Synthesis,Characterization And Antibacterial Activity Of Som Metals(II) With L-Histidine Complexes

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Abstract In this work study metals(II) coordination compound of L-Histidine were preparation and characterized using by infrared and UV-V is spectroscopy technique and Magnetic Susceptibility Measurements(BM).The complexes were studied for antibacterial activities. The stoichiometric the reaction between the metal(II) ion and ligand ion molar ratio(1:2) [where M= Ni, Co, Zn and L-Histidine].

Keywords *preparation of complexes, UV-V is spectroscopy technique ,infrared and Magnetic Susceptibility Measurements(BM) and antibacterial activities.*

1. Introduction

L-Histidine is an optically active α-amino acid and is a tridentate ligand that has an imidazole ring, amino and carboxylate groups. Amino acids are the potential candidates for optical second harmonic generation because they contain chiral carbon atom and crystallize in non-centro symmetric space groups and it is an essential criterion for nonlinear application [1,2].The amino acid, histidine, is the most frequently occurring ligand of zinc in the active centre of zinc containing enzymes[3,4].Complexes of transition metal with amino acids in proteins and peptides are utilized in numerous biological processes, such as oxygen conveyer, electron transfer and oxidation. In these processes the enzymatic active site which is very specific, forms complexes with divalent metal ions [5,6]. Both catalytic and structural zinc in enzymes are always coordinated by at least one histidine donor [7,8]. Of the metal ligating amino acids bearing N, O and S containing donors in their side chains histidine are the most prominent ones for zinc [9,10]. Zn^{2+} can create inert chelate complexes by accepting the free electron pairs of O-, N-, S- from certain amino acid motifs. Not only it does play a crucial role in a variety of biochemical processes, but it can also participate in numerous reactions in organometallic chemistry. Nickel is usually found in biological compounds as Ni^{2+}, since many enzymes are complexes of Ni^{2+} [11-16].The role of Ni in bioinorganic chemistry has been developed only since 1975, when the urea's was shown to be a nickel-containing enzyme[17].

Hence the objective of this work was to synthesize, characterize and determine the antibacterial activities of coordination compounds of (L-His) with metal-ligand ratio 1:2.

2-MATERIALS AND METHODS

2.1. Synthesis of Complexes

The Zn(II),Ni(II) and Co(II) complexes of L-Histidine ligand were prepared in1:2 [metal: ligand] ratio by the addition of 0.01M of appropriate metal salt (0.362gm, 0.525gm and 0.499gm for Zn^{+2} ,Ni^{+2} and Co^{+2} respectively) to a solution of the L-Histidine 0.03M (1.39gm) dissolved with stirring in distilled water with the addition of $NaSO_4$(0.71gm) dissolved in 1ml distilled water with stirring then add to mixture drop by drop. The mixture was then heated on a water bath for 3h. An immediate precipitation was obtained for majority of the complexes, while some required further concentration and cooling. The products obtained were filtered, washed with ethanol and dried in air.

2. 2 Preparation of the extracts

The 1.72gm from complexes $[Zn(L\text{-}His)_2]$,$[Ni(L\text{-}His)_2]$,$[Co(L\text{-}His)_2]$ powder in 100mL from distilled water at 100 rpm in a shaker incubator for 24 h at room temperature then solution was filtered through What number 1 sterile filter paper then the extracts were evaporated by dryness by Clock bottles in the air at Room temperature [18,19]. It was dissolved in 2.5ml of distilled water and the extracts were placed in sealed glass tubes for preservation and kept in the refrigerator at a temperature of 4°C until use [20].

Test organisms

Escherichia coli and *streptococcus, Eusy pseudomonas.* The bacterial strains which obtained from Al Marj hospital.

2.3 Antibacterial activity determination

The following microorganisms were tested: Gram negative- *Escherichia coli*; Gram positive *streptococcus*, were cultivated and stored in Nutrient Agar (NA), the Muller-Hinton agar medium was used for antibacterial assay. the agar diffusion method was used to assess the antimicrobial activity of the extracts Equip the bacterial suspension by take from 3-5 colonies of bacteria and put in 3-4ml normal saline then take from suspension 100µl and put in all agar plates by Sterile cotton swab. containing bacterial cultures incubated for 24 hours at 37°C then, the extracts were applied directly on agar plates using the drop method (100µL) [21].Then the prepared extracts are poured in to the well in the standard concentration (100µL). All the plates were incubated for 24 hours at 37°C. Then the presence of zone of inhibition could be measured on the plates. All tests were performed in triplicate, and clear zones greater than 7mm were

considered as positive results because Cork borer was 7mm in diameter [22].By Sterile cotton swab. containing bacterial cultures incubated for 24 hours at 37°C then, the extracts were applied directly on agar plates using the drop method (100µL) [21].Then the prepared extracts are poured in to the well in the standard concentration (100µL). All the plates were incubated for 24 hours at 37°C .Then the presence zone of inhibition could be measured on the plates. All tests were performed in triplicate, and clear zones greater than 7 mm were considered as positive results because Cork borer was 7 mm in diameter [22].

2.4 UV-visible spectroscopy

The UV-Visible transmittance spectra of the complexes were recorded on a Shimadzu UV-Vis 160 spectrophotometer, in quartz cells at the desired wave length region. 3mM solution of complexes in DMSO was used in all UV-Visible measurements.

2.5Magnetic Susceptibility Measurements(BM)

Magnetic susceptibility measurements have been widely used in studying the complexes of transition metals, if most of these metals possess a single electron and show characteristics. From the calculations and values of magnetic measurements, you can determine the Moluclure formula and the geometery as well as the complex geometrical shape. Also from the obtained result, M-L is concluded to be a high spin complex or M-L as a low spin complex [23,24]. Magnetic susceptibility measurements are used to determine the extent of electron pairing, the stereochemistry and metal-metal interactions in the complexes.

3. RESULTS AND DISCUSSION

3.1. Physicochemical Properties

The complexes showed a wide range of colors that were in agreement with those obtained for similar coordination compounds.

Table1. Some physical properties of the prepared complexes :

complexes	*Color*	*MP (C^0)*	*Wt of product (gm)*	*%Yield*
$[Zn(His)_2]^{+2}$	creamy	349.6	2.7243	86.7
$[Co(His)_2]^{+2}$	brown	349.3	2.1744	59.7
$[Ni(His)_2]^{+2}$	purple	350.6	2.272	92.42

3.3Magnetic Susceptibility Measurements(BM)

The magnetic susceptibility values of the complexes are Co(II) complex exhibited magnetic moment of (d^7)(3.46M.B) with paramagnetic indicating the low spin distorted tetrahedral geometry of the complex. The Ni(II) complex exhibited magnetic moment of (d^8)(2.44M.B) with paramagnetic indicated the Low spin nature of the complex and have octahedral geometry. Also Zn(II) complex exhibited magnetic moment of (d^{10}) with diamagnetic indicated the Low spin nature of the complex and have tetrahedral geometry.

3.4 Infrared Spectra

The Infrared spectra results study includes the figures**(a,b,c)** where comparing their vibration frequency with those of L-histidine with metal ion.

3.4.1.L-histidine-Complexes

The Infrared spectra for L-histidine indicate broad band at 3308cm^{-1}-294102cm^{-1} and a medium band 1575.38cm^{-1}correspond to -NH_2 stretching. Where this band free ligand is shifted in this spectra of the complex.

New band at 898cm^{-1}-816$cm^{-1}$and 781cm^{-1}-712cm^{-1} were includes to the [M-N] and [M-O] bond stretching band frequencies, respectively and served as further evidence of coordination via the nitrogen and oxygen atoms of the ligand. While Ni(II) complex at 3272cm^{-1} , 3003cm^{-1} and Zn(II) complex at 3006cm^{-1}, 2823cm^{-1} and Co(II) complex at 3125cm^{-1} ,2871cm^{-1}.

These results correspond with literature value being similar to other metal complex with amino acide [25-27].

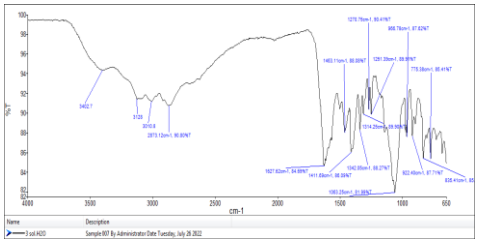

Fig.(a).IR Spectra of $[Ni(L\text{-}His)_2]^{2+}$

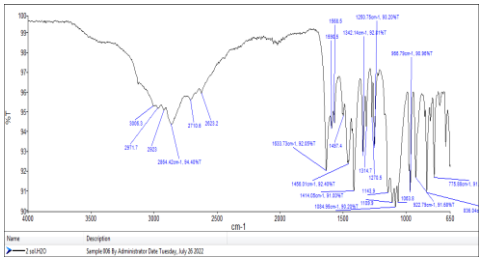

Fig.(b)IR Spectra of $[Zn(L\text{-}His)_2]^{2+}$

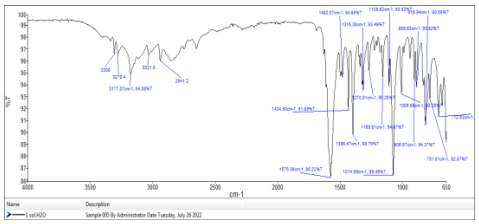

Fig.(c)IR Spectra of $[Co(L\text{-}His)_2]^{2+}$

3.5-Electronic Spectra and UV visible spectra

The electronic spectral data of the complex are give figures(d,e,f) of the prepared complexes show that the band of the ligand which is corresponding to n→π* is changed to higher wavelength in $[Zn(His)_2]^{+2}$, $[Ni(His)_2]^{+2}$ and $[Co(His)_2]^{+2}$ indicating to combination of H_2N:⟶M and N:⟶M LMCT transition.

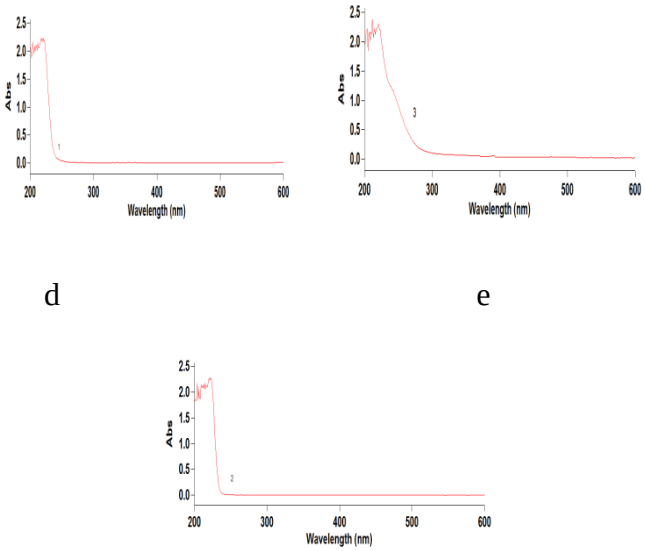

Fig.(d,e,f)UV/Vis Spectra complexes(Ni(II),(Co(II),Zn(II) with L-Histidin

The absorption band of complex showed ligand to metal charge transfer corresponded to the fig.(d, e, f).The d-d transition of the Co(II) complex have only absorption band in visible region due to the $^4A_2(F)\longrightarrow{}^4T_1(P)$ transition tetrahedral geometry and d-d transition suggesting that the Ni(II) complex are coordinated where octahedral geometry and transition $^3A_{2g}\longrightarrow{}^3T_{2g}$,$^3T_{2g}\longrightarrow{}^3T_{1g}$ and $^3A_{2g}\longrightarrow{}^3T_{1g}$.

The d-d transition of the Zn(II) complex transition suggesting d-d transfer is intense charge transfer transition which are assigned to (INCT) [28-31].

3.6. Antibacterial activity There is no effect for free L-Histidine on the types of bacteria *Escherichia Coli*, *Streptococcus* and *Easy domonas* and as well as the effect of the complexes Ni(II), Zn(II) while the found one complex an effect on only one type of bacteria *Easy domonas* from the Co(II) complex as shown in the (**table2**) [32-33].

Table2. Antibacterial for the L-Histidine and their Co(II),Ni(II)and Zn(II) Complexes:

	Escherichia Coli	*Streptococcus*	*Easy domonas*
L-histidine	Resist	Resist	Resist
$[Ni(L\text{-}His)_2]^{2+}$	Resist	Resist	Resist
$[Co\ (L\text{-}His)_2]^{2+}$	Resist	Resist	+
$[Zn(L\text{-}His)_2]^{2+}$	Resist	Resist	Resist

3.7.The effect of some antibiotics on the growth of laboratory bacteria:

Looking at the results in the (table3) recorded the effects of 3 commercial antibiotics available in pharmacies, which are the most common used and effective where we find that the antibiotic is the most effective of those antibiotics on *Esherichia Coli* bacteria is *Chloramphenicol* effect on different types of bacteria. As for the *CLINDAMYCIN* antibiotic, it had an effect on only one type of bacteria *Streptococcus* while the antibiotic *Ampicill/Sulbactam* dose not have any effect on these bacteria.

Table3. The effect of some antibiotics on the growth of bacteria:

	Escherichia Coli	*Streptococcus*	*Easy domonas*
Chloramphenicol	+	+	+
CLINDAMYCIN	Resist	+	Resist
Ampicill/Sulbactam	Resist	Resist	Resist

4.Conclusion

This study indicates that the bonding of the metals ionic with L-Histidine is bidentate through nitrogen and oxygen atoms. This was confirmed by Characterization of IR ,UV. Spectra and Magnetic Susceptibility.

Antibacterial activity no effect on L-Histidine and complexes but found type only one effected on Co(II)complex is *Easy domonas*. Also effect of some antibiotics on the growth of laboratory bacteria find of the effect *Escherichia Coli*, *Streptococcus* and *Easy domonas* bacteria is *Chloramphenicol* and also effect CLINDAMYCIN on *Streptococcus* only.

References:

1-R V., A. Albert Irudayaraj, A Dhayal Raj, S Karthick, G Jayakumar *Mechanics, Materials Science & Engineering, April 2017 – ISSN 2412-5954*

2-P. P. Kumar, V. Manivannan, S. Tamilselvan, S. Senthil, V. Antony Raj, P. Sagayaraj, J. Madhavan, *Growth and characterization of a pure and doped nonlinear optical L-Histidine acetaten single crystal, Optics Communications 2008, 281, 2989-2995. 10.1016/j.optcom.2008.01.058.*

3-P. R. REDDY , M. RADHIKA and P. MANJULA *J. Chem. Sci., Vol. 117, No. 3, May 2005, pp. 239–246. © Indian Academy of Sciences.*

4-B. I, L. C, M. W and Z. M (eds) *1986 Zinc enzymes (Boston: Birkhaused).*

5-F. Hassan, A. Al-Jeboori and T. A. Mussa *Journal of Chemical and Pharmaceutical Research, 2013, 5(11):318-321*

6- R Griffith; A Norins; C Kagan. *Dermatologica, 1978, 156(5), 257-267.*

7- C .D W *1991 Adv. Protein Chem. 42 281*

8-V.B. L , A. D S *1993 Acc. Chem. Res. 26 5433*

9-B. K (ed.) *1990 Biocoordination chemistry: Coordination equilibria in biologically active systems*

(New York: Ellis Horwood)

10-R. M, G. M , V. H *2002 Inorg. Chim. Acta 334 25*

11-N.T. Rahmouni, S. Djebbar, O.B. Baitich *ICAIJ, 8(2), 2013 [41-49] ISSN : 0974 - 746X*

12- J.R.Lancaster Jr; *The bioinorganic chemistry of Nickel, VCH,Weinheim, (1988).*

13-J.Costamagna, J.Vargas, R. Latorre; *Coord.Chem. Rev., 67, 119 (1992).*

14-H.Seigel;*Metal ions in biological systems,NewYork (1973).*

15-G.L.Bichorn; *Inorganic Biochemistry, Elsevier, Amsterdam, (1973).*

16-G. Wilkinson; *Comprehensive Coordination*

Chemistry, Pergamon Press Oxford, 2, 751, 4, 634, 5,687, 6,166, 494, 638 (1987).

17-N.E.Dixon,T.C.Gazzolo,R.L.Blakely,B.Zermer;J.A m.C *em.Soc., 97, 4131 (1975)*

18- R., P. S and Parekh, K. S. *1981. Antibactrial activity of Indian seaweed extracts. Bot. Mar. 24: 577-582.*

19-V., V; Critchley, A. T and Vonholy, A. *1996. Establishment of aProtocol for testing antibacterial Activity in Southern African macroalgae.Microbios:115-123.*

20-F. F. Kammoun, M. Hammami, N. Mchirgui, R. A. Belbahri, L. Gargouri,Y. Miled, N. B. Re bah, F. *2011. Chemical composition and some biological activities of marine algae collected in Tunisia. Cien. Mar. 37(2): 113–124.*

21- C., S; Azzolina, R; Furnari, G; Cormaci,M and Grasso, S. *1981. Antimicrobial and anfiviral activities of some marine algae from eastern Sicily. Bot.*

22-A.M.Yimer,*journal homepage: http://www.pakinsight.com/?ic=journal&journal=96.Review of Catalysts, 2015, 2(1): 14-25*
23-N. Raman, S. Ravichandran, and C. Thangaraja, *"Copper(II), cobalt(II), nickel (II) and zinc (II) complexes of schiff base derived from benzil-2,4-dinitrophenylhydrazone with aniline," Journal of the Chemical Society, Indian Academic Scociety, vol. 4, pp. 116- 215, 2004.*
24-F. Hassan ,A. A.Jeboori , T. A. Mussa. *Journal of Chemical and Pharmaceutical Research, 2013, 5(11):318-321. Research Article ISSN : 0975-7384CODEN(USA) : JCPRC5*

25-P. Mejnikov; P. Corbi; C Aguila. *J. Alloys comp. **2000**, 307(1-2), 179-183.*

26-C. Batiu; C. Jelic; N. Leopold; O Cozar; L David, *J. Mol. Struct. **2005**, 325-330, 744-747,*

27-M. S. mohamad, *Acta Chim. Pharm. Indica: 3(2), 2013, 140-148ISSN 2277-288X*

28-A. P. Mishra, A. Tiwari and K. J. Rajendra, *Advanced Materials Letters, 3(3), 213-219 (2012).*

30-A. A. S. Al-Hamdani and S. A. Shaker, *Oriental J. Chem., 27(3), 835-845 (2011).*

31-A. S. Munde, A. N. Jagdale, S. M. Jadhav et al., *J. Serb. Chem. Soc., 75(3), 349-359 (2010).*

32- F. A. Abd Al-Jabar and A. S. Ahmed *Journal of Al-Nahrain University Science Vol.19 (3), September, 2016, pp.114-118*

33-L., K.B.I., Victoria, R.B.I., Mathias, M., Mina, D., Mukesh, P., Martin, M. and Artur, S. "*Antimicrobial activity of histidine-rich peptides is dependent on acidic condition. Biochem Biophys Acta". 2007, 1768(11): 2667-8.*