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RESEARCH PAPER

Mononuclear Erbium (III) Complex with Tetradentate N2O2 Schiff Base Ligand

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ABSTRACT:

The synthesis of a tetradentate Schiff-base ligand bis(salicylidene)ethylenediamine from salicylaldehyde and ethylenediamine , are important class of ligands . The results of the C.H.N study revealed the formation of a 1:1 [M:L] ratio. .$[Er(Salen)(NO_3)_2]^-$, square antiprismatic geometry, is the proposed structure of lanthanide metal complex. ^{1}H-NMR, FT-IR, UV-Visible spectral mesurements, and molar conductance were used to estimate the synthesized Schiff-base ligand and its complex.

The stoichiometry of the complex has been found to be 1:1 (Er:Salen) matching with C.H.N. analysis. After deprotonation, spectral studies revealed that the ligand was tetradentately coordinated to the metal ion (N_2O_2) through azomethine nitrogen and phenolic oxygen. The biological activities of the Schiff base (Salen , H_2L) and Er(III) complex against E.coli and Staphylococcus bacteria were examined, Schiff base ligand being less active than Erbium (III) complex.

KEY WORDS: Salen ligand , ONNO donor atoms, Er(III) , antibacterial studies
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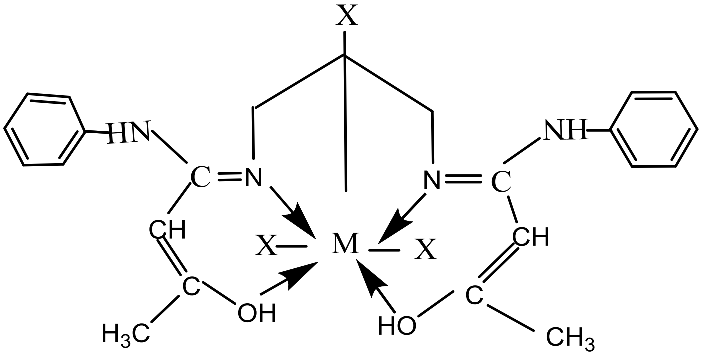
1.INTRODUCTION :

Schiff bases and their metal complexes have taken a central role in the expansion of co-ordination chemistry, the synthesis of tetradentate Schiff-base ligands from diamines and the corresponding salicylaldehyde derivative is an important reaction. Fig.1. shows the proposed structure for the known lanthanide complexes (Jadhav etal, 2017).



X= Cl^- , NO_3^- , NCS^-
M= Sm(III) , Gd(III) , Dy(III)

Fig.1. Proposed structure for the identified lanthanide complexes

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An comprehensive series of inquiries into the [bis(salicylidene)ethylenediamine-Erbium(III)] complex and other Complexes within this family has been performed (Holt and Post, 1971). (Lodewyckx etal.,2001) (Rao and colleagues, 2002) (Varghese and Muraleedharan, 2012) Schiff-bases are an essential class of organic compounds with many biological applications, including proteins, visual pigments, enzymic, alodolization, and decarboxylation reactions. Furthermore, some Schiff-bases and their metal ion complexes have antibacterial, antiviral, and antitumor properties. Because of the inclusion of the (-HC=N-) group (Athira et al.,2011), it is biologically important (Shelke etal, 2012) (R.V. Deun and Binnemans, 2001) (Abdel-Kader and El-Ansary, 2009) (Hayvali and Dal.H., 2004) . Lanthanides are metals that are highly electropositive and reactive. Except for Yb(III) , their reactivity tends to be proportional to their size, with Eu having the largest metal radius being the most reactive (Greenwood, 2012). Ethylenediamine is a highly basic amine with the formula $C_2H_4(NH_2)_2$, it’s a colorless liquid with an ammonia-like odor (Kotova etal.,2008). Ethylenediamine is a bidentate ligand that can bind to a variety of metal ions and form very stable complexes with lanthanide metal ions or transition metal ions. (Endale and Desalegn, 2018) (Taha etal. 2011) (T.A. Al-Diwan,2011) (Maher and Mohammed ,2015). The present study aimed to synthesis of Erbium(III) complex with tetradentate N_2O_2 Schiff -Base ligand , as possible antibacterial agents. Some authors (Acuña-Cueva, 2003) noted that salen ligand with central metal ions gives rigid compounds .

2. Experimental

2.1-Chemicals and reagents

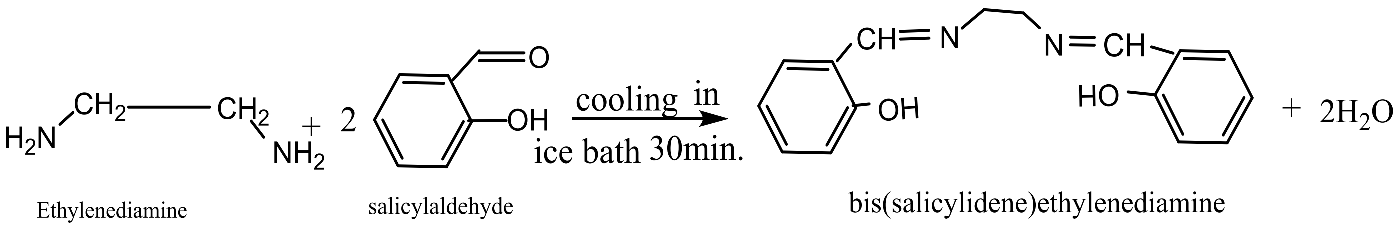
All the chemicals used in the present work were of analytical grade. Salicylaldehyde, ethylenediamine (Sigma Aldrich), $Er(NO_3)_3.5H_2O$ as metal salt (Fluka), and solvents such as DMSO, distilled water, ethanol, methanol, and diethyl ether from Sigma Aldrich and BDH were used in this work .

2.2-Measurements

A Jenway conductivity meter 4200(0.93cell constant) (UK) was used to measure the conductivity of the complex in (DMSO). Electrothermal 9100 was used to calculate melting points (UK). In a shimadzu spectrophotometer, FT-IR spectra were registered using KBr discs in the 4000-400 cm^{-1} range. In the education college –Chemistry Department Salahaddin university –Erbil- Iraq, UV-Visible spectra were reported in DMSO on a Shimadzu 1800 UV-Visible. In Al-al-Bayt Central Labs (Jordan), 1H-NMR was performed on a Bruker ultra-shield 300MHZ with TMS as internal references. At Marash University, carbon, hydrogen, and nitrogen (C.H.N) analysis was performed using a Euro EA elemental analyzer 3000/Italy. The oxalate–oxide method was used to evaluate erbium metal (Vogel, A.I.,1963). The Erbil Medical Technical Institute of Erbil Polytechnic University in Iraq conducted biological activity studies.

2.3- Synthesis of ligand H_2L (salen)

The Schiff base ligand H_2L bis(salicylidene)ethylenediamine was synthesized by directly mixing (2mmol,0.244g) salicylaldehyde dissolved in 25ml absolute ethanol with (1mmol,0.0601g) of (en) according to a published method (Cozzi,P.G.,2004). For around 30 minutes, the reaction mixtures were cooled in an ice bath and vigorously stirred. The solution turned a bright yellow color, indicating that the Schiff base had developed. Filtration was used to extract the precipitate, which was then washed with ethanol and dried in an oven. the yields were 80% and m. p 127°C , M.wt.268.31. The preparation Reaction for the H_2L is outlined in Scheme .1.



Scheme.1.Preparation reaction of (Salen) Ligand

2.4 -Synthesis of $[Er(salen)(NO_3)_2]^-$ Complex

The complex was made by dissolving [1 mmol (0.443 g)] of the metal salt Er $(NO_3)_2.5H_2O$ in 20 mL absolute ethanol and stirring it thoroughly for several minutes. [1mmol (0.268g)] H_2L dissolved in 10ml ethanol was applied to the resulting solution. The resulting mixture was heated under reflux for two hours on a magnetic stirrer, the pale brown precipitate was filtered, washed in ethanol, dried, and the m.p. was measured at 280 ^oC . In order to make complex, the metal to ligand ratio must be 1:1. The C.H.N results based on the elemental analysis data for $[Er(salen)(NO_3)_2]^-$ complex Calc.. C,34.28%, H,2.5% &, N,10 % - Found C,34.15 %, H,2.44% , N,10.11 %, and Er(III) percentage is 30% . The prepared complex in aqueous solutions and non-popular organic solvents such as ether, acetone, benzene, and carbon tetrachloride is insoluble, but it dissolves readily in DMF and DMSO. In acidic solutions, Erbium complex dissociate slowly, in acidic solution limiting their use to basic media.

3. Result and Discussion

3.1- IR Spectra

The ligand exhibits a medium intensity band at 1637cm^{-1}, which is typical of ʋ(C=N) stretching vibration; however, in the Erbium(III) complex, the band is shifted around 17cm^{-1} , suggesting that the azomethine nitrogen is involved in coordination to the metal ion (PalS and Pal.S,2002). The hydrogen bond package in the ligand and complex structure presence at 3186-3008 cm^{-1} . Stretching vibrations of the ʋ(C=C) type occur in the ligand at 1498 cm^{-1} and are moved to 1483 cm^{-1} when the erbium complex suffered bathochromic shifted. The assignable strong band in the spectrum of the ligand caused by phenolic ʋ(C-O) at 1284 cm^{-1} has shifted to 1280 cm^{-1} low intensity band in the spectrum of the erbium complex due to the participation of phenolic oxygen in coordination with metal ion. The presence of bands at 449cm^{-1} and 528cm^{-1} in the complex spectrum, which correspond to the stretching vibrations of the M-O and M-N bands, respectively, suggest that the salen ligand coordinated to the metal ion in the complex via a N and O atom (Toyssie P. and Charatte ,1963). The coordinated nitrate ion as a bidentate ligand is responsible for the new bands observed in the Er(III) complex at 1375-875 cm^{-1} medium bands (Agarwal etal ,2005). The I.R spectra Figures 2&3 show the Salen ligand and Er(III) complex .

3.2-^{1}H - NMR spectrum of Schiff base ligand

The ^{1}H-NMR spectrum of the Salen ligand recorded in DMSO-d_6 (Sabir et al, 2017). Fig. 4. Show the spectrum of Salen Ligand by ^{1}H-NMR. Because of the presence of the (ph-OH) proton, the ligand ^{1}H-NMR spectrum shows a signal at 13.33 ppm and at 8.4 ppm there is a sharp singlet signal for the -CH=N- proton in ligand spectrum Aromatic protons in (H_2L) appeared in multiplets ranging from 7.7 to 6.5 ppm and were unaffected by temperature.

3.3- Electronic transition spectra of ligand and its complex

In Er(III) ion 4f - orbitals do not engage in bonding because they are well protected by the $5S^2$ and $5p^6$ orbitals. The ligand has little effect on their spectroscopic and magnetic properties (Hebbink G., 2002). Fig.5. depicts the electrical spectrum of the Er(III) metal ion. The observed wave length in the (40.000-12.500) cm^{-1} range is transitioned by 4f-4f. As a result of Er(III) absorption spectrum are usually sharp, line-like spectra, as opposed to the extensive absorption of transition metals. The 4f orbitals in lanthanides are buried deep within the atom, reducing the impact of ligand vibrations on the broadening effect (Hussein et al ,2018). Ligand to metal charge transfer bands appears as a strong band .The presence of the -CH=N- band is indicated by two maximum spectrum observed in the Er(III) complex (35.714-26.315)cm^{-1} assigned to the π - π^* and n-π^* transitions (Mohammed et al, 2013). Fig .6. illustrates the combined UV-Vis. spectrum of Salen ligand and Er(III) complex.

3.4- Molar conductivity - The electrical conductance measurements for the Er (III) complex indicate that it is electrolytic nature (1:1) the calculated value is 178 $\Omega^{-1}cm^{-1}mol^{-1}$.

3.5- Antibacterial activity.

The antibacterial function of the Salen ligand and Erbium(III) complex was investigated. The organization of Salen ligand and Erbium(III) complex with two bacteria species, E.coli and Staphylococcus aureus, was investigated (FI.F.H.S., 2015) (F.H. Kamel and S.S. Sabir, 2017) at 37°C for 24 hours, Using (DMSO) as a solvent and a control were examined , the concentration of the compounds in this solvent was 25mg per one milliliter using disc sensitivity test and as compared with control, that the inhibition with the aid of using steel chelates is better than that of ligand . Inhibition zones were measured in millimeters . The $[Er(salen)(NO_3)_2]^-$ complex has been found to have higher antibacterial activity than the ligand. Fig.7. show the antibacterial activity of Schiff base Ligand and Er(III) complex.

Conclusion

A specific chelating Schiff base is formed when two equivalents of salicylaldehyde react with a diamine such as (en). There is a palace for two nitrate ions open to additional ligands for raising the coordination number to eight square antiprismatic geometry, salen ligand with four coordinating sites as tetradentate ligand (NOON) donor atoms sequence towards Er(III). In fact, by forming chelating complexes, Schiff bases can increase the stability of several metal ion complexes of various oxidation numbers. (N.R.Bader,2010) (Gueye,M.N.2017) Fig..8.,show the suggested structure of $[Er(salen)(NO_3)_2]^-$ is exceptional example of single ionic lanthanide complex coordinating with Schiff base ligands (Sui, Y. etal ,2015).

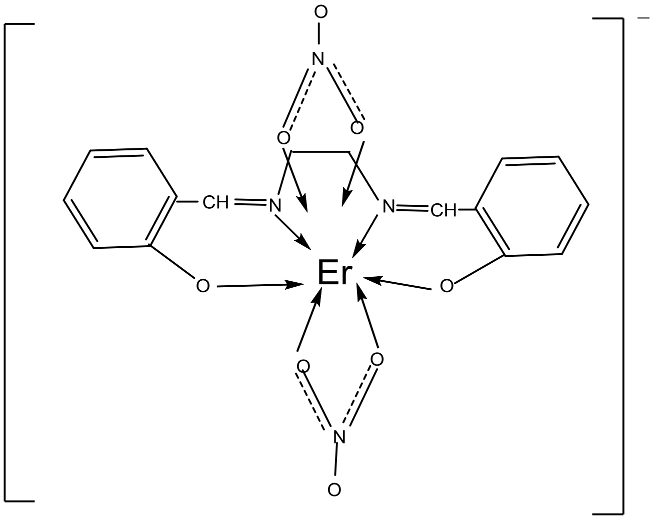


Fig. 8. Suggested structure of $[Er(salen)(NO_3)_2]^-$ complex .

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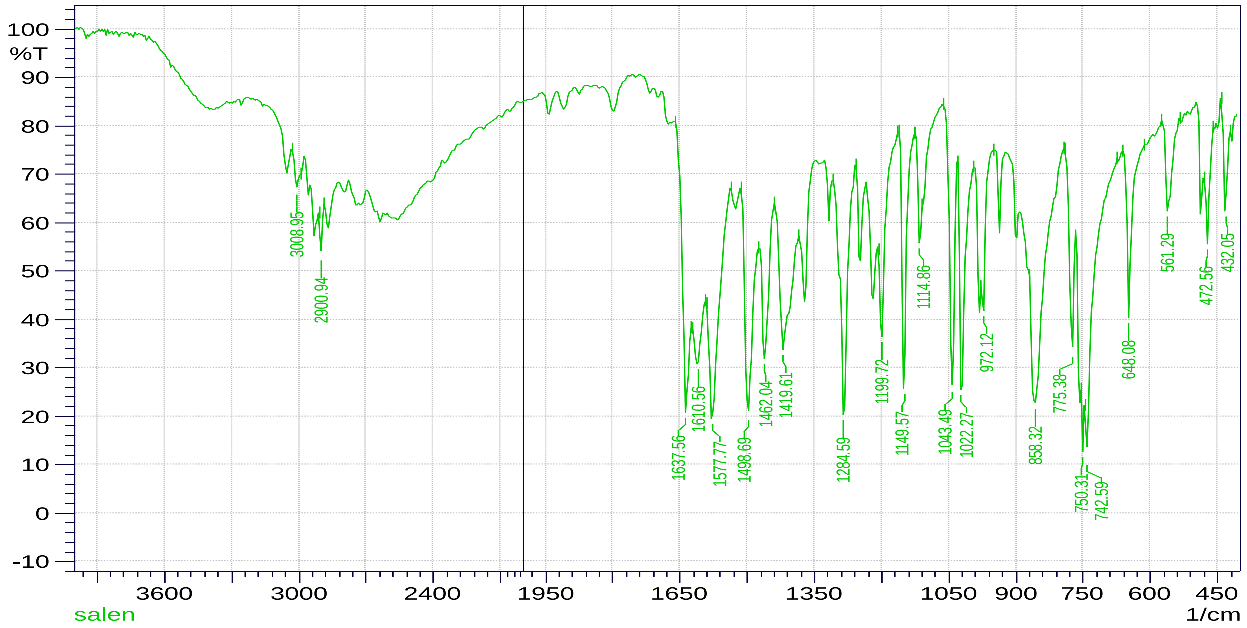

Fig.2. The IR spectrum of Salen Ligand.

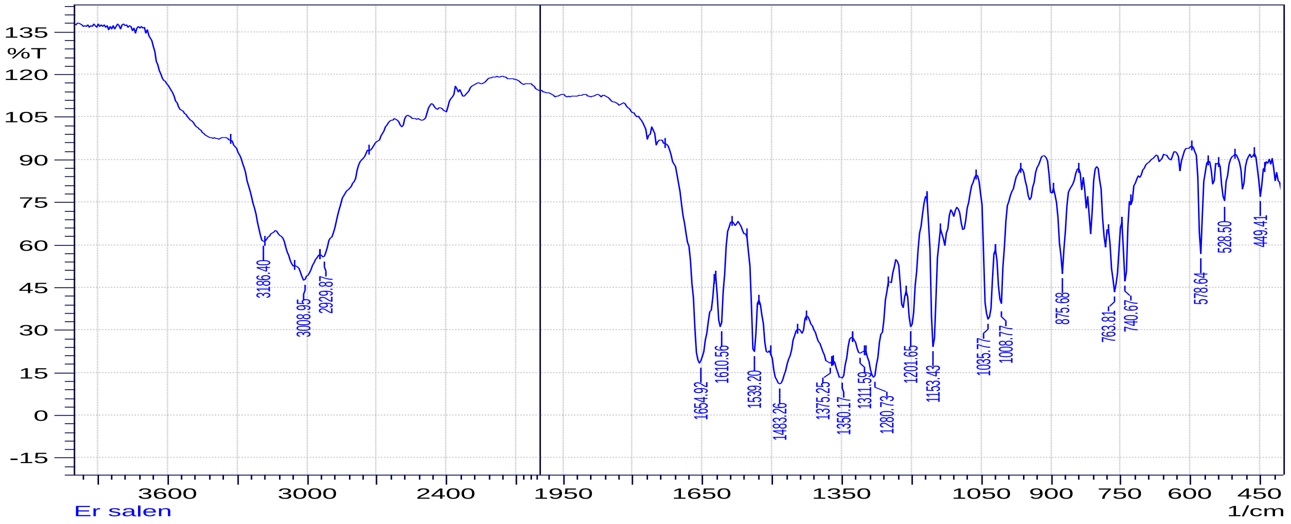

Fig.3. The IR spectrum of $[Er(salen)(NO_3)_2]^-$

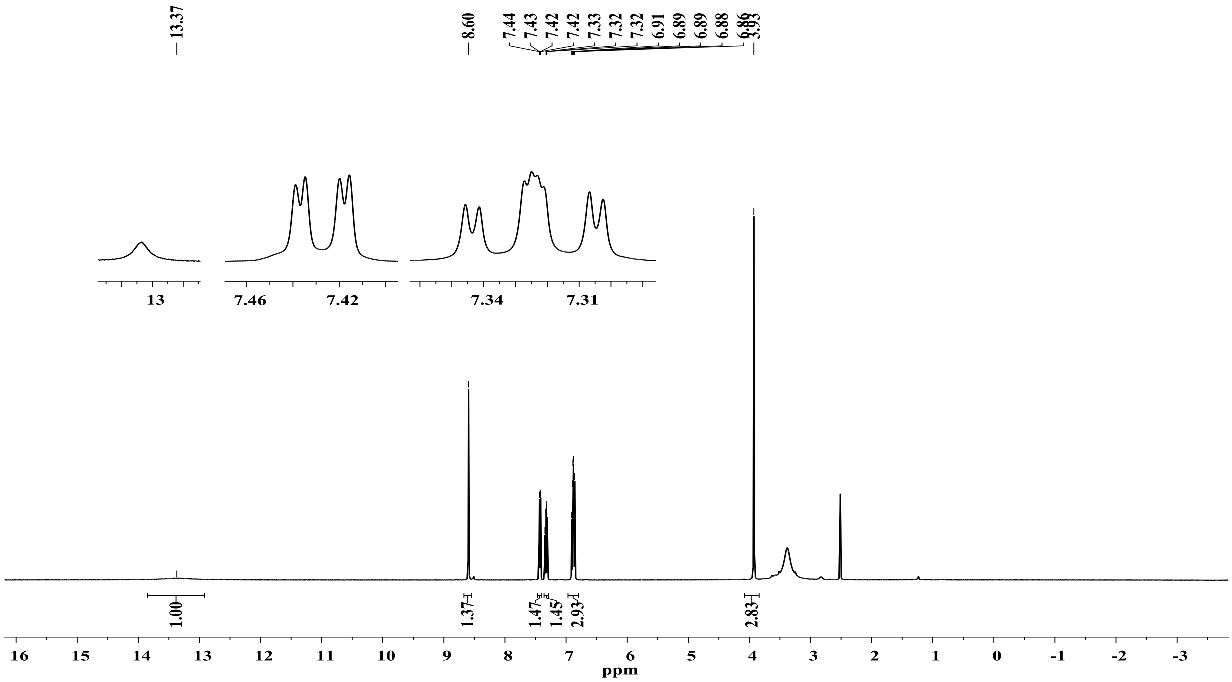

Fig.4. ^{1}H-NMR spectrum of Salen Ligand

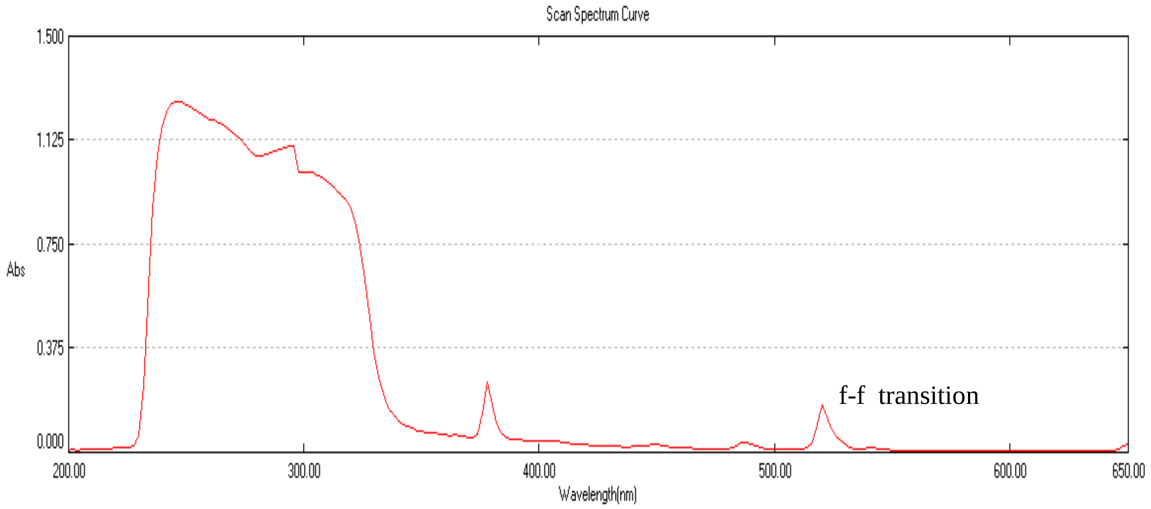

Fig.5. UV-Visible Spectrum of Er(III) Metal ion in methanol solvent .

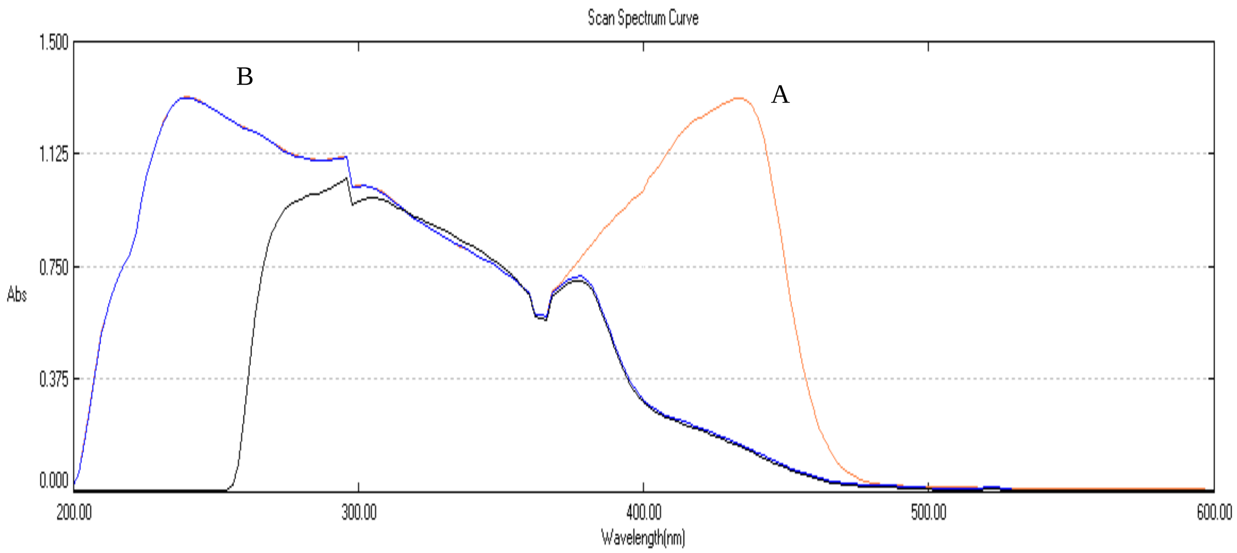

Fig.6.Combined UV-Visible Spectrum of Salen ligand (A) & Er (III) complex in DMSO solvent (B).

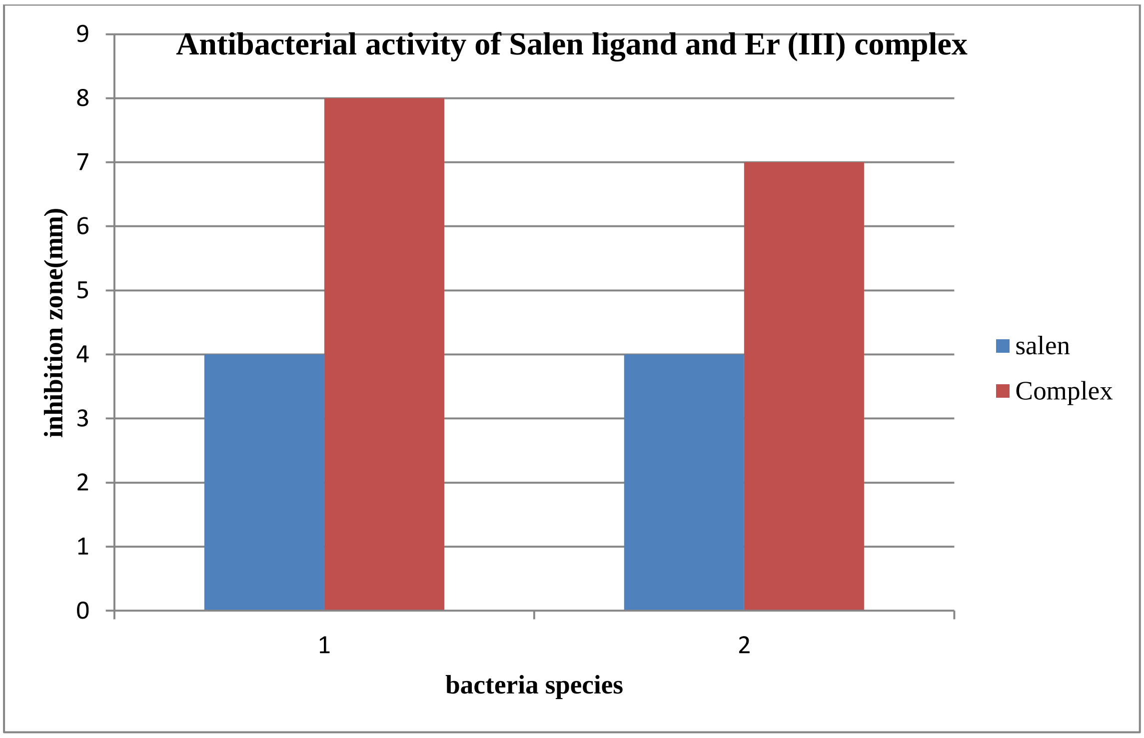

Fig.7. The antibacterial activity of Schiff base Ligand and Er (III) complex.

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