Synthesis, Spectroscopic Characterization and Antibacterial Activity of mixed ligand complexes of Cr(III),Fe(III), and La(III) with

1-nitroso-2-naphthol and L-leucine

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Abstract :

The mixed ligand complexes of Cr(III), Fe(III) and La(III) with 1-nitroso-2naphthol $(C_{10}H_7NO_2),$ symbolized(NNPhH)] and amino acid[L-, symbolized (Leu H), were $leucine(C_6H_{13}NO_2)$ synthesized and characterized by: Melting points, Solubility, Molar conductivity. determination the percentage of the metal in the complexes by flame(AAS), magnetic susceptibility measurements, chloride ion content. Spectroscopic Method [FT-IR and UV-Vis], and Program [Chem office-CS. Chem.- 3D pro 2004] was used.

The results showed that the deprotonated tow ligands acts as a bidentate ligand, (leu⁻) was coordinated to the metal ions through the oxygen of the carboxylic group and the nitrogen of the amine and

the 1-nitroso-2-naphthol ligand was coordinated to the metal ions through the oxygen. Octahedral geometry for Cr(III),Fe(III),and La(III) are proposed.

المعقدات المحضرة بلورات صلبة درست من النواحي الأتية:



درجات الانصبهار، التوصيلية الكهربائية المولارية، الذوبانية، الخواص المغناطيسية،تقدير النسبة المئوية للأيون الفلزي في المعقدات بوساطة مطيافية الامتصاص الذري، الدراسات الطيفية: وتضمنت أطياف(الأشعة تحت الحمراء، الأشعة فوق البنفسجية – المرئية الطيفية: وتضمنت (Chem. Office – Cs. chem – 3D pro 2004) في رسم أشكال

INTRODUCTION:

1-nitroso-2-naphthol ($C_{10}H_7NO_2$) is crystalline solid, sparingly soluble in water and readily soluble in alcohol ,ether and common organic solvent. Its melting point is equal to 103–106 °C , Orthosubstituted nitrosonaphthols can undergo tautomerisation to give oxooximes.(Figure- 1) In the case of 1-nitroso-2-naphthol, the equilibrium is greatly displaced toward the keto-form and the compound has, in the solid state and in solution, a predominately which is a hybrid of resonance forms of the type ⁽¹⁻⁵⁾.

-11-nitroso-2-naphtholis currently used as a complexing agent in the analysis of cobalt and it is also a sensitive and specific reagent for floury metric determinations of tyrosine residues in proteins and peptides ⁽⁶⁾.



Figur-1:Tautomerisation in 1-nitroso-2-naphthol -

Metal amino acid complexes have long been of interest as models for metal – Ligand systems and interaction which may occur in nature⁽⁷⁾. Biological importance of several amino acids their complexes with transition metals is well documented⁽⁸⁻⁹⁾. The amino acid L- leucine and various transition metals are important in the biological functions of



humans, animals, and plants. L- leucine is one of the twenty major amino acids and is considered an essential amino

acid (10).

In this paper we present the synthesis and study of {Cr(III),Fe(III) and La(III)} complexes with 1-nitroso-2naphthol as a primary ligand and amino acid (L-leucine) as a secondary ligand have been used, respectively.

Experimental part :

a- Reagents and instruments: L-leucine and 1-nitroso-2-naphthol were purchased from (Merck), metals chloride and solvents from (B.D.H)& Fluka. The reagents were used without further purification .

b- Instruments: FT-I.R spectra were recorded as KBr discs using Fourier transform Infrared Spectrophotometer Shimadzu 24 FT-I.R 8400s. Electronic spectra of the prepared complexes were measured in the region (200- 1100) nm for 10^{-3} M solutions in ethanol at 25°C using shimadzu-U.V-160 . A Ultra Violet Visible- Spectrophotometer with 1.000 ± 0.001 cm matched quartz cell. While metal contents of the complexes were determined by Atomic Absorption (A.A)Technique using Japan A.A-67G Shimadzu. Electrical conductivity measurements of the complexes were recorded at 25°C for 10^{-3} M solutions of the samples in ethanol using pw9527 Digital conductivity meter (Philips). Melting points were recorded by using Stuart melting point apparatus. chloride ion content were also evolution by (Mohr method),Magnetic susceptibility measurements were measured using Bruker magnet BM6. The proposed molecular structure of the complexes were determinated by using chem. office prog, 3DX (2004).

C-Synthesis of the complexes :

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1) Sodium leucinate (Na⁺ Leu⁻):L-leucine [0.131 gm, 1 m mol] was dissolved in 10 ml ethanol and added to 10 ml of ethnolic solution containing [0.04 gm (1mmol)] of the sodium hydroxide , the solution was deprotonated according to the following reaction scheme (1)



scheme (1): Synthesis of the Sodium leucinate(Na⁺Leu⁻)

2) Sodium 1-Nitroso-2-naphtholate (Na⁺NNPh⁻):

1-nitroso-2-naphthol ((NNPhH)]) [0.346 gm(2mmol)] was dissolved in 10 ml ethanol and added to 10 ml of ethanolic solution containing [0.08 gm (2mmol)] of the sodium hydroxide,the solution was deprotonated according to the following reaction (scheme -1)



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scheme (2): Synthesis of the sodium 1-Nitroso-2-naphtholate (Na⁺NNPh

-)

3)Synthesis of complexes:

The complexes were prepared by the addition of ethnolic solutions of the (Na⁺NNPh⁻) and (Na⁺Leu⁻) to warm stirred ethanolic solution of the

La(II), Cr (III), Fe(III) chloride(1 m moles in) 15 mL ethanol)in the stoichiometric ratio (1:2:1) (M:2NNPh⁻:Leu⁻) under continuous stirring , the metallic complexes are precipitates.

The solid products are filtered, washed with ethanol and dried in vacuum over anhydrous $CaCl_2$. according to the following reaction scheme (3)xxxxxxx



scheme (3): Synthesis of the $[M(C_{26}H_{24}N_3O_6)]$ complexes

4) Preparation of Microorganism suspension

A) The micro- organism suspension was prepared by taking 2–4 colonies from all the studied micro- organism. Then it was inserted in the physiological solution in 0.85% concentration and was compared with Macferr land tube number 0.5 which is equal to 1.5×108 cell/mm. It is used for Petri dish preparation for the examination of biological activity against the under studied chemical compound.



B) Inhibition Activity Selection for the complexes in studied Microorganism

The agar well diffusion method was used to see the effect of under studied chemical complexes on the micro-organism growth. This is done by using 20–25 ml from Nutrient agar medium for each Petri dish.

The dish was incubated in incubator for 24 hours at (37°C) to make sure that no contamination would occur in the dish.

The dish was wetted in 10 milliliters of micro-organism which was prepared as mentioned in the previous paragraph which include 1.5×10^8 cell/mm. Distributed evenly on the Nutrient Agar medium surface by using spreader. Bore was made on the cultured medium surface by using cork borer. The chemical complexes were made as 100 m ml per bore and left the central bore containing only D.M.F. The dishes were left for 1/2 hour in refrigerator at 4°C^[11]. The dishes were incubated at (37°C) for 24 hours. The biological activity for the complexes was defined by measuring the diameter of the inhibition area surrounding each bore in millimeters⁻

Results and Discussion:

Physical properties of the prepared complexes:

Table (1)shows the physical data for the prepared complexes which show different melting points. All the complexes are colored, non-hygroscopic and thermally stable solids (Table 1), indicating a strong metal-ligand bond. The complexes are insoluble in water but soluble in common organic solvents such as ethanol, ethyl alcohol, acetone, chloroform ,DMF and DMSO. The observed molar conductance values measured in ethanol in 10⁻³ M solution lie in the (9.87-12.11) ⁻¹ cm²mol⁻¹



¹ range, the conductivity measurements in ethanol indicated the non electrolyte behavior⁽¹²⁾.

Atomic Absorption :

The atomic absorption measurements (Table-1) for all complexes (figure 2)gave approximated values for theoretical values.

Fourier-transform infrared spectra_and mode of coordination :

The most important infrared spectral bands that provide conclusive structural evidence for the coordination of the ligands to the central metal ions .

The assignment of some of the most characteristic FT-IR band of the complexes are shown in Table (2) together with those of two ligands recorded for comparative purposes and facilitate the spectral analysis.

Figure (3), Table (2), displays the (FT-IR) spectrum for the (L-leucine)exhibited a band around (3417)cm⁻¹ that corresponds to the stretching vibration of υ (N-H) + υ (O-H), while another strong absorption band at (3070) cm⁻¹ is due to the υ (N-H₂)sym while the bands at (1585) cm⁻¹ and (1415)cm⁻¹ were assigned to the υ (-COO)_{asy} and υ (-COO)_{sym} respectively. υ (-COO)_{asy-sym} =170 cm⁻¹. ⁽¹⁴⁾ Figure (4) ,Table (2), displays the (FT-IR) spectrum for the(2-nitroso-1-naphthol) which exhibits very strong band at (1616)cm⁻¹ due to (C=O) stretching vibration ⁽¹³⁻¹⁵⁾ .The band at (3425)cm⁻¹ is due to the (O–H) stretching vibration ^[14]. The band at (1523)cm⁻¹ is due to the (C=N) while the bands at (1450) and (2790)cm⁻¹ were assigned to the (C=C) aromatic and (C–H) aromatic stretching respectively. The band at (3066)cm⁻¹



were assigned to (HO---H) hydrogen bonding $^{(15,16)}$ and the band at (1153) cm⁻¹ is due to the (N-O) stretching vibration. The weak bands at

(552cm⁻¹) and (478 cm⁻¹) refer to υ (Fe-N) and υ (Fe-O) bands respectively^(14,15). The weak bands at (552cm⁻¹) and (439 cm⁻¹) refer to υ (Cr-N) and υ (Cr -O) bands respectively^(14,15).

The bands at (675cm^{-1}) and (525cm^{-1}) refer to υ (La-N) and υ (La-O) bands respectively ⁽¹⁵⁾.

Electronic spectra & Magnetic studies :

The electronic spectral data of the free ligands 1-nitroso-2naphthol and

L-leucine and their complexes are summarized in table-3. The U.V- V is spectra of the free ligand (1-nitroso-2-naphthol) in ethanol solvent appeared a high, intense absorption bands at (383nm) (15772cm⁻¹) ($\max = 2238 \mod 1.$ cm⁻¹) and at (304nm) (26109cm⁻¹) ($\max = 937 \mod 1.$ cm⁻¹). These bands are attributed to $(n \rightarrow \pi^*)$ and $(\pi \rightarrow \pi^*)$ transitions respectively. The electronic spectra of L-leucine show an

absorption band at 305 nm (32786cm⁻¹)in ethanol is attributed to $(\pi \rightarrow \pi^*)$ transition. (16,17)

The magnetic moments of the complexes shown in Table (3) were calculated from the measured magnetic susceptibilities after employing diamagnetic corrections and revealed their diamagnetic nature as expected for La(III) with



4f ^o configuration. The magnetic moment shows the Cr(III) ion to be (3.30BM) with d^3 (T₂g³ eg) configuration in a distorted octahedral environment. The magnetic moment shows the Fe(III) ion to be (5.7BM) with d⁵ configuration in a octahedral environment. ^(17,18)

Different bonding and structural behavior were related during the study of coordination chemistry of the different new complexes. The **Racah** and other ligand field parameters which illustrate the bonding nature between metal ion and donor atoms of the ligand were calculated for Fe(III), Cr(III) complex using (Tanabe-Sugano) diagram⁽¹⁹⁻²⁰⁾

 $Cr(C_{26}H_{24}N_3O_6)$:d³ The spectrum of Red- Brown complex exhibited the following absorptions at (19920) cm⁻¹, (22075)cm⁻¹ and(25380) cm⁻¹ wave numbers these bands are characteristic of octahedral Cr(III) complex and were assigned to the transitions ${}^{4}T_{2g}$ ${}^{4}A_{2g}$ transition energy = 10Dq = ${}_{0}$ = 19920 cm⁻¹

$${}^{4}T_{1g}(F) \qquad {}^{4}A_{2g} \ , {}^{4}T_{1g}(P) \qquad {}^{4}A_{2g}$$

Peak positions for some octahedral Cr(III) complex (in cm ⁻¹).							
Complex	1	2	3	2/ 1	1/ 2	В	/B
Cr(C ₂₆ H ₂₄ N ₃ O ₆)	19920	22075	25380	1.10	0.686	1030	19.33

Fe $(C_{26}H_{24}N_3O_6)$:d⁵ -The spectrum of Dark - green complex showed two bands in the d-d transition region at 11402 cm⁻¹ and 25575 cm⁻¹,



bands can be assigned to the following transitions fom Tanabe-Sugano diagram for d⁵ octahedral field.

⁶ A₁g
$${}^{4}T_{1}g(11,402 \text{ cm}^{-1}) = 10\text{Dq}$$

⁶A₁g ${}^{4}T_{2}g(25,575\text{ cm}^{-1})$

From Tanabe-Sugano diagram for d^5 octahedral field the value of 10Dq equal to (11,402 cm⁻¹)

. Peak positions for some octahedral Fe(III) complex (in cm ⁻¹).							
Complex	1	2	3	2/ 1	1/ 2	В	/B
$Fe(C_{26}H_{24}N_3O_6)$	11,402	25,575	-	2.24	0.44	1090	10.46

La $(C_{26}H_{24}N_3O_6)$:F⁰ - The spectrum of cream-yellow complex showed one

absorption band at 277 nm (36101cm⁻¹) is attributed to $(\pi \rightarrow \pi^*)$ transition.

Discussion of the biological effect results for prepared complexes:

The biological activity of the $Cr(C_{26}H_{24}N_3O_6)_2$ $Fe(C_{26}H_{24}N_3O_6)$ and La $(C_{26}H_{24}N_3O_6)$ complexes was studied by using inhibition method for three types of pathogenic bacteria. One type of bacteria was gram position which is *staphylococcus*. The second one was gram negative which is *Klebsiella SPP*. The third one was gram variability which is **Bacillus**⁽²¹⁾

The zone inhibition of bacterial growth were measured in mm depending upon the diameter as shown in Table (4) **Figure**s (10-11)



The rate of inhibition diameter was varied according to the variation in the complex type and Bacterial type.

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Table (1) The physical properties of the complexes

					Me		
Compound	M.wt	Color	M.p°c (de)	Ат µS.cm².Mol ⁻¹	theor y	exp	Cl%
C ₆ H ₁₃ NO ₂ (leu)	130. 18	white	289	1.24	-	-	-
1-nitroso-2-naphthol (C ₁₀ H ₆ N ₂ O ₄)	172.17	dark-Brown	106	1.77	-	-	-
Cr(C ₂₆ H ₂₄ N ₃ O ₆)	526.51	Red- Brown	244 de	9.87	9.88	11	Nill
Fe(C ₂₆ H ₂₄ N ₃ O ₆)	530.36	Dark - green	250 de	11.88	10.03	11.8	Nill
La (C ₂₆ H ₂₄ N ₃ O ₆)	613.39	cream-yellow	>300	12.11	22.65	24.03	Nill

Table (3) : Electronic Spectra of the studied complexes and two ligand

Compounds	λ (nm)	ט'(cm ⁻¹)	Assignment	µeff (BM)
C ₆ H ₁₃ NO ₂ (leu)	305	32786	$\pi { ightarrow} \pi^*$	-



1-nitroso-2-naphthol	304	32894	$\pi \rightarrow \pi^*$	
$(C_{10}H_6N_2O_4)$	383	26109	$n \rightarrow \pi^*$	-
Cr(C ₂₆ H ₂₄ N ₃ O ₆)	502 453 394	19920 22075 25380	${}^{4}A_{2}g(F) \rightarrow {}^{4}T_{2}g(F)$ ${}^{4}A_{2}g(F) \rightarrow {}^{4}T_{1}g(F)$	3.30
			${}^{4}A_{2}g(F) \rightarrow {}^{4}T_{1}g(P)$	
Fe(C ₂₆ H ₂₄ N ₃ O ₆)	391	25575	${}^6\!A_1g \rightarrow {}^4\!T_1g$	5.7
	877	11402	${}^{6}A_{1}g \rightarrow {}^{4}Eg$	
La (C ₂₆ H ₂₄ N ₃ O ₆)	277	36101	$\pi \rightarrow \pi^*$	Di mag

C.T= (Chargtransfer)

 Table (4) Showed the inhibition circle diameter in millimeter for the bacteria after 24

 hour incubation paid and 37°C for L-leucinee and 1-Nitroso-2-naphthol complexes

Compound	Bacill	Klebsiella	Staph
Control DMF	10.9	9.9	13.3
L-leucine	12.9	10.9	16
1-nitroso-2-naphthol	17.9	13.9	20.7
$Cr(C_{26}H_{24}N_{3}O_{6})$	18.5	15.9	28.6
$Fe(C_{26}H_{24}N_3O_6)$	20	18.1	22.2
$La(C_{26}H_{24}N_{3}O_{6})$	25	26	32

Nomenclature of prepared complexes :

Table (5) shows empirical formula and nomenclature (IUPAC) with abbreviated .

Table (5) Nomenclature of prepared complexes

Complexes	Name	Abbreviation
$Cr(C_{26}H_{24}N_3O_6)$	(L-leucinato) bis(1-nitroso-2-naphtholato) chromium(III)	[Cr NNPh) ₂ (leu)]



Fe(C ₂₆ H ₂₄ N ₃ O ₆)	(L-leucinato) bis (1-nitroso-2-naphtholato) iron(III)	Fe NNPh) ₂ (leu)]
La (C ₂₆ H ₂₄ N ₃ O ₆)	(L-leucinato) bis (1-nitroso-2-naphtholato) Lanthanum (III)	La (NNPh) ₂ (leu)]



Figure (3) FT- IR spectrum of leucin $C_6H_{13}NO_2$



Figure. (4)FT- IR spectrum of 1-nitroso-2-naphthol ($C_{10}H_6N_2O_4$)



Figur. .(4)FT- IR spectrum of Cr(C₂₆H₂₄N₃O₆)



Figure.(5)FT- IR spectrum of $La(C_{26}H_{24}N_3O_6$

Figure (6)The (UV-Vis) Spectra of L-leucin



Figure.(7)The (UV-Vis) Spectra of 1-nitroso-2-naphthol



Figure.(8)The (UV-Vis) Spectra of $Cr(C_{26}H_{24}N_3O_6)$



Figure.(9)The (UV-Vis) Spectra of La(C₂₆H₂₄N₃O₆)

Conclusion:

The bidentet two ligands were reacted with appreparative metal salt in ethanol, different colored complexes were obtained, they were studied and identified by spectroscopic, magnetic and conducting measurements, which have been non-electrolyte. All complexes indicative of coordination through nitrogen and oxygen atoms.

Biological activity:

bacterial growth were measured in mm The zone inhibition of11&10depending upon the diameter as shown in Table (6) Figures (



Figure(10) shows the antimicrobial activity of (L1&L2) (appear the inhibition zones agenist some pathogenic bacteri (a-Bacillus,b-Klebsiella S.P.P,c-Staphylococcus S.P).









(1) $[Cr(C_{26}H_{24}N_3O_6)]$ La(C₂₆H₂₄N₃O₆)

(2) $Fe(C_{26}H_{24}N_3O_6)$

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Figure(11) shows the antimicrobial activity of complexs(1-3) (appear the inhibition zones agenist some pathogenic bacteri (a-Bacillus,b-Klebsiella S.P.P,c- Staphylococcus S.P).

Compound	υ(N-H)+ υ (O-H)	υ (C-H) _{cy} (C-H) _{ali}	υ(C=O)	υ(C=N)	υ(N-O)	υ(-COO) _{asy}	v (- COO) _{sym}	M-N	М-О
(L-leu)	3417m	1580s	-	-	-	1585vs	1415vs	-	-
1-nitroso-2-naphthol	3425s- br- 3066w	2790vw	1616vs	1523vs	1153m	-	-	-	-
$Cr(C_{26}H_{24}N_3O_6)$	3032m	2957s	1589vs	1512vs	1134s	1485s	1354 s	536w	w 439
Fe(C ₂₆ H ₂₄ N ₃ O ₆)	3444vs 3059w	2950m	1589vs	1550w	1145vs	1508vs	1357vs	624m	470m
La (C ₂₆ H ₂₄ N ₃ O ₆)	3455s- br-	2890vw	1500vs	1556m	1195vs	1595 vs	1415s	675m	525m

) FT-IR spectral data of the Ligands $% \left({{{\rm{A}}_{{\rm{B}}}} \right)$ and there complexes 2 Table (

v = stretching, asy= asymmetric, sym=symmetric

