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# Binuclear Manganese (II) complexes of a new Schiff-base as Ligand: Synthesis, Structural characterization, and antibacterial activity

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**Abstract :** A binucleating new amino schiff base ligand with a phenylene spacer afforded by the condensation of amino acids with*o*-pthalaldehyde has been served as an octadentate$N_4O_4$ligand in designing some binuclear complexes of manganese(II), binding manner of the ligand to the metal and the composition and geometry of the metal complexes were examined by elemental analysis, conductivity measurements, magnetic moments, IR,$^1$H,$^{13}$C NMR, Mass and electronic spectroscopies, and TGA,DTA measurements, there are two different coordination/chelation environments present around two metal centres of each binuclear complex .The composition of the complexes in the coordination sphere was found to be $[M_2(L)(H_2O)_4]xH_2O$ (where M=Mn(II). All the above metal complexes have shown moderate to good antibacterial activity against Gram-positive and Gram –negative bacteria.
**Keywords :** Binuclear complexes, Schiff base: synthesis, structural characterization, antibacterial activity.

## Introduction

Hugo Schiff was the first scientist who described Schiff bases in 1864. [1]The condensation of primary amine with either an aldehyde or ketene yields Schiff base [2-4] Schiff bases have a variety of applications in biological, clinical,and pharmacological areas. The synthesis and application of Schiff bases and their coordination compounds have been highly considered in inorganic, organic and biological fields, since their structural properties similar to some of the biological systems.[5-10] The transition metal complexes with Schiff bases have expanded with wide and diversified subjects comprising vast areas of organmetallic compounds[11] and various aspects of bio coordination chemistry [12] The design and synthesis of symmetrical Schiff-bases, derived from the 1:2 stepwise condensation of carbonyl compounds. With alkyl or aryl diamines. And a wide range of aldehyde or ketenes functionalities, as well as their metal (II) complexes have been of interest due to their preparative accessibility, structural variability and tuneable electronic properties allowing to carry out systematic reactivity studies based on ancillary ligand modifications [13] In recent years much efforts has been put in synthesis and characterization of mono-and bi- nuclear transition- metal complexes. Schiff-base ligands that are able to form binuclear transition metal complexes are useful to study the relation between structures and magnetic exchange interactions [14]. And to mimic bimetallic biosites in various proteins and enzymes [15]. The complexes thus play an important role in developing the coordination chemistry related to catalysis and

enzymatic reactions, magnetism and bioinorganic modelling studies [16,17] In this regard, there is much current interest in designing binucleating ligands and their transition metal complexes.

The multidentate binucleating Schiff bases with inbuilt spacers can take up two same or different metal ions. Various mono-and dialdehyde/ketones have been employed to condense amines or amino acids to explore multidentatebinucleating Schiff bases to design a variety of binuclear transition metal complexes [13,18,19,20-23].Shakirand Verkey.[24].Have reported on the synthesis characterization of macrocyclic binuclear Cu(II),Ni(II),Zn(II) complexes by template condensation of diethylenetrimine with dicarboxylic acids, Similarly, the binuclear Ni(II) and Pd(II) complexes have been prepared and characterized by Al-Kubaisi[25].Recently ,B. Geeta et al developed various co-ordination compounds including Schiff-base macro cycles derive from o-Phthalaldehyde and different amines[26-36].Further ,we also disclosed the excellent catalytic and antibacterial activity of the macro cyclic Schiff-bases and their metal complexes in our recent reports[26-36].However, to our knowledge the combination of o-Phthalaldehyde and amino acids has never been used to synthesize Schiff-base ligands.Herein, we have noticed that amino Schiff bases with several potential donor atoms could be a good choice to condense with o-Phthalaldehyde to develop binucleating Schiff-base ligands.In this connection it was interesting to synthesize and study the transition metal complexes

With Schiff-base produced from condensation reaction of O-Phthalaldehyde with glycyl-glycine amino acid(see Scheme1).A description on characterization data using analytical, spectroscopic, thermal and magnetic data has been systematically presented.Furthermore,the application of these metal complexes as potential antibacterial agents has also been demonstrated.

## 2. Experimental

### 2.1. Physical measurements

All the chemicals used of annular grade. Solvents were purified and dried before use according to the Standard procedures. The metal contents were determined by gravimetric procedure using dimethylglyoxime as precipitating agent. Elemental analysis (C, H, N) was obtained using Perkin-Elmer elemental analyser, The Infrared spectra were recorded in KBr/CsBr/Nujoll on Perkin-Elmer-283 spectrophotometer in the range of 4000-200$cm^{-1}$ and electronic spectra in MeOH were obtained using Shimadzu UV-265 Spectrometer.$^{1}H$ and $^{13}C$ NMR spectra in $CDCl_3$/DMSO were recorded on a Brucker WH 300 (200MHz) and Varian Gemini(200MHz) spectrometer using TMS as an internal reference. Conductance measurements were carried out at room temperature on freshly prepared $10^{-3}$M EtOH solutions using a coronation digital conductivity meter. The magnetic studies were carried out at room temperature on a Gouy balance carried with Hg $[Co(SCN)_4$.all the mass spectra were recorded using MALDI Autoflex time-of-flight mass spectrometer. The TG-DTG thermo grams of the complexes were recorded on Mettler Toledo star system. The antibacterial activity of the compounds was determined by the cup plate method and minimum inhibitory concentration by liquid dilution method[37-40].

### 2.2 Materials

Manganese, Iron salts, Ortho-Phthalaldehyde, amino acids and other chemicals were purchased from Aldrich, USA and all the compounds are analytical grade. The solvents were distilled and stored over molecular sieves. The purity of compounds was checked by TLC using Merck 60F254 silica gel plates. The antibacterial activity of the compounds was determined by the cup plate method and the minimum inhibitory concentration by liquid dilution method[37-41].The hydrogenation unit consists of three –necked, double-walled glass drain, which in turn is connected to a double - walled hydrogen burette through which water at the desired temperature from a thermostat is circulated.

The eight amino acid Schiff base lignds, *viz*.2-{[(E)-1-1-(2-{[C1-carboxyethyl)imino]methyl] phenyl}phenyl) methylidene] amino} propanoic acid (CEIMPA), 2-{[(E)-1-(2-{[C1-carboxy -2-Carboxyphenylethylimino] methyl} phenyl)methylidene] amino}-3-phenyl propanoic acid(CPEIAP),2-({(E)-1-[2-({1-carboxy-2-(4-hydroxyphenyl)ethyl]imino}methyl)phenyl]methylidene}amino)-3-(4-hydroxyphenyl) propanoicacid(CPEIMP).2-({2-[(E)-1{2-[(carboxymethyl)amino]-2-oxoethyl} imino]methyl} phyenly) methylidene)amino)acety)amino)actic acid (CMAIPA).2-({(E)-1[2-({[1-carboxy-2-(3,4-dihydroxyphenyl)-1-

methyl/ethyl]imono}methyl)phenyl]methylidene}amino)3-(3,4-dihydroxyphenyl)-2-methyl propanoic acid (CPMIMP).

2-{[(E)-1-(2-{[1,3dicarboxypropyl)imino]methyl}phenyl]methylidene}amino)pentanedioic acid (DCPIMP), 2-({(E)-1-[2-({[1-corboxypropyl-2-(1H-3-indoly)ethyl]imino}methyl)phenyl]methylidene}amino)-3-(1H-3-indolyl)propanoic acid (CEIMAP).

2-({2-[(E)-1{2-[(carboxy-2-(1H-5-imidazolyl)ethyl)imino]methyl}phenyl]methylidene}amino)-3-(1H-5imidazolyl)propanoic acid(CIMPAP) were prepared as previously reported,[42.43].Our synthetic route of Schiff-base ligand is shown in Scheme.1.

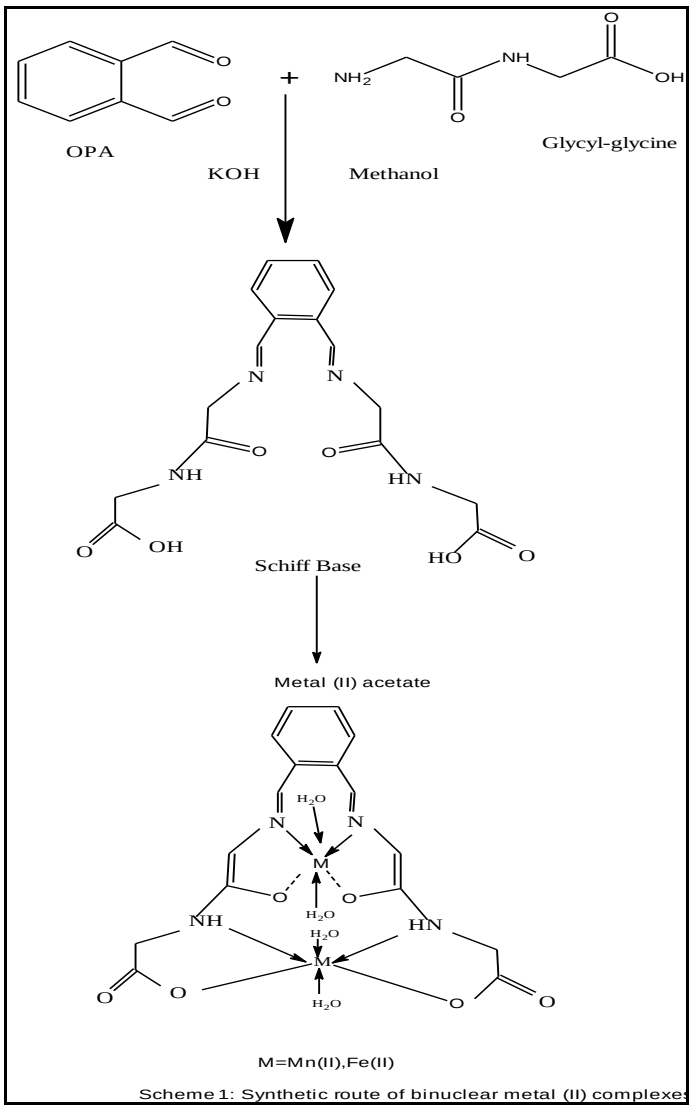
### 2.3. Synthesis is amino Schiff base Mn(II)compounds

A solution of manganese (II) acetate is taken in a round bottom flask of 100 mL, 25mL of manganese(II) acetate(1.2g in 30 mL of methanol and 30 mL of Schiff base ligand solution. (0.005mol,*viz*.,0.332g of CEIMPA,0.321g of CPEIAP,0.337g of CPEIMP, 0.381g of CPMIMP, 0.316g of DCPIMP, 0.375g of CEIMAP, 0.325g of CIMPAP, 0.302g of CMAIPA in methanol) were mixed with continuous stirring. The resulting solution was concentrated to 5 mL under reduced pressure and a few millilitre of diethyl ether was added to initiate crystallization the resulting precipitate was separated by suction filtration, washed with diethyl ether, vacuum dried to obtain a recrystallized using chloroform and methanol solvent mixture and dried in vacuum desiccators .The physical and analytical data are in agreement with the proposed molecular formula. $[Mn_2L\ (H_2O)_4]3H_2O$ is taken in table x And the synthetic route of binuclear manganese (II) complexes is given scheme 1.

Compound **1**: Yield 79%; pale brown; reaction time: 75 min; Anal. found(%) : C 41.69, H 6.00, N 6.95, Mn 13.62; Calcd for $C_{14}H_{24}N_2O_8Mn$: C 41.71, H 6.21, N 6.98, Mn 13.68, Compound **2**:Yield 86%; dirty brown, reaction time: 65 min; Anal. found (%): C 58.70, H 6.02, N 5.07, Mn 9.94, Calcd for $C_{27}H_{33}N_2O_7Mn$: C 58.73, H 6.08, N 5.15 Mn 9.91, Compound 3: Yield 86%; dark brown; reaction time: 70 min; Anal. found(%): C 55.03, H 5.68, N 9.87, Mn 9.68; Calcd for $C_{26}H_{32}N_4O_7Mn$: C 55.05, H 5.71, N 9.84, Mn 9.71. Compound **4**: Yield 83%; light brown; reaction time: 90 min; Anal. found(%) C 53.43, H 5.44, N 4.45, Mn 8.73, Calcd for $C_{28}\ H_{34}N_2O_{11}Mn$(%) : C 53.46, H 5.48, N 4.48, Mn 8.76, Compound **5** : Yield 82%; pale brown; reaction time: 105 min; Anal.found (%): C 41.63, H 5.43, N 5.39, Mn 10.58, Calcd for C 41.68, H 5.48, N 5.39, Mn 10.61, Compound **6 :** Yield 85%; thick brown; reaction time: 75 min; Anal found(%) ; C 44.87, H 5.27, N 15.76, Mn 10.26, Calcd for $C_{20}H_2N_6O_8Mn$(%) : C 44.90, H 5.30, N 15.79, Mn 10.2, Compound **7:** Yield 82%; dark brown; reaction time 90 min; Anal.found(%) : C 56.51, H 6.01, N 8.79, Mn 8.62, Calcd for $C_{30}H_{38}N_4O_8Mn$(%) : C 56.54, H 6.03, N 8.81, Mn 8.82, Compound **8**: Yield 98%; light brown ; reaction time 95 min; Anal found (%) : C 35.38, H 5.94, N 10.31, Mn 10.11, Calcd for $C_{16}H_{32}O_{13}N_4Mn$ (%): C 35.40, H 5.97, N 10.34, Mn 10.14.

## 3. Result and discussion

All the complexes are soluble in methanol and water. The elemental analysis data and the physical properties of the complexes are listed in Table 1.The complexes can be represented as $[M_2L(H_2O)_4].xH_2O$ whereas(M=Mn(II), (L=ligand). The molar conductance values of the complexes in dichloromethane measured at $10^{-3}$M concentration are in the range of 8-19 indicate that all the complexes behave as non electrolytes.[41]




Scheme 1: Synthetic route of binuclear metal (II) complexes

### 3.1 Infrared spectral analysis

All the infrared frequencies of the Schiff base ligand and its Mn(II), complexes exhibit broad bands in the 3440-3564 $cm^{-1}$ range and this may be attributed to the presence of coordinated or lattice water molecule. A strong IR absorption band observed in the free Schiff base around 1565-1600 $cm^{-1}$ assignable to the $\nu_{asym}$ ($COO^{-}$) absorption of ligands was shifted to higher frequency in the 1572-1587 $cm^{-1}$ range and the $\nu_{sym}$ ($COO^{-1}$) visualizes the coordination of carboxyl oxygen to the metal ions along with imino nitrogen atom[45]. In the low frequency regions. Bands detected around 518-533 $cm^{-1}$ ranges are assigned to M-N (imino nitrogen) and the bands at 420-480 $cm^{-1}$ ranges are assigned to M-O (carboxylate oxygen atom)[27,36,42,46].

### 3.2.N .M.R. spectral data

Further evidence for the presence of coordinated Schiff base ligands in the Metal complexes is provided by the $^{1}H$ n.m.r.spectra of the complexes. The integral intensities of each signal were found to agree with the number of different types of protons present in the complexes. A signal appeared in the ligand $^{1}H$ –n.m.r spectrum at 8.12 $\delta$ is due to CH=N protons. However, in the spectra of Mn(II)complex the signal moved down field at 8.22 $\delta$ suggests the coordination of imino nitrogen to manganese ion [47] the carbonyl proton of the ligand was observed at 11.49 ppm. However it was not present in the complex spectrum due to the involvement of carboxyl oxygen in chelation through deprotonation [48].Further, a broad signal found in the complex spectrum at 6.2 ppm corresponds to NH proton, which was shifted from 5.64 ppm of ligand give evidence to the coordination of NH group[15].

**Table 1. Infrared spectroscopic data and molar conductance values of Mn (II) compounds**

| S.No | Complex | Selected IR bands($cm^{-1}$) | | | |
|---|---|---|---|---|---|
| | | υC=N | υM-N | υM-O | $(\Omega]^{-1}cm^2mol^{-1})$ |
| 1<br>L-1 | $[Mn_2CEIMPA(H_2O)_2]2H_2O$<br>CEIMPA | 1613<br>1640 | 520 | 432 | 8.8<br>---- |
| 2<br>L-2 | $[Mn_2CPEIAP(H_2O)_2]H_2O$<br>CPEIAP | 1618<br>1625 | 525 | 420 | 9.5<br>---- |
| 3<br>L-3 | $[Mn_2CPEIMP(H_2O)_2]H_2O$<br>CPEIMP | 1623<br>1640 | 518 | 460 | 10.2<br>---- |
| 4<br>L-4 | $[Mn_2CPMIMP(H_2O)_2]H_2O$<br>CPMIMP | 1608<br>1620 | 530 | 438 | 9.0<br>---- |
| 5<br>L-5 | $[Mn_2DCPIMP(H_2O)_2]2H_2O$<br>DCPIMP | 1609<br>1619 | 522 | 428 | 8.6<br>---- |
| 6<br>L-6 | $[Mn_2CEIMAP(H_2O)_2]2H_2O$<br>CEIMAP | 1614<br>1630 | 528 | 450 | 9.5<br>---- |
| 7<br>L-7 | $[Mn_2CIMPAP(H_2O)_2]2H_2O$<br>CIMPAP | 1600<br>1618 | 533 | 480 | 9.8<br>---- |
| 8<br>L-8 | $[Mn_2CMAIPA(H_2O)_4]3H_2O$<br>CMAIPA | 1632<br>1643 | 520 | 468 | 10.0<br>---- |

### 3.3.$^{13}$C NMR Spectral analysis

In the $^{13}$C NMR spectra of Mn(II) complexes, a down field shift of CH=N group was observed in between 169.5-175.6 ppm and for carbonyl carbon at 194.9 ppm it signifies that the ligand coordination through the nitrogen atom of CH=N[34,35,49] and through the oxygen of carboxyl group of the ligand[34,35,48]. Furthermore, the down- field of shifting of amide adjacent carbonyl (C-O) describes the coordination of this site to manganese ion however, the enolic carbon peak shifted to 108.4 – 116.2 $\delta$ suggesting that coordination of C-O group to the metal by DE protonation. The $^1$H and $^{13}$C NMR spectrum of $[Mn_2L]$

### 3.4. Mass spectral data

The molecular ion peaks and isotopic pattern of amino Schiff base Mn(II) compounds shows different m/z values with different intensities presented in "supplementary material."

### 3.5. Molar conductance and thermal studies

A Digisun digital conductivity meter, DI-909 model was used for the conductance measurements. The cell used for measuring the molar conductivity was calibrated with 0.1 M KCl solution. These values are in the range of 8.8 to 10.0 $\Lambda\_M\ [(\Omega]\hat{}(-1)\ cm\hat{}2\ mol\hat{}(-1)$ suggesting that they are non electrolytes. The thermogravimetric analysis of the Mn(II) Schiff base compounds were obtained using less than 10 mg of the compound, and the TGA and DTA of Schiff base Mn(II) complexes were critically examined to ascertain the presence of lattice held coordinated water molecules and decomposition patterns, lattice water will usually be lost at temperatures ranging from 69-130 $^o$Cwhere as coordinated water requires a temperature of 145 C or above. The thermograms of the Mn(II) complexes show initial weight loss in the temperature range of 87.5-110.8 C. and also, the DSC curve of these complexes shows an endothermic peak in the above range further giving evidence for the presence of water molecules.

The loss of water molecule in this temperature range indicates that they are present in the lattice water [50] The percentage weight loss in this temperature range indicates that there are two water molecules each in Mn(II) complexes of CEIMPA, DCPIMP, CEIMAP and CIMPAP; the complexes of CPEIAP, CPEIMP and CPMIMP have one water molecule and the complex of CMAIPA has three water molecules as lattice-held water. The thermograms of all the Mn(II) complexes exhibit weight loss in the temperature range 162.2-178.5 C. Also, the DSC curve of the complexes shows an endothermic peak in the above temperature range further giving evidence for the presence of coordinated water molecules.[51,52,53] The percentages weight loss in this temperature ranges indicates that there are water molecules in all the Mn(II) complexes. The final products of decomposition in all the complexes above 500C corresponds to Manganese oxide. The analysis of thermograms gives further support to the composition of the complexes proposed on the basis of elemental and thermal analysis.

### 3.6. Electronic spectra and magnetic susceptibility

The electronic spectrum of binuclear Mn(II) complex with the ligand exhibits weak absorption bands around 18573 ($\nu_1$) , 23642($\nu_2$) , 27716 ($\nu_3$) and 38874 $cm^{-1}$($\nu_4$) characteristic of octahedral geometry corresponding to $^6A_{1g}$------$^4T_{1g}$($^4G$), $^6A^{1g}$ ------$^4T_{2g}$ (4D), $^6A_{1g}$--------$^4T_{1g}$ ($^4P$) , $^6A_{1g}$------$^4E_g$(4G) transitions respectively. The complexes showed the magnetic moment value in the range of 5.35-5.94B.M which is in the range of octahedral geometry for Mn (II) complexes[54].

***Table 2:*** **Electronic spectral band and magnetic moments (B.M.) of Mn(II) compound**

| **Complexes** | $\lambda_{max}{}^{b}$ | $\mu_{eff}$ |
|---|---|---|
| $[Mn_2L(H_2O)_4]3H_2O$ | 18573, 23642, 27716, 38875 | 5.35-5.94 |

### 3.7. Anti-bacterial activity

Antibacterial activity of the ligand CMAIPA and its Mn(II), complexes against two Gram- positive (*B.Subtilis* and *S. aureus*) and two Gram-negative (*E.Coli* and *K. pneumonia*) bacteria were studied using three existing antibacterial drugs *Viz.* streptomycin, ampicillin and rifampicin. Preliminary screening for the complexes was performed at the fixed concentration of 1000µg/mL .Inhibition was recorded by measuring the diameter of the inhibition zone at the end of 24 h for bacteria. Among the compounds tested the two metal complexes showed good inhibition towards all tested strains (Table 3). The activity of all these complexes were further confirmed by determining the minimum inhibitory concentration [37,38.55] values by liquid dilution method in which the effectiveness was observed at lower concentrations. The comparison of MICS (in µg/mL) of all the complexes and standard drugs against tested strains are presented in fig. 1 (Table 3). It was found that Mn(II), complexes have good activity against all bacterial strains with MIC value(5-20 µg/mL), in particular two metal complex showed excellent activity (MIC range 5-10 µg/mL) against all the bacterial strains even than standard drugs streptomycin and ampicillin. The results from these studies have also shown that complexation of metal to CMAIPA serves to improve the antimicrobial of the ligand. This higher antibacterial activity of the metal complexes compared to ligand is may be due to the changed in structure due to coordination and chelating trend to make metal complexes acts as more powerful and potent bacteriostatic agent, thus inhibiting the growth of the bacteria. Furthermore, chelation reduces the polarity of the metal ion mainly due to the partial sharing of its positive charge with the donor group within the chelate ring system. such chelation increases the lipophilic nature of central metal atom, which favour its permeation more efficiently through the lipid layer of the microorganism, thus destroying them more forcefully [31,56,57] Thus all the complexes showed more increased activity than the corresponding ligand and two antibacterial drugs. The activity of ligand, complexes and standard drugs against different bacteria were found to be

CMAIPA (L) < Streptomycin <$Mn_2L(H_2O)_4.3H_2O$ =Ampicillin<Rifampicin for *S aureus*
*CMAIPA(L) = streptomycin < Ampicillin*< $Mn_2L(H_2O)_4.3H_2O$ <Rifampicin *for B.subtilis*,
Streptomycin<CMAIPA(L)= Ampicilin< $Mn_2L(H_2O)_4.3H_2O$ < Rifampicin for *E.coli*
and Streptomycin <Ampllicin<CMAIPA(L) <$Mn_2L(H_2O)_4.3H_2O$<Rifampicin for *K. Pneumonia*

**Table 3.Zone of inhibition of CMAIPA and its Mn(II), Fe(II) complexes against different bacteria.**

| Ligand/Complexes (1000 µg/mL) | Zone of inhibition (mm) | | | |
|---|---|---|---|---|
| | Gram positive bacteria | | Gram-negative bacteria | |
| | S. aureus | B. subtilis | E. coli | K. pneumonia |
| CMAIPA | 12 | 11 | 09 | 09 |
| $[Mn_2L(H_2O)_4]3H_2O$ | 16 | 22 | 15 | 20 |
| Streptomycin | 12 | 10 | 07 | 07 |
| Ampicillin | 13 | 11 | 09 | 08 |
| Refampicin | 48 | 51 | 48 | 45 |
| | | | | |

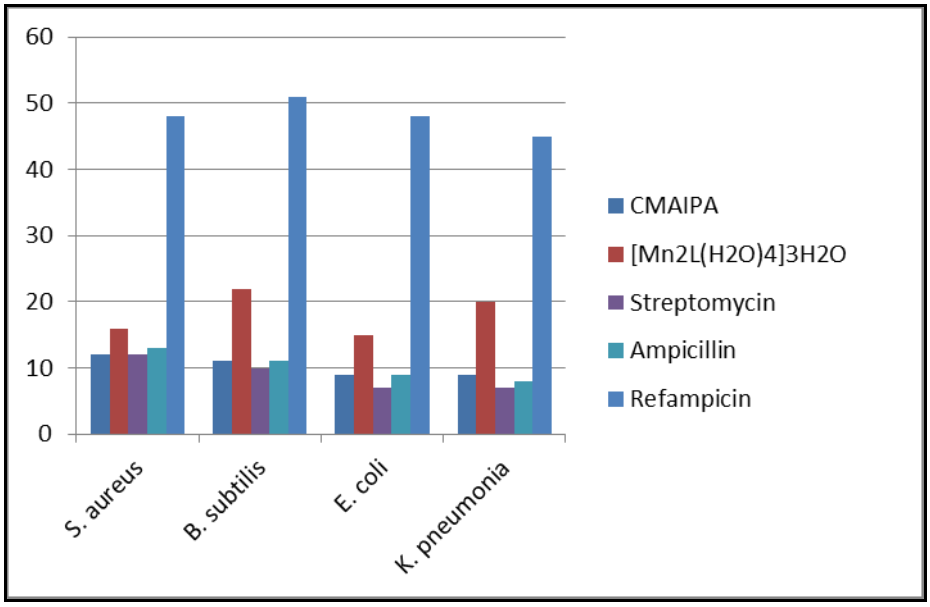



**Fig.1Comparison of MIC values (in µg/mL) of complexes and standard drugs against different bacteria.**

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