

RESEARCH ARTICLE

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Biologically Important Drugs**

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Synthesis, Structural Characterization and Antimicrobial Activity Evaluation of Manganese(II) Complexes with Biologically Important Drugs

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Abstract

The mononuclear Mn(II) complexes of the type $[Mn(L)_n(H_2O)_2Cl_2]$ (where $n=1$ or 2) were prepared with biologically important drugs viz. Clomiphene citrate (CPC), Imipramine hydrochloride (IMH), Diphenylpyraline hydrochloride (DPH), Embramine hydrochloride (EBH), and Dothiepin hydrochloride (DOT), and characterized by using elemental analysis, infra-red (IR), UV-visible spectra, X-ray powder diffraction studies and thermogravimetric analysis. The molar conductance measurement of all the complexes in DMF solution corresponds to non-electrolytic nature. All complexes were of the high-spin type and found to have six-coordinate octahedral geometry. The antimicrobial activity of these complexes has been screened against two gram-positive and two gram-negative bacteria. Antifungal activity against two different fungi has been evaluated and compared with standard drug. All the complexes inhibit the growth of both gram positive and gram negative bacteria to competent level.

Keywords: Mn complexes; spectral studies; X-ray powder diffraction; antimicrobial activity.

1. Introduction

Metal ions play a vital role in a vast number of biological processes. Uses of metal ions in therapeutic agents are known to accelerate drug action and their efficacy is enhanced upon coordination with a metal ion [1, 2]. The antimicrobial properties of metal complexes have been recognized for centuries and have represented some of the most fundamental breakthroughs in medicinal history [3].

Mn is an essential trace element for all forms of life. The synthesis and characterization of the complexes of Mn(II) of different ligands are of growing interest in coordination chemistry [4]. Many Mn complexes were synthesized as functional models ranging from Mn catalase enzyme [5] to benzyl alcohol oxidation [6], C-H bond activation [7], and cis-dihydroxylation and epoxidation of alkenes [8]. The coordination chemistry of Mn complexes with nitrogen donor moieties is of interest as these complexes give information about the functional role of Mn(II) in biological system [9]. The problem of antibiotic resistance has now reached a crisis and there is a need to redouble efforts towards the design of new drugs. A number of reports show the use of Mn complexes as both antibacterial and antifungal agents [10-14].

In the present work, we synthesized and analyzed the IR, electronic spectra and did elemental analysis, magnetic susceptibility, conductance measurements, X-ray powder diffraction studies and thermogravimetric analysis of Mn(II) complexes (Figure 1) of some biologically important drugs. In view of the biological activity of the complexes and diverse coordinating ability of the ligands, we were provoked to study the Mn(II) complex of nitrogen based ligand against microbial strains, viz. *E. coli*, *S. aureus*, *P. aeruginosa*, *B. subtilis* and fungal strains *A. flavus* and *A. niger*, to study the role of the complexes as antimicrobial compounds.

2. Methods

2.1. Material

The ligands CPC (Clomiphene citrate, Cipla Ltd., India); IMH (Imipramine hydrochloride, Sun Pharmaceuticals Ltd., India); DPH (Diphenylpyraline hydrochloride and EBH (Embramine hydrochloride, SKF Ltd., India); and DOT (Dothiepin hydrochloride, Intas Laboratories Ltd., India), were received from as gift sample and used as received.

Among the solvents employed DMF and DMSO were of spectroscopic grade and remaining solvents were of AR grade. The commercial ethanol sample was refluxed over calcium oxide for 6 h, distilled and used.

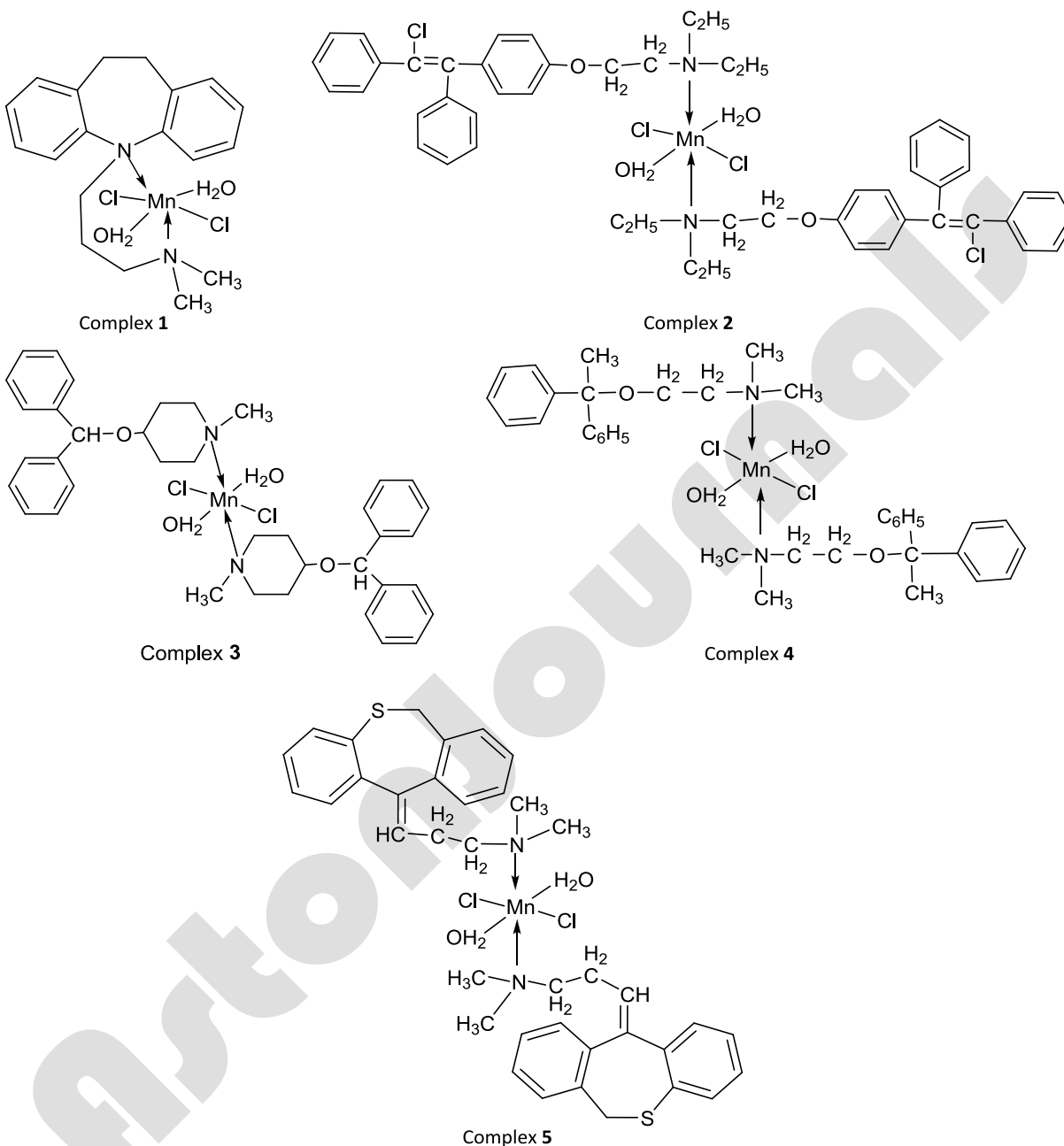


Figure 1: Suggested structure of the prepared of complexes (1-5).

2.2. Physical measurements

Elemental analyses (C, H, N) were carried out using an Elementar Vario EL-III instrument. FTIR spectra for samples were recorded using Jasco FT-IR- 4100 spectrometer. $^1\text{H-NMR}$ spectra were recorded in DMSO-d_6 on AMX-400 FT-NMR spectrometer. Electronic spectra of the complexes in the UV-visible region (200-900 nm) were measured using a Jasco UVIDEc-610 double beam spectrophotometer with quartz cells. Electrical conductance measurements of the prepared complexes were done using an Elico CM-180 conductometer. Melting points were determined in an open capillary tube on Mel-temp apparatus. Magnetic susceptibility data in the room temperature were obtained from Gouy method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant. The TG and DTA patterns of the

complexes were recorded on a Perkin Elmer US TGA-7 analyzer in the atmosphere of air. X-ray diffraction patterns were obtained with a DE-CER P12 X-ray diffractometer using Cu-K α radiation filtered by a nickel foil over a range of diffraction angle $2\theta = 3-50^\circ$ and $3-60^\circ$ in the complexes studied. The wavelength of the radiation was 1.5412 Å. Metal and chloride contents in the complexes were estimated volumetric and gravimetric method, respectively by using standard procedures [15].

2.3. General procedure for the preparation of complexes

A volume of 50 mL ethanolic solution containing 5 mmol ligand (IMH) was slowly added to 50 mL of 5 mmol ethanolic solution of the Mn(II) chloride or 50 mL of 2.5 mmol of Mn(II) was used in the case of other ligands (CPC, DPH, EBH and DOT). The mixture was then refluxed on a water bath at 60-70 °C for 2 h with continuous stirring. The precipitate obtained in each case after cooling to room temperature were filtered and washed several times with alcohol, finally with ether and dried over anhydrous CaCl₂.

3. Results and Discussion

All the prepared Mn(II) chloride complexes are crystalline solids. All the Mn(II) complexes obtained were having light brown color and the decomposition temperature of the complexes are reported in Table 1. The complexes are stable ordinary conditions and are non-hygroscopic. All the complexes are insoluble in water and common organic solvents but readily soluble in DMF and DMSO. The analytical data of the complexes in Table 1 and Table 2 indicate that the 1:1 (metal:ligand) stoichiometry for Mn(II) chloride complex of IMH having the general formula [Mn(IM)(H₂O)₂Cl₂]. Whereas the stoichiometry was 1:2 for Mn(II)chloride complexes of CPC, DPH, EBH and DOT with the general formula [Mn(L)₂(H₂O)₂Cl₂], where L = CP, DP, EB, DOT.

The molar conductance data of Mn(II) complexes in dimethyl formamide at 10⁻³ M are presented in Table 2. The molar conductance values lie in the range 16.3-19.4 Ohm⁻¹ cm² mol⁻¹ indicating the non-electrolytic nature of the complexes. The non-zero values are due to slight solvolysis of the complexes [16].

Table 1: Physical and analytical data of the metal complexes.

Complex	Mol. Wt.	M.P. °C	Found (Calc.) %			
			C	H	N	M
1 [Mn(IM)(H ₂ O) ₂ Cl ₂]	442.28	196-198	50.34 (51.55)	6.09 (6.33)	6.84 (6.33)	13.26 (12.43)
2 [Mn(CP) ₂ (H ₂ O) ₂ Cl ₂]	973.84	221-223	65.19 (64.07)	5.78 (6.16)	3.06 (2.87)	4.96 (5.64)
3 [Mn(DP) ₂ (H ₂ O) ₂ Cl ₂]	724.64	190-192	61.35 (62.92)	6.22 (6.89)	4.13 (3.86)	7.87 (7.58)
4 [Mn(EB) ₂ (H ₂ O) ₂ Cl ₂]	858.48	213-214	49.23 (50.32)	6.18 (5.59)	3.88 (3.26)	6.90 (6.40)
5 Mn(DOT) ₂ (H ₂ O) ₂ Cl ₂]	752.78	202-204	61.79 (60.57)	6.82 (6.11)	4.23 (3.71)	7.76 (7.30)

3.1. Magnetic susceptibility

Mn(II) complexes obtained in the present investigation are paramagnetic having the effective magnetic moment values 5.79-5.96 BM (Table 2). The contribution to the magnetic moment is from spin only value [17]. The observed magnetic moment values show the presence of five unpaired and reflect a high-spin octahedral geometry involving d²sp³ hybridization around Mn(II) ion.

Table 2: Electronic spectra and magnetic moments of the metal complexes.

Complex	Electronic spectral bands (cm ⁻¹)	Λ Ohm ⁻¹ cm ² mol ⁻¹	μ_{eff} (BM)
1	13699, 15940, 21865	17.4	5.83
2	13562, 22453, 34167	16.3	5.79
3	13878, 16977, 22262	19.4	5.96
4	13699, 15873, 21470	17.2	5.93
5	13677, 15940, 21865	17.4	5.88

3.2. Electronic spectra

The majority of Mn(II) complexes are high-spin. In octahedral fields this configuration gives spin-forbidden as well as parity-forbidden transitions, thus accounting for the extremely pale colour of such compounds [18]. In tetrahedral environments, the transition are still spin-forbidden but no longer parity-forbidden, therefore, the compounds have noticeable pale yellow-green colour. The solution spectra was recorded for the Mn(II) complexes and the resultant data are presented in the Table 2 and the spectra are given in Figure 2. The electronic spectral bands observed in the region 13562-13878, 15873-16977 and 21470-22262 cm^{-1} in the spectra of Mn(II) complexes may be assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4A_{1g}, {}^4E_g$, respectively [19]. The band at 34000 cm^{-1} has been regarded as ligand-metal charge transfer band [20]. The electronic spectral data of Mn(II) complexes suggest an octahedral arrangement of ligand atoms around Mn(II) ion [21-23].

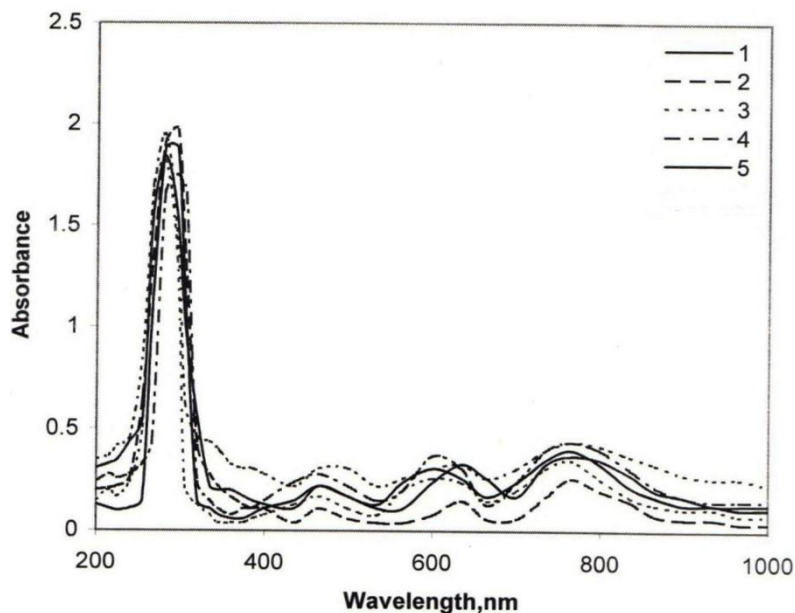


Figure 2: Electronic spectra of (1) $[\text{Mn}(\text{IM})(\text{H}_2\text{O})_2\text{Cl}_2]$; (2) $[\text{Mn}(\text{CP})_2(\text{H}_2\text{O})_2\text{Cl}_2]$; (3) $[\text{Mn}(\text{DP})_2(\text{H}_2\text{O})_2\text{Cl}_2]$; (4) $[\text{Mn}(\text{EB})_2(\text{H}_2\text{O})_2\text{Cl}_2]$; (5) $[\text{Mn}(\text{DOT})_2(\text{H}_2\text{O})_2\text{Cl}_2]$.

3.3. IR spectra

The IR spectra of ligands and their Mn(II) complexes data are presented in Table 3. In complex 1 the broad band around 3000-2850 cm^{-1} and 2830-2300 cm^{-1} obtained for IMH has completely disappeared indicating the heterocyclic nitrogen and nitrogen atom of the side chain are the site of coordination [24].

Table 3: Characteristic IR bands (cm^{-1}) of the ligands and their Mn(II) complexes.

Complex	$\nu(\text{N-CH}_3)$	$\nu(\text{N-CH}_2)$	$\nu(\text{OH})$	$\nu(\text{Mn-N})$	$\nu(\text{Mn-Cl})$
IMH	3000-2850	2830-2300	—	—	—
CPC	$\nu(\text{N-C}_2\text{H}_5)$ 2760-2320	—	—	—	—
DPH	3015-2850	—	—	—	—
EBH	2700-2300	—	—	—	—
DOT	2700-2300	—	—	—	—
1	—	—	3610	440	324
2	—	—	3520	435	333
3	—	—	3480	423	326
4	—	—	3460	422	350
5	—	—	3300	413	344

The IR spectra of the ligand DPH, show a strong and broad band in the region $3015\text{--}2850\text{ cm}^{-1}$, which can be assigned to heterocyclic nitrogen atom with alkyl group. In the spectra of complex 3, this broad band has disappeared indicating that the heterocyclic nitrogen atom of the ligand is the site of coordination. The ligand CPC, EBH and DOT shows strong and broad bands in the region $2760\text{--}2320\text{ cm}^{-1}$, which can be assigned to tertiary nitrogen of the side chain. In the spectra of corresponding complexes 2, 4 and 5 this band has disappeared thereby indicating that the tertiary nitrogen atom of the side chain in the ligand is the site of coordination. The bands at $1150\text{--}1050\text{ cm}^{-1}$ which can be attributed to $\nu\text{C-O-C}$ in the ligand CPC, DPH and EBH remains unaffected in the respective Mn(II) complexes suggesting that the oxygen atom was not involved in the bonding with Mn(II) ion. The $\nu\text{C-S-C}$ vibrations in the ligand DOT and its complex were observed in the region 760 cm^{-1} suggests that the sulphur atom was not involved in the bonding. In the spectra of all the new complexes of Mn(II) a new band appeared in the region $3600\text{--}3300\text{ cm}^{-1}$ is due to νOH vibration of coordinated water molecule. The presence of coordinated water is also confirmed from TG studies. The new bands at $410\text{--}430\text{ cm}^{-1}$ and $320\text{--}350\text{ cm}^{-1}$ are assigned to $\nu\text{Mn-N}$ and $\nu\text{Mn-Cl}$, respectively.

3.4. X-ray powder diffraction studies

The x-ray diffractogram obtained for the complex $[\text{Mn}(\text{IM})(\text{H}_2\text{O})_2\text{Cl}_2]$ records 23 reflections between $3\text{--}60^\circ$ (2θ). All the peaks have been indexed [25, 26] and their $\sin^2\theta$ values compared with calculated one, which reveal that there is a good agreement between calculated and observed values of $\sin^2\theta$. The unit cell parameters were calculated by trial and error method [27-29]. The unit cell parameter obtained for the complex are $a = 27.3520\text{ \AA}$, $b = 10.3670\text{ \AA}$, $c = 12.4896\text{ \AA}$, $\beta = 118.656^\circ$ with cell volume $V = 3107.74\text{ \AA}^3$.

The x-ray diffractograms obtained for the complexes of $[\text{Mn}(\text{DOT})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ and $[\text{Mn}(\text{DP})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ (Figure 3), records 22 and 21 reflections between 10 and 60° (2θ), respectively. The unit cell parameter obtained for the $[\text{Mn}(\text{DOT})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex are $a = 16.9531\text{ \AA}$, $b = 10.9649\text{ \AA}$, $c = 14.9625\text{ \AA}$, $\beta = 90.974^\circ$ with cell volume $V = 2780.97\text{ \AA}^3$ and for $[\text{Mn}(\text{DP})_2(\text{H}_2\text{O})_2\text{Cl}_2]$ complex are $a = 27.2915\text{ \AA}$, $b = 4.3962\text{ \AA}$, $c = 17.5044\text{ \AA}$, $\beta = 101.438^\circ$ with cell volume $V = 2058.44\text{ \AA}^3$.

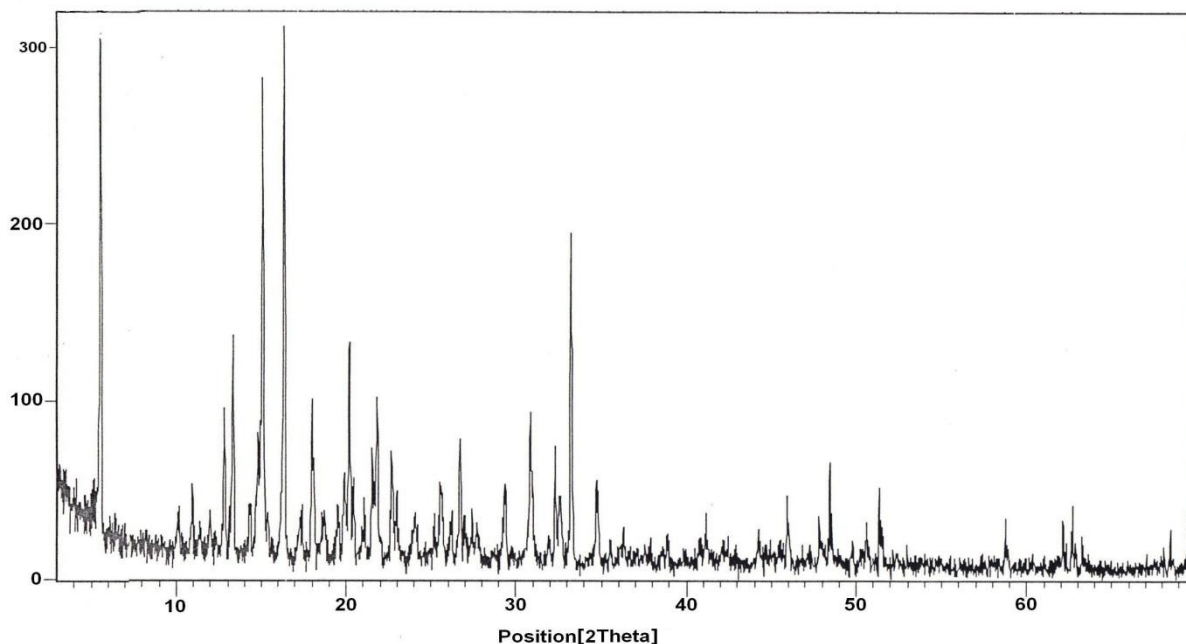


Figure 3: X-ray diffractogram of $[\text{Mn}(\text{DP})_2(\text{H}_2\text{O})_2\text{Cl}_2]$.

3.5. Thermogravimetric analysis

All other complexes of Mn(II) chloride with IMH, EBH, DOT, CPC and DPH follow the same trend in the thermal degradation (Table 4). The first step was followed by a mass change in the range $152\text{--}230^\circ\text{C}$ corresponds to the

loss of two molecules of water. The second thermal degradation step of Mn(II) complexes occurs at the temperature range 230-460 °C and the weight loss in this step corresponds to the expulsion of one molecule of IM ligand and two molecules of CP, EB, DOT and DP ligands. In the third thermal degradation step of Mn(II) complexes occurs at the temperature range 460-620 °C. The weight loss in this step was in full agreement with the present weight calculated on the basis of stoichiometry proposed for the complexes.

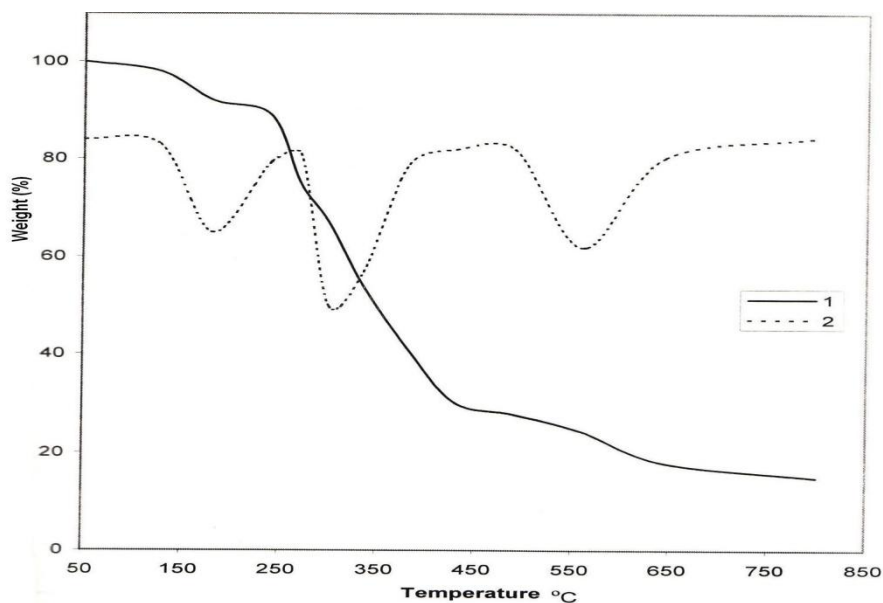


Figure 4: (1)TGA and (2)DTA curves of the complex $[\text{Mn}(\text{CP})_2(\text{H}_2\text{O})_2\text{Cl}_2]$.

The final residue of the decomposition at above 530 °C in the Mn(II) complexes corresponds to Mn(II) oxide, which was in conformity with the observed and calculated weight of pyrolysis products. Thermal analyses data supports the 1:1 (metal:ligand) stoichiometry for Mn(II) chloride complexes with IMH and 1:2 stoichiometry for Mn(II) chloride complexes with CPC, DPH, EBH and DOT. Thermogravimetric data also support the presence of coordinated water. All the complexes are anhydrous and thermally stable.

Table 4: Stepwise thermal degradation data obtained from TGA curves.

Complex	Temp. Range (°C)	Degradation of products	% Weight loss		% Residue (MnO)	
			Cal.	Expt.	Cal.	Expt.
1	174-210	2 H ₂ O	8.13	7.66	16.04	16.40
	220-360	IM	63.39	62.93		
	400-580	2 Cl	16.03	15.86		
2	152-205	2 H ₂ O	3.69	4.22	7.38	7.92
	230-380	2 CP	83.37	81.78		
	440-620	2 Cl	3.64	3.05		
3	190-240	2 H ₂ O	4.96	4.22	9.79	9.02
	290-460	2 DP	77.66	75.58		
	520-600	2 Cl	9.78	8.92		
4	170-205	2 H ₂ O	4.19	3.98	8.26	7.91
	250-308	2 EB	81.14	79.41		
	360-570	2 Cl	8.25	7.52		
5	185-210	2 H ₂ O	4.78	4.28	9.42	8.38
	235-430	2 DOT	78.49	76.94		
	460-580	2 Cl	9.41	8.14		

3.6. Antimicrobial studies

Antimicrobial activity of Mn(II) chloride complexes of IMH, CPC, DPH, EBH and DOT was determined against *E. coli*, *S. aureus*, *P. aeruginosa* and *B. subtilis* by disk diffusion method. Antifungal activity of the prepared compounds was tested against two fungi, *A. flavus* and *A. niger* by *B.* poisoned food technique. The activities of the compounds were compared with those of standard Chloramphenicol for antibacterial and Griseofulvin for antifungal activity. The results of the percentage inhibition of both bacterial and fungal growth are presented in Tables 5 and 6.

Table 5: Antibacterial screening data of the ligands and their metal complexes.

Compound	Percentage Inhibition Zone (\pm)							
	<i>S. aureus</i>		<i>E. coli</i>		<i>P. aeruginosa</i>		<i>B. subtilis</i>	
	30 μ g	60 μ g	30 μ g	60 μ g	30 μ g	60 μ g	30 μ g	60 μ g
IMH	0.0	3.5	0.0	2.4	0.0	3.0	0.0	4.2
CPC	1.1	6.7	0.6	6.5	1.2	6.7	0.8	6.2
DPH	1.7	9.7	1.4	8.2	2.1	9.4	2.2	10.3
EBH	0.0	3.2	0.0	3.4	0.0	2.9	0.0	4.0
DOT	0.0	2.4	0.0	2.3	0.0	3.5	0.0	3.2
1	5.2	11.0	5.7	9.4	6.9	12.8	5.8	12.6
2	7.3	14.4	5.5	12.8	8.1	12.3	7.7	13.9
3	16.2	28.2	9.5	23.3	10.0	22.4	11.1	25.4
4	3.3	9.1	2.5	6.2	4.3	11.0	3.6	10.4
5	3.5	7.2	2.1	6.0	3.6	8.0	3.1	8.5
Chloramphenicol	100	100	100	100	100	100	100	100

DMSO showed no inhibition, each value is the average of four replicates.

Table 6: Antifungal screening data of the ligands and their metal complexes.

Compound	Percentage Inhibition Zone (\pm)			
	<i>A. flavus</i>		<i>A. niger</i>	
	30 μ g	60 μ g	30 μ g	60 μ g
IMH	0.0	2.2	0.0	4.1
CPC	2.3	3.3	1.7	3.4
DPH	11.7	22.4	12.2	24.0
EBH	0.0	2.4	0.0	1.9
DOT	0.0	2.2	0.0	2.3
1	4.2	13.3	5.6	16.2
2	7.6	17.9	8.2	16.1
3	23.5	48.8	24.4	54.3
4	2.8	9.7	3.3	11.4
5	2.5	12.3	2.7	12.5
Griseofulvin	100	100	100	100

DMSO showed no inhibition, each value is the average of four replicates.

The results clearly indicate that the compounds have both antibacterial and antifungal activity against the tested organisms. The antimicrobial activity of the complexes is higher than that of parent ligands. The results of the inhibitory activity of the synthesized complexes on the organisms show that in lower concentration the complex did not affect much on the bacterial and fungal growth. It shows that as the concentration of the complex increases, the inhibition of bacterial and fungal growth also increases. Mn(II) complexes containing DPH and CPC predominantly showed good activity among the synthesized Mn(II) complexes.

4. Conclusion

In conclusion, the IR spectral data indicate that the ligands CPC, DPH, EBH and DOT act as neutral monodentate, while IMH acts as bidentate ligand. The molar conductance of all the complexes in DMF indicates non-electrolytic nature thus showing that the anions are coordinated to the metal ion. The electronic spectral data and magnetic moment values support the octahedral structure for all the complexes of Mn(II). The results clearly indicate that the studied complexes have both antibacterial and antifungal activity against the tested organisms.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

KSP and LSK interpreted the analytical and spectral data and were involved in the preparation of manuscript. BJ carried out biological studies and HDR reviewed the manuscript thoroughly. BV carried out the main experimental work.

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References

- West DX, Liberta AE, Padhye SB, *et al.*, 1993. Thiosemicarbazone complexes of copper(II): structural and biological studies. *Coordination Chemistry Review*, 123:49-71.
- Sanchez-Delgado RA, Lazardi K, Rincon L, *et al.*, 1993. Toward a novel metal-based chemotherapy against tropical diseases. Enhancement of the efficacy of clotrimazole against *Trypanosoma cruzi* by complexation to ruthenium in $\text{RuCl}_2(\text{clotrimazole})_2$. *Journal of Medicinal Chemistry*, 36:2041-2043.
- Elsome MA, Hamilton-Miller JMT, Brmfitt W, *et al.*, 1996. In-vitro and in-vivo antibacterial activity of plaunotol, a cytoprotective antiulcer agent, against *Helicobacter pylori*. *Journal of Antimicrobial Chemotherapy*, 37(5):911-918.
- Elayaperumal R, Dharmalingam P, 2012. In-vitro microbicidal activity of Mn(II) complex of N, N'-Dimethyl-N, N' Bis (Pyrid-2-Lmethyl) Ethylenediamine. *International Journal of Chemical and Analytical Science*, 3(5):1391-1393.
- Oelrijk AEM, Khangulov SV, Dismukes GC, 2000. Mechanism of hydrogen peroxide dismutation by a DiMn catalase mimic dominant role of an intramolecular base on substrate binding affinity and rate acceleration. *Inorganic Chemistry*, 39:3020-3028.
- Zondddervan C, Hage R, Feringa BL, 1997. Selective catalytic oxidation of benzyl alcohols to benzaldehydes with a dinuclear Mn(IV) complex. *Chemical Communication*, 5:419-420.
- Bolm C, Meyer N, Raabe G, Weyermuller T, Bothe E, 2000. A novel enantiopure proline-derived triazacyclononane: synthesis, structure and application of its Mn complex. *Chemical Communication*, 24:2435-2436.
- De Boer JW, Brinksma J, Browne WR, Meetsma A, Alsters PL, Hage R, Feringa BL, 2005. Cis-Dihydroxylation and epoxidation of alkenes by $[\text{Mn}_2\text{O}(\text{RCO}_2)_2(\text{tmtacn})_2]$: Tailoring the selectivity of a highly H_2O_2 -efficient catalyst. *Journal of American Chemical Society*, 127:7990-7991.
- Wieghardt K, 1989. The active sites in Mn-containing metalloproteins and inorganic model complexes. *Angewandte Chemie*, 28:1153-1172.
- Sharma RC, Parashar K, 1988. Synthesis and microbicidal activity of N-(2-substituted) phenyl ureas and their metal complexes. *Journal of Inorganic Biochemistry*, 32:163-169.
- Casey MT, McCann M, Devereux M, *et al.*, 1994. Synthesis and structure of the Mn(II) complex salt $[\text{Mn}_2(\text{oda})(\text{phen})_4(\text{H}_2\text{O})_2][\text{Mn}_2(\text{oda})(\text{phen})_4(\text{oda})_2] \cdot 4\text{H}_2\text{O}$ (odaH₂=octanedioic acid): a catalyst for H_2O_2 disproportionation. *Journal of Chemical Society, Chemical Communication*, 22:2643-2645.
- McCann M, Casey MT, Devereux M, *et al.*, 1997. Mn(II) complexes of hexanedioic and heptanedioic acid and $[\text{Mn}(\text{phen})_2(\text{H}_2\text{O})_2][\text{Mn}(\text{O}_2\text{C}(\text{CH}_2)_5\text{CO}_2)(\text{phen})_2(\text{H}_2\text{O})](\text{O}_2\text{C}(\text{CH}_2)_5\text{CO}_2) \cdot 12.5\text{H}_2\text{O}$. *Polyhedron*, 16:2741-2748.
- McCann M, Casey MT, Devereux M, *et al.*, 1997. Syntheses, X-ray crystal structures and catalytic activities of the Mn(II) butanedioic acid complexes $[\text{Mn}_2(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)_2(\text{phen})_2(\text{H}_2\text{O})_4] \cdot 2\text{H}_2\text{O}$ and $[\text{Mn}(\text{O}_2\text{C}(\text{CH}_2)_2\text{CO}_2)(\text{bipy})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$. *Polyhedron*, 16:2547-2552.
- Geraghty M, McCann M, Devereux M, 1998. Synthesis, X-ray crystal structure and catalytic activity of *cis*- $[\text{Mn}(\text{phen})_2(\text{H}_2\text{O})_2]\text{penda} \cdot 5\text{H}_2\text{O}$ (penda= pentanedioic acid; phen = 1,10-phenanthroline). *Inorganica Chimica Acta*, 277:257-262.
- Vogel AI, 1975. *A Text Book of Quantitative Inorganic Analysis*, 3rd edition. ELBS and Longman, London, 267-569.

16. Geary WJ, 1971. The use of conductivity measurements in organic solvents for the characterisation of coordination compounds. *Coordination Chemistry Review*, 7:81-122.
17. Pandey PK, Pandey AK, Mishra AN, *et al.*, 2012. Physico chemical studies of Mn(II), cobalt(II), zinc(II) and copper(II) complexes derived from 2-substituted benzaldehyde thiosemicarbazones. *Indian Journal of Scientific Research*, 3(1):119-122.
18. Cotton FA, Wilkinson G, 1972. *Advanced Inorganic Chemistry, A Comprehensive Text*, 3rd edition. Interscience, New York.
19. Ballhausen CJ, 1962. *Introduction to Ligand Field Theory*. McGraw-Hill, New York.
20. Warratz R, Aboufadi H, Bally T, *et al.*, 2009. Electronic structure and absorption spectra of biferrocenyl and bisfulvalenide diiron radical cations: detection and assignment of new low-energy transitions. *Chemistry - A European Journal*, 15(7):1604–1617.
21. Qian M, Gou S, Chantrapromma S, *et al.*, 2000. Synthesis of dinuclear metal complexes of a macrocyclic ligand with multiligating pendant-arms. Crystal structures of its manganese(II) and cadmium(II) complexes. *Inorganica Chimica Acta*, 305:83–90.
22. Toshio N, Kenshin N, Shino U, *et al.*, 2001. Novel dinuclear Mn(III) complexes with bi- or tridentate and bridging tetradentate Schiff base ligands: preparation, properties and catalase-like function. *Polyhedron*, 20:191–201.
23. Rosu T, Gulea A, Nicolae A, *et al.*, 2007. Complexes of 3dⁿ metal ions with thiosemicarbazones: synthesis and antimicrobial activity. *Molecules*, 12:782-796.
24. Keshavan B, Gowda K, 2001. Dioxobridged complexes of molybdenum (IV) and tungsten (IV) with N-alkylphenothiazines and their interactions with L-cysteine and L-histidine. *Proceeding of Indian Academy of Science (Chem. Sci.)*, 113(3):165–172.
25. Cullity BD, 1978. *Elements of X-ray Diffraction*, 2nd edition. Wiley Interscience, New York.
26. Henry NFM, Lipson H, Wooster WA, 1951. *Interpretation of X-ray Diffraction Photographs*. McMillan, London, 123.
27. Berger MJ, 1953. *X-ray Crystallography*. Wiley, New York, 100.
28. Peiser H, Rooksey HP, Wilson AJC, 1956. *Institute of Physics*, London, 344.
29. Kennon NT, 1978. *Patterns in Crystals*. John Wiley and Sons, New York, 197 pp.