MANSOURA JOURNAL OF CHEMISTRY
Official Journal of Faculty of Science, Mansoura University, Egypt
E-mail: scimag@mans.edu.eg ISSN: 1687-5060

Synthesis, spectral and biological studies of some metal chelates complexes of Schiff-bases derived from phthalaldehyde and benzylamine

Abdusalam M. Hamil[1]*, Khalifa M. Khalifa[1], Eman I. Mobark[1] and Y.A. Alkhayali[2]

1. Chemistry Department, Faculty of Science, Sabha University, Sabha, Libya
2. Botany Department, Faculty of Science, Sabha University, Sabha, Libya

*** Correspondence to AM Hamil:** *E-mail: abdsalam_1956@yahoo.com*, Tel.: +218923022760

Received: 14/9/2019
Accepted: 24/9/2019

Abstract: Three transition metal complexes derived from the condensation product of (*9E*)-*N*-(*E*)-(benzylimino)methylidene phenylmethanamine with phthalaldyde and benzyl amine have been synthesized and characterized. The geometries of the isolated chelate compounds were investigated by physical, elemental analyses (CHN), conductance, molar susceptibility, mass spectra, ^{1}H-NMR, FTIR and electronic spectra data. The elemental analyses showed that the isolated chelates have 1:1 [M:L] ratio. The values of conductance showed that the all the chelates are electrolytic in nature except the compound with the formula, $[CuL(H_2O)_2Cl_2].2H_2O$, which is non-electrolytic. Also, the results of spectral and the values of magnetic moments of the Cr^{3+}, Ni^{2+} and Cu^{2+} chelates exhibit that the compounds are paramagnetic in nature and characterized by octahedral geometries. The IR spectral data displayed the main coordination sites on coordination toward lower wavenumbers.

keywords: Schiff Base Metal complexes, Spectroscopic Study, Biological Activity

1. Introduction

The compounds contain the azomethine group (-HC=N-) are known as Schiff-bases and obtained by the reactions of different kinds of ketones or aldehydes with primary amines and the first example was first reported by Hugo Schiff in 1864 [1]. The common feature of these compounds is the presence of the azomethine group and have the general formula, RHC=N-R, where R and R′are alkyl, aryl, cycloalkyl or heterocyclic groups which may be variously substituted. Schiff-bases derived from aliphatic aldehydes are unstable and are easily polymerized. On the other hand, the use of aromatic aldehydes leads to form stable compounds due to the existence of conjugation system within the compounds.

Triazole Schiff-bases were reported to possess antimicrobial, antianxiety, antidepressant and plant growth regulatory activity [2]. Two novel chelates obtained from Ni(II) and Pd(II) salts with Schiff-base derived from 5-chloro isatin with 4-phenyl-3-thiosemicarbazid have been synthesized in absolute EtOH. The structures of the isolated solid chelates have been studied using elemental analyses and infrared and electronic spectra. The ligand was further characterized by mass spectrum [3]. Schiff-base complexes of 4-(2-hydroxbenzalo-deamino)-3-hydrox naphthalene-1-sulfonic acid have been isolated and investigated by elemental analyses, (C,H,N,S), IR, electronic spectra, molar conductivity and magnetic moment measurements [4]. These compounds are also known as anils, imines or azomethines [5] are also known Schiff-base compounds. Two new Schiff-base ligands, [**HL^{1}**, ($C_{15}H_{11}N_3O_3$)] and [**HL^{2}**, ($C_{15}H_{11}N_3O_2S$)], were synthesized from the condensation products of semicarbazide and/or thiosemicarbazide with salicylaldehyde in EtOH. The isolated Cu^{2+} chelates with the general formulae, $C_{15}H_{11}N_3O_3Cu$ and $C_{15}H_{11}N_3O_2SCu$, were prepared. The Schiff-bases and their chelates showed moderate to strong antimicrobial activity [6]. The chemistry of thiosemicarbazones chelates were resumed due to their broad profile of pharmacological activity that provides a diverse variety of compounds with different activities [7-10]. Moreover, the Schiff-bases synthesized from amino and carbonyl groups are an important class of compounds having the ability to coordinate to the metal ions *via* azomethine nitrogen and. In azomethine derivatives, the C and N linkage is essential for biological activity and several azomethine have

been reported to possess remarkable antibacterial, antifungal, anticancer and antimalarial (Prakash *et al*, 2011)**[11]**.

In the present investigation we reported a literature survey on the synthesis, characterization and applications of Schiff-bases and their chelates derived from 2-hydroxyacetophenone and primary amines including applications of Schiff-bases and their chelates in qualitative analysis, biological activity and synthesis for chemical analysis. The chemicals used to get Schiff-bases and chelates with appreciable stability lead to get important compounds in the field of chemistry. The uses of Schiff-bases and their chelates as biological reagents suggest enlisting an important type of research to be considered among Chemists and in solving recent problems in the living aspects **[12]**

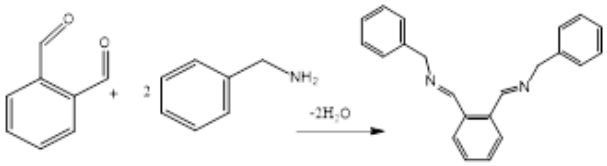
2. Materials and methods

2.1. Materials

All chemicals as well as solvents used in this investigation were of BDH and Aldrich quality. Phthalaldyde, benzyl amine and metal salts, ($CrCl_3.6H_2O$, $NiCl_2.6H_2O$, and $CuCl_2.2H_2$)], absolute ethanol, glacial acetic acid, ammonia solution, ether and dimethyl foramide (DMF) were pure and used as supplied. The solvents were of pure grades or purified by the recommended methods.

2.2. Synthesis of Schiff base

(*9E*)-N-(*E*)-(benzylimino)methylidene)phenyl-methanamine (**L**) was synthesized by adding (6.702 g, 0.05 mole) of phthalaldyde drop wise to benzyl amine (5.358g, 0.05 mole) in 50 cm^3 of absolute ethanol. The reaction mixture was refluxed for 3 h. The product was left to cool at room temperature, filtered and recrystallized from EtOH, dried under vacuum and kept at room temperature. The product has a brown precipitate (yield 76%; **Scheme 1)**.



Scheme 1: Synthesis of (*9E*)-N-(*E*)-(benzylimino) methylidene)phenyl- methanamine (**L**)

2.3. Synthesis of Complexes

The chelates were obtained by adding the Schiff base (3.124g; 0.01 mole) in 50 cm^3 absolute ethanol to 0.01 mole of the metal salts of $CrCl_3.6H_2O$, $NiCl_2.6H_2O$ and $CuCl_2.2H_2O$, (2.665 g, 2.377 g and 1.705 g, respectively, in absolute ethanol. The reaction mixtures were held under reflux for 3 hs and the isolated the solid products were filtered off, recrystallized from ethanol and finally kept in a desiccator over silica gel**.**

2.4. Bacteria assay

The Schiff-base and its complexes with Cr^{3+}, Ni^{2+} and Cu^{2+} complexes were tested against *Pseudomonas aeruginosa* and *Bacillus subtilis* bacteria species in a mixture of DMF and H_2O. The diffusion methods were used in the antibacterial activity determination**.**

3. Results and discussion

3.1. Microanalysis and molar conductance measurements of the Schiff-bases chelates

(9E)-N-(E)-(benzylimino)methylidenephenyl-methanamine **(H_2L)** was synthesized by adding phthalaldyde drop wise to benzyl amine with stirring. The synthesized Schiff-base was subjected to CHN elemental analyses, mass spectra, IR, UV and ^{1}H-NMR. The molar conductance values of the complexes in DMF solvent lie in the range of 27-146 ohm^{-1} cm^2 mol^{-1} indicating the Cu^{2+} chelate is non-electrolytic while the of Cr^{3+} and Ni^{2+} chelates are electrolytic and some physical properties are listed in **Table 1**. The results show a good agreement between the calculated and experimental values.

Table (1): *Elemental analyses and some physical data of* ***H_2L^1*** *and its chelates*

Ligands/Complexes	Color	M.wt.	M.P.; °C	% Calcd. **(Found)**			Λ_m Ω^{-1} cm^2 $.mol^{-1}$	BM
				C%	H%	N%		
$C_{22}H_{20}N_2$; **H_2L^1**	Dark brown	312.41	115	84.58 **(83.89)**	6.45 **(6.68)**	8.97 **(8.17)**	-	-
$[Cr(\mathbf{H_2L^1})Cl_2(H_2O)_2]Cl$	Dark green	506.79	158	52.14 **(52.15)**	4,77 **(4.19)**	5.53 **(6.06)**	87	3.68
$[Ni(\mathbf{H_2L^1})(H_2O)_4]$ $Cl_2.5H_2O$	Brown	604.14	170	43.74 **(44.13)**	43.74 **(44.11)**	4.12 **(4.56)**	146	2.71
$[Cu(\mathbf{H_2L^1})(H_2O)_2Cl_2].3H_2O$	Light green	536.94	180	49.21 **(48.78)**	5.64 **(6.25)**	5.22 **(5.79)**	27	1.79

3.2. Mass spectrum of H_2L^1

The molecular weight from the mass spectrum of **H_2L^1** (**Figure 1**) shows M^+ peak at 312.41 corresponds to the molecular formula, $C_{22}H_{20}N_2$.

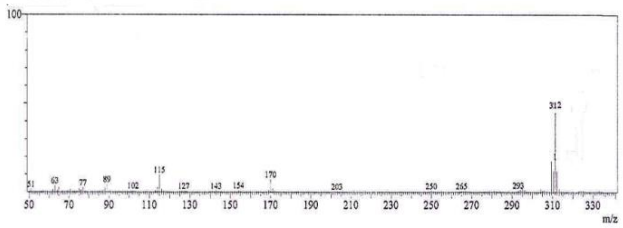


Fig. 1. Mass spectrum of the free ligand

3.3. ^{1}H-NMR spectrum of ligand

^{1}H-NMR spectrum in d_6-DMSO solvent was carried out on a Jeol- 90 Fourier Transform (200 MHz). The Schiff-base **(H_2L^1)** shows peaks (**Figure 2**) at 3.56, 6.916-8.857 and 9.985 ppm, downfield of TMS, attributable to the protons of CH_2, phenyl and –HC=N-, respectively **[13].**

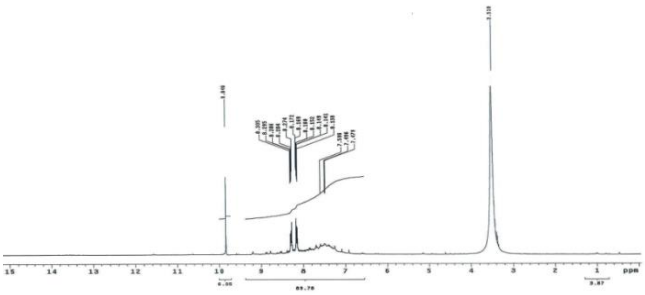


Fig. 2. ^{1}H-NMR spectrum of the free ligand

3.4. Spectra and antibacterial activity studies

The spectral data of **H_2L^1** and its chelates are summarized in **Table (2)** and illustrated in **Figs**. 3-6. UV spectrum of the Schiff-base **(H_2L^1)** shows two bands at 265 nm (37735 cm^{-1}) and 346 nm (28901 cm^{-1}) corresponding to π→π* and n→π* transitions, respectively **[14,15]**.

Table (2): *IR and electronic spectral data of the ligand (H_2L^1) and its complexes*

Ligand/ Complexes	Wave number (υ, cm^{-1})				UV/Vis λ_{max} (cm^{-1})
	υ(CH_2)	υ(C=N)	υ(M-N)	υ(M-O)	
H_2L^1; ($C_{22}H_{20}N_2$)	3360	1636	-	-	37735, 28901
[Cr(**H_2L^1**)$Cl_2(H_2O)_2$]Cl	3378	1648	620	513	16343, 16000, 28653
[Ni(**H_2L^1**)$(H_2O)_4$]Cl_2.5H_2O	3404	1643	589	458	14084, 17035, 28409
[Cu(**H_2L^1**)$(H_2O)_2Cl_2$].3H_2O	3413	1640	634	570	15432, 17391, 27932

Spectrum of Cr^{3+}chelate exhibits three bands at 13643, 16000 & 28653 cm^{-1} corresponding to $^4A_{2g(F)} \rightarrow {}^4T_{2g(F)}$, $^4A_{2(F)} \rightarrow {}^4T_{1g(F)}$ and charge transfer, respectively, while three absorption bands were observed for Ni^{2+}L at 14084, 17035 & 28409 cm^{-1} corresponding to $^3A_{2g(f)} \rightarrow {}^3T_{1g(f)}$, $^3A_{2g(f)} \rightarrow {}^3T_{1g(p)}$ and $^3A_{2g(f)} \rightarrow {}^3T_{1g(f)}$ transitions, respectively **[16,17]**. The electronic spectrum of Cu^{2+}**(H_2L^1)** shows three bands at 17391 cm^{-1}, 15432 cm^{-1} & 27932 cm^{-1} assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2E_g \rightarrow {}^2T_{2g}$ and charge transfer (CT) bands **[18,19]**.

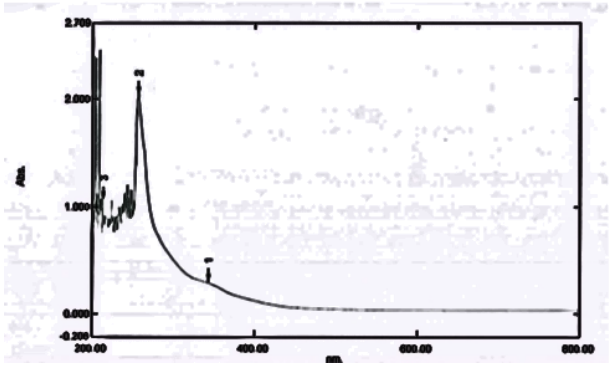


Fig. 3. UV spectrum of the free ligand **(H_2L^1)**

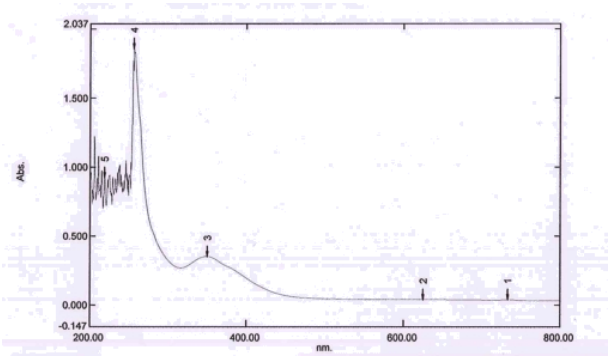


Fig. 4. Electronic spectrum of Cr^{3+} complex

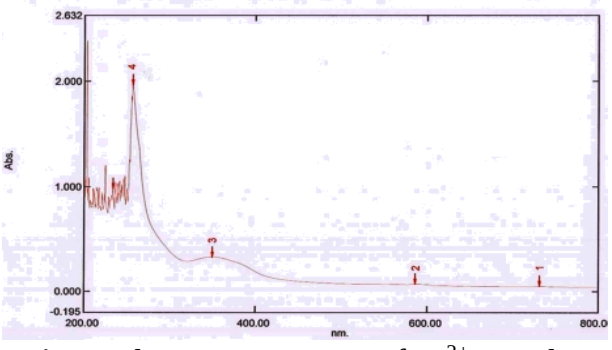


Fig. 5. Electronic spectrum of Ni^{2+} complex

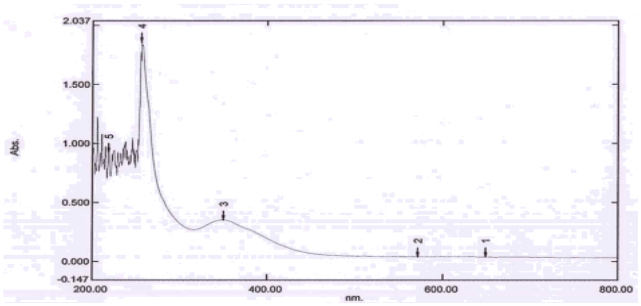


Fig. 6. Electronic spectrum of the Cu^{2+} complex

3.4.1. IR spectra

FTIR spectral data of the Schiff-base and its chelates are recorded in **Table 2** and their spectra are shown in **Figs. 7-10**. IR spectrum of Schiff-base shows a band at 3360 cm^{-1} due to the presence of υ(CH) group [20]. The same spectrum displays a band at 1636 cm^{-1} attributed to the existence of υ(HC=N) vibration [21]. In the chelates, the shifting of bands at 1638, 1643 and 1640 cm^{-1} to higher frequency compared with the free Schiff-base suggests the bonding of the metal ions through the nitrogen of azomethine group υ(HC=N).

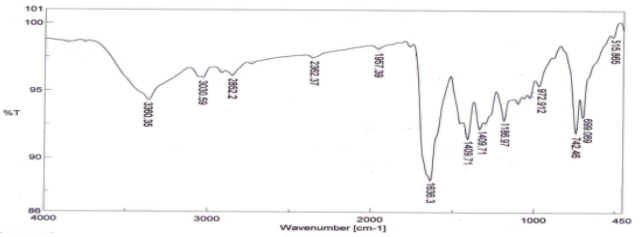


Fig. 7. IR spectrum of free ligand **(H_2L^1)** in KBr

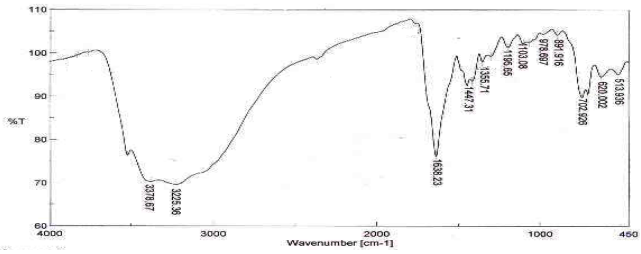


Fig. 8. IR spectrum of Cr^{3+} complex

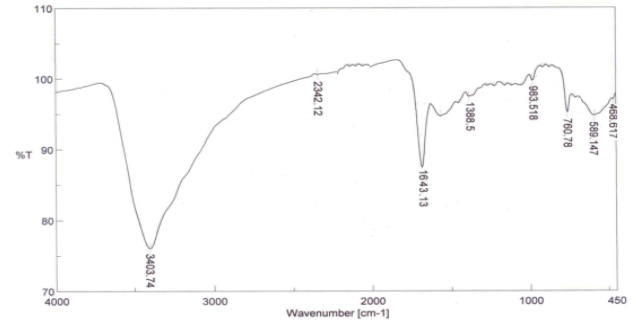


Fig. 9. IR spectrum of Ni^{2+} complex

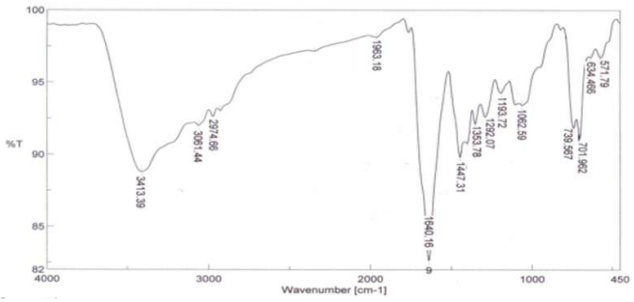


Fig. 10. IR spectrum of Cu^{2+} complex

The IR spectra of the chelates exhibit bands in the range of 3378-3414 cm^{-1} assigned to the presence of water molecules as hydrated and/or coordinated [22]. New bands which are obscured in the spectrum of free ligand observed at 458-571 cm^{-1} attributed to υ(M-N) vibration. The appearance of υ(M-N) vibration supports the involvement of nitrogen atoms in chelation with the metal ions under investigation [23].

3.4.2. Antibacterial activity [Newman – keuls test (at α = 0.05)]

Schiff-base and its complexes showed inhibitory activity against all used bacteria species (*Proteus sp*., *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Bacillus subtilis*) for the free Schiff-base 17-16 mm and 16-10 mm for complexes, the antibacterial results (mm) are summarized in **Table 3**.

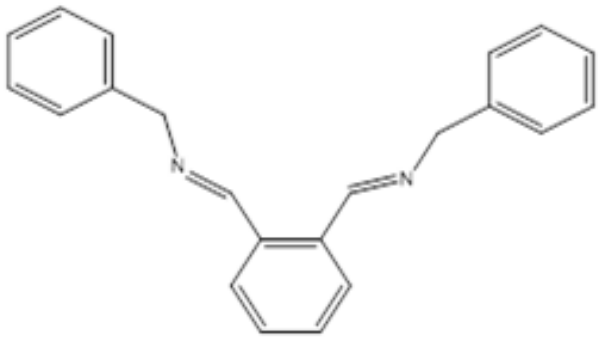
Table (3). Antibacterial activity results (mm) of Schiff-base and its chelates

Ligand/ Chelates	*Bacillus subtilis*	*Staphylococcus aureus*	*Pseudomonas aeruginosa*	*Proteus sp.*
(H_2L); ($C_{22}H_{20}N_2$)	^{b}7.6±8.1	^{b}14.60±1	^{a}17.7 ±1	^{ab}15.6±8
[Cr(**L**)$Cl_2(H_2O)_2$]Cl	^{c}10.6±1.7	^{c}9.5±1.3	^{c}10.1 ±3	^{c}10.6±1
[Ni(**L**)$(H_2O)_4$]$Cl_2.5H_2O$.	^{dc}6 ±7.10	^{d}4.3±1.4	^{a}16.9 ±1	^{dc}6 ±7.1
[Cu(**L**)$(H_2O)_2Cl_2$].$3H_2O$	^{b}7.6±8.1	^{d}3.9±1.5	^{d}3.4 ±2	^{d}3.8±6

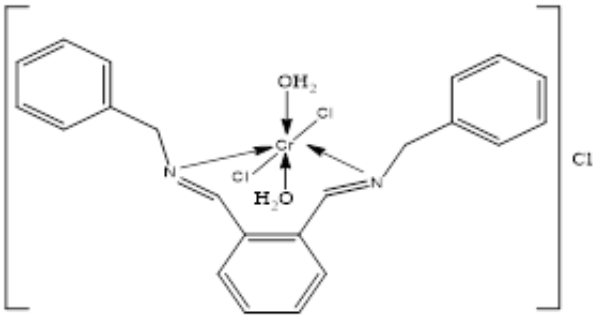
Means (3 replications) fallowed by the same letters are not significantly different fallowing

CONCLUSION

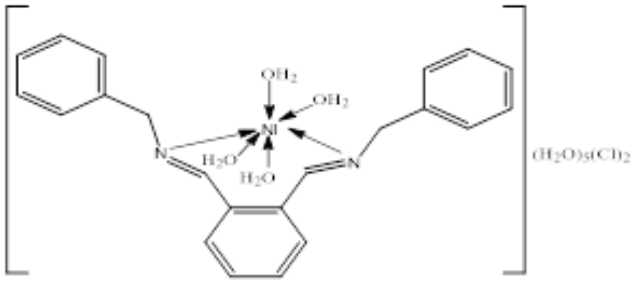
Based on the elemental composition, electronic and IR spectral studies, the structures (1-4) are proposed for the synthesized ligand and its complexes.



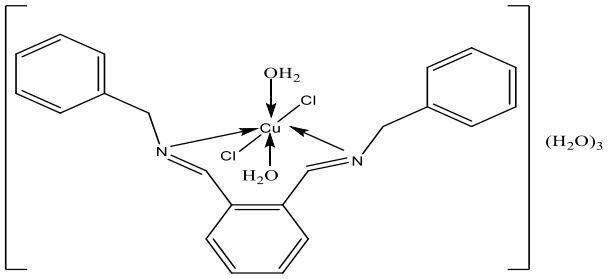
Structure 1 H_2L ($C_{22}H_{20}N_2$)



Structure 2 [Cr(**(H_2L)**)$Cl_2(H_2O)_2$]Cl



Structure 3 [Ni**(H_2L)**$(H_2O)_4$]$Cl_2.5H_2O$



Structure 4 [Cu**(H_2L)**$Cl_2(H_2O)_2$].$3H_2O$

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الملخص العربي

تحضير والدراسة الطيفية ودراسة النشاط البكتيري لبعض مركبات العناصر الانتقالية Cu^{2+}, Ni^{2+}, Cr^{3+} مع قاعدة شف المشتقة من فثلدهيدوبنزايل امين

عبدالسلام معتوق هميل[1] , خليفة مصباح خليفة[1] , إيمان ابراهيم امبارك[1] , يونس الخيالي[2]

١ -قسم الكيمياء , كلية العلوم , جامعة سبها , ليبيا.

٢ - قسم النبات, كلية العلوم , جامعة سبها , ليبيا.

تم تحضير مرتبط قاعدة شيف من تكثيف (*E*)-N-(*9E*)- بنزيل ايمنو ميثيل دايين فينيل ميثان امين, وتمت دراسته بواسطة التقنيات مثل التحليل العنصري والأشعة فوق بنفسجية والأشعة تحت الحمراء والرنين النووي المغناطيسي ومطياف الكتلة, وحضر منها متراكبات لقواعد شيف بتكثيفها مع أيونات Cr(III), Ni(II) وأيون Cu(II). وتم تحديد الاشكال الفراغية للمتراكبات بواسطة الطرق الطيفية والمغناطيسية, وإقترحت جميع المتراكبات ثمانية السطوح, كما أجريت لها تطبيقات على بعض أنواع من البكتيريا bactetia *Pseudomonas aeruginosa, Proteus, Staphylococci* and *Bacillus subtilis* **.**