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Preparation, Characterization of Mn(II),Mn(III), and Mn(IV) Complexes with Schiff Base Ligands Derived from Salicylic acid Hydrazide have N,O Donors and Biological Activity Study

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Abstract

Mn(II), Mn(III), and Mn (IV) complexes with two Schiff base ligands derived from salicylic acid hydrazide with 4-dimethylaminobenzaldehyde and 4-Nitrobenzaldehyde have been prepared and characterized by several techniques, including, infrared and electronic spectra, magnetic measurements, molar conductance measurements, and the metal content in complexes were estimated by gravimetric analysis. Based on these studies square pyramidal structure for Mn (III) complexes and octahedral structure for the Mn (II) and Mn (IV) complexes were proposed. The antimicrobial activity against two Strain Gram +ve bacteria (Staphalococcus auras, Enterococcus) and two Strain Gram -ve bacteria (E.coli, P.aeruginosa) and yeast Candida albicans to assess their inhibiting potential, the results showed all ligands and their complexes inactive against Staphalococcus auras and they have moderate activity against the rest microorganisms.

تحضير وتشخيص معقدات المنغنيز(II)، المنغنيز(III) والمنغنيز (IV) مع قواعد شيف المشتقة من السالسيلك أسيد هيدرازايد الحاوية على النتروجين الأوكسجين كذرات مانحة ودراسة فعاليتها البايولوجية

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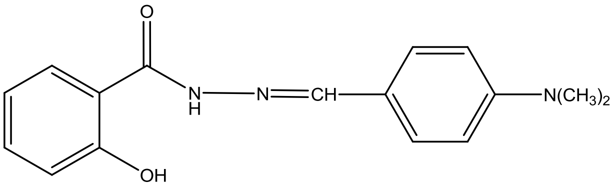
الخلاصة

تم تحضير معقدات للمنغنيز بحالات تاكسدية (II) و(III) و(IV) مع اثنين من قواعد شيف المشتقة من السالسيلك أسيد هيدرازايد مع 4- داي مثيل امينوبنز الديهايد و4- نانتروبنزالديهايد وتم تشخيصها بعدة تقنيات مثل طيف الأشعة تحت الحمراء والأطياف الالكترونية فوق البنفسجية والمرئية، التوصيلية المولارية، الحساسية المغناطيسية وتم تقدير نسبة الفلز في المعقدات باستخدام التحليل الكرافامتري، اعتمادا على نتائج هذه الدراسات تم فرض شكل فراغي ثماني السطوح لمعقدات المنغنيز (II) و(IV) وشكل هرم رباعي لمعقدات المنغنيز(III). تم دراسة الفعالية البايولوجية لقواعد شيف ومعقداتها ضد نوعين من البكتريا الموجبة والسالبة (Staphalococcus auras, P.aeruginosa, E.coli, and Enterococcus) وضد الخميرة Candida albicans أظهرت النتائج انه جميع الليكاندات والمعقدات غير فعالة ضد Staphalococcus auras والبقية متوسطه الفعالية تجاه الإحياء المجهرية الباقية.

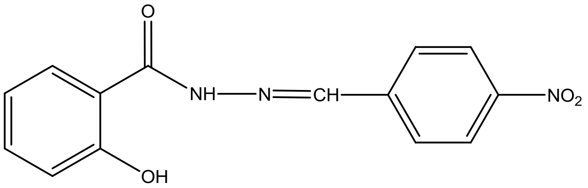
Introduction

From more than last one decade, there has been a dramatic growth of interest in inorganic complexes based material that exhibit unusual properties. Schiff bases derived from an amine and aldehyde/ketones are an important class of ligands coordinate to metal ion via azomethine nitrogen and have been studied extensively(1). Manganese complexes play important roles ranging from bioinorganic chemistry to solid- state physics. The coordination chemistry of manganese is dominated by stable manganese (II) and manganese (III) ions(2). In this context, two Schiff base ligand derived from salicylic acid hydrazide with 4-dimethylaminobenzaldehyde and 4-Nitrobenzaldehyde had been taken as potential (N,O) bidetentate ligand containing two donor atoms.



N'-(4-(dimethylamino)benzylidene)-2-hydroxybenzohydrazide

La



2-hydroxy-*N*'-(4-nitrobenzylidene)benzohydrazide

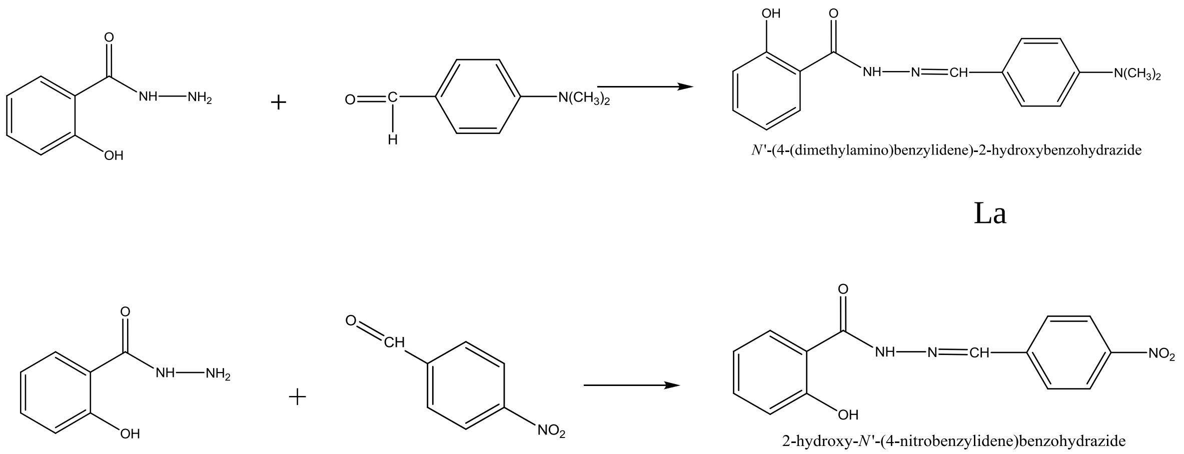
Lb

The aim of the present study is to prepare, characterize, and determine the antimicrobial activity of Mn (II), Mn (III), Mn (IV) complexes with two Schiff base ligands derived from aroyl hydrazide containing (O,N) donor atoms.

Material and Methods

All chemicals used in this work were of analytical reagent grade and used us received from supplies. Melting points were recorded with Stuart melting points apparatus SMP30 and were uncorrected. FTIR spectra were recorded on SHIMADZU FTIR-8400 spectrophotometer in the frequency range 4000-400 Cm^{-1}, the measurements were carried out with samples in KBr disc, magnetic susceptibility measurements were measured by using the equation $\mu_{eff}=2.82\ (X_MT)^{1/2}$ BM, and carried out on Magnetic Susceptibility Brucker B.M at room temperature UV-Visible spectra were recorded in DMF on JENAY 6405 UV/VIS. spectrophotometer, the metal content in complexes were estimated by gravimetric analysis (3) and the molar conductivities of complexes measured by using Martin instrument, Mi 805, and the antimicrobial activity of the prepared complexes were evaluated by the agar well diffusion, the organisms used were local (Staphalococcus auras, Enterococcus, E.coli, P.aeruginosa and yeast Candida albicans) and they were characterized.

- **Preparation of Schiff base ligands:** To solution of 0.005 mole (0.76) g of salicylic acid hydrazide in 25 ml of absolute ethanol, 0.005 mole (0.746) g of 4-dimethylaminobenzaldehyd, or 0.005 mole (0.755)g of 4-nitrobenzaldehyde were added separately and the mixtures were refluxed for 4 hours, where by yellow solids were precipitated. The solids were filtered, washed with ethanol several times, dried in vacuum in presence of $CaCl_2$, and recrystalzied in ethanol (4) Scheme (1).



La

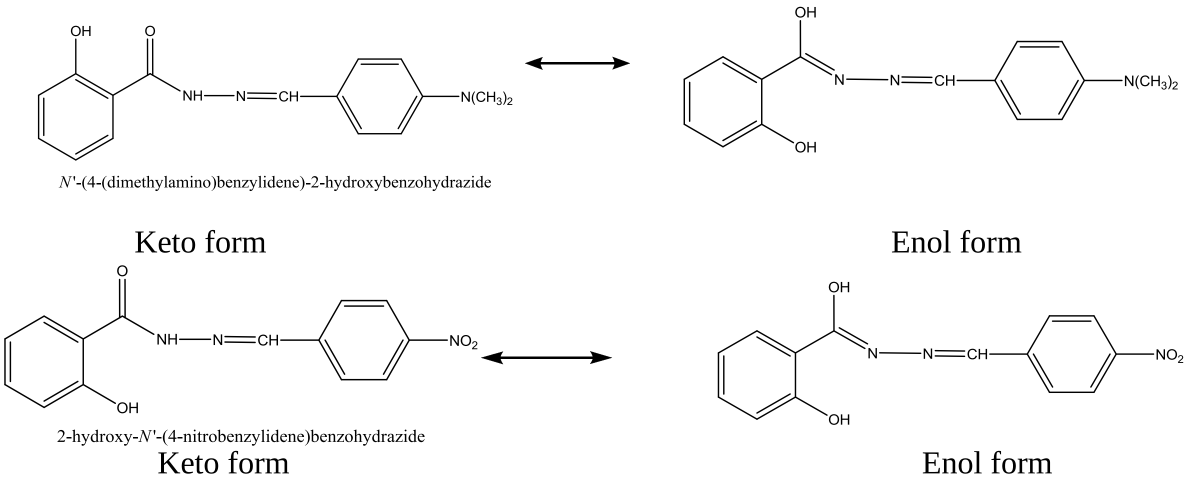
Lb

Scheme (I). The preparation of two Schiff base ligands

- **Preparation of Mn(II), Mn(III) complexes:** The Mn (II) and Mn (III) complexes of the Schiff base ligands were prepared by mixing solutions of MnCl2.4H2O 0.001 mole (0.198) g and anhydrous MnCl30.001 mol (0.161) g in ethanol with the solution of the corresponding Schiff base ligands 0.002 mole (0.56) g La and (0.57) g Lb in ethanol in 1:2 molar ratio respectively with stirring. The pH of the reaction mixtures were adjusted to 7.5-8.5 by adding 10% ethanolic ammonia solution and refluxed for 4 hours. The color compounds formed were filtered, washed with ethanol and dried in a desiccators over CaCl2 for one day (5).
- **Preparation of Mn(IV) complexes:** The Mn (II) complexes were exposed to dioxygen by bubbling air into the solutions in DMSO for 4 hours. The resulting dark brown solids were collected by filtration, washed with little cold ethanol and diethyl ether(2).
- **Antimicrobial activity:** The overnight cultures (0.2 ml) of each bacterium was dispensed into 20 ml sterile nutrient broth and incubated for about 3-5 h to standardize the culture. A loopful of the local cultures was used for the antibacterial assay. Muller Hilton agar was prepared and 20 ml of sterilized media was poured in petriplates and allowed for solidification. The bacterial lawn culture was made using sterile cotton swab and labelled. The plates were incubated immediately at 37 ^{0}C for 24 h. Activity was determined by measuring the diameter of zones showing complete inhibition (mm) (5).

Results and discussion

Aroylhydrazide are N and O donor atoms,which potentate the formation of polydentate Schiff base ligands. The lactam (keto) or lactim (enol) tautomeric forms Scheme (2) give variation the donating properties of the ligands.



N'-(4-(dimethylamino)benzylidene)-2-hydroxybenzohydrazide

Keto form

Enol form

2-hydroxy-*N*'-(4-nitrobenzylidene)benzohydrazide

Keto form

Enol form

Scheme (2). Keto and enol forms o Schiff base ligands

All the complexes are colored, solids and are stable in air. All complexes melt over 350 ^{0}C, they are soluble in DMSO and DMF.Table (1).

Table (1) The analytical and physical data of Schiff base ligands and its complexes

Compound	Formula	Color	Solubility	m.p C^0	% Of metal (cal) obs.
La	$C_{16}H_{17}N_3O_2$	yellow	ethanol	255	–
Lb	$C_{14}H_{11}N_3O_4$	yellow	ethanol	268	–
$[Mn(La)_2(H_2O)_2]$	$C_{32}H_{40}MnN_6O_6$	Green	DMSO,DMF	>350	(8.33) 7.96
$[Mn(La)_2Cl]$	$C_{32}H_{36}ClMnN_6O_4$	Brown	DMSO,DMF	>350	(8.34) 7.73
$[Mn(La)_2Cl_2]$	$C_{32}H_{36}Cl_2MnN_6O_4$	Dark brown	DMSO,DMF	>350	(7.91) 7.32
$[Mn(Lb)_2(H_2O)_2]$	$C_{28}H_{24}MnN_6O_8$	Green	DMSO,DMF	>350	(8.76) 7.65
$[Mn(Lb)_2Cl]$	$C_{28}H_{24}ClMnN_6O_8$	Brown	DMSO,DMF	>350	(8.29) 7.21
$[Mn(Lb)_2Cl_2]$	$C_{28}H_{24}Cl_2MnN_6O_8$	Dark brown	DMSO,DMF	>350	(7.87) 7.55

- **Infrared Spectra**: In order to study the bonding mode of ligands to metal ions in the complexes, IR spectrum of the free ligands were compared with the spectra of metal complexes. The most characteristic IR spectral bands of the ligands and their complexes are discussed in Table (2). The IR spectra of the tow ligands showed that the ligands coordinate to manganese atom through the azomethine nitrogen and carbonyl group. This inferred from the absence of υ(C=O), υ(N-H) and downward Schiff of υ(CH=N) in the spectra for all complexes(6). There are additional new vibrations between 1145-1150 Cm^{-1} due to υ(C-O) of enol form of ligands and two peaks of υ(M-O) and υ(M-N) in the region 445-655 Cm^{-1}(7).

Table (2) The most characteristic IR bands spectral bands of ligands and its complexes in Cm^{-1}

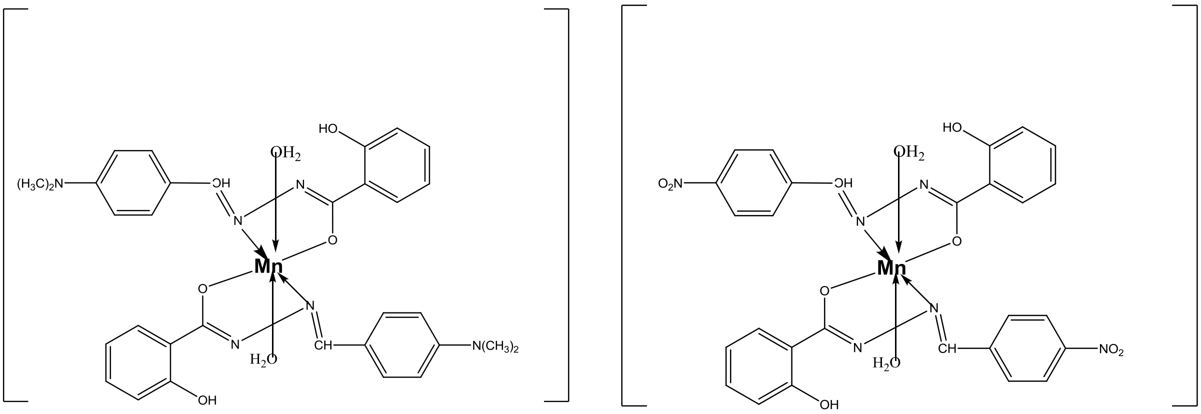
Compound	υ(OH)	υ(N-H)	υ(C=N)	υ(C=O)	υ(C-O)	υ(Mn-O)	υ(Mn-N)	υ(OH_2)
La	3100	3250	1620	1650	------	------	--------	
Lb	3010	3225	1620	1650	------	------	--------	
$[Mn(La)_2(H_2O)_2]$	3099	------	1585	------	1145	585	445	3427
$[Mn(La)_2Cl]$	3099	------	1581	------	1148	597	468	
$[Mn(La)_2Cl_2]$	3100	------	1586	------	1150	608	505	
$[Mn(Lb)_2(H_2O)_2]$	3015	------	1585	------	1146	620	510	3448
$[Mn(Lb)_2Cl]$	3014	------	1588	------	1148	594	490	
$[Mn(Lb)_2Cl_2]$	3010	------	1590	------	1150	655	440	

- **Electronic Spectral and Magnetic Moment Data:** The electronic spectra and magnetic moments of the ligands and their metal complexes are disused in Table (3).

Table (3) The electronic spectra, magnetic moments, and molar conductivity of ligands and its complexes in 1X10^{-3}M in DMSO

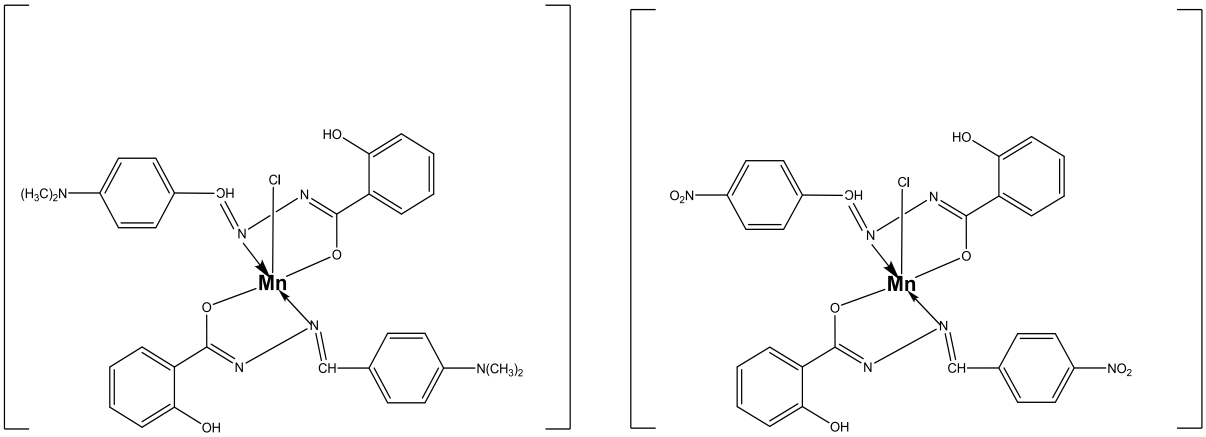
Compound	Abs. bands In Cm^{-1}	Assignment	μ_{eff} B.M	Mho Cm^2.mol^{-1} DMSO	Structure
La	39000 26000	π →π*, n→π*	-	-	
Lb	39000 26000	π →π*, n→π*	-	-	
$[Mn(La)_2(H_2O)_2]$ $[Mn(Lb)_2(H_2O)_2]$	16422 Cm^{-1} 23750 Cm^{-1} 28225 Cm^{-1}	$^6A_1g \rightarrow {}^4T_1g$ $^6A_1g \rightarrow {}^4T_2g$ LMCT	5.65	6.1 5.7	Octahedral
$[Mn(La)_2Cl]$ $[Mn(Lb)_2Cl]$	14100 Cm^{-1} 16987 Cm^{-1} 20203 Cm^{-1} 28270 Cm^{-1}	$^5B1 \rightarrow {}^5B_2$ $^5B_1 \rightarrow {}^5A_2$ $^5B_1 \rightarrow {}^5E$ LMCT	4.6	6.54 7.45	Square pyramidal
$[Mn(La)_2Cl_2]$ $[Mn(Lb)_2Cl_2]$	17000 Cm^{-1} 32000 Cm^{-1}	d-d transitions π →π*, n→π*	3.7	5.88 7.49	Octahedral

The absorption bands of the complexes will help to give an idea of their structure. The electronic spectra of the ligands in DMSO consists of an intense band centered at (370 nm) 39000 Cm^{-1} attributed to the n→π* transition of the non-bonding electrons present on the nitrogen of the azomethine group. Another intense band in the higher energy region of the spectra of the free ligands was reflected to the π→π* transition of the benzene ring at (258 nm) 26000 Cm^{-1}(8). The electronic spectra of Mn (II) complexes showed three bands at 16422, 23750, and 28225 Cm^{-1} assignable to $^6A_1g \rightarrow {}^4T_1g$, $^6A_1g \rightarrow {}^4T_2g$ and charge transfer respectively, the magnetic moment of the two Mn(II) complexes were (5.65-5.85) μ_B which indicate a high spin d^5(9,10), octahedral structure for these complexes were proposed.



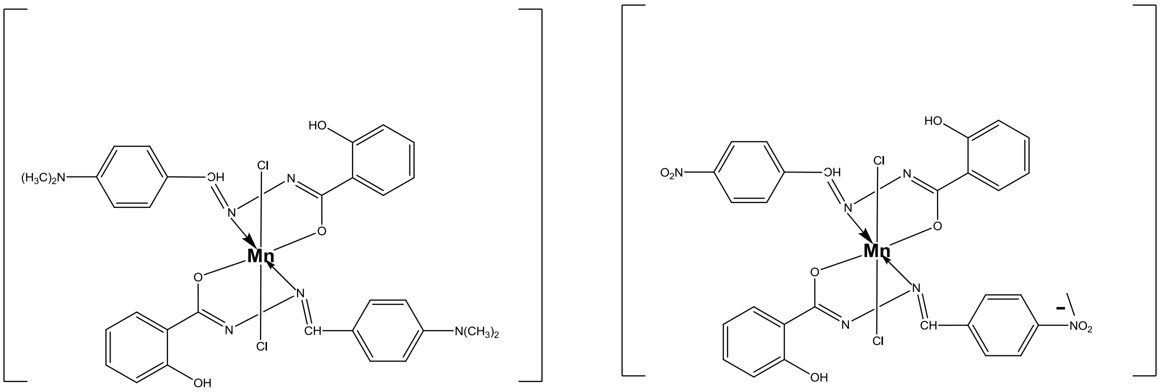
The proposed structures of Mn (II) complexes:

The electronic spectra of Mn (III) two complexes exhibit an intense band at 28270 Cm-1 which may be due to ligand to metal charge transfer (LMCT) transition. In the second region three d-d bands are observed at 14100, 16987, 20203 Cm-1 which may be due to 5B1→5B2, 5B1→5A2, 5B1→5E transitions respectively. The magnetic moments of Mn (III) complexes were (4.6-4.65) µB which indicates a high spin d4 system, this results suggest pyramidal geometry around the Mn (III) atoms (11).



The proposed structures of Mn **(III) complexes**

The magnetic moment of Mn (IV) two complexes were (3.7-3.8)μ_B which indicate a high d^3 system. For octahedral Mn (IV) complexes, the electronic spectra of Mn (IV) two complexes expected to show three spin-allowed d-d transition $^4A_2g\rightarrow{}^4T_2g$,$^4A_2g\rightarrow{}^4T_1g(F)$, $^4A_2g\rightarrow{}^4T_1g$. But one d-d transition band at 17000 Cm^{-1} and intense at 32000 Cm^{-1} probably due to interaligand transition in the UV region (2).



The proposed structure of Mn (IV) complexes

- **Conductivity Measurement:** The molar conductance of the complexes determination at concentration of $1x10^{-3}$ M at room temperature in DMSO and DMF solvents, Table (3). Show values in range (5.2-7.49) Mho $Cm^2.mol^{-1}$ for all complexes, indicating that the complexes are non electrolyte(12). In addition to that when $AgNO_3$ in water solution added to the solutions of complexes in DMSO there were no precipitate of AgCl, this mean there is no Cl ion outside the coordination sphere.
- **Antimicrobial Activity:** The Schiff base ligands and its manganese complexes were evaluated for antimicrobial activity in concentration of 100 ppm in DMSO solvent. against two strain gram +ve bacteria (Staphalococcus auras, Enterococcus) and two strain gram –ve bacteria (E.oli, P.aeruginosa) and the yeast Candida albicans (13). The antimicrobial results are given in Table (4). These observations showed that the two Schiff base ligands and their complexes inactive against staphalococcus auras, with low activity against the other microorganisms and the majority of the compounds are in some cases ligands and its complexes have similar activity against

the other bacteria and fungus, but the [Mn(Lb)$_2$Cl] has more activity against (P.aeruginosa, enterococcus auras, and C.albicans fungus) than the ligands and other complexes except [Mn(Lb)$_2$Cl$_2$] was more activity against E.coli. It has been suggested that the ligands with the N and O donor system might have inhibited enzymes production, since enzymes which require free hydroxyl groups for their activity appear to the especially susceptible to deactivation by the ions of the complexes (14). The variation in the activity of different metal complexes against different microorganisms depends on the impermeability of the cell or differences in the ribosomes in the microbial cells. The lipid membrane surrounding the cell favours the passage of any lipid soluble material and it is known that liposolubility is an important factor controlling antimicrobial activity (15).

Table (4) Antimicrobial activity of ligands and its complexes in (mm) concentration of 100 ppm in DMSO solvent

Compound	Staphalococcus	E.coli	P.aeruginosa	Enterococcus	C.albicans
La	------	4.7	4.2	3.7	3.33
Lb	------	4.1	4.3	4.1	4.2
[Mn(La)$_2$(H$_2$O)$_2$]	------	4.2	4.43	4.81	5.21
[Mn(La)$_2$Cl]	------	6.11	4.11	5.51	7.4
[Mn(La)$_2$Cl$_2$]	------	8.31	10.2	6.74	6.21
[Mn(Lb)$_2$(H$_2$O)$_2$]	------	7.75	7.31	6.22	5.11
[Mn(Lb)$_2$Cl]	------	8.45	13.31	9.27	8.33
[Mn(Lb)$_2$Cl$_2$]	------	9.11	9.6	7.4	6.23

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