Synthesis, Characterization and Antibacterial Activity of Nd(III),Gd(III),Dy(III) and Er(III) Complexes with 2-[(2,4-dinitro-phenyl)-hydrozono methyl]-phenol

Zahraa Abdul Mahdi Jaber Alwasti
Department of chemistry, College of Science for Women
University of Baghdad

Abstract

The 2-[(2,4-dinitro-phenyl)-hydrozono methyl]-phenol was prepared by the reaction of salicylaldehyde with 2,4-dinitrophenylhydrazine, the prepared ligand was identified by Microelemental Analysis, FT.IR and UV-Vis spectroscopic techniques. Treatment of the prepared ligand with the following selected metal ions (Nd^{III},Gd^{III},Dy^{III} and Er^{III}) in aqueous ethanol with a 1:3 M:L ratio, yielded a series of complexes of the general formula $[M(L)_3]$. The prepared complexes were characterized by using flame atomic absorption, (C.H.N) Analysis, FT.IR and UV-Vis spectroscopic methods as well as conductivity measurements. From the obtained data the octahedral structure was suggested for all prepared complexes.

Keywords:- spectral studies, complexes, lanthanide, transition metals.

Introduction

The term Schiff base was invented by Hugo Schiff for the condensation reaction between an aldehydyde and ketone with amine. Schiff base ligands are able to coordinate with metal ion through the imine group and another side group in aldehyde or ketone(1,2). Schiff base derivatives are very importants in coordination chemistry. Therefore, Schiff base complexes containing transition metals have been shown broad range in research areas, such as structural chemistry(3). A large number of Schiff bases and their complexes have been well known for their easy synthesis, stability and several application, such as catalytic and biological properties(4-9).

Recently, the complexes of Schiff base ligands have been investigated for their interesting important applications, such as biological, biochemical, analytical, antimicrobial, antibacterial, anticancer, antitumor and antifungal activity(10-14).

The present paper reports the synthesis and characterization of new Nd^{III},Gd^{III},Dy^{III} and Er^{III} complexes.

Experimental

Instrumentation

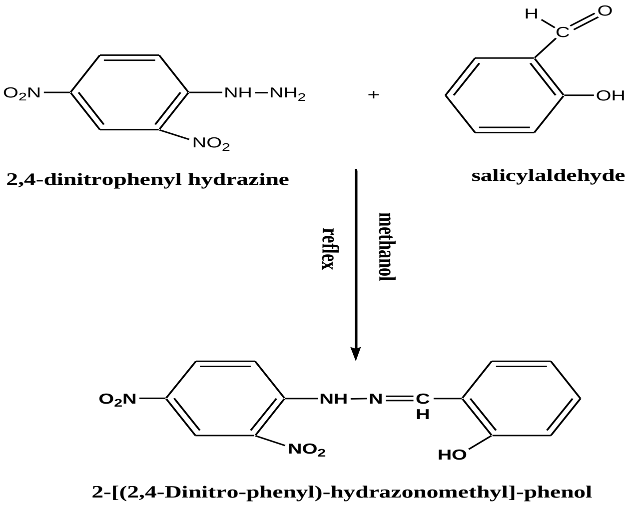
UV-Vis spectra were recorded on a (Shimadzu UV-160 A) Ultra Violet-Visble Spectrophotometer. I.R-spectra were taken on a (Shimadzu, FTIR-8400 S) Fourier Transform Infrared. Spectrophotometer (4000-400) cm^{-1} with samples prepared as KBr discs. Atomic Absorption was obtained by using a (Shimadzu A.A-160A) Atomic Absorption/Flame Emission Spectrophotometer. Microelemental analysis (C.H.N) was performed in the central service laboratory, College of Education for pure Sciences/Ibn Al-haitham by using (Euro EA 3000 Elemental Analyzer). Conductivities were measured for 10^{-3}M of complexes in DMF at 25°C by using (Philips PW-Digital Conductimeter). In addition, melting points were obtained by using (Melting Point Apparatus).

Materials

The following chemicals were used as received from suppliers; salicylaldehyde,2,4-dinitrophenylhydrazine, Neodymium chloride hexahydrate 98.8%, Gadolinium chloride hexahydrate 99.9%, Dysprosium chloride hydrate 98% and Erbium chloride 98.8% (Merck).

Synthesis of Schiff base (L)(15)

(0.26ml,1mmole) of salicylaldehyde was added to methanolic solution of (3.24g,1mmole) of 2,4-dinitrophenylhydrazine.The solution mixture was stirred and refluxed for 3 hours, yellow crystalline precipitate observed. The resulting precipitate as filtered off recrystallized from menthol and dried at 50°C. The preparation method of the ligand (L) is represented in scheme-1.



(Schem-1): Preparation Method of the Ligand (L)

Preparation of Metal Complexes (general procedure)

An aqueous solution of the metal salts containing 0.131g, 0.148g, 0.121g and 0.146g (1mmole) of $Nd(NO_3)_3.6H_2O$, $Gd(NO_3)_3.6H_2O$, $Dy(NO_3)_3.H_2O$ and $Er(NO_3)_3.5H_2O$ respectively was added gradually with stirring to ethanolic solution (0.301g,3mmol) of the ligand by using stichiometric amount (1:3) Metal to Ligand molar ratio. The mixture was refluxed with constant stirring for 3 hour. The mixture was cooled at room temperature dark precipitate was formed, filtered and recrystillized from ethanol.

Study of Biological Activity

Three selected types of bacteria were used including , *Esherichia Coli (E. Coli)* as Gram Negative Bacteria, *Staphylococcus Aureus (Staph. Aureus)* as Gram Positive Bacteria and *Psedomonas Aeruginosa (Ps. Aeruginosa)* in Neutrient Agar medium, using (DMSO) as a solvent and as a control, the concentration of the compounds in this solvent was 10^{-3}M, using disc sensitivity test. This method involves the exposure of the zone of inhibition toward the diffusion of micro- organism on agar plate. The plates were incubated for 24hr. at $37C^{o}$.

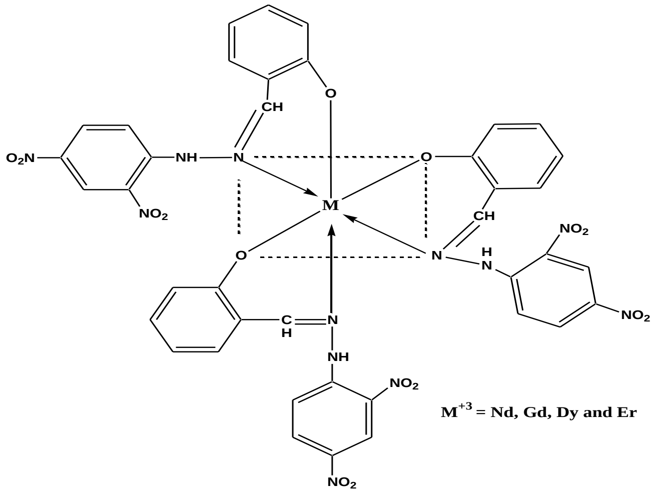
Results and Discussion

The ligand (HL) was prepared by condensation reaction between salicylaldehyde and 2,4-dinitrophenylhydrazine. The ligand was sparingly soluble in water but soluble in organic solvents such as DMSO and DMF, stable toward air and moisture. Synthesized ligand (HL) was characterized by FT-IR, Elem.Anal.(C,H,N) and UV-Vis spectroscopic technique. The solid complexes were prepared by reaction of alcoholic solution of the ligand with the aqueous solution of the metal ions in a (M:L) of (1:3). The (C.H.N) analysis with metal contents of these complexes were in good agreements with the calculated values (Table-1) includes some physical properties and elemental analysis.

The molar conductance of the complexes as (10^{-3}M) in DMSO indicating their non-electrolytic nature(16), the data were recorded in (Table 2). The UV-Vis spectra data for the free ligand and all metal complexes are listed in (Table-2). The UV-Vis spectrum of the ligand (L) (Fig-1) shows two peaks at 268 nm and 405 nm assigned to (π–π*) electronic transitions(17,18). The electronic spectra of the complexes (Fig-2) showed peaks at 281 nm, 270 nm, 277 nm and 280 nm due to ligand field. The absorbance peaks at 358 nm, 382 nm, 390 nm and 380 nm were assigned to charge transfer. The spectra of the complexes appear absorbance peaks at 520 nm, 533 nm, 541 nm and 537 nm were found to be caused by (f-f) electronic transition(19).

In order to study the binding mode of the ligand with the metal ions, a comparison was made for the FT.IR spectra of the free ligand and those of the prepared complexes and the data was tabulated in (Table-3). The IR spectrum of the ligand (L) (Fig-3) exhibited band at 3278 cm^{-1} was assigned to ν(OH) stretching frequency. This band was absent in the spectra of the prepared complexes, which indicated deprotonation and involvement of the enol oxygen in chelation(20,21). The bands at 3105 cm^{-1} and 3066 cm^{-1} in the ligand spectrum ascribed to ν(CH) aromatic(22). The band at 1622 cm^{-1} due to ν(C=N), shifted to lower frequency with change in shape in spectra of the complexes, which is an indication of the engagement of this group in the coordination with the metal ion(23,24). The bands in the ligand spectrum at 1595 cm^{-1} and 1512 cm^{-1} were assigned to ν(C=C)(25). The new bands observed at (467-580) cm^{-1} are tentatively assigned to ν(M-N) and ν(M-O) (Metal-Ligand) stretching bands(26,27).

According to the results obtained and spectral analysis an octahedral structure has been suggested to these complexes, the molecular structure represented in Scheme-2 .



(Schem-2): Preparation of Metal Complexes.

Compounds	Color	M.P°C	Yield %	Analysis Calc (Found)			
				M%	C%	H%	N%
Ligand(L)	yellowish orange	185	85	-	51.82 (50.88)	2.99 (2.63)	18.60 (17.38)
$[Nd(L)_3]$	yellow	211	77	13.79 (12.89)	44.82 (44.17)	2.29 (1.96)	16.09 (15.86)
$[Gd(L)_3]$	orange	218	72	14.85 (13.95)	44.27 (43.94)	2.27 (2.03)	15.89 (14.75)
$[Dy(L)_3]$	yellow	220	74	15.33 (14.85)	44.02 (43.78)	2.25 (1.97)	15.80 (14.67)
$[Er(L)_3]$	yellow	232	73	15.65 (14.83)	43.86 (42.92)	2.24 (1.88)	15.74 (14.88)

Table(1):- Physical properties and elemental analysis of the complexes.

Table(2):- UV-Vis and conductance measurements data.

Compounds	(λ nm)	ABS	ϵ_{max} $(L.mol^{-1}.cm^{-1})$	$\Lambda_m(S.cm^2.mol^{-1})$ In Absolute ethanol
Ligand(L)	268 405	0.513 1.315	513 1315	-
$[Nd(L)_3]$	281 358 520	0.735 0.977 1.847	735 977 1847	13.82
$[Gd(L)_3]$	270 382 533	0.519 1.108 1.768	519 1108 1768	10.36
$[Dy(L)_3]$	277 390 541	0.473 1.037 1.475	473 1037 1475	7.83
$[Er(L)_3]$	280 380 537	0.358 0.837 1.357	358 837 1357	9.72

Table(3):- The Main Frequencies of the Ligands and It's Complexes(cm^{-1}).

Compounds	**υ(OH)**	**υ(CH) aromatic**	**υ(C=N)**	**υ(C=C)**	**υ(M-N)**	**υ(M-O)**
Ligand(L)	3278 br.	3105 w.	1622 sh.	1595 sho. 1512 s.	-	-
$[Nd(L)_3]$	-	3106 w.	1610 s.	1596 sho. 1512 sh.	543 w.	471 w.
$[Gd(L)_3]$	-	3107 w.	1614 s.	1591 sho. 1512 s.	580 w.	530 w.
$[Dy(L)_3]$	-	3106 w.	1607 sh.	1593 sho. 1512 s.	519 w.	482 w.
$[Er(L)_3]$	-	3105 w.	1606 sh.	1595 sho. 1512 sh.	530 w.	467 w.

br = broad, sh = sharp, sho =shoulder, s = strong, w =weak

Finally, the biological activities of the ligand and their complexes have also been tested against selected type of bacteria, (Table-4) show the deactivation capacity against the bacteria specimen of the prepared compounds under study.

Table(4):- Diameters (mm) of Deactivation of Bacteria for the Phenylalanine and It's Complexes

Compounds	**Staphylococcus Aureus**	**Escherichia Coli**	**Psedomonas Aeruginosa**
Ligand(L)	++	-	++
$[Nd(L)_3]$	-	+	-
$[Gd(L)_3]$	+	-	+
$[Dy(L)_3]$	-	++	-
$[Er(L)_3]$	++	+	++

(-) = No inhibition.

(+) =Inhibition diameter (6-8) mm.

(++) =Inhibition diameter (8-10) mm.

(+++) =Inhibition diameter (10-20) mm.

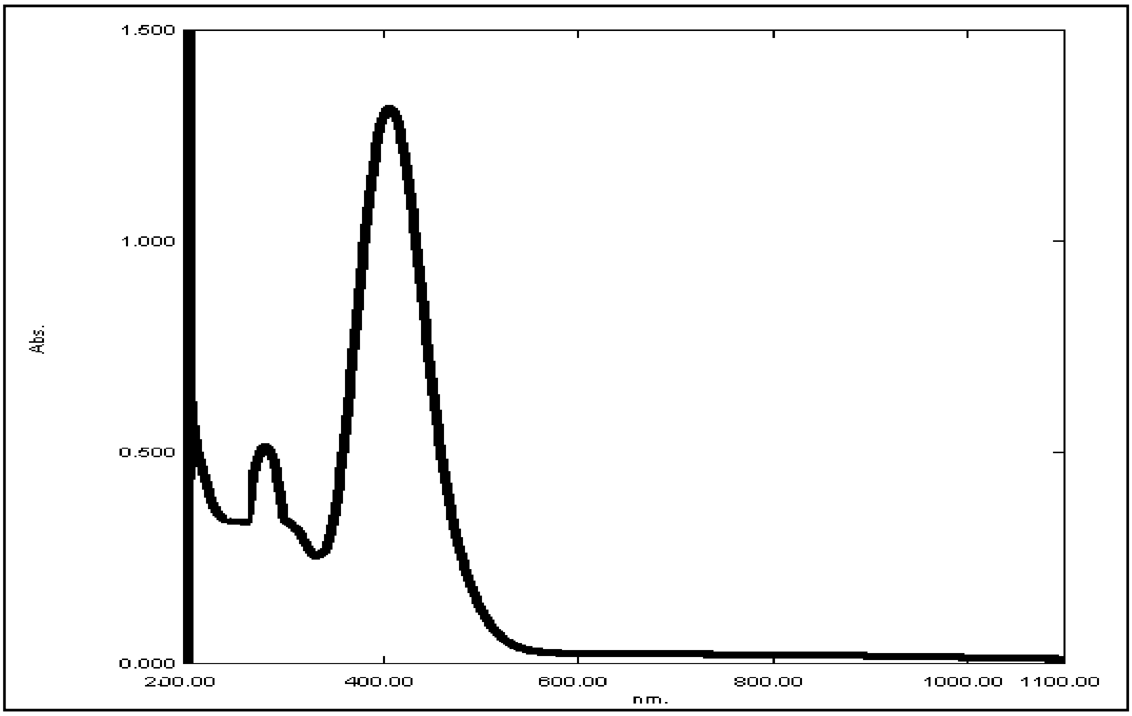


Fig.(1):- UV-Vis spectrum of the ligand.

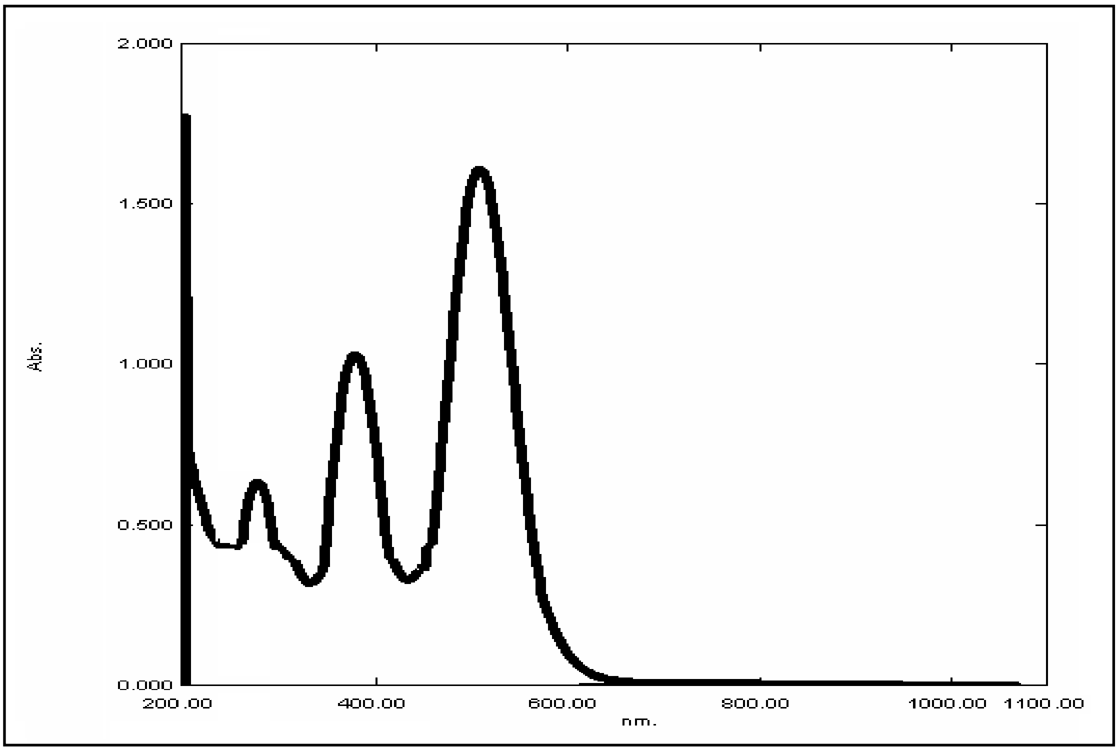


Fig.(2):- UV-Vis spectrum of the $[Gd(L)_3]$ complex.

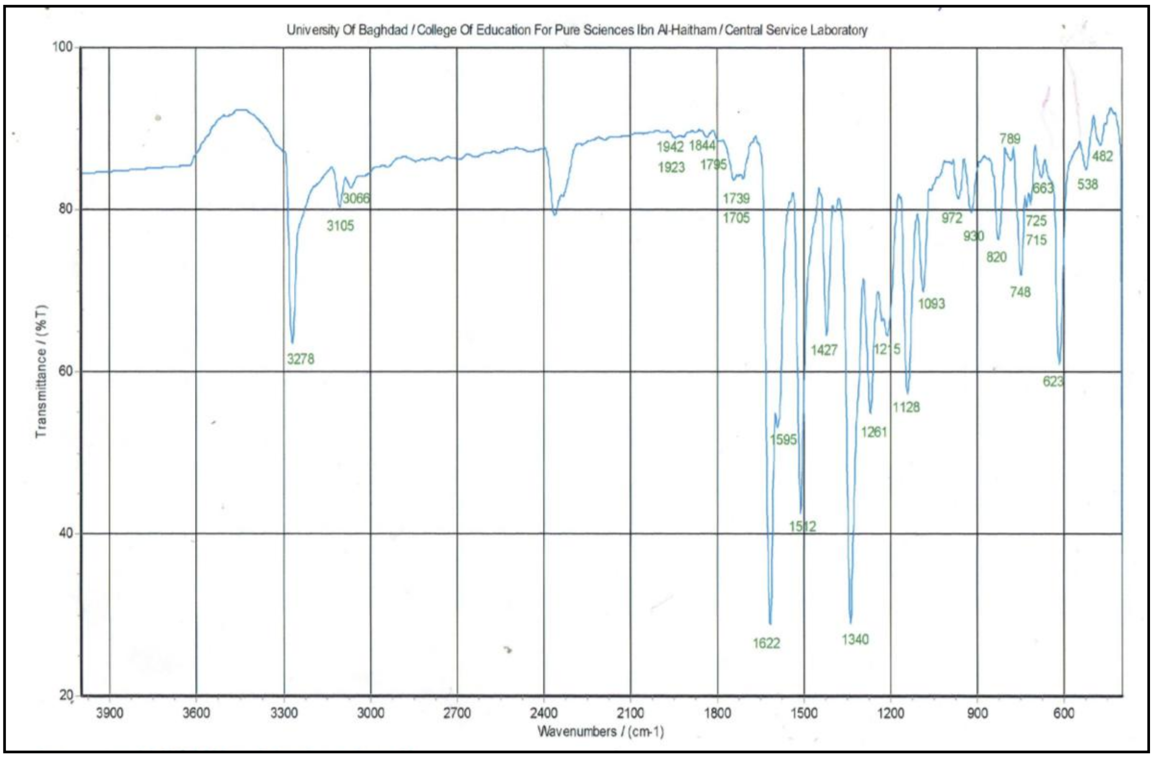


Fig.(3):- FT-IR spectrum of the ligand.

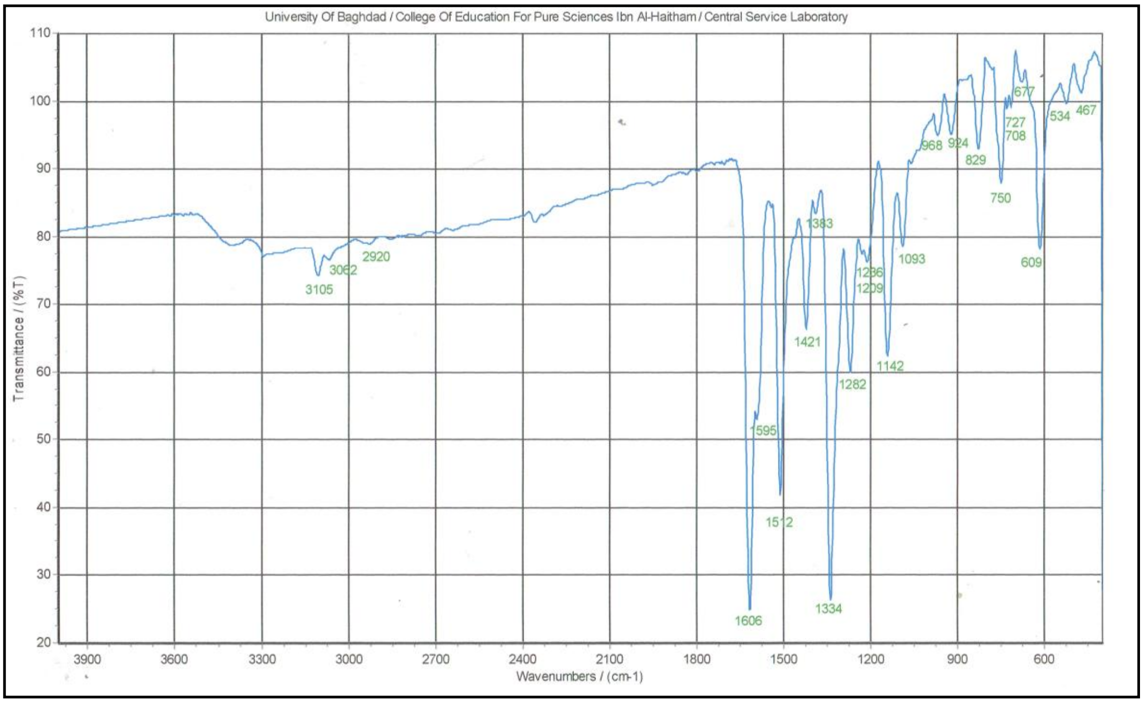


Fig.(4):- FT-IR spectrum of $[Er(L)_3]$ complex.

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تحضيرو تشخيص ودراسة الفعالية البايولوجية لمعقدات النيوديوم(III)، الكادلينيوم(III)، الديسبريسيوم(III) والأريبيوم(III) مع 2-(4،2- ثنائي نايترو- فنيل) هايدروزونو مثيل- فينول.

زهراء عبد المهدي الواسطي

قسم الكيمياء- كليةالعلوم للبنات- جامعة بغداد

الخلاصة

تم تحضير الليكاند 2-(4،2- ثنائي نايترو- فنيل) هايدروزونو مثيل- فينول من تفاعل السلسلديهايد مع 4،2- ثنائي نايترو فنيل هايدرازين. شخص الليكاند المحضر بواسطة اطياف الأشعة تحت الحمراء وفوق البنفسجية – المرئية والتحليل الدقيق للعناصر(C.H.N) . تمت مفاعلة الليكاند مع ابونات Nd(III),Gd(III),Dy(III) and Er(III) وبنسبة مولية (3:1) فلز: ليكاند. شخصت المعقدات المحضرة بوساطة التحليل الدقيق للعناصر(C.H.N)؛ تقنية الإمتصاص الذري اللهبي واطياف الأشعة تحت الحمراء وفوق البنفسجية – المرئية، فضلا عن قياسات التوصيلية الكهربائية، ومن النتائج التي تم الحصول عليها هي اقتراح الشكل ثماني السطوح للمعقدات المحضرة. لقد تمت الإفادة من الليكاندات والمعقدات قيد الدراسة حول إمكانية دراسة الفاعلية البايولوجية ووجد أن لهذه المعقدات قابلية متباينة على قتل الأنواع المنتخبة من البكتريا.

الكلمات المفتاحية: الدراسات الطيفية، المعقدات، اللانثانات، العناصر الإنتقالية.