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Synthesis, Investigation and Biologically Activity of Iron (II) Complexes with Diammie Complexes

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ABSTRACT

Iron diammin complexes can be possess biological activities, these complexes were synthesized via the reaction equimolar quantity of diphenyl carbizon {HNNCO(NH)2(C6H5)} (L1) or 4-Nitrophenylehydrazine { O2NC6H4(NH)(NH2} (L2) or 2 ,4-dinitrophenylhydrazine {(O2N)2C6H3(NH)(NH2)} (L3) with the iron solute {FeCl2} in ration (1:1) to form complexes [{HNNCO(NH)2(C6H5)FeCl2}] [FeL1], {O2NC6H4(NH)(NH2)}FeCl2] [FeL2] and[{(O2N)2C6H3(NH)(NH2)}FeCl2] [FeL3] respectively. They characterized by using Fourier Transform Infrared (FT-IR) and UV-Visible spectroscopy. A variable temperature study of these complexes were follow by using UV-Visible spectroscopy to follow electronic transform behaviors under temperature control. A coordination number of these complexes in five and four geometry may be assigned. These complexes are found to shown increased deferent inhibition to the growth of bacterial strains of Bacillus spp & Klebsiella spp & E.coli & proteus spp & pseudomona spp) while all complexes were in deferent's concentration (0.001, 0.2 and 1M) and the result as evidenced from the presence.

Keywords: diphenyl carbizon} (L1), 4-Nitrophenylehydrazine (L2), 2 ,4-dinitrophenylhydrazine (L3), Iron complex, variable temperature study, increased deferent inhibition to the growth of bacterial.

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INTRODUCTION

Complexes of transition metal have received a great attention because of their biological activities, including anti-tumour, antibacterial, antiviral, antifungal and anticarcinogenic properties [1-5]. Some of complexes ability biological activities are essentially due to their of coordinate tetradentate chelate with heavy metal ions, bonding through sulfur and nitrogen [6, 7]. The interest in Schiff base complexes and development of the field of bioinorganic chemistry has increased with highly interest, since it has been recognized that many of these complexes may serve as models for biologically important species [8, 9]. Iron complexes with Schiff base ligands, design, synthesis and characterization and play a relevant role in the coordination chemistry of iron due to their importance as synthetic models for the iron-containing enzymes [10, 12], oxidation catalysts [13, 14] and stable molecular materials based on temperature, pressure or light induced spin-crossover behaviours [15, 16]. The demonstration of amine-carbonyl condensation constitutes the number of enzyme-mediated and understanding mechanism of amine-carbonyl condensation have received great attention by D. Barton et al. [17] Thiourea compound has been used for anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity in experimental animals. [18] El-ajaily et al.[19] have Sanitized and investigated some complexes derived from salicylaldhyde and histidine and they found to have antibacterial activation on some pathogenic bacteria. Schiff base of types 3-enehydrazono-2-salicylidindolinone and there Complexes incorporating Co(II), Ni(II), Cu(II) and Zn(II) and they have activated for some antibacterial such Staphylococus aureus, Enteroccus, Proteus mirabilis, Escherichia coli, Bacillus anthracis, Pseudomonas aeruginosa and Candida albicans.[20]

MATERIALS AND METHOD

All chemical were used as received from supplied. Penhyle carbizon produced by BHD chemical company, 4-Nitro phenylehydrazine produced by Riedel-dehean chemical company, Ethanol production company PSPARK chemical company and Ethanol production company CARLOERBA chemical company. The metal salt iron chloride produced by (Laboratory Reagent) chemical company. Solvents used were purified by distillation.

Synthesis of [(phenyl carbizon) iron(II) dichloro] [FeL1]

In double nick flask (2 g) of iron dichloride ($FeCl_2$) in 15 ml of distal water was add equimolar quantity of diphenyl carbizon {$HNNCO(NH)_2(C_6H_5)$} (**L1**) (3.78 g) in 30 ml of ethyl alcohol drop wise in room temperature with steer, then temperature rise up in gradually to reflux for five hours. In during that time the color has been observed a changed in color from pink to reddish brown then the mixture of ammonia and water in (1:1) to the reaction and former left for an five hours on heating, where observed color of the solution changed from reddish-brown to brown. Then a brown solid was nominated from hot solution in filtration, dried and after recrystallization we acquired the brown crystals in percentage of 53% (Scheme 1).

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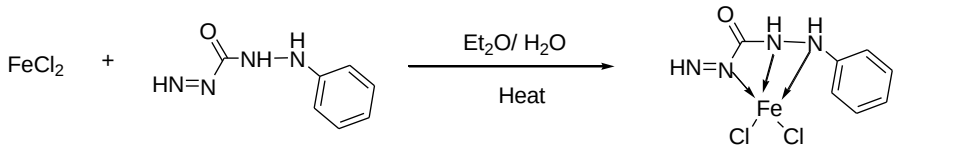
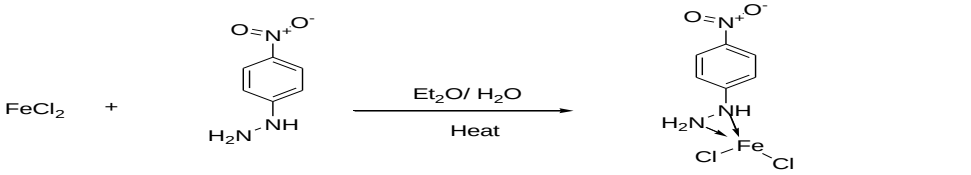


iron(II) chloride phenyl carbizon [(phenyl carbizon) iron (II) dichloro]

Scheme 1: preparation of [{HNNCO(NH)$_2$(C$_6$H$_5$)FeCl$_2$}] [FeL1]

Synthesis of [{4-Nitro phenylehydrazine} iron (II) dichloro] [FeL2]

In double nick flask (2 g) of iron dichloride ($FeCl_2$) in 20 ml of distal water was add equimolar quantity of 4-Nitrophenylehydrazine {$O_2NC_6H_4(NH)(NH_2$} (**L2**) (2.41g) in 30 ml of ethyl alcohol drop wise in room temperature with steer, then temperature rise up in gradually to reflux for five hours. In during that time the color has been observed a changed in color from pink to reddish brown then the mixture of ammonia and water in (1:1) to the reaction and former left for an five hours on heating, where observed color of the solution changed from dark brown to light brown. Then a light brown solid was nominated from hot solution in filtration, dried and after recrystallization we acquired the brown crystals in percentage of 70% (Scheme 2).

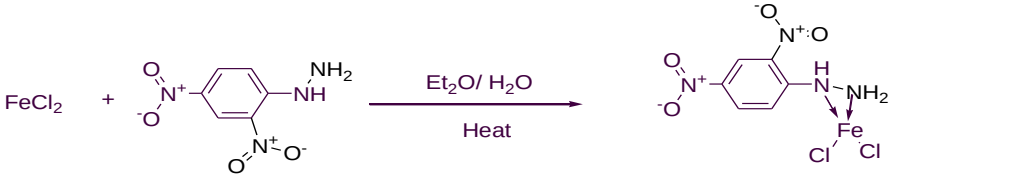


iron(II) chloride 4-Nitrophenylhydrazin [(4-Nitrophenylhydrazin) iron(II) Dichloro]

Scheme 2: Preparation of [{(O$_2$NC$_6$H$_4$(NH)(NH$_2$)}FeCl$_2$] [FeL2]

Synthesis of [(2 ,4-dinitrophenylhydrazine) iron (II) dichloro] [FeL3]

In double nick flask (2 g) of iron dichloride ($FeCl_2$) in 15 ml of distal water was add equimolar quantity of 2,4-dinitrophenylhydrazine {$(O_2N)_2C_6H_3(NH)(NH_2)$} (**L3**) (3.12g) in 30 ml of ethyl alcohol drop wise in room temperature with steer, then temperature rise up in gradually to reflux for five hours. In during that time the color has been observed a changed in color from pink to reddish brown then the mixture of ammonia and water in (1:1) to the reaction and former left for an five hours on heating, where observed color of the solution changed orange to dark brown. Then a dark brown solid was nominated from hot solution in filtration, dried and after recrystallization we acquired the brown crystals in percentage of 77% (Scheme 3).



iron(II) chloride (2,4-dinitrophenylhydrazin) [(2,4-dinitrophenylhydrazin) iron(II) dichloro]

Scheme 3: preparation of [{(O$_2$N)$_2$C$_6$H$_3$(NH)(NH$_2$)}FeCl$_2$] [FeL3]

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RESULT AND DISCUSSION

The all complexes were characterized using, melting point determination, Fourier Transform Infrared (FT-IR) and UV-Visible spectrometer studies and thermal analyses.

The melting points of the complexes were carried out on a Bamslead Electro thermal melting point apparatus. The IR spectrum was recorded in the range 400 – 4000 cm-1 on a Fourier Transform Infrared (FT-IR) spectrometer Bruker tensor 37 Gemany (ATR). The electronic spectra in ethanol solution were recorded in the range 200 – 900 nm on a Schimadzu UV – VIS 9200 spectrophotometer Japan. TG and DTG analyses were done on a Perkin Elmer thermal analyzer in nitrogen atmosphere.

The antibacterial studies were conducted with bacterial stains of *Escherichia Coli* and *Bacillus Subtills* in cultural medium of nutrient Agar. This Agar medium was prepared in distilled water and inoculation was done in petry dishes using platinum wire. The compounds were dissolved in mixture of water and ethanol (10:1 ml) and 3mm diameter blotting paper disc are dipped in this solution and then dried in an incubator. This was applied on the bacteria and plates were kept in incubator at 37^{o}C for 24hours. The zone of inhibition was measured in mm and its percentage is calculated.

Spectrometers studies

UV-Vis. spectral Study

[FeL1] was examined in spectrally by using a ultraviolet and visible radiation UV-Vis. has given peaks absorption of initial at 318 nm in frequency (3144 Cm^{-1}) which's demonstrates the transmission of the type n → π* and the second absorption peak at 243 nm in frequency (4115 Cm^{-1}) which is indicates the transmission of type π→π* and these identical with those reported in some literature [21,22]. Follow the thermal behavior of this complex spectrally by using the device mentioned above with different temperatures ranging from (303-330K) was noted the emergence of two peaks at 200 nm and 320 nm in the frequency of (5000 Cm^{-1} and 3125 Cm^{-1}) respectively, after a raising temperature to the range of 383-343 K, the observed was appearance to the third peak in addition to the previous peaks at a wavelength of 738 nm in frequency (1355Cm^{-1}) this is due to type d-d. The observed data are given in the table 1 and scheme 4.

[FeL2] was examined in spectrally by using a visible UV-Vis. Radiation in the vicinity of Ph=7, has given peaks absorption of initial at 299 nm in frequency (3344 Cm^{-1}) which's demonstrates the transmission of the type n → π* and the second absorption peak at 287 nm in frequency (3484 Cm^{-1}) which is indicates the transmission of type π →π* and these identical with those reported in some literature [21,22]. Follow the thermal behavior of this complex spectrally by using the device mentioned above with different temperatures ranging from (303-353K) was noted the emergence of two peaks at 200 nm and 400 nm in the frequency of (5000 Cm^{-1} and 2500 Cm^{-1}) respectively, after a raising temperature to the range

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of (363-383 K), the observed was appearance to the third peak in addition to the previous peaks at a wavelength of 606 nm in frequency (1605 Cm^{-1}) this is due to type d-d. Again **[FeL3]** was examined in spectrally by UV-Vis. radiation in the vicinity of Ph=7, has given peaks absorption of initial at 252 nm in frequency (3968 Cm^{-1}) which's demonstrates the transmission of the type n → π* and the second absorption peak at 360 nm in frequency (2777 Cm^{-1}) which is indicates the transmission of type π → π* and Thirdly peak at 396 nm in frequency (2525 Cm-1) due d-d transition. These identical with those reported in some literature [21,22]. A thermal behavior of this complex spectrally by using the device mentioned above with different temperatures ranging from (303-343K) was noted the emergence of two peaks at 200 nm and 400 nm in the frequency of (5000 Cm^{-1} and 2500 Cm^{-1}) respectively, after a raising temperature to the range of (353-383 K), the observed third peak in addition to the previous peaks at a wavelength of 741 nm in frequency (1349 Cm^{-1}) this is due shifted to type d-d (Table 1).

Table 1: Thermal behavior of complexes **[FeL1]**, **[FeL2]** and **[FeL3]**

[FeL1]			[FeL2]			[FeL3]		
K	**nm**	**A**	**K**	**Nm**	**A**	**K**	**nm**	**A**
303	318	3.08	**303**	299	1.699	**303**	396	2.465
	243	2.512		287	2.694		360	2.256
				255	2.751		252	2.273
313	317	3.147	**313**	399	1.633	**313**	398	2.453
	244	2.531		283	2.479		254	2.257
				257	2.505			
323	320	2.931	**323**	398	1.635	**323**	397	2.477
	244	2.531		285	2.382		360	2.245
				250	2.400		254	2.257
333	320	2.855	**333**	400	1.647	**333**	397	2.477
	244	2.480		285	2.515		360	2.233
				245	2.330		254	2.257
343	364	0.559	**343**	401	1.675	**343**	683	0.200
	322	2.897		285	2.289		406	2.591
	246	2.469		230	2.294		254	2.284
353	735	0.152	**353**	255	2.275	**353**	741	0.187
	321	2.845		290	2.255		408	2.611
	283	2.512		403	1.721		338	2.167
							280	2.215
							254	2.249
363	735	0.132	**363**	330	2.025	**363**	425	2.100
	320	3.733		606	1.753		359	2.239
	270	2.498						
373	738	0.250	**373**	407	1.210	**373**	425	2.211
	317	3.2		287	2.030		300	2.222
	260	2.522		259	2.660		250	2.253
383	720	0.358	**383**	407	1.793			
	314	2.836						
	245	2.495						

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FT-IR spectral Study

As studying a complex **[FeL1]** in Fourier transform Infrared (FT-IR) spectroscopy, to make sure the appearance some of function to be in the complex. An absorption peak at 3125 Cm^{-1} indicate the presence of the association of N-H stretching frequency and appearance absorption at 3080 Cm^{-1} that indicate the presence of association C-H (Ar) stretching frequency, whiling the appearance absorption at 1120 Cm^{-1} which indicate the presence of association C-N stretching frequency, finally appearance absorption peak at 1050 Cm^{-1} indicate the presence association N=N, the shift of frequency is due to the coordinate bonding of nitrogen- nitrogen to the metal[23-25], willing the frequencies 1751, 1620, 3080 and 440 Cm^{-1} and the function of these to existences of C=O, C=C (Ar), C-H (Ar) and Fe-N stretching frequency in respectively and all these are identical with those reported in the literature [26-28] . From previous data, we can prove to be complex in type of penta-geometry. Again when the **[FeL2]** was examining in FT-IR spectroscopy showed absorption peak at 3125 Cm^{-1} indicate the presence of N-H stretching frequency, the peak appearance at 3010 Cm^{-1} indicate for C-H (Ar), whiling presence peak at 1150 Cm^{-1} indicate for (Ar)C-NH stretching and finally appearance absorption peaks at 1020, 1150, 1600, 1640 and 440 Cm^{-1} indicates for H_2N-NH, (Ar)C-N(O_2), C=C(Ar), NO and Fe-N respectively. All these bonds stretching are identical with perversely reported in the literature [26-28] and complex **[FeL1]**. **[FeL3]** was tested in (FT-IR) and showed first peak at 3120 Cm^{-1}, 1600 Cm^{-1} and 1100 Cm^{-1} for N-H, C=C (Ar) N-C (Ar) stretching respectively. Plus those peaks, appearance peak at 1050 Cm^{-1} indicate for N-N stretching, other peaks were appearance 1781 Cm-1, 3120 Cm^{-1}, 1600 Cm^{-1} and 440 Cm^{-1} indicates for N=O, C-H, N-O and Fe-N stretching respectively. From these information we can find all peaks are related to complex **[FeL3]** and also have Compared with the previously publication [26-28] and complexes **[FeL1]** and **[FeL2]**.

Antibacterial Studies

The antibacterial studies were tested on the five species of the bacteria such (Bacillus spp & Klebsiella spp & E.coli & proteus spp & pseudomona spp) while all complexes were in deferent's concentration (0.001, 0.2 and 1M) and the result is given in Tables .2, 3 and 4. In concentration of 0.001M, complex [Fe(L2)] Showed a positively influence on only one type of bacterial in species Bacillus spp., whiling the other complexes showed low influential on the five species of the bacteria mentioned above, the result is given in Table 2 and figure 1.

Table 2 Antibacterial Activities in concentration 0.001M

Complex	E. Coli		Bacillus spp		Sraphiaureus		Klebsiella spp		Pseudomonas spp	
	Activity	Percentage	Activity	Percentage	Activity	Percentage	Activity	Percentage	Activity	Percentage
[FeL1]	_	5%	—	50%	_	5%	_	5%	_	5%
[FeL2]	—	5%	++	50%	—	5%	—	5%	—	5%
[FeL3]	_	5%	_	5%	_	5%	_	5%	_	5%

Percentage of Inhibition: Below 5mm = (–) low active, 5mm – 10mm = (+) Active, 10mm – 15mm = (++) mildly active & 15mm – 20mm = (+++) moderately active, (20 mm, up) = (++++) highly active

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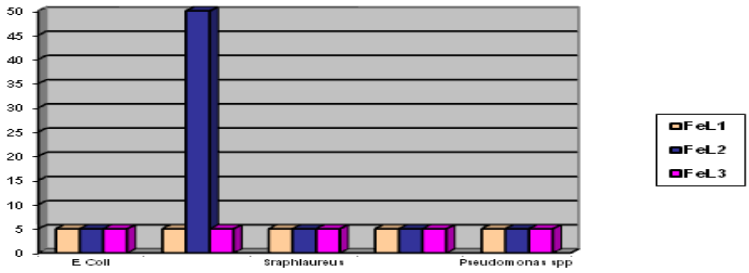

Fig. 1 antibacterial activities in percentage in concentration 0.001

In concentration of 0.02M, complex **[FeL3]** Showed a positively influence on only three types of bacterial in species Bacillus spp., Shaphiaureus and Klebsiella spp. whiling the other complexes showed low influential on the five species of the bacteria mentioned above, the result is given in Table 3 and figure 2.

Table 3 Antibacterial Activities in concentration 0.02M

Complex	*E. Coli*		*Bacillus spp*		*Sraphiaureus*		*Klebsiella spp*		*Pseudomonas spp*	
	Activity	*Percentage*	*Activity*	*Percentage*	*Activity*	*Percentage*	*Activity*	*Percentage*	*Activity*	*Percentage*
[FeL1]	_	*5%*	_	*5%*	_	*5%*	_	*5%*	_	*5%*
[FeL2]	_	*5%*	_	*5%*	_	*5%*	_	*5%*	_	*5%*
[FeL3]	_	*5%*	+++	*75%*	++	*50%*	++	*50%*	_	*5%*

Percentage of Inhibition: Below 5mm = (–) low active, 5mm – 10mm = (+) Active, 10mm – 15mm = (++) mildly active & 15mm – 20mm = (+++) moderately active, (20 mm, up) = (++++) highly active

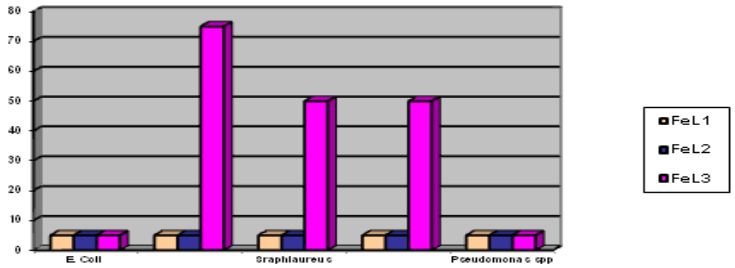

Fig. 2 antibacterial activities in percentage in concentration 0.02

In concentration of 1M, complex [FeL3] Showed a positively influence on only three types of bacterial in species Bacillus spp., Sraphiaureus and Klebsiella spp., but was low activity effect on E.Coli and Pseudomas. whiling the [FL1] and [FeL2] showed medium influential on the Becillus and Sraphiaureus species of the bacteria. Others were low influece, the result is given in Table 4 and figure 3.

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Table 4 Antibacterial Activities in concentration 1M

Complex	E. Coli		Bacillus spp		Sraphiaureus		Klebsiella spp		Pseudomonas spp	
	Activity	Percentage	Activity	Percentage	Activity	Percentage	Activity	Percentage	Activity	Percentage
[FeL1]	_	5%	++	50%	_	5%	_	5%	_	5%
[FeL2]	_	5%	+++	75%	_	5%	_	5%	_	5%
[FeL3]	+	25%	+++	75%	+++	75%	++	50%	_	5%

Percentage of Inhibition: Below 5mm = (-), 5mm – 10mm = (+) Active, 10mm – 15mm = (++) mildly active
15mm – 20mm = (+++) moderately active, (20 mm, up) = (++++) highly active

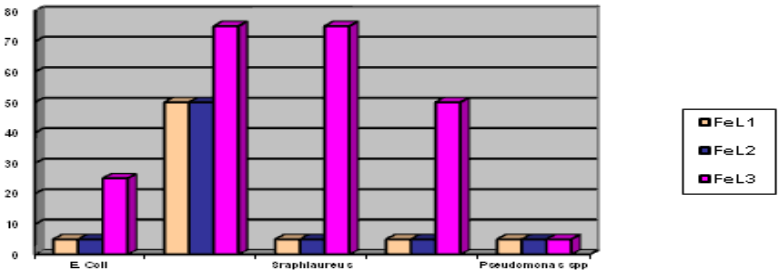

Fig. 3 antibacterial activities in percentage in concentration 1

CONCLUSION

The chemistry presented in this paper shows that the chelating diammdes of Fe(II) are accessible. The data we get it from FT-IR showed a type of complexes are suggested to be tridentate coordinate with four and five coordination. The Coordination around the Fe(II) centre is best described as distorted tetra-and penta-hedral, therefore the research initiated to examine under thermal behavior of all complexes in fireball temperatures by follow UV-Vis. Study and showed completely deferent behavior for etch complexes, this behavior comes affects in increased antibacterial activity under deferent concentration.

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