Preparation, Characterization And Biological Study of New Azo-Oxime Ligand And Some of Its Metal Complexes

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الخلاصة

مركبات كلابية جديدة مع الصيغة العامة $[M\ (HL)_2(H_2O)_2]$. عندما $[M= Co(II), Ni(II), Cu(II)]$، و $[M\ (HL)_2].(H_2O)_2$ لل Zn(II) وCd(II). حضرت بواسطة تفاعل أملاح الكلوريدات لهذه العناصر مع ليكاند آزو-أوكزيم جديد 2-Hydroxy(3-trifloromethylphenylazo)-benzaldehydeoxime (H_2L). والمُحضر بإزواج ملح الديازونيوم لل 3-مثيل انلين مع السالسلديهايد. شخص ليكاند الازو-أوكزيم الجديد ومعقداته الكلابية بالتقنيات المتاحة، وأظهرت النتائج إن المعقدات الكلابية لكل من Co(II) و Ni(II) و Cu(II) ذات شكل ثماني السطوح، وان Zn(II) و Cd(II) لها شكل رباعي السطوح. تم اختبار الليكاند ومعقداته الفلزية ضد كائنات حساسة متمثلة ب *Staphyllococcus aureus, Streptococcus mutants, Escherichia coli* and *Proteus mirabilis* كمضادات بكتيرية و *Aspergillus flavus, Aspergillus terreus* كمضادات فطرية. وأظهرت البيانات أن للمعقدات الفلزية فعالية أعلى كمضادات بكتيرية وفطرية من ليكاندها الحر.

Abstract

New chelate compounds, with general formula $[M\ (HL)_2(H_2O)_2]$. when [M= Co(II), Ni(II), and Cu(II)] and $[M\ (HL)_2].(H_2O)_2$ for Zn(II) and Cd(II), were prepared by reacting chloride salts of these metal with new azo-oxime ligand 2-Hydroxy(3-trifloromethylphenylazo)-benzaldehydeoxime (H_2L), which was prepared by coupling of diazonium salt of 3-Methylanilin with Salicylaldoxime. The new azo-oxime ligand and its chelate complexes were characterized by available techniques and the results showed that Co(II), Ni(II), and Cu(II)] chelate complexes have octahedral geometry where Zn(II) and Cd(II), have tetrahedral geometry. The ligand and their metal complexes was tested invitro against the sensitive organisms *Staphyllococcus aureus*, *Streptococcus mutants*, *Escherichia coli* and *Proteus mirabilis* as antibacterial and *Aspergillus flavus*, *Aspergillus terreus* as fungicidal. The activity data show that the metal complexes higher antibacterial and antifungus activity than the free ligand.

Keywords: *preparation***,** *Azo -oxime, chelate complexes***,** *Biological Study*.

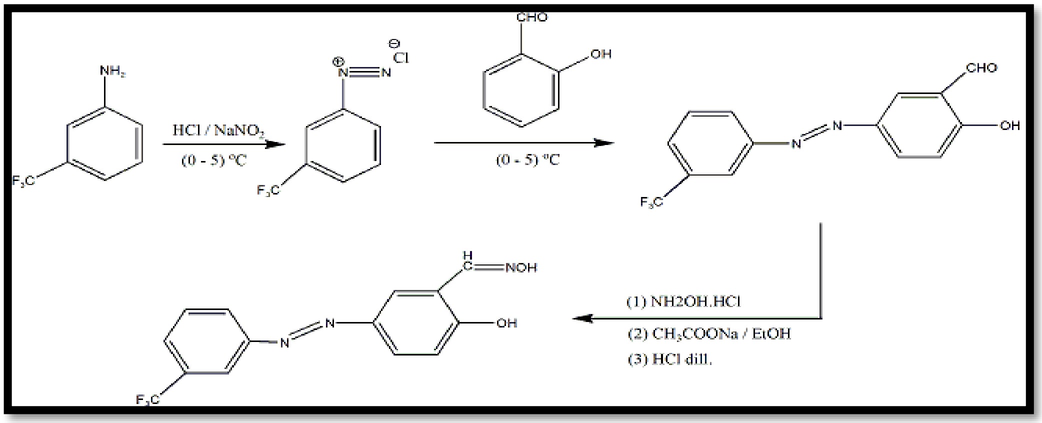
1. Introduction

Compounds of Azo-oxim are characterized by containing oxime and azo groups in its chemical structure. Azo-oximes are relatively recent when compared to the oximes and azo compounds. Both of these groups include in their chemical structure a nitrogen atom with a non-bonding pair of electrons that give it many physical and chemical properties. Due to their versatile application in various fields such as biomedical applications, textile dyes and advanced application in lasers, ink-jet printers, liquid crystalline displays, organic synthesis and electro-optical devices. Azo-oxime compounds are considered as the largest class of industrially synthesized organic dyes(1).

The oxime groups are good donors and can form stable chelate complexes with transition metal ions. These oximes and their metal chelate complexes play a major role in the advancement of inorganic chemistry. They are widely involved in a variety of biochemical(2) and analytical applications(3). It was also discovered that there is a possibility that they attention due to their possible antimicrobial applications (4). The *ortho*-hydroxy-aryloximes act as excellent bidentate ligands through the nitrogen and oxygen donor atoms. Their metal complexes are well-recognized ants extract that find industrial applications in extractive metallurgy and separation science (5).

2. Experimental

Preparing 2-[Hydroxy-5-(3-trifluoromethyl-phenylazo)-benzaldehyde]-oxime **(H_2L)** This type of ligand is prepared in two steps, the first step will be combining the azo compound with the carbonyl compound that was prepared in advance in order to obtain its oxime derivative in the second step. The azo-coupled 2-hydroxybenzaldehyde was synthesized using the known coupling methods(6). 2-Hydroxybenzaldehyde (3.2 ml, 0.03 mol) was dissolved in 25mL of a mixture of distilled water and alcohol which contained (1.2 g, 0.03 mol) of sodium hydroxide, pieces of ice were added for cooling purpose. Whilst the mixture of (3.7 ml, 0.03 mol) of *m*-trifloromethylanilin and 6 ml of concentrated hydrochloric acid dissolved in 50 ml of distilled water, the mixture was cooled with pieces of ice. This was followed by the addition of (2.1 g, 0.03 mol) sodium nitrite solution, the resulting solution was added slowly to the solution of Basal aldehyde solution at 0-5 ^{o}C. The product was then filtered washed by using cold distilled water and dried and re-crystallized using hot ethanol. The azo-oxime compound was prepared using the following method: Hydroxylamine hydrochloride (0.115 g, 0.0012 mol) and 2-hydroxy-5-[(*E*)-phenyldiazenyl] benzaldehyde (0.294 g, 0.001 mol) were dissolved in 30 mL of EtOH with Sodium acetate (0.163 g, 0.0012 mol). The solution was refluxed for 1 hour and left at room temperature, cold distilled water was then added to it, this was followed by the acidic acid equation of the mixture with the addition of drops of diluted hydrochloric acid. The mixture was then cooled and left for the next day to precipitate more. The crystals were then filtered, washed with cold distilled water and then dried under vacuum at 80 ^{o}C overnight. They were re-crystallized using hot ethanol.



Scheme 1: syntheses of the (H_2L) ligand

Preparation of metal complexes

The metal complexes (1 mol) were prepared by dissolving 0.618 g of the ligand in 20 ml ethanol which was added drop by drop whilst stirring, to produce a stoiciometric molar ratio of 1:2 (metal:ligand). The following salts Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were dissolved in 15 mL of hot distilled water. The colored precipitates formed at room temperature and were filtered off, washed using distilled water in order to remove any traces of the unreacted starting materials and were then dried at 70 °C overnight.

Antimicrobial activity studies

Antibacterial activity

The invitro biological screening effects of the investing compounds were tested against the bacteria *staphyllococcous aureus*, *Streptococcous mutans*, *Escherichia coli* and *Proteus mirabilis* by the well-diffusion method using Muller-Hinton agar as medium (7). Wells of 6 mm in diameter were made in the agar plates by using sterile cork borer , then agar surfaces were inoculated with each bacterium. The tested compounds were dissolved in dimethylformamide (DMF) to obtain a solution 1000 ppm concentration. The plates were incubated at 37 ^{0}C overnight; the zones of inhibition formed were measured in mm. Each experiment was performed in triplicate and the average of the three ages of the three determinations was recorded.

Antifungal activity

The fungicidal activities of the compounds were evaluated by the well-diffusion method (8). Against the fungi viz *Aspergillus flavus*, *Aspergillus terreus* at 10, 100 and 1000 ppm concentrations with triplicate determinations in each case. The average percentage inhibition was calculated using the following formula (9).

Inhibition (%) = (C – T) 100 / C.

Were C is diameter of colony fungus in center plates and T is diameter of the colony fungus in the test plates.

3. Results and discussion

The results of the elemental analyses of the azo-oxime ligand and its metal chelates are in good agreement with the theoretical expectations. The elemental analyses of the coordination compounds show that the metal:ligand ratios are 1:2 in all the metal complexes. The molar conductivities of the metal chelates in DMF at 25 °C are in the range of 11.75-21.37 Ω^{-1} cm^2 mol^{-1}, indicating nonelectrolytes in solution(10). The conductivity measurement of complexes summarized in table 3.

IR spectroscopy

The infrared spectra of the free azo-Oxime ligand (H_2L) and its metal complexes with Co(III), Ni(II), Cu(II), Zn((II) and Cd(II) are given in Table 1. The IR spectrum of the ligand and cobalt(II) complex is given in Figure 1 and 2 respectively. The observed band in the range 1618 cm^{-1} is due to ν (C=N) group of the ligand(11). These bands are shifted to lower region during the complex formation indicating its participation in coordination with the metal ions. The spectra of the metal complexes showed the hydroxyl group with a location, shape and intensity different from the free ligand spectrum, which is due to the association of the υ(O─H) with the metal ions after the loss of proton at the formation of the complex. The sharp band in the range (804 cm^{-1}) are due to ν (C–F)(12). In the metal complexes, the aromatic C-H stretching bands were observed between 3080 and 3045 cm^{-1}(13). The infrared spectra of the complex showed a weak beam to medium intensity and at frequencies (3600-3200 cm^{-1}), which are due to the asymmetric and asymmetric vibrations of the H-O-H that indicate the presence of water molecules(14). The vibration band of the azo group both in the ligand and the complexes was seen at range (1479 – 1481 cm^{-1})(15), the constant value of its vibration both in the ligand and the complexes indications that there is no coordination between the azo group and the metal ions. However, there were two new bands, which were not seen in the spectrum of the ligand, appearing also in the spectra of the complexes; the first one was the (M-O) stretching bands seen between (520 cm^{-1}) and (507 cm^{-1}), which indicated that the ligand was coordinated with the metals through the phenolic hydroxyls, and the second weak band was (M-N) vibrations seen at (468 – 478) cm^{-1}(16).

Table 1: IR frequencies (in cm^{-1}) of the azo-Oxime ligands and their complexes

No.	compounds	υ(O─H)	υ(C=N)	υ(N=N)	υ(C─F)	υ(M─O)	υ(M─N)
1	**H_2L_1**	3427	1618	1481	804	-----	-----
2	**$[Co(HL_1)_2(H_2O)_2]$**	3445	1602	1478	804	513	468
3	**$[Ni(HL_1)_2(H_2O)_2]$**	3419	1604	1475	804	511	472
4	**$[Cu(HL_1)_2(H_2O)_2]$**	3417	1602	1473	804	507	476
5	**$[Zn(H_2L_1)_2].2H_2O$**	3415	1600	1479	804	520	470
6	**$[Cd(H_2L_1)_2].2H_2O$**	3418	1598	1473	804	516	478

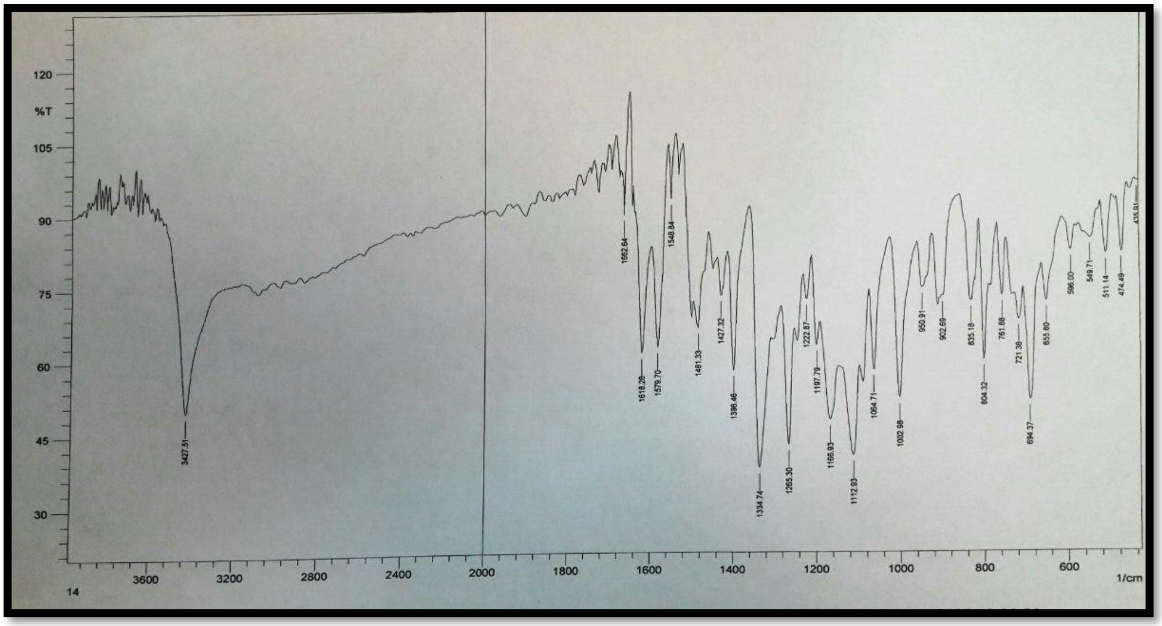


Figure 1 : IR spectroum of(H_2L) ligand

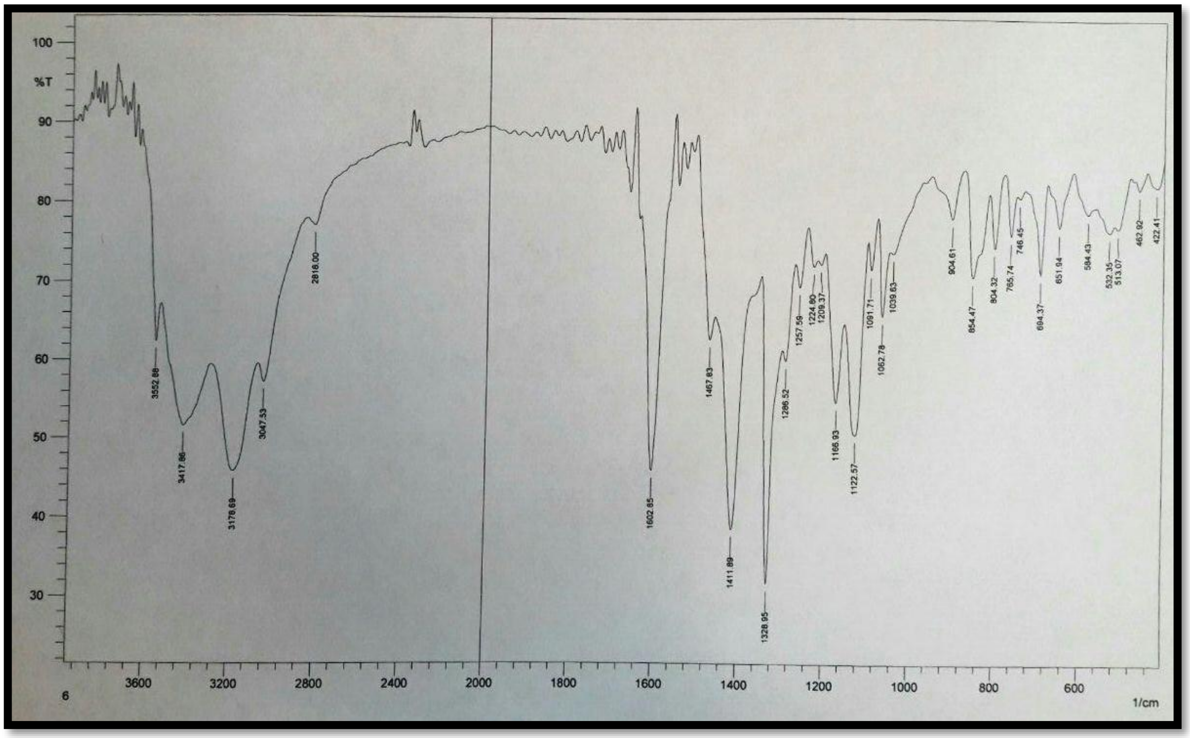


Figure 2: IR spectroum of the[Co(HL)$_2$(H$_2$O)$_2$] chelate complex

Elemental Analysis

The elemental analysis data of the ligand and it's metal complexes are given in table 2. They were consistent with the calculated results from the empirical formula of each compound. It has been found that the theoretical values are in good agreement with the found values**.**

Table 2: The analytical data of the ligands and their complexes

No.	**Compounds**	Symbol	Molecular formula (Mo.Wt)	Found (Calc.)%			
				C	H	N	M
1	$C_{14}H_9N_2O_2F_3$	HA	294	56.89 (57.14)	3.01 (3.06)	9.62 (9.52)	------
2	$C_{14}H_{10}N_3O_2F_3$	H_2L	309	54.13 (54.37)	3.16 (3.23)	13.41 (13.59)	------
3	$[Co(C_{14}H_{10}N_3O_2F_3)_2(H_2O)_2]$	(A_1)	710.93	47.11 (47.26)	2.99 (3.09)	11.69 (11.81)	8.01 (8.28)
4	$[Ni(C_{14}H_{10}N_3O_2F_3)_2(H_2O)_2]$	(A_2)	710.7	47.15 (47.27)	2.96 (3.09)	11.56 (11.81)	7.91 (8.25)
5	$[Cu(C_{14}H_{10}N_3O_2F_3)_2(H_2O)_2]$	(A_3)	715.5	46.69 (46.96)	2.98 (3.07)	11.52 (11.74)	8.26 (8.87)
6	$[Zn(C_{14}H_{10}N_3O_2F_3)_2].2H_2O$	(A_4)	717.4	46.61 (46.83)	2.92 (3.06)	11.49 (11.75)	8.78 (9.11)
7	$[Cd(C_{14}H_{10}N_3O_2F_3)_2].2H_2O$	(A_5)	764.41	43.72 (43.95)	2.69 (2.87)	10.72 (10.98)	13.98 (14.70)

Electronic Spectra

The UV/Vis spectra of azo-oxime ligand (H_2L) and its metal complexes were measured in DMF at room temperature, and the absorbance maxima are presented in Table 3. The H_2L ligand was characterized mainly by two absorption bands. The bands at 21.786 (459) and 27.700 cm^{-1} (361) were assigned to *($n\rightarrow\pi^*$)* and *($\pi\rightarrow\pi^*$)* transitions respectively in the azo and hydroxyimine groups in the phenyl azo- linked hydroxyimino ligand H_2L. The UV-visible spectrum of the H_2L azo-oxime ligand in DMF solution is shown in Figure 3. UV/Vis spectra can often provide quick and reliable information about the ligand arrangement in metal complexes. The cobalt(II) complex exhibited three bands, which are expected from an octahedral structure. The UV/Vis spectrum of the Co(II) complex displayed 2 well-defined spectral bands at 9500 cm^{-1} and 21.221 cm^{-1} . The third d-d transition band, which may be obscured. These spectral bands may have corresponded to ${}^4T_{1g} \rightarrow {}^4T_{2g}$, ${}^4T_{1g}\rightarrow{}^4A_{2g}$ and ${}^4T_{1g} \rightarrow {}^4T_{1g}$ transitions, respectively, which are characteristic of 6-coordinated geometry around cobalt(II)(17). The measured magnetic moment value (3.93 B.M.) of the Co(II) complex. The electronic spectrum of the $[Ni(H_2L)_2(H_2O)_2]$ complex showed 3 well-defined bands assignable to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}$ transitions in an octahedral structure, respectively(18). The observed magnetic moment of the Ni(II) complex was 2.82 B.M. The UV-visible spectrum of the Nickel complex is shown in Figure 4. The UV/Vis spectrum of copper(II) complex showed 3 absorption bands at 10.905 , 11.428 and 21.691 cm^{-1} associated to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively. The magnetic moment of Cu(II) complex was 1.79 B.M., indicating the presence of one unpaired electron(19). The electronic absorption spectrum of showed 2 bands at 24.038 and 34.482 cm^{-1} , which were assigned to the charge transfer. The bands at 28.248 and 34.722 cm^{-1} in the UV-visible spectrum of the $[Cd(H_2L)_2].2H_2O$ The spectroscopic data are given in Table 3. The Zn(II) and Cd(II) complexes spectra did not show any peaks of (d–d) transitions because they had electrically charged orbitals (nd^{10}).

Table 3. Electronic spectral data for azo-oxime ligand and its chelate complexes in DMF.

No.	Complex	Assigument	Absorption band(cm^{-1})	μ_{eff} (B.M)	Proposed Structure	Λ_M ($S.cm^2.mol^{-1}$) In (DMF)
1.	$[Co(HL_1)_2(H_2O)_2]$	$^4T_1g \rightarrow {}^4T_2g$	9500	4.23	Oh	21.37
		$^4T_1g \rightarrow {}^4T_1g$	21.221			
		$^4T_1g \rightarrow {}^4A_2g$	-			
2.	$[Ni(HL_1)_2(H_2O)_2]$	$^3A_2g \rightarrow {}^3T_2g$	10.976	3.82	Oh	11.76
		$^3A_2g \rightarrow {}^3T_1g$	14.727			
		$^3A_2g \rightarrow {}^3T_1g$	22.075			
3.	$[Cu(HL_1)_2(H_2O)_2]$	$^2B_1g \rightarrow {}^2A_1g$	10.905	1.49	Oh	16.02
		$^2B_1g \rightarrow {}^2B_2g$	11.428			
		$^2B_1g \rightarrow {}^2Eg$	21.691			
4.	$[Zn(HL_1)_2].2H_2O$	C. T.	……	Dia	Th	13.74
5.	$[Cd(HL_1)_2].2H_2O$	C. T.	……	Dia	Th	12.81

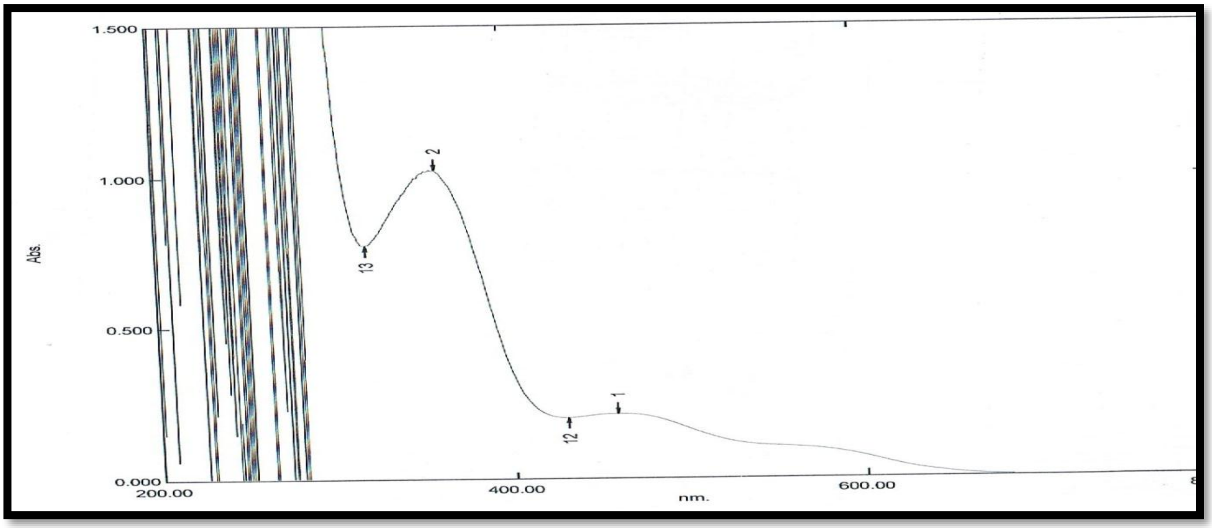


Figure 3: Uv-Visible spectroum of the ligand(H_2L)

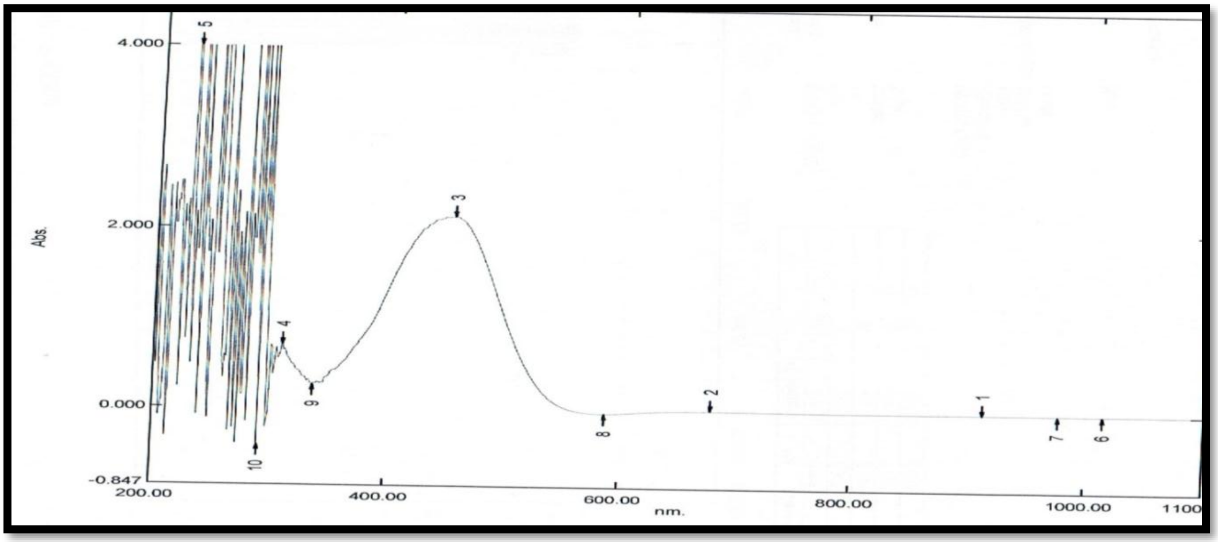


Figure 4: Uv-Visible spectroum of the[$Ni(HL_1)_2(H_2O)_2$]

Mass spectrum

The mass spectrum was obtained for the ligand. The mass spectrum of (H_2L) ligand was presented in figure 5. The most important peaks were observed in the mass spectrum data of ligand. The parent peak of ligand at m/z = 308.1 is due to the $[C_{14}H_{10}N_3O_2F_3]^+$ ion. The different competitive fragmentation pathways of ligand give the peaks at different mass numbers at 95.1, 143.1, 145.1 and 187.1. It was in good agreement with the molecular weight of the proposed structures and pathways of fragment for the ligand(20).

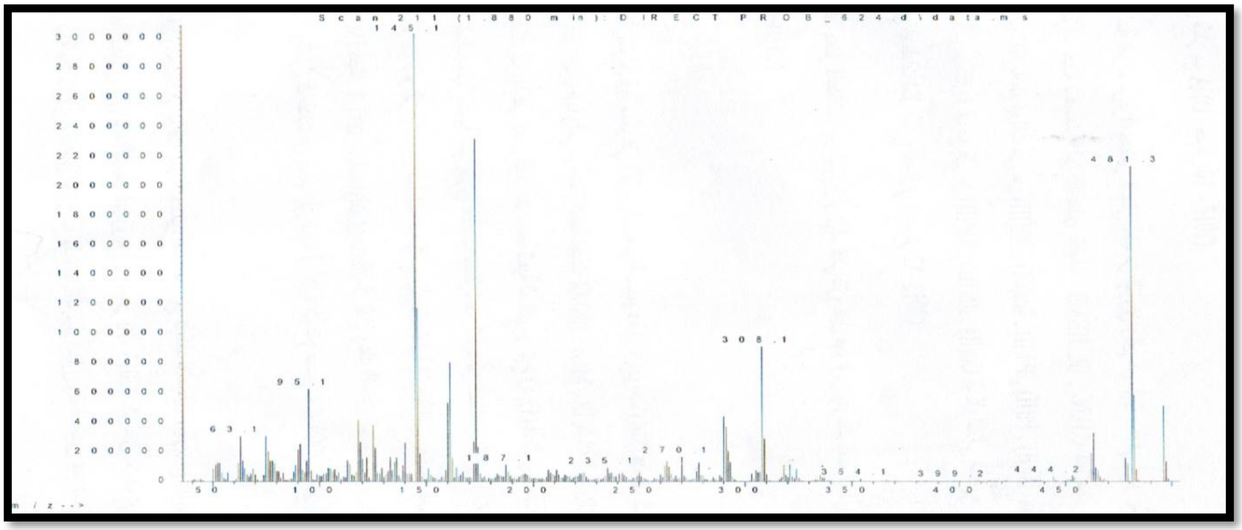


Figure 5: The mass spectrum of azo-Oxime ligand (H_2L)

^{1}H-NMR spectra

The ^{1}H-NMR spectrum of the azo-oxime ligand is shown in Figure 6. The Multiple peaks observed in the range of 7.19 – 8.80 ppm in ^{1}HNMR spectrum of H_2L were attributed to the aromatic protons, while the proton of the oxime group produced a signal that interleaved the range; it appeared as a single signal at the value of 8.50 ppm within the range mentioned above. As for the proton hydroxyl phenolic group of the salsaldehyde ring appeared as a single signal at 10.29(21,22).

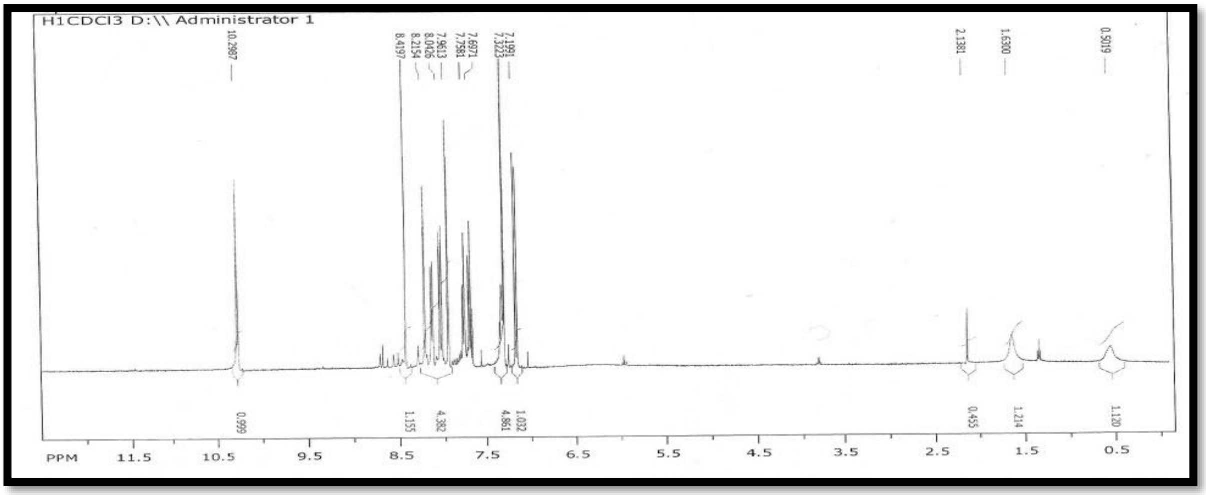
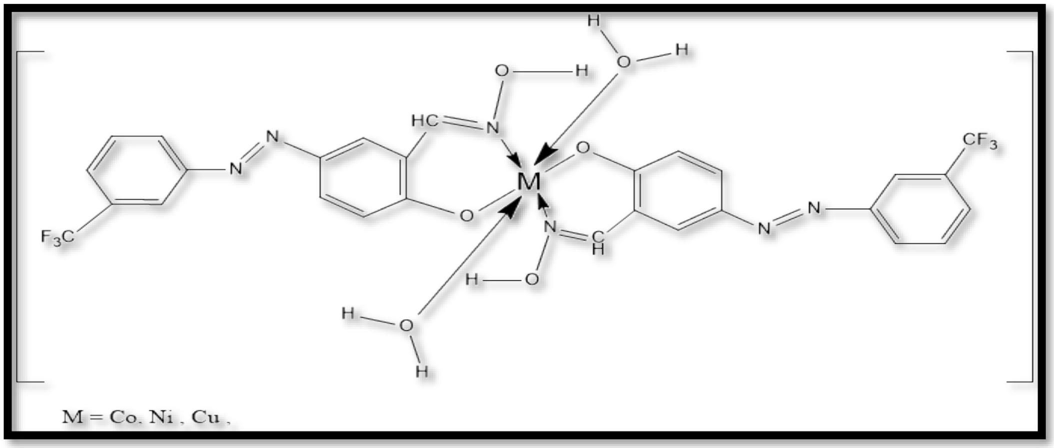
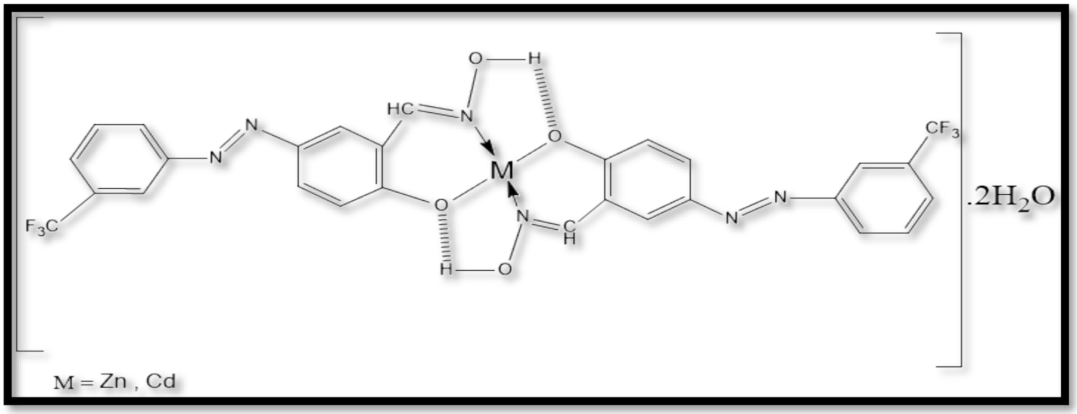


Figure 6: The ^{1}H-NMR spectrum of azo-Oxime ligand (H_2L)



Schem 3: The suggested geometry of Co(II), Ni(II), Cu(II), Chelate complexes



Schem 4: The suggested geometry of Zn(II) or Cd(II), Chelate complexes

Antimicrobial activity studies

Biological activity studies of the ligand and its chelate complexes have been tested for invitro growth inhibitory against *S.aureus, Str.mutans, E.coli and P.mirablilis* by well–diffusion method. Their zones of inhibition against different bacteria are presented in table 4 and its statistical presentation is shown in figure 7. The results show that the complexes display more potency and the ligand has less potency against same pathogenic bacterial strains under same experimental conditions. The ligand shows moderate effect to most bacteria with the exception of S.aureus and Str.mutans slight and high activity respectively. The Cd(II), and Ni(II), complexes were exhibited high potency against all bacteria. The Zn(II) complex has high potency as antibacterial for *S.aureus and Str.mutans except E.coli and P.mirabilis* moderate effect. The Cu(II) complex has high effect against *Str.mutans and P.mirablilis* with the exception of *S.aureus* and *E.coli* moderate effect, the Co(II) complex shown moderate potency against most tested

bacteria except Str.*mutans* high effect. From invitro fungicidal activity table 5, the results demonstrated that chelate complexes indicate high activity than the free ligand. A comparative study of the compounds was shown significant toxicity at 1000 ppm concentration, for all species

of fungi. However, all chelate complexes are more active the ligand and antifungal activity decrease on dilution. Also, it was observed that compounds exhibited more significant effect *A.terreus* than *A.flavus*. This would suggest that the chelation of the complex easily cross a cell membrane (23). Furthermore, when the comparison for the compounds was made between bacteria and fungi, it was observed that the compounds found to be more active against fungi than bacteria. Variation in the effectiveness of different biocidal species against microorganisms depends on the impermeability of the cell of the microbes or on differences in ribosomes of microbial cells(24). The higher biological activity of chelate complexes than that free ligand. This is probably due to the greater lipophilic nature of the metal complexes. The increased activity of the metal chelates can be explained by Overtone's concept and Tweedy's chelation theory. On chelation, metal ion polarity is reduced to a greater extent due to the overlapping of ligand orbital ad partial sharing of positive charge of metal ion with donor groups(25). Further, the delocalization of the π-electron is increased over the whole chelate sphere and enhances the lipophilicity of the complex. The lipophilic nature of the central metal atom is also increased upon chelation, which subsequently favors the permeation through the lipid layer of cell membrane(26). The mechanism of action of antimicrobial agents can be discussed under five headings, (1)inhibition of cell wall synthesis, (2)inhibition of cell membrane function, (3)inhibition of protein synthesis, (4)inhibition of folate metabolism and (5)inhibition of nucleic acids synthesis(27). The differences in antimicrobial activity are due to the nature of metal ions and also the cell membrane of the microorganisms.

Table 4: Antibacterial activity data (zone of inhibition in mm) of the ligand and their metal complexes

Bacteria / Compounds	*G(+Ve)*		*G(-Ve)*	
	S.aureus	Str.mutans	E.coli	P.mirabilis
H_2L	8	15	10	9
$[Co(HL)_2(H_2O)_2]$	10	18	11	11
$[Ni(HL)_2(H_2O)_2]$	13	20	13	16
$[Cu(HL)_2(H_2O)_2]$	12	18	12	14
$[Zn(HL)_2].2H_2O$	15	19	11	12
$[Cd(HL)_2].2H_2O$	17	22	16	15

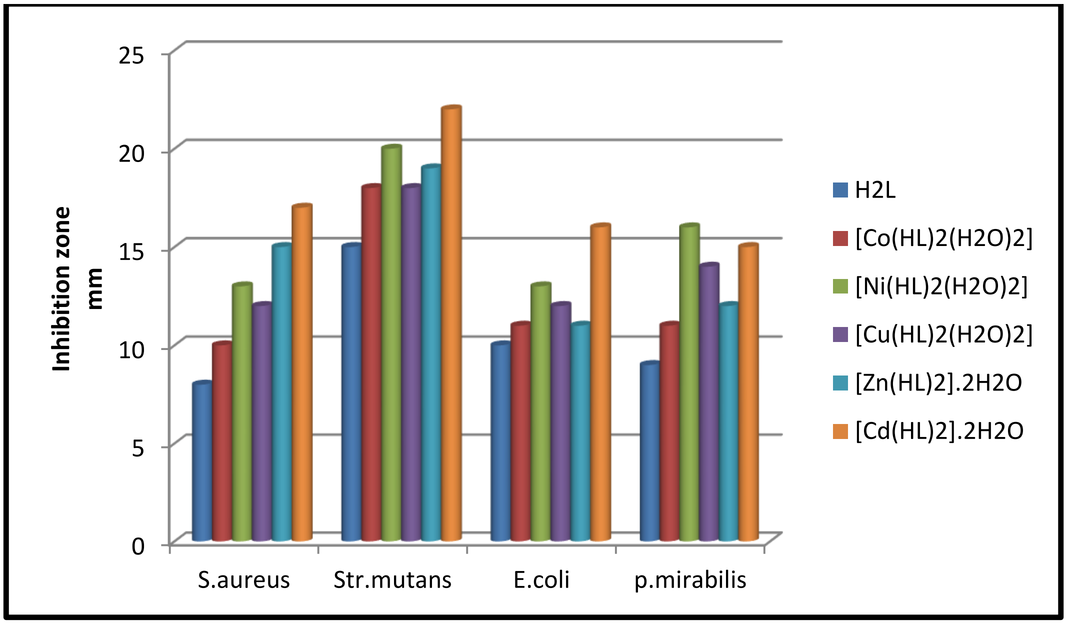


Figure 7: Statistical representation for antibacterial activity of ligand (H_2L) and its metal complexes

Table 5: Antifungal activity data of the ligand and their metal complexes

Compound	**Average percentage inhibition (%) after 72h**					
	A.flavus			***A.terreus***		
	10	**100**	**1000**	**10**	**100**	**1000**
H_2L	70	72.2	78.9	78.9	82.2	84.4
$[Co(HL)_2(H_2O)_2]$	67.8	74.4	77.8	78.9	83.3	87.8
$[Ni(HL)_2(H_2O)_2]$	72.2	76.7	80	84.4	88.9	91.1
$[Cu(HL)_2(H_2O)_2]$	70	76.7	82.2	83.3	87.8	88.9
$[Zn(HL)_2].2H_2O$	78.9	81.1	83.3	81.1	83.3	85.6
$[Cd(HL)_2].2H_2O$	75.5	77.8	84.4	80	86.7	90

Conclusion

In this work, a new azo-oxime ligand 2-[Hydroxy-5-(3-trifluoromethyl-phenylazo)-benzaldehyde]-oxime (H_2L) derived from 2-[Hydroxy-5-(3-trifluoromethyl-phenylazo)]-benzaldehyde and hydroxylamminehydrochloride and some of its transition metal complexes was prepared. The analytical data and the spectroscopic studies suggested that the complexes had the general formula $[M(HL)_2(H_2O)_2]$, where M is copper(II), nickel(II), or cobalt(II), and $[M(HL)_2].2H_2O$, where M is zinc(II), or cadmium(II). Based on th infrared, elemental analysis, electronic absorption, mass spectroscopic, nuclear magnetic resonance, electron paramagnetic resonance and molar conductance measurements data of the *m*-triflourophenylazo linked oxime ligand, H_2L was coordinated to the metal ion through the hydroxyimino nitrogen and phenolic oxygen atoms. Azo-oxime derivative H_2L probably forms a octahedral complexes with Co(II), Ni(II), Cu(II), and square planar complex with Zn(II) ion and Cd(II), with a metal:ligand ratio of 1:2. Based on the above spectral and analytical data. The observations of antimicrobial activity prove that compounds exhibit antimicrobial properties chelates show more inhibitory effects than the parent ligand.

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