ml)

Complexes	Diameter of zone of inhibition (mm)											
	<i>T. reesei</i>			<i>A. niger</i>			<i>P. funiculosum</i>			<i>F. oxysporium</i>		
	40	80	100	40	80	100	40	80	100	40	80	100
[Mn(C ₁₅ H ₂₈ O ₃ N ₂)(OAc)](OAc) ₂	--	8	12	6	10	12	--	12	12	10	10	12
[Mn(C ₂₀ H ₃₀ O ₃ N ₂)(OAc)](OAc) ₂	--	10	11	--	11	12	--	10	12	--	11	15
[Mn(C ₂₅ H ₃₂ O ₃ N ₂)(OAc)](OAc) ₂	--	12	14	12	14	16	4	13	15	--	12	14
[Fe(C ₁₅ H ₂₈ O ₃ N ₂)Cl]Cl ₂	8	12	13	12	12	14	--	12	12	--	10	14
[Fe(C ₂₀ H ₃₀ O ₃ N ₂)Cl]Cl ₂	6	10	14	10	11	14	--	10	12	8	9	12
[Fe(C ₂₅ H ₃₂ O ₃ N ₂)Cl]Cl ₂	--	11	13	8	9	11	--	11	14	10	13	13
Ketakenazole	12	14	18	14	16	18	12	14	16	12	15	18

4. Conclusion

In the present work metal complexes were synthesized successfully. On the basis of elemental analyses, molar conductances, magnetic measurement, H¹NMR, IR and mass spectral studies, a hexacoordinated environment around the metal ion is proposed for all the complexes. The antimicrobial screening of synthesized complexes carried out against the bacteria *Streptomyces griesus*, *Escherichia coli*, *Staphylococcus aureus*, *Pseudomonas aeruginosa* and fungi *Trichoderma Reesei*, *Aspergillus niger*, *Penicillium funiculosum*, *Fusarium oxysporium*. It is observed that Fe(III) complexes show more inhibitory activity as compared to Mn(III) complexes.

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References

- [1] S Ilhan and H Temel (2007) Synthesis and characterization of a new macrocyclic schiff base derived from 2,6-diaminopridine and 1,10-bis(2-fromyl phenyl)-1,4,7,10-tetraoxadecane and its Cu(II), Ni(II), Pb(II), Co(III) and La(III) complexes, *Transition Metal Chemistry* 32:1039-1046.
- [2] A Chaudhary, N Bansal, A Gajraj and R V Singh (2003) Antifertile, antibacterial, antifungal and percent disease incidence aspects of macrocyclic complexes of manganese(II), *Journal of Inorganic Biochemistry* 96(2):393-400.
- [3] D Parker and J A G Williams (1996) Getting excited about lanthanide complexation chemistry, *Journal of Chemical Society, Dalton Transaction* 18:3613-3628.
- [4] Anupma, S Chandra, D Jain and S Soam (2015) Spectroscopic Approach of Macrocyclic Complexes of Mn(II) with a New Azamacrocyclic Tetra Dentate Ligand, *International Journal Of Advance Research In Engineering Technology & Sciences* 2(5):1-4.
- [5] R D Guy and C L Chakrabarti (1976) Studies of metal-organic interaction in model systems pertaining to natural waters, *Canadian Journal of Chemistry* 54(16):2600-2611.
- [6] W. C. Still and I. Galyner (1981) Chemical consequences of conformation in macrocyclic compounds: An effective approach to remote asymmetric induction, *Tetrahedron* 37:3981-3996.
- [7] K Sharma, Parveen, D P Singh and R Chopra (2015) Antibacterial and spectroscopic studies of biologically active macrocyclic complexes of divalent metal ions, *Der Pharma Chemica* 7(2):292-300.
- [8] M T H Tarafder, N Saravanan, K A Crouse and A M B Ali (2001) Coordination chemistry and biological activity of nickel(II) and copper(II) ion complexes with nitrogen-sulphur donor ligands derive from S-benzylthiocabazate (SBDC), *Transition Metal Chemistry* 26(6):613-618.
- [9] S Chandra, K Gupta and S Sharma (2001) Synthesis and spectral studies of transition metal complexes with 5,7,12,14-tetramethyl-14,8,11-tetraazacyclotetradeca-4,7,11,14-tetraene, a fourteen-membered tetradentate macrocyclic ligand, *Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry* 31(7):1205-1215.
- [10] S Chandra and K Gupta (2002) Chromium(III), manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes with a pentadentate, 15-membered new macrocyclic ligand, *Transition Metal Chemistry* 27:196-199.
- [11] D Luneau, J M Savariault, P Cassoux and J P Tuchaques (1988) Polynuclear manganese(II) complexes with Robson-type ligands: Synthesis, characterization, molecular structure and magnetic properties, *Journal of Chemical Society, Dalton Transitions* 5:1225-1235.
- [12] Y Agnus, R Louis, J P Gisselbrecht and R Weiss (1984) Dicopper(II) Choro and Azido Inclusion Complexes of the [24-ane-N₂S₄] Binucleating Macrocycles. Synthesis, Crystal and Molecular Structures, and Spectral, Magnetic and Electrochemical Properties, *Journal of the American Chemical Society* 106(1):93-102.
- [13] Rajni and L Singh (2013) A review on synthesis and application of macrocyclic ligands and their transition metal complexes, *International Journal of Advanced Engineering Applications* 6(6):74-88.
- [14] S Chandra, D Jain, A K Sharma and P Sharma (2009) Coordination Modes of a Schiff Base Pentadentate Derivative of 4-Aminoantipyrine with Cobalt(II), Nickel(II) and Copper (II) Metal Ions: Synthesis, Spectroscopic and Antimicrobial Studies, *Molecules* 14:174-190.
- [15] A A Khndar, S A H Yazdi, M Khatamina, P McArdle and S A Zarei (2007) Synthesis, characterization and

- structure of nickel(II) complexes of a 16-membered mixed-donor macrocyclic Schiff base ligand, potentially hexadentate, bearing two pendant alcohol, *Polyhedron* 26(1):33-38.
- [16] D Kumar and Sandhya (2014) Synthesis, spectral and antimicrobial studies of tetraazamacrocyclic complexes of bivalent transition metal ions of bioinorganic relevance, *Journal of Chemical and Pharmaceutical Research* (6):746-750.
- [17] R N Prasad and A Jain (2007) Synthesis and spectral characterization of zinc(II) complexes of 12-membered oxa-azamacrocycles, *Indian Journal of Chemistry* 46A:1782-1786.
- [18] H I Ugras, I Basaran, T Kilic and U Cakir (2006) Synthesis, Complexation and antifungal, antibacterial Activity Studies of a New Macrocyclic Schiff Base, *Journal of Heterocyclic Chemistry* 43:1679-1684.
- [19] A Martinez, C Hemmert, C Loup, G Barre and B Meunier (2006) Synthesis of New Macrocyclic Chiral Manganese(III) Schiff Bases as Catalyst for Asymmetric Epoxidation, *Journal of Organic Chemistry* 71:1449-1457.
- [20] R Sharma, Prabhat, R Singh, S Pawar and A Chauhan (2010) Studies of Transition Metal Complexes and Their Antibacterial Activities, *Journal of American Science* 6(9):559-564.
- [21] R N Prasad and M Mathur (2006) Cr^{III}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II} and Zn^{II} complexes of 26- and 28-membered tetraazamacrocycles, *Journal of Indian Chemical Society* 83:208-213.
- [22] El A I Heiba, R M Dessau and W J Kowhljr (1969) Oxidation by metal salts. III. Reaction of manganic acetate with aromatic hydrocarbons and the reactivity of the carboxymethyl radical, *Journal of the American Chemical Society* 91(1):138.
- [23] I Ahmad and A J Beg (2001) Antimicrobial and phytochemical studies on 45 indian medicinal plants against multi-drug resistant human pathogens, *Journal of Ethnopharmacology* 74:113-123.
- [24] D P Singh and R Kumar (2007) Trivalent metal ion directed synthesis and characterization of macrocyclic complexes, *Journal of the Serbian Chemical Society* 72(11):1069-1074.
- [25] K Shanker, M Ashok, P M Reddy, R Rohini and V Ravinder (2009) Spectroscopic characterization and antibacterial activities of Mn(III) complexes containing the tetradentate aza Schiff base ligands, *International Journal of ChemTech Research* 1(3):777-783.
- [26] T Kurahashi and H Fujii (2011) One-Electron Oxidation of Electronically Diverse Manganese(III) and Nickel(II) Salen Complexes: Transition from Localized to Delocalized Mixed Valence Ligand Radicals, *Journal of the American Chemical Society* 133:8307-8316.
- [27] S K Gupta and Y S Kushwah (2001) Mononuclear iron(III) macrocyclic complexes derived from 4-methyl-2,6-di(formyl/benzoyl)phenol and diamine: synthesis, spectral speciation and electrochemical behavior, *Polyhedron* 20(15):2019-2025.
- [28] R N Prasad, S Chaudhary and A Jain (2014) Synthesis and spectral studies of chromium(III) and iron(III) complexes of trioxadiazamacrocycles, *Journal of the Indian Chemical Society* 91:137-141.
- [29] K K Narang and A Agarwal (1974) Salicylaldehyde salicylhydrazone complexes of some transition metal ions, *Inorganica Chimica Acta* 9:137-142.
- [30] R N Prasad, M Mathur and A Upadhyay (2007) Synthesis and spectroscopic studies of Cr (III), Fe (III) and Co (II) complexes of hexaazamacrocycles, *Journal of the Indian Chemical Society* 84:1202-1204.
- [31] J Costamagna, G Ferraudi, M Villagran and E Wolcan (2000) Ligand luminescence and photoinduced charge separation in bis(naphthalene) substituted fourteen-membered tetraazamacrocyclic complexes of Cu^{II} and Ni^{II}, *Journal of the Chemical Society, Dalton Transactions*:2631-2637.
- [32] D P Singh and V B Rana (1995) Binuclear chromium(III), manganese(III) iron(III) and cobalt(III) complexes bridged by diaminopyridine, *Polyhedron* 14(20):2901-2906.