
Synthesis, Spectroscopic Investigation and Antibacterial Activity of some new Schiff Base Chelates

A.M.Hamil¹, M.M. El-ajaily^{2*}, M. Abdelkarem³, H.A.Boghdadi⁴ and M. Himmet⁵

¹Chemistry Department, Faculty of Science, Sebha University, Sebha, Libya. .

²Chemistry Department, Faculty of Science, Benghazi University, Benghazi, Libya. .

³Chemistry Department, Faculty of Science, Sudan University of Science and Technology, Sudan.

⁴Botany Department, Faculty of Science, Sebha University, Sebha, Libya.

⁵Chemistry Department, Faculty of Science, Omdorman Islamic University, Sudan.

Abstract

New divalent and trivalent transition metal complexes of 2-[(4 -[(Z)-1-(2-hydroxyphenyl)ethylidene]aminobutylethanimidoyl]phenol] were synthesized. The synthesized complexes were subjected to CHN, molar conductivity, magnetic moments, infrared, electronic and electron paramagnetic resonance spectra. The CHN elemental analyses showed the formation of 2:1 [M:L] ratio, The molar conductance measurements revealed the presence of non-electrolytic nature. infrared spectral results displayed the involvement of azomethine nitrogen atom and hydroxyl groups in coordination to the central metal ion. On the basis of electronic and electron paramagnetic resonance spectral studies, an octahedral structure was proposed for all complexes. Also the antibacterial activity of the Schiff base and its chelates were screened on some pathogenic bacteria.

Introduction

Schiff bases are normally using for applications after coupling with inorganic compounds, to increase the activity of it.⁽¹⁾ Chohan et al.⁽²⁾ reported the synthesise of some chelates derived from the salicylaldehydes and then forwarded to their applications for antifungal, antibacterial and antitumor activities. Anticancer activity via Schiff base complexes derived from 4-hydroxysalicylaldehyde and amines have been reported.⁽³⁾ El-ajaily *et al.*⁽⁴⁾ have synthesized and investigated some

complexes derived from salicylaldehyde and histidine and they found to have antibacterial activity on some pathogenic bacteria. Schiff base of types 3-enehydrazono-2-salicylidindolinone and their complexes incorporating Co(II), Ni(II), Cu(II) and Zn(II) ions have antimicrobial activity for some pathogenic bacteria and fungi, such *Staphylococcus aureus*, *Enterococcus*, *Proteus mirabilis*, *Escherichia coli*, *Bacillus anthracis*, *Pseudomonas aeruginosa* and *Candida albicans*.⁽⁴⁾

This study aims to synthesis , characterize Schiff base and its chelates with Co(II), Ni(II), Cr(III), Cu(II) and La(III) ions and screen their biological activity on some pathogenic bacteria.

Experimental

Materials and Methods

Analytical grade reagents (BDH) were used. The molar conductance measurements were performed on a BC 3020 Professional Benchtop Conductivity Meter. Magnetic susceptibility was determined using a Johnson Matthey instrument at room temperature (25 °C) with Hg[Co(SCN)₄] as blank. The infrared spectra were recorded as KBr disc on a Perkin – Elmer 1430 IR Spectrophotometer. The UV-Vis spectra were recorded on a Unicam Model UV-2 spectrophotometer . The EPR spectra were recorded by using EMX ESR spectrometer (Bruker) 1998 Y. All analyses were done at microanalytical center, Cairo University, Giza, Egypt.

Synthesis of Schiff base

The Schiff base under investigation was used. The stock mixtures of compounds synthesized by adding (6.02 cm³, 0.05 mmole) of 2-hydroxyacetophenone dropwise bacteria species were used in this study to 1,4-butanediamine (4.40 g, 0.05 mmole)(*Escherichia coli* , *Proteus Pseudomonas* in 50 cm³ of absolute ethanol. Then, the *aeruginosa* and *Staphylococcus aureus*). mixture was refluxed for three hours, and thenAntibacterial activity was determined by allowed to cool at ambient temperature,the well (6 mm diameter) diffusion filtered, recrystallized from ethanol and driedmethod. Petri dishes containing Mueller under vacuum to get yellow precipitate (m.p.Hinton agar medium were seeded with a 194.1 °C ; yield 79 %).

Synthesis of chelates

The following chelates were synthesized by adding of Schiff base (3.24 gm; 0.01 mole) in 50 cm³ absolute ethanol to 0.01 mole of the salts of CoCl₂.6H₂O, NiCl₂.6H₂O, CuSO₄.5H₂O, CrCl₃.6H₂O and LaCl₃.7H₂O (2.3793gm, 0.01mole), (2.3769gm, 0.01mole), (2.4968 gm, 0.01mole) , (2.6650 gm, 0.01mole) and (3.7137 gm, 0.01mole), respectively, in the same amount of the absolute ethanol. The reaction mixtures were condensed for three hours. The obtained chelates were filtered, recrystallized from suitable solvents and finally kept in a desiccator over silica.

Bacterial culture

The Schiff base and its Co(II), Ni(II), Cr(III) and Cu(II) chelates were added separately to the (1:1) mixture of DMF and H₂O solvents. The obtained mixtures were further purified and filtrated by using Whatman filter paper No 1. The stock solutions of the extracts were sterilized by filtration using a Millipore membrane filter of 0.2 µm pore size. The sterile mixtures resulted from the compounds were stored at 4⁰C for further 24 hour culture of the bacterial species were growth on nutrient agar. Each well was filed with 50µl of the compound.

Solvents were used as a negative control. Inoculated plates were Incubated at 37 °C for 24 hour. The assessment of antibacterial activity was based on the measurement of the diameter of inhibition formed around the well.

Results and Discussion

CHN analyses and molar conductivity

The CHN elemental analysis data of the Schiff base and its chelates are listed in Table 1. agree with the proposed composition and the synthesized chelates were formed in 2:1[M:L] ratio. The obtained molar conductance values of the chelates in DMF solvent lie in the range of 5.66-29.80 ohm⁻¹ cm² mol⁻¹ indicating their non electrolytic behavior. Thus, the chelates may be formulated as [M(L)X_n(H₂O)_n]nH₂O. ⁽⁵⁾

Table 1: Elemental analyses and some physical data of the Schiff base and its chelates

L/ Chelates	Color	M.wt.	M.P., ⁰ C	Found (Calc.) %			Λ	BM
				C%	H%	N%		
L; (C ₂₀ H ₂₄ N ₂ O ₂)	Yellow	324.00	>194	71.87 (72.03)	7.64 (7.46)	8.37 (8.64)	-	-
[Co ₂ LCl ₂ (H ₂ O) ₆]	Violet	619.15	>315	38.76 (38.79)	5.90 (5.53)	4.43 (4.52)	5.67	4.75
[Ni ₂ LCl ₂ (H ₂ O) ₆]	Pale green	618.40	>288	38.22 (38.82)	5.72 (5.54)	4.81 (4.53)	12.71	2.63
[Cr ₂ LCl ₄ (H ₂ O) ₄]2H ₂ O	Green	605.39	>295	36.46 (35.52)	4.86 (4.07)	4.25 (4.14)	24.80	3.98
[Cu ₂ LCl ₂ (H ₂ O) ₆].H ₂ O	Pale blue	628.00	>294	38.17 (37.16)	5.31(5.61)	4.06 (4.33)	19.17	1.70
[La ₂ LCl ₄ (H ₂ O) ₄].H ₂ O	Pale yellow	813.82	>300	29.49 (28.87)	3.89 (3.88)	356 (3.37)	12.30	0.00

Infrared spectra

The assignments of the significant infrared bands of the Schiff base and its chelates are listed in Table 2. Figs.(1-5) In principle, the Schiff base exhibits a band at 1612cm⁻¹ due to νC=N vibration which is shifted to lower wave number in the chelates indicating the

participation of the azomethine group in complexation through nitrogen atom. ⁽⁶⁾ This is also confirmed by the appearance of new band which is absent in the free Schiff base in the range of 417-448 cm⁻¹ attributed to the νM-N vibration. ⁽⁷⁾ A band at 3475 cm⁻¹ due to νOH group in the free Schiff base. ⁽⁸⁾ which is changed during the chelate formation indicating

its involvement in chelation with metal ions. The broad band which observed in the spectra of the chelates displays the existence of the water molecules in the chelates. ⁽⁹⁾ The involvement of the

oxygen atom of the hydroxyl group is confirmed by the appearance of new bands in the range of 492-545 cm^{-1} assigned to the $\nu\text{M-O}$ vibration. ⁽¹⁰⁾

Table 2: Infrared and electronic spectral data of the Schiff base and its chelates

L\ chelates	IR Bands (cm^{-1})				Uv-Vis, nm (cm^{-1})
	$\nu\text{OH}(\text{H}_2\text{O})$	$\nu\text{C}=\text{N}$	$\nu\text{M-O}$	$\nu\text{M-N}$	
L; $\text{C}_{20}\text{H}_{24}\text{N}_2\text{O}_2$	3475	1612	-	-	240, 290 , 425
$[\text{Co}_2\text{LCl}_2(\text{H}_2\text{O})_6]$	3557	1622	545	417	550, 570, 630, 645
$[\text{Ni}_2\text{LCl}_2(\text{H}_2\text{O})_6]$	3078	1611	501	448	560, 580
$[\text{Cr}_2\text{LCl}_4(\text{H}_2\text{O})_4].2\text{H}_2\text{O}$	3386	1605	492	444	570) , 630
$[\text{Cu}_2\text{LCl}_2(\text{H}_2\text{O})_6].\text{H}_2\text{O}$	3487	1533	502	436	450, 590
$[\text{La}_2\text{LCl}_4(\text{H}_2\text{O})_4].\text{H}_2\text{O}$	3561	1619	545	424	560

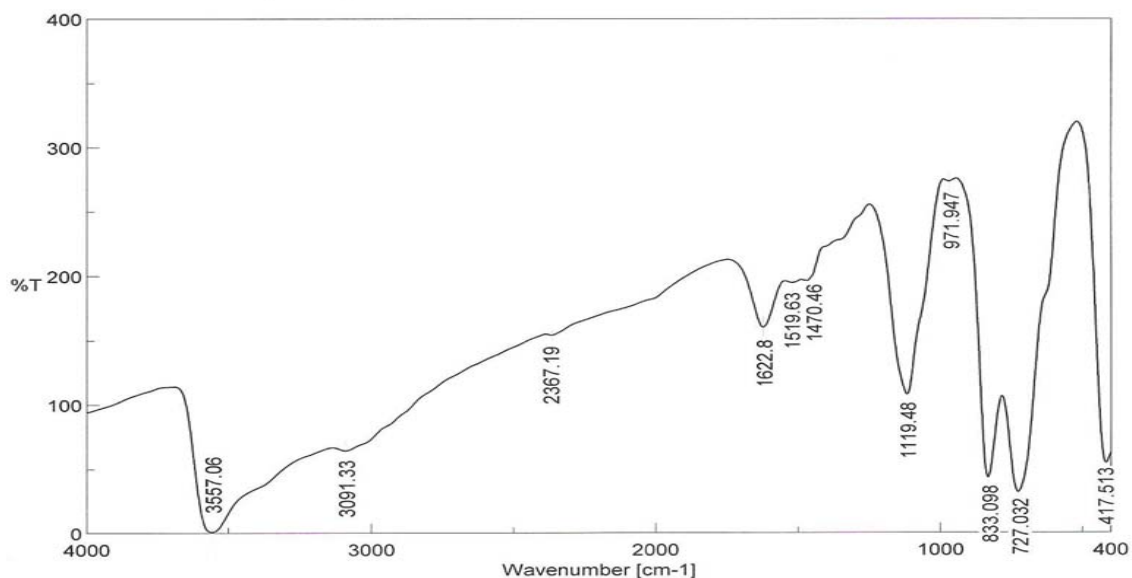


Fig.(1): IR spectrum of $\text{Co}_2\text{-L}$ complex

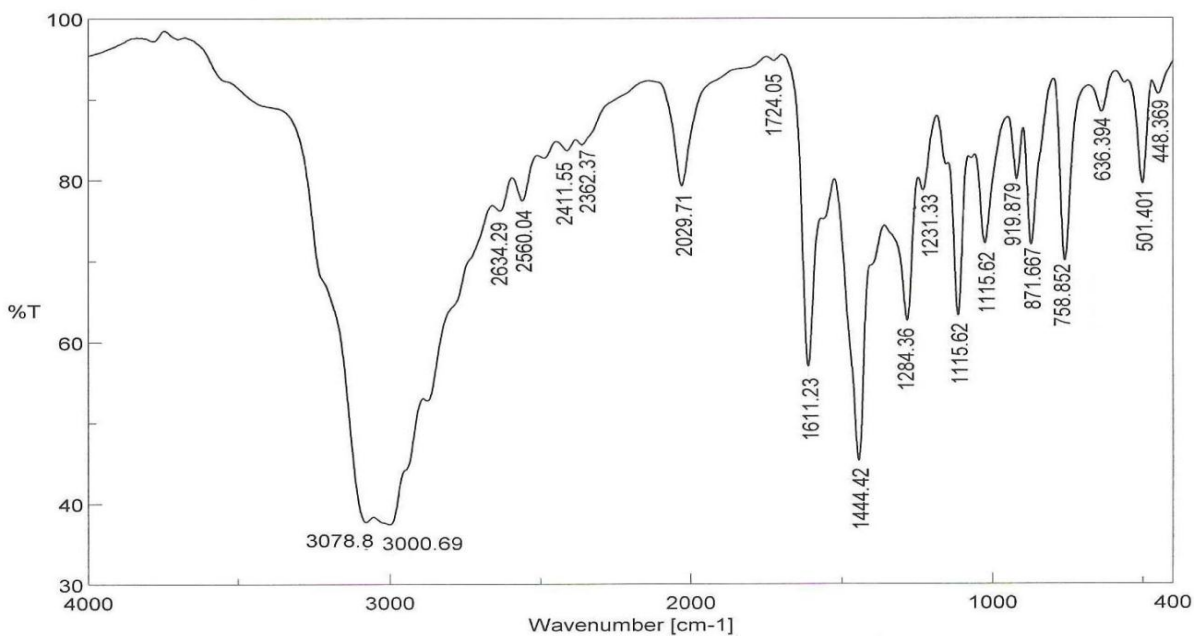


Fig.(2): IR spectrum of Ni₂-L complex

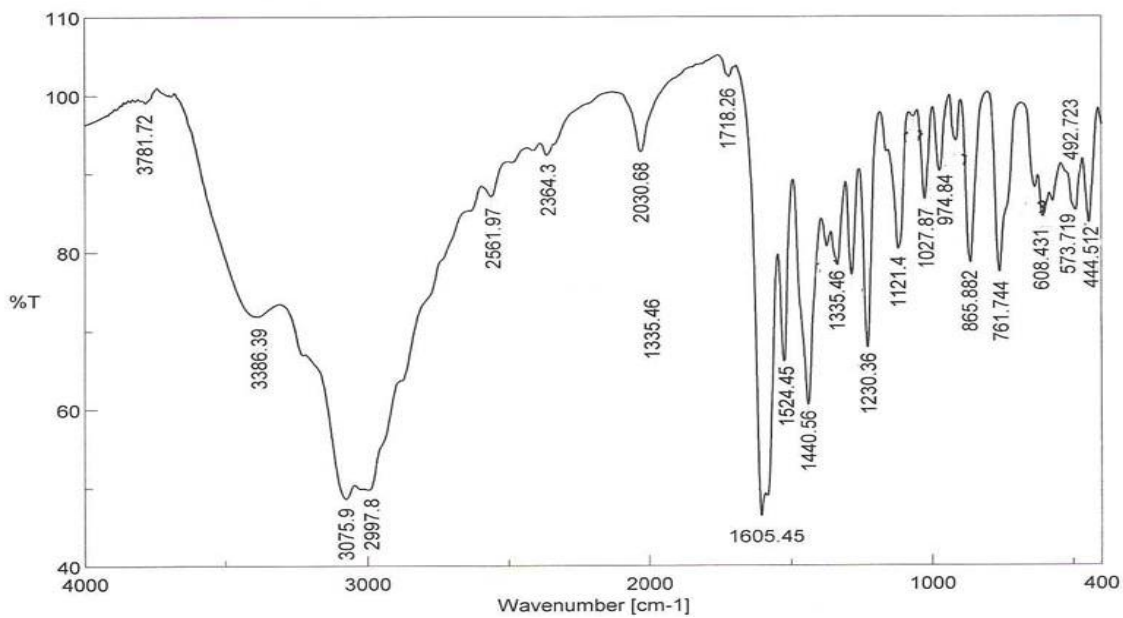


Fig.(3): IR spectrum of Cr₂-L complex

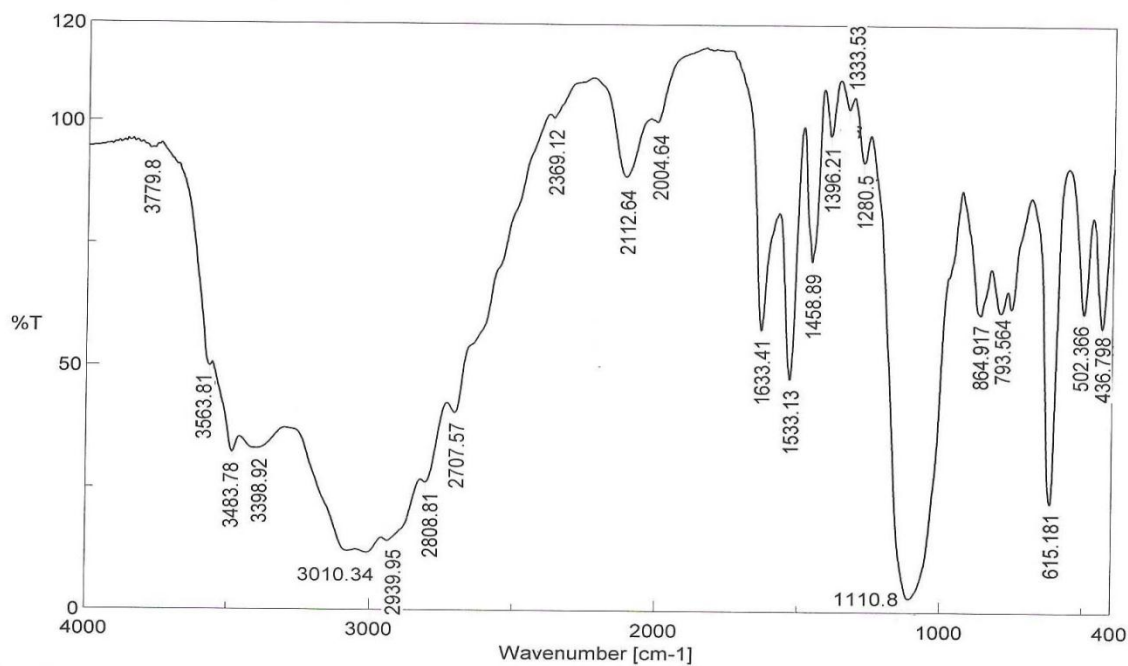


Fig.(4): IR spectrum of Cu₂-L complex

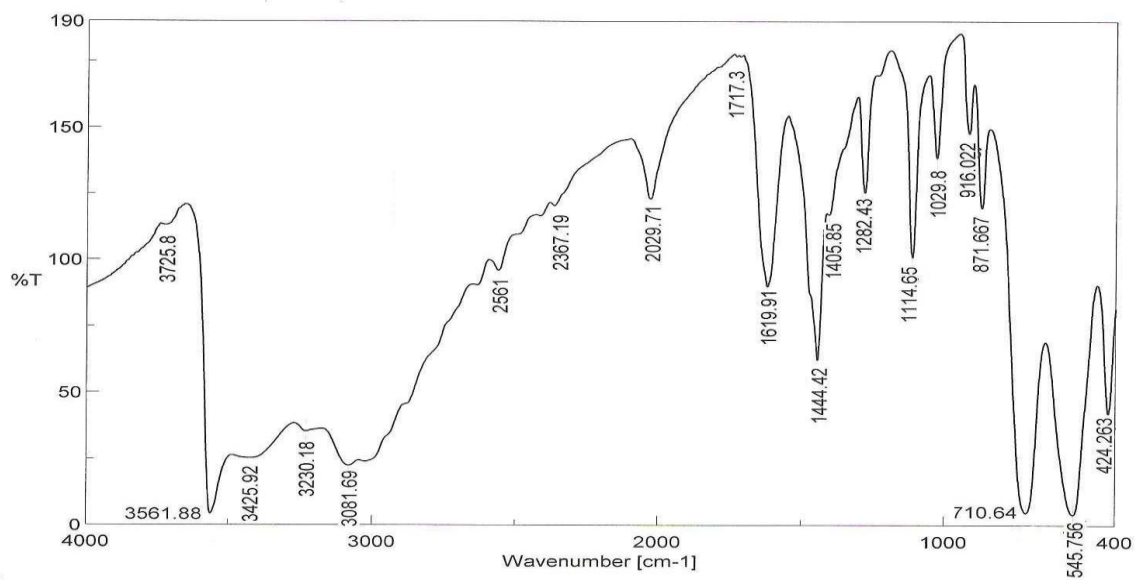


Fig.(5): IR spectrum of La₂.L complex

Electronic spectra and magnetic moments

The spectrum of the Schiff base exhibits three bands at 240, 290 and 425 nm, the first two bands due to the $\pi \rightarrow \pi^*$ (phenyl ring) and $n \rightarrow \pi^*$ ($-\text{C}=\text{N}$) and the third one assigned to charge transfer transitions.⁽¹¹⁾ Co(II) chelate displays several bands (Table 2) corresponding to the ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$ transitions. The intensity of the bands and the magnetic moment value (4.75 BM) confirmed the presence of an octahedral structure around Co(II) ion.⁽¹²⁾ It is well known that Ni(II) ions form large number of chelates whose their coordination number varies from 4 to 6. The electronic spectral data of Ni(II) chelate exhibit two bands (Table 2) attributed to ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}(\text{F})$ and ${}^3\text{A}_{2g} \rightarrow {}^4\text{T}_{1g}(\text{F})$ transitions. The

paramagnetic phenomena and the nature of the bands support the existence of an octahedral geometry.⁽¹³⁾ The spectrum of Cr(III) chelate shows two bands at 570 nm, 630 nm, these bands can be due to ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ and ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$ transitions including an octahedral geometry around the Cr(III) ion.⁽¹⁴⁾ The magnetic moment value of the chelate (3.98BM) reveals the presence of three odd electrons in its 3d orbital of Cr (III) ion. the Cu(II) chelate shows bands at 450 nm and 590 nm which can be assigned to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ and charge transfer transitions, the paramagnetic behavior of the chelate supports the presence of an octahedral structure around Cu(II) ion.⁽¹⁵⁾ For La(III) chelate, the electronic spectrum displays a band at 560 nm which could be due to the existence of a charge transfer transition and an octahedral geometry was suggested for the chelate,⁽¹⁶⁾ **Figs.(6-10)**

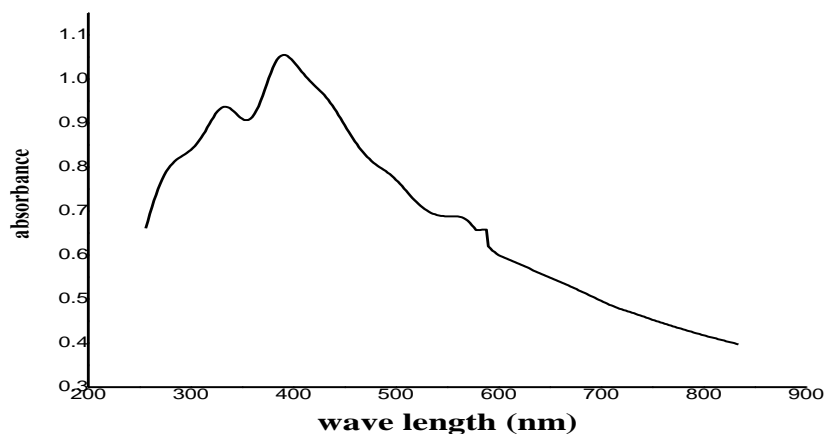


Fig.(6): Electronic spectra of Co₂L complex

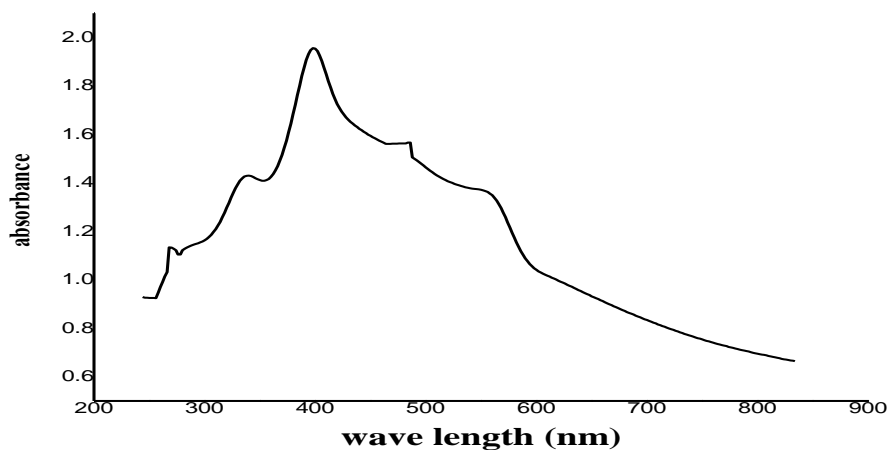


Fig. (7): Electronic spectrum of Ni₂.L complex

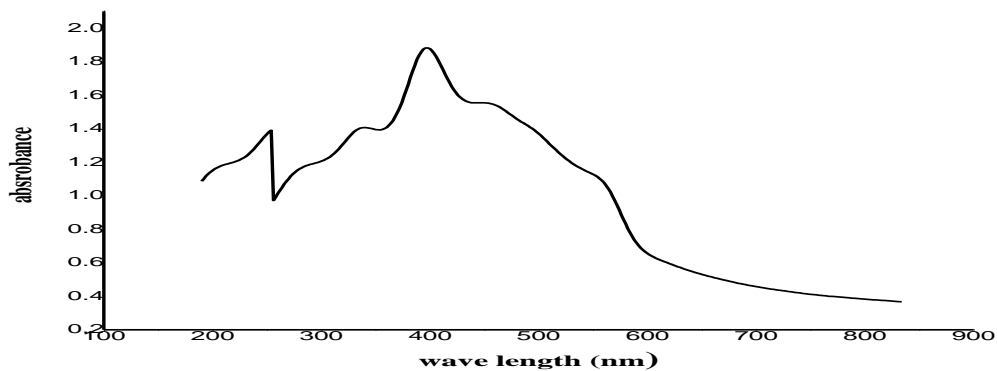


Fig.(8): Electronic spectrum of Cr₂.L complex

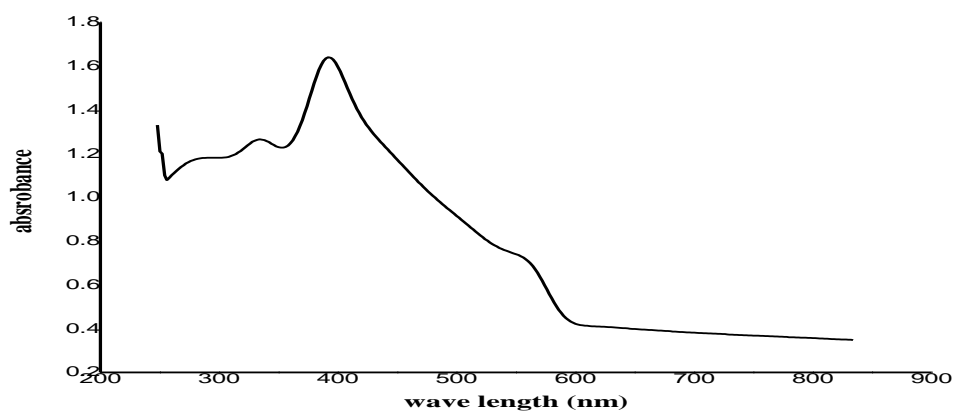


Fig.(9) : Electronic spectrum of Cu₂.L complex

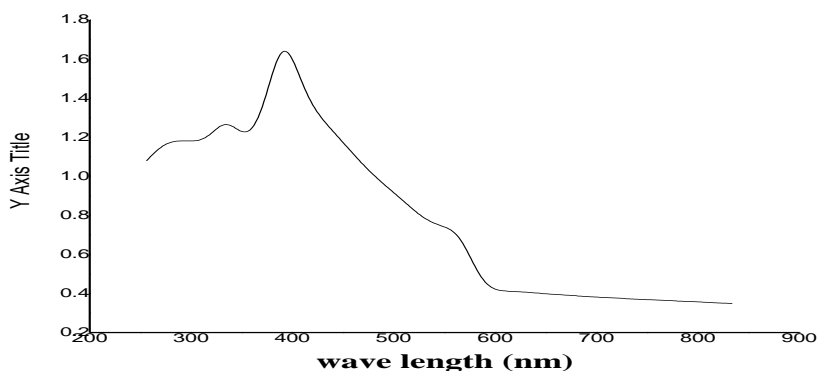


Fig.(10) :Electronic spectrum of La₂.L complex

Electron paramagnetic resonance spectra

The e. p. r spectra Figs.(10-14) of the Co(II), Ni(II), Cr(III) and Cu(II) chelates exhibit g values at 2.9919, 2.05856, 1.97824 and 2.00798, respectively. The

observed deviation from the ideal value (2.0023) suggesting that there is a good agreement with the covalent character of the metal- ligand bond and support the existence of an octahedral geometry around the metal ions.⁽¹⁷⁾

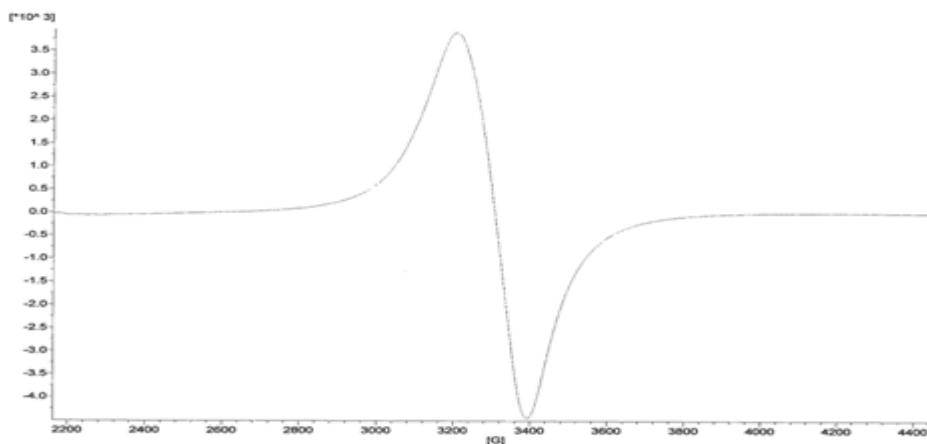


Fig. (11): Electron paramagnetic resonance spectrum of Co₂.L complex

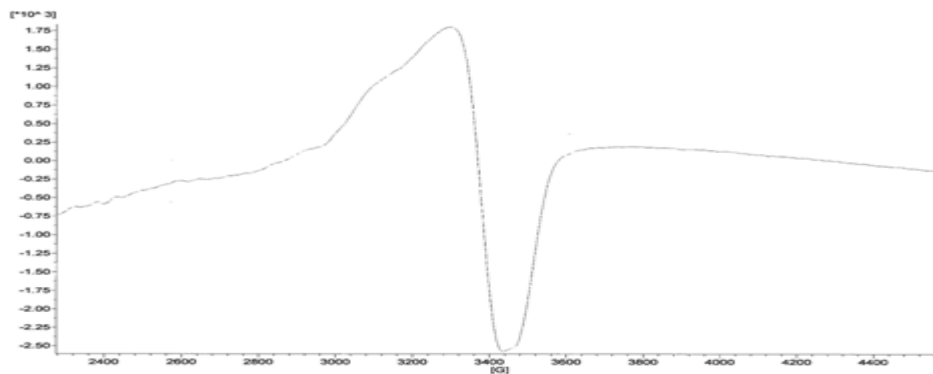


Fig. (12): Electron paramagnetic resonance spectrum of Ni₂-L complex

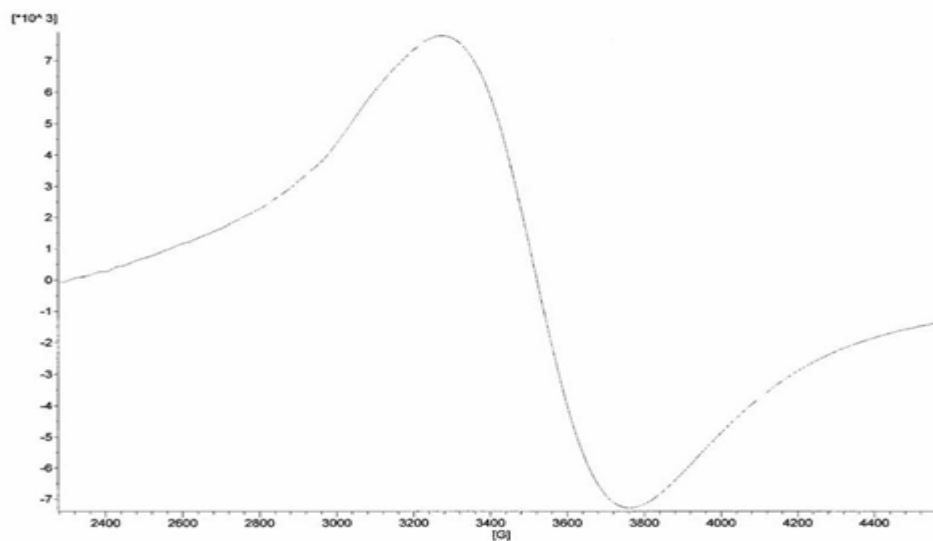


Fig. (13): Electron paramagnetic resonance spectrum of Cr₂-L complex

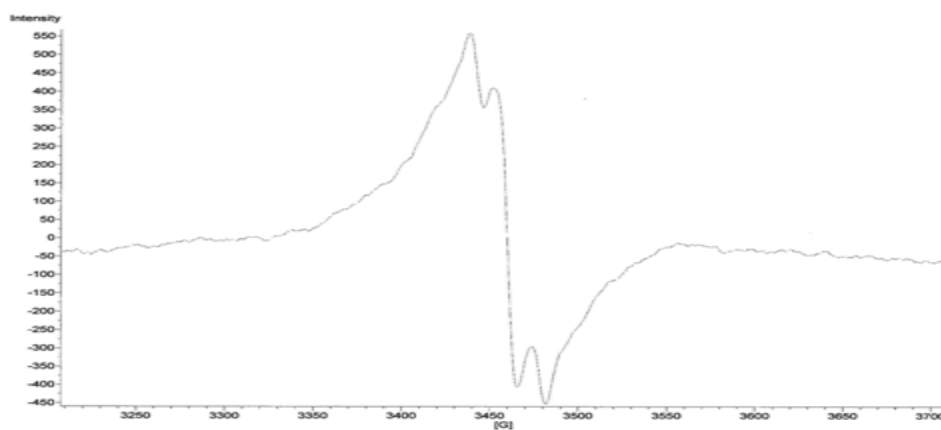


Fig. (14): Electron paramagnetic resonance spectrum of Cu₂-L complex

Antibacterial activity

The obtained data of the most compounds (Table 3) exhibit antibacterial activity against at least two bacteria species tested.. Although the compounds differ significantly in their activities against the tested pathogenic bacteria species. The screened Schiff base showed various inhibitory effects (9 mm and 16 mm) against *E. coli* and *Proteus* species. The inhibition zones vary depending on bacteria species and type of the used compound. The largest zone of inhibition was observed for the Schiff base against *E. coli* (16 mm), and no inhibitory activity against *P.aeruginosa* and *S.aureus*. [La₂LCl₄(H₂O)₄].H₂O chelate shows inhibitory activity against all bacteria

specie (9 – 12 mm). The lowest zone of inhibition was observed from [La₂LCl₄(H₂O)₄].H₂O chelate against *P.aeruginosa* (9mm). Whereas, for the [Cr₂LCl₄(H₂O)₄].2H₂O chelate, there is an effect against *S.aureus* (9 mm), *Proteus Sp* (10mm) and *P.aeruginosa* (11mm). The inhibitory activity of [Ni₂LCl₂(H₂O)₆] chelate against *Proteus Sp*, *P. aeruginosa* and *S.aureus* (12, 10 and 11 mm), respectively, was observed. Also, the [Co₂LCl₄(H₂O)₄] chelate shows high activity against *S.aureus* (14 mm) and low activity against *P.aeruginosa* (10 mm). No inhibitory activity was observed by [Co₂LCl₂(H₂O)₆], [Ni₂LCl₂(H₂O)₆] and [Cr₂LCl₄(H₂O)₄].2H₂O chelates against *E. coli*.

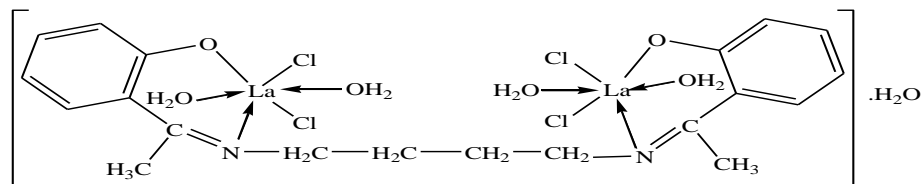
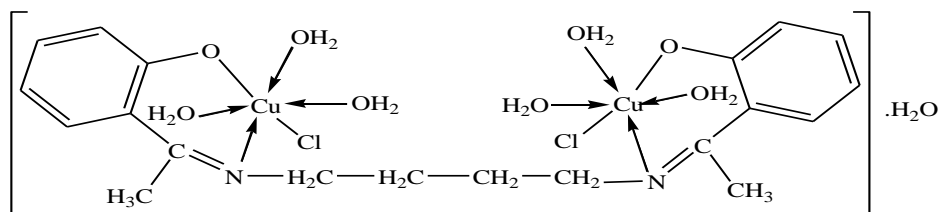
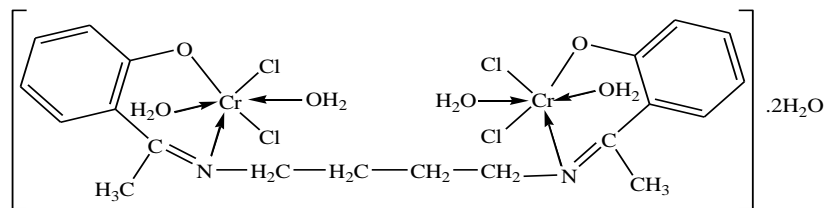
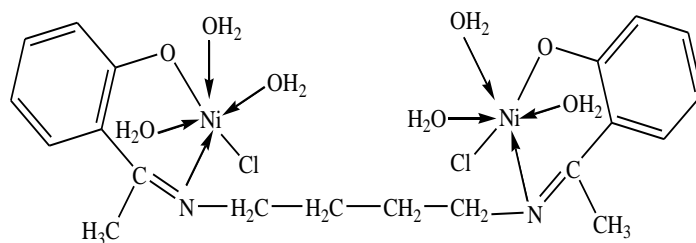
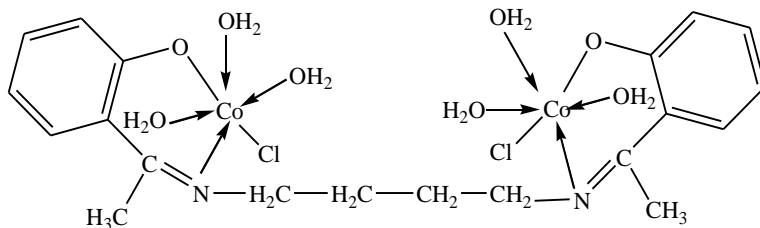
Table 3: Antibacterial activity of the Schiff base and its Co(II), Ni(II), Cr(III) and La(III) chelates.

Schiff base(L) /its complexes	bacteria species			
	<i>E. coli</i>	<i>Proteus Sp</i>	<i>P.aeruginosa</i>	<i>S.aureus</i>
L ;(C ₂₀ H ₂₄ N ₂ O ₂)	16	13	-	-
[Co ₂ LCl ₂ (H ₂ O) ₆]	-	13	10	14
[Ni ₂ LCl ₂ (H ₂ O) ₆]	-	12	10	11
[Cr ₂ LCl ₄ (H ₂ O) ₄].2H ₂ O	-	10	11	9
[La ₂ LCl ₄ (H ₂ O) ₄].H ₂ O	11	12	9	12

-: NOT active.

Conclusion

From the previous results, one can suggest the chemical structures for the synthesized complexes are as follows:



تخليق وتشخيص ودراسة التأثير المضاد البكتيري لبعض المتراكبات الجديدة لقواعد شيف

عبدالسلام ههيل، مرعي العجيلي، محمد عبدالكريم، محمد همت، حامد البغدادي

الملخص

تم تخليق متراكبات ثنائية وثلاثية التكافؤ لبعض العناصر الانتقالية مع المرتبط

2-[4 -[(Z)-1-(2-hydroxyphenyl)ethylidene]aminobutylethanimidoyl]phenol];

وكذلك تشخيصها باستخدام تقنيات فيزيائية عديدة، أهمها: التحليل العنصري (CHN)، القياسات المولارية الجهدية، القياسات المغناطيسية، الأطياف تحت الحمراء (IR)، الالكترونية (UV- Vis)، الكتلة والرنين الألكتروني البارامغناطيسي (E.P.R). بينت نتائج التحليل العنصري تكون مركبات قواعد شيف بنسبة 2:1 [M:L] وحددت القياسات المولارية الجهدية إن جميع المتراكبات المحضرة غير الكتروليتية في طبيعتها. وبينت قيم تحليل القياسات المغناطيسية وجود الكترولونات مفردة، اما نتائج مطيافية الأشعة تحت الحمراء قد اظهرت السلوك التناسقي لمركبات قواعد شيف المحضرة اتجاه جميع الايونات الفلزية المستخدمة باتجاه مجموعة الازوميتن (C=N) والهيدروكسيل (OH). كما اوضحت نتائج المطيافية الالكترونية لمركبات قواعد شيف ومتراكباتها وايضا الاشكال الهندسية المتوقعة للمتراكبات المحضرة ودعم تحديد الاشكال الهندسية بواسطة التحليل الالكتروني البارامغناطيسي الرنيني، واقترحت ان جميع المتراكبات تكون على هيئة ثماني السطوح. وتم دراسة تأثير مركبات قواعد شيف المحضرة ومتراكباتها المختلفة على عدد من انواع البكتريا الممرضة، وكان لها تأثير فعال عليها.

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