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Synthesis and Characterization of Schiff base [(2S)-3-phenyl-2-((E)-((1S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)amino)propanoic acid] and their metal complexes

Nuha H. Al-Saadawy[1]

[1] **Department of Pharmaceutical Chemistry,**
College of Pharmacy, University of Thi-Qar,
Thi-Qar, Iraq.

Abstract

The reaction of camphor with phenylalanine under showed conditions yielded Schiff base as a ligand. The structures of Cu(II), Ni(II), Co(II) and Fe(II) with schiff base compound have been joined by the reacting between copper bromide, hexahydrate nickel chloride, hexahydrate cobalt chloride and iron bromide and ligand in 1:2 mole ratio. The free ligand and their metal structures have been in the solid state. The spectroscopic data of the structures suggest their 1:2 buildings structures which are inspected by elemental analysis (CHN), FT-IR, ^{1}H NMR spectroscopy. The spectroscopic studies proposed the octahedral structure for the all structures and the results are represented and analyzed underneath.

Keywords: *Complexes, metal complexes, phenylalanine, camphor, heptan-2-ylidene.*

I. INTRODUCTION

Camphor is a waxy, white or transparent solid with a strong aromatic odour**(1,2)** which sublimates at room temperature and melts at 180 °C**(3,4)**.It is practically insoluble in water, but soluble in alcohol, ether, chloroform and other organic solvents. It is a terpenoid (1,7,7-trimethylbicyclo[2.2.1]-2-heptanone) with a chemical formula of C10H16O and exists in two enantiomeric forms: (1*S*)-(−)- and (1*R*)-(+)-camphor. These two enantiomers have a similar camphoraceous odour, but how the stereochemistry impacts on the biological activity is still unknown.(5-7) Scientifically, numerous biological activities have been attributed to camphor including antibacterial, antifungal, antimutagenic, antitussive and insecticidal properties, but it is important to note that bioactivity was determined in many cases using an essential oil rich in camphor and not pure camphor. Schiff base named after Hugo Schiff [1864] is a nitrogen analog of an aldehyde or ketone in which the C=O group is replaced by a carbon – nitrogen double bond (C=N) with the nitrogen atom connected to an aryl or alkly group, the Schiff base makes a stable aldimines or ketoimines(8). A series of Schiff base ligands were synthesized from camphor(9). Schiff base-camphorsulfonyl amide legends synthesized (10). The study of the nature of interactions between donor and acceptor in a charge transfer complexes has attracted the attention of both theoretical and experimental (11, 12). chemists worldwide. A study of the electrical properties of charge-transfer (CT) complexes of 2-aminopyrimidine and 2-aminopyrazine Schiff bases with nitrobenzene derivatives has been done (13). The electrical conductivities of some Schiff bases and their charge transfer complexes with 2,4-dinitrophenol and picric acid as acidic acceptors indicate that they behave as semiconductors within the investigated range of temperature (14). Charge-transfer complexes of quinaldine-arylidenschiff bases with fluoranil and 2,4-dinitrofluoro-benzene have been investigated (15). Charge-transfer (CT) complexes of pyrimidine Schiff bases, derived from condensation of 2-amino-pyrimidine and substituted benzaldehydes with some aromaticpolynitro compounds were prepared and investigated (16). Structural,spectral and thermal stability of charge-transfer (CT) complexes(17).

2. EXPERIMENTAL

2.1 Chemicals and Apparatus

Chemicals acquired from Sigma-Aldrich, Fluka and BDH utilized without filtration. Liquefying point was dictated by utilizing open hairlike tube dissolving point mechanical assembly. ^{1}H NMR spectra was recorded on Bruker 300 MHz spectrometers with TMS as an inner reference utilizing DMSO-d_6 dissolvable. Infra-red spectra were recorded with KBr circles utilizing a FTIR spectrophotometer Shimadzu model 8400 S in reach 4000-400 cm-1. Essential examination for Carbon, Hydrogen and Nitrogen were performed by utilizing an Euro vector EA 3000A

Elemental Analysis (Italy). Dissolving purposes of every single strong compound were resolved utilizing a MPS10 electrically warmed liquefying point mechanical assembly.

2.2 Synthesis of Schiff base:-

The following compound was synthesized as described in literature. [(2S)-3-phenyl-2-((E)-((1S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)amino)propanoic acid] was prepared by the following general method: (18)

Preparation of L ($C_{19}H_{25}NO_2$): camphor (0.1 mole) and phenylalanine (0.1 mole) was mixed together in 50 ml. of absolute alcohol: water (1:1) and refluxed on water bath for about 5 hrs. The solution obtained after reflux gave white crystalline compound. It was filtered and washed with water and finally recrystallised from absolute alcohol, yield 73%, m. p. 180 - 181°C. L is soluble in many organic solvents, but insoluble in water.

2.3 Synthesis of Cu(II), Ni(II), Co(II), Zn(II) and Fe(II) complexes:

All the new complexes were prepared by the same procedure: A hot ethanolic solution of the ligand of [(2S)-3-phenyl-2-((E)-((1S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)amino)propanoic acid] **(L)** (0.001 mol) and (0.1 gm) of sodium hydroxide in absolute ethanol (10 ml) was prepared and then $CuBr_2$, $NiCl_2{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $ZnCl_2$ and $FeBr_2$ (0.0005 mol) in distill water (10 ml) was added to the hot solution of **(L)** ligand. The mixture of ligand and metal halide were heating to 70 °C and stirring for 3 hrs. The product colored solution was cooling. The product was filtered to obtain precipitate washed with cooled absolute ethanol. Recrystallized from glacial acetic acid then dried. The analytical and physical data of the complexes are listed in Table 1.

Table 1

Physical and analytical data for ligand and complexes *1-4*

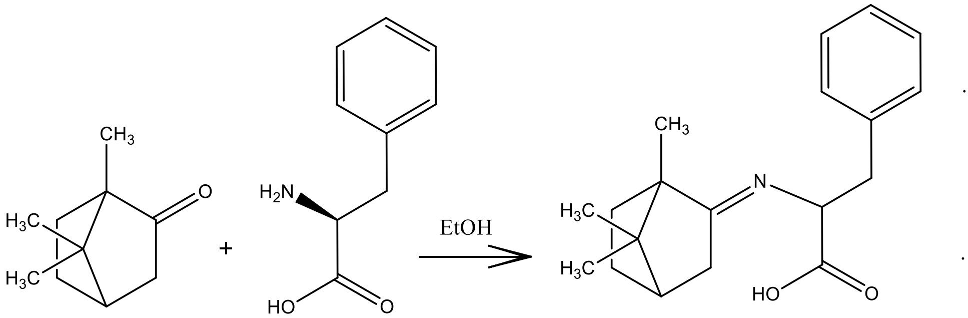
Comp.	color	Melting point	Analysis (%)[a]	Yield %

		(℃)				
			C	**H**	**N**	
Ligand	white	180-181	76.22 76.47	8.42 8.93	4.68 4.70	91
$Cu(L)_2(H_2O)_2$ [1]	Gray	218-220	65.54 65.93	7.53 7.41	4.02 4.70	57
$Fe(L)_2(H_2O)_2$ [2]	Reddish-brown	204-206	66.27 66.43	7.61 7.76	4.07 4.43	74
$Ni(L)_2(H_2O)_2$ [3]	Green	258-260	66.00 66.34	7.58 7.35	4.05 4.62	63
$Co(L)_2(H_2O)_2$ [4]	Dark brown	228-230	65.98 65.61	7.58 7.51	4.05 4.45	61

[a] *calculated values are in parentheses*

3. Results and discussion:

The Schiff base **(L)** is formed in good yield by the condensation of camphor **structure 1** with phenylalanine occurred in the 1:1 ratio as in structure **2** (Scheme 1).

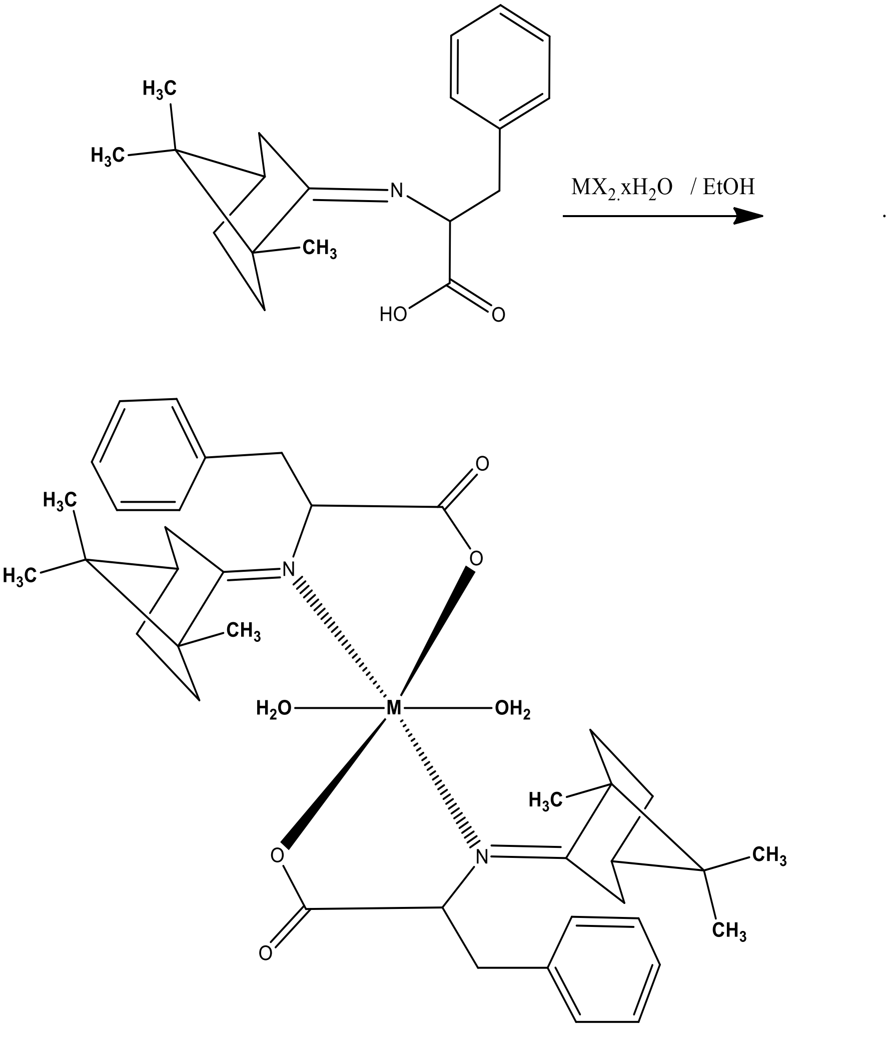


1

2

SCHEME 1. Preparative method for **base [(2S)-3-phenyl-2-((E)-((1S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)amino)propanoic acid]**

Schiff base is crystalline in nature and is soluble in common organic solvents. The metal – ligand complexes were synthesized and obtained in pure form. Reactions of (Cu-, Ni-, Co- and Fe- halides) with [(2S)-3-phenyl-2-((E)-((1S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)amino)propanoic acid] in 1:2 molar ratio in ethanol and water are represented in Scheme 2. It's formed well defined and crystalline complexes with of Cu(II), Ni(II), Co(II) and Fe(II) ions. The results of elemental analysis (CHN) with molecular formula and the melting points are presented in Table 1. The results obtained are in good agreement with those calculated for the suggested formula and the melting points are sharp, indicating the purity of the prepared Schiff base and their complexes. The structures of the Schiff base and their complexes under study are given below (Scheme 2). The structure of these Schiff bases is also confirmed by CHN analysis, IR and ^{1}H NMR spectra, which will be discussed in a detailed manner.



Where $MX_2.xH_2O = NiCl_2.6H_2O$; $CoCl_2.6H_2O$, $CuBr_2$ or $FeCl_2$

SCHEME 2. Preparative methods for complexes (1:2) molar ratio

3.1 Infrared spectra :

The IR spectra for all prepared complexes (1-4) and ligand are listed in Table 2 and some of these spectra are shown in the Figures (1 - 5). All compounds 1-4 and ligand shows a strong band in the range (1739 -1741) cm^{-1} which it’s attributed to (C=O) bond for phenylalanine group

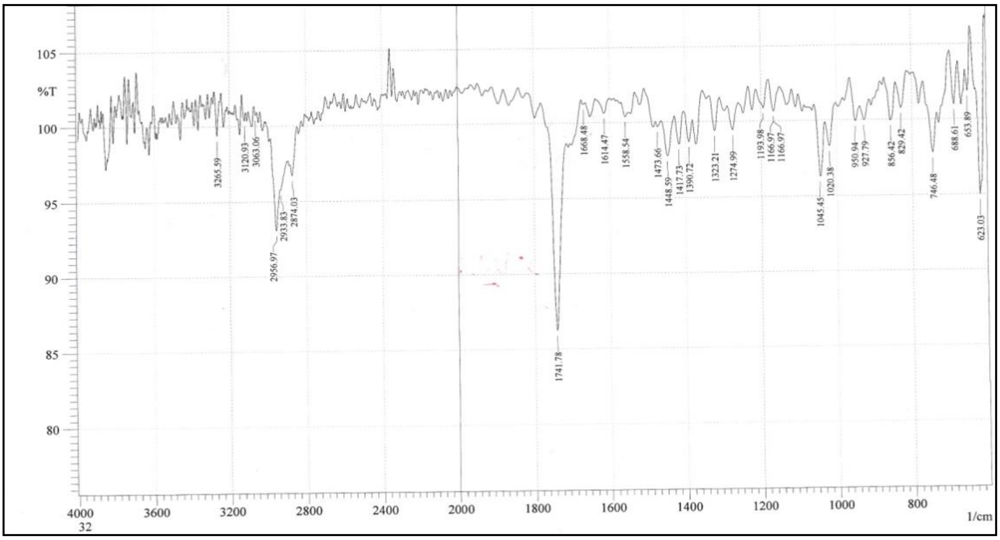


Figure (1): IR spectra for ligand

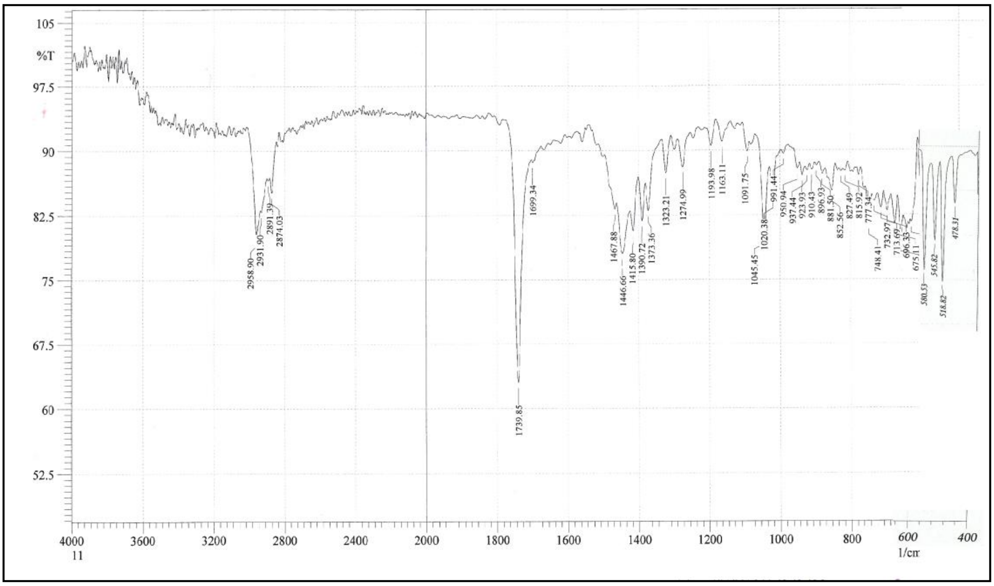


Figure (2): IR spectra for complex 1

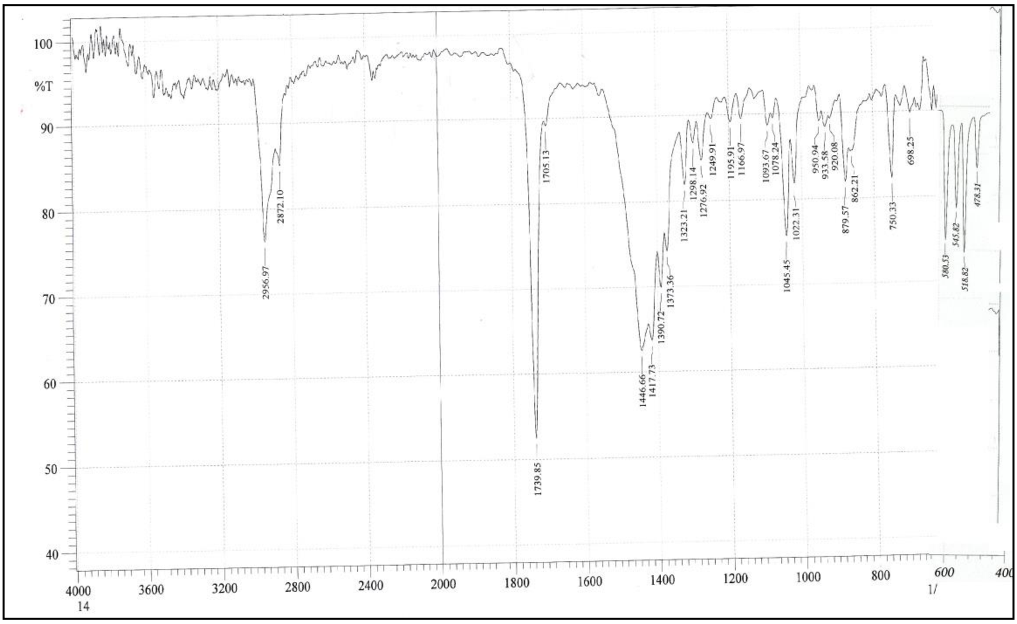


Figure (3): IR spectra for complex 2

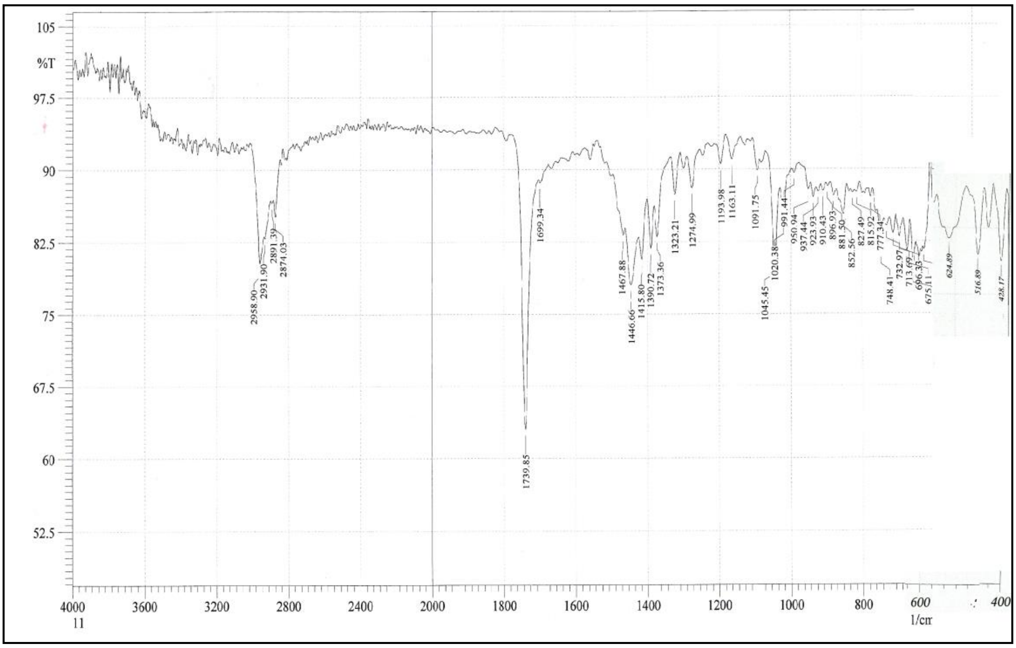


Figure (4): IR spectra for complex 3

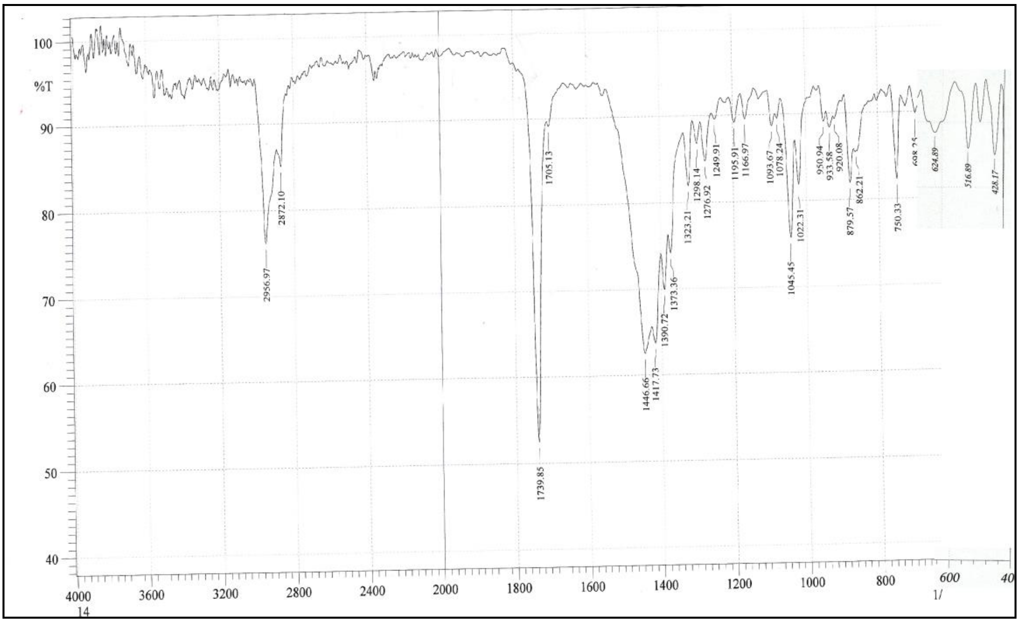


Figure (5): IR spectra for complex 4

stretching vibration which are in agreement with previous reported data.**(19, 20)** The IR spectra of the ligands and complexes synthesized are shows two strong bands appeared at the range (3063 - 2956) cm^{-1} and (2956 - 2872) cm^{-1} due to stretching aromatic (C-H) and aliphatic (C-H) respectively. **(19, 20)**The IR spectra of the complexes were compared with of the free ligand in order to determine the coordination sites that may be involved in chelating. There was some guide peaks in the spectra of the ligands, which were helpful in achieving this goal. The position and/or the intensities of these peaks are expected to change upon chelating. New peak is also guide peak, as M-N in chelating. This guide peak are shown in Table 2. Upon comparison This band was shifted to higher or lower wave numbers in the complexes, indicating the participation of the azomethine nitrogen in coordination (M-N). A strong bands appeared in the range (516 - 518) cm^{-1} it's attributed to stretching of band (M-N). (21) New bands are found in the spectra of the complexes in the regions (428 - 478) cm^{-1} which are assigned to υ(M-O) stretching vibrations for metal complexes. (19, 20) Several medium intensity bands appeared in the (1446 - 1448) cm^{-1} region of the spectra are due to the stretching of various (C=C) vibrations. The IR spectra of the ligand and complexes synthesized are shows two strong bands appeared at 1045 cm^{-1} and the range (1274 - 1276) cm^{-1} due to stretching aliphatic (C-N) and (C=N) respectively. (19, 20)

Table 2. IR Spectroscopic data for Ligand and compounds *1-4*

Ligand/ complexes IR (cm^{-1})	λ_{max} in nm (ε in M^{-1}cm^{-1})
Ligand	3063cm^{-1} ν(C-H) Ar., 2956 cm^{-1} ν(C-H) aliph., 1448 cm^{-1} ν(C=C) Ar., 1274 cm^{-1} ν(C=N), 1045 cm^{-1} ν(C-N) aliph, 1741 cm^{-1} ν(C=O), 3265 cm^{-1} ν(O-H).
$Cu(L)_2(H_2O)_2$ [1]	2958 cm^{-1} ν(C-H) Ar., 2874 cm^{-1} ν(C-H) Aliph., 1446 cm^{-1} ν(C=C) Ar., 1739 cm^{-1} ν(C=O), 1274 cm^{-1} ν(C=N), 1045 cm^{-1} ν(C-N) Aliph.,478 cm^{-1} ν(M-O), 518 cm^{-1} ν(M-N).
$Fe(L)_2(H_2O)_2$ [2]	2956 cm^{-1} ν(C-H) Ar., 2872 cm^{-1} ν(C-H) Aliph., 1446 cm^{-1} ν(C=C) Ar., 1739 cm^{-1} ν(C=O) Ar., 1276 cm^{-1} ν(C=N), 1045 cm^{-1} ν(C-N) Aliph., 478 cm^{-1} ν(M-O), 518 cm^{-1} ν(M-N).
$Ni(L)_2(H_2O)_2$ [3]	2958 cm^{-1} ν(C-H) Ar., 2874 cm^{-1} ν(C-H) Aliph., 1446 cm^{-1} ν(C=C) Ar., 1739 cm^{-1} ν(C=O) Ar., 1274 cm^{-1} ν(C=N), 1045 cm^{-1} ν(C-N) Aliph., 428 cm^{-1} ν(M-O), 516 cm^{-1} ν(M-N).
$Co(L)_2(H_2O)_2$ [4]	2956 cm^{-1} ν(C-H) Ar., 2872 cm^{-1} ν(C-H) Aliph., 1446 cm^{-1} ν(C=C) Ar., 1739 cm^{-1} ν(C=O) Ar., 1276 cm^{-1} ν(C=N), 1045 cm^{-1} ν(C-N) Aliph., 428 cm^{-1} ν(M-O), 516 cm^{-1} ν(M-N).

A wide band in 3265 cm^{-1} can be alluded to (O-H) bond in free ligand yet This crest will be vanished in IR spectra of edifices was great and clear confirmation to event of response by hydroxyl bunch in free ligand. Accordingly; from the IR spectra it is inferred that the ligand acts as an unbiased bidentate ligand facilitated to the metal particle by means of azomethine N while ligand carries on as monodentate and deprotonated hydroxyl bunch. (19, 20) The Figures (1-5) are explained all spectra for ligand and it's complexes.

3.2 ^{1}H NMR spectra

^{1}H NMR spectra of ligand and it's complexes (1-4) were recorded in DMSO-d_6 and are shown in Figures 7 – 12 depending on the suggest structure (Figure 6), and are presented in Table 3., The ^{1}H NMR spectra of the Schiff base exhibits multisignals within the 7.18 – 7.32 ppm range are assigned to the corresponding protons of phenyl ring (H16, H17, H18, H19 and H20) at ligand and it's complexes. The spectra of the complexes are examined in comparison with those of the parent Schiff base. The ^{1}H NMR spectra of the Schiff base synthesized from camphor and phenylalanine revealed a signal at 10.27 ppm (singlet) due to the proton OH (H22) and The proton OH has disappeared in ^{1}H NMR spectra of complexes Schiff base, indicating that the OH proton is removed by chelation with the metal ion.(19)

Table 3. ^{1}H NMR Spectroscopic data for Ligand and compounds *1-4*

Ligand/ complexes	Chemical shift (ppm)
Ligand	7.26 - 7.32 (m, 5H, Ar.), 6.73 – 6.78 (q, 2H, H14), 1.11 – 1.16 (m, 2H, H8), 1.36 – 1.38 (m, 5H, H1 & H7), 1.40 - 1.52 (m, 6H, H10 & H11), 2.05 – 2.14 (m, 2H, H5), 2.72 – 2.76 (m, 1H, H13), 2.89 – 2.91 (m, 1H, H6), 10.27 (s, 1H, H22)
$Cu(L)_2(H_2O)_2$ [1]	7.18 - 7.32 (m, 10H, Ar.), 6.46 – 6.51 (q, 4H, H14), 1.12 (d, 4H, H8), 1.52 (t, 10H, H1 & H7), 1.60 - 164 (m, 12H, H10 & H11), 2.52 – 2.56 (m, 4H, H5), 2.66 – 2.70 (m, 2H, H13), 3.21 – 3.65 (m, 2H, H6).
$Fe(L)_2(H_2O)_2$ [2]	7.18 - 7.32 (m, 10H, Ar.), 6.46 – 6.51 (q, 4H, H14), 1.12 (d, 4H, H8), 1.61 (d, 10H, H1 & H7), 1.63 (q, 12H, H10 & H11), 2.55 (q, 4H, H5), 2.66 (q, 2H, H13), 3.21 – 3.65 (m, 2H, H6).

Ni(L)$_2$(H$_2$O)$_2$ [3]	7.18 - 7.32 (m, 10H, Ar.), 6.49 – 6.51 (q, 4H, H14), 1.12 (d, 4H, H8), 1.52 (t, 10H, H1 & H7), 1.61 - 164 (m, 12H, H10 & H11), 2.52 – 2.56 (m, 4H, H5), 2.66 – 2.70 (m, 2H, H13), 3.21 – 3.65 (m, 2H, H6).
Co(L)$_2$(H$_2$O)$_2$ [4]	7.18 - 7.32 (m, 10H, Ar.), 6.46 – 6.51 (q, 4H, H14), 1.12 (d, 4H, H8), 1.61 (s, 10H, H1 & H7), 1.62 (d, 12H, H10 & H11), 2.55 (d, 4H, H5), 2.67 (t, 2H, H13), 3.21 – 3.65 (m, 2H, H6).

The spectra of the considerable number of mixes demonstrate a quartet signal at the range 6.73 – 6.78 ppm refers to the protons H14 at the ligand in Schiff base while at the complexes H14 has been appeared at the range 6.46 – 6.51 ppm as multiple signal. The doublet signals at 1.12 ppm recommended the attribution of the proton H8 in ligand while appeared at the range 1.11 – 1.16 ppm as a multiple signal.(23) The spectra of the ligand show a multiple signal at the range 1.40 – 1.52 ppm due to proton H10 and H11, a multiple signal at the range 1.60 – 1.64 ppm due to the proton H10 and H11 of the copper and nickel complexes, a quartet signals at 1.63 ppm refer to iron complex and H10 and H11 for cobalt complex has been appeared at 1.62 ppm as doublet signal.(23)

The spectra of the ligand show a multiple signal at the range 2.05 – 2.14 ppm due to proton H5, band at the range 2.52 – 2.56 ppm due to the proton H5 of the copper and nickel complexes as a multiple signal, H5 in iron and cobalt complexes appered at 2.55 ppm as a quartet and doublet signals.(23)

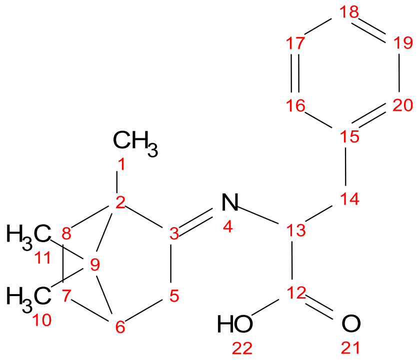


Figure (7): ^{1}H NMR spectra for ligand

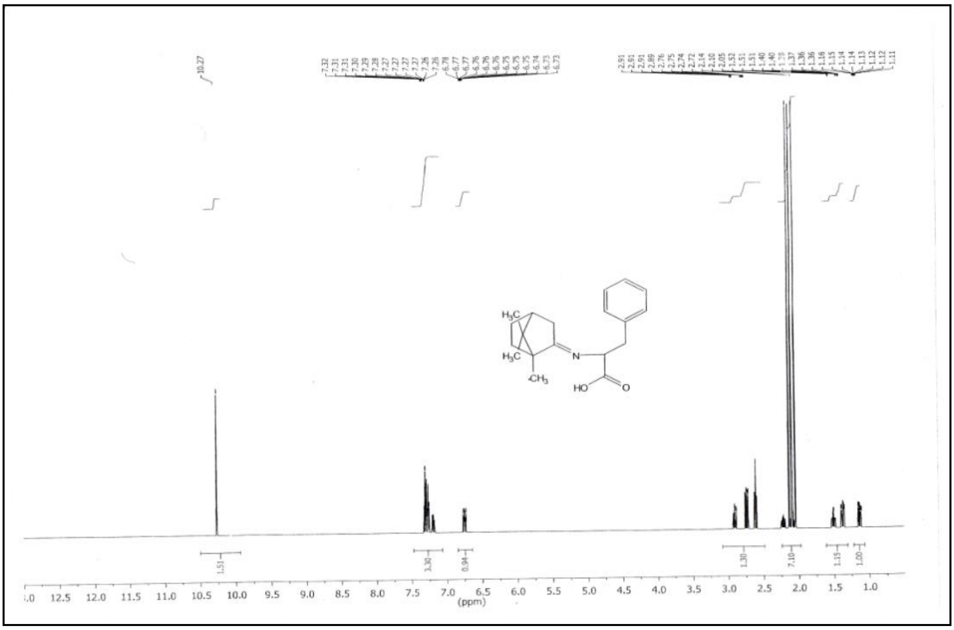


Figure (7): ^{1}H NMR spectra for ligand

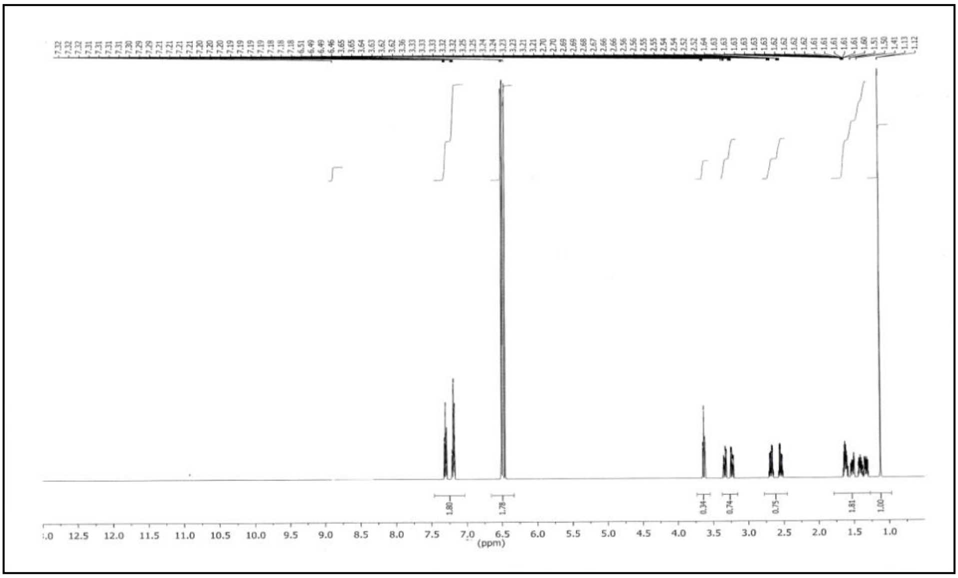


Figure (8): ^{1}H NMR spectra for complex 1

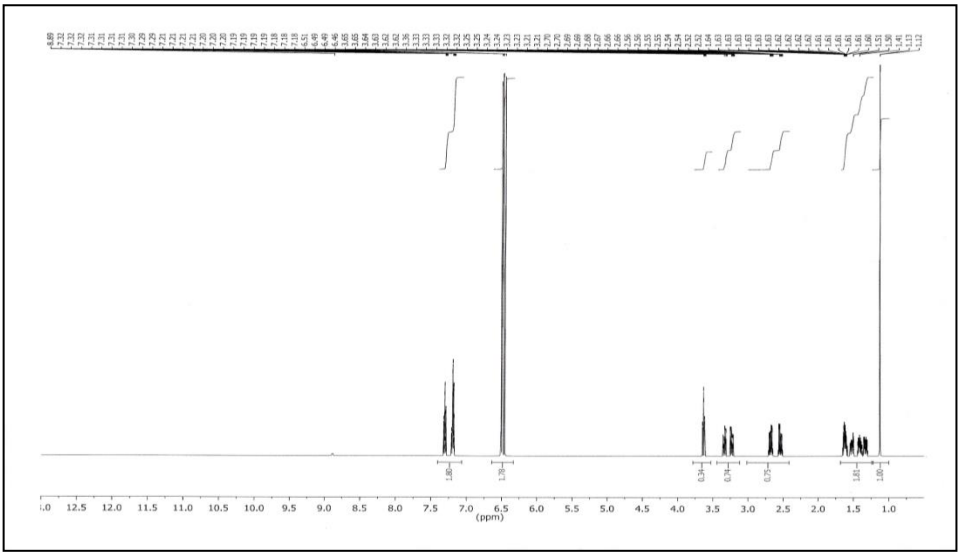


Figure (9): ^{1}H NMR spectra for complex 2

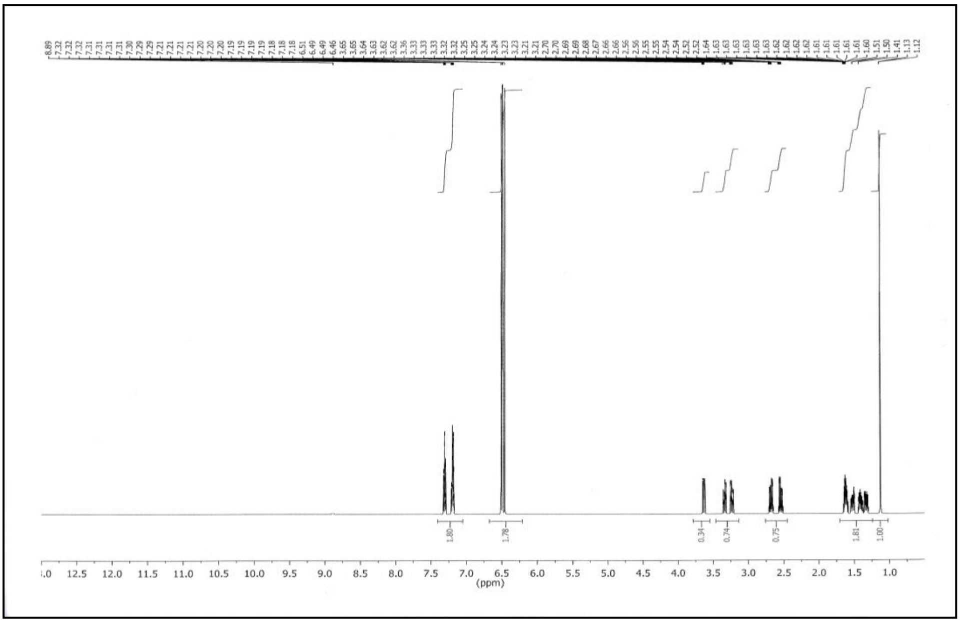


Figure (10): ^{1}H NMR spectra for complex 3

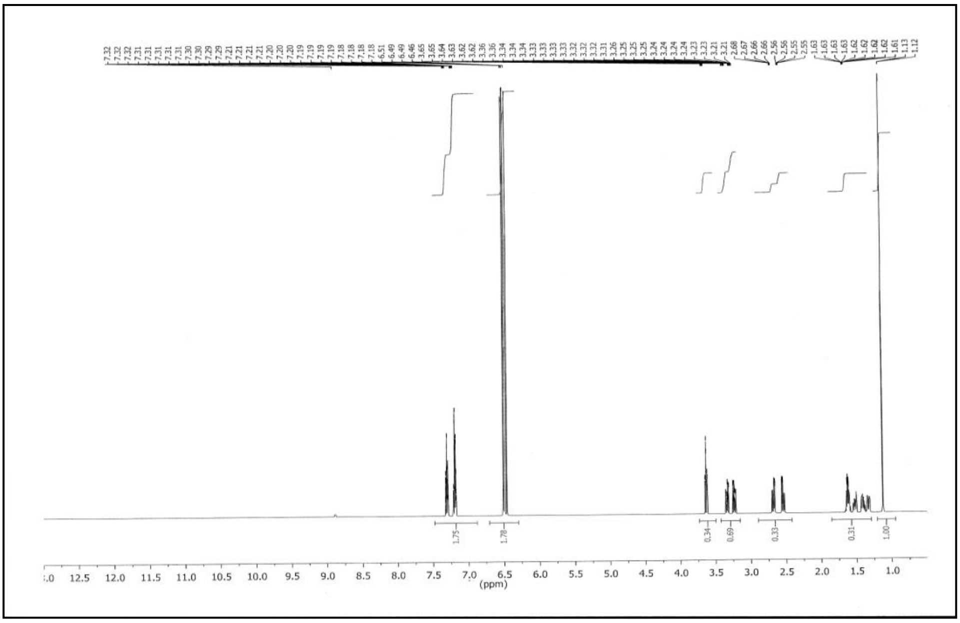


Figure (11): ^{1}H NMR spectra for complex 4

The ^{1}H NMR spectrum of ligand, Fig. 7, shows a multiple signal at the range 2.72 – 2.76 ppm due to H13 in ligand, a triplet signal centered at 2.67 ppm can be attributed H13 in cobalt complex,**(19, 20, 23)** a quartet signal can be appeared at 2.66 ppm may be attributed to H5 in iron complex, a multiple signal at 2.66 – 2.70 ppm can be assigned to H5 in copper and nickel complexes,**(19, 20, 23)** a multiple signal at the range 2.89 – 2.91 ppm refer to H6 in Schiff base (ligand), also a multiple signal appeared at the range 3.21 – 3.65 ppm can be referred to H6 in all complexes,**(19 , 20)** Fig. 8, 9, 10 and 11, Table 3.

Conclusion:

Another complexes has been set up by the reaction between schiff base derived from camphor and phenylalanine as ligand bidntate with metal halide. Explanatory IR, ^{1}H NMR and elemental examination (CHN) revealed a 1:2 mole ratio in which one of Schiff base and metal halide. In another study will be utilized this edifices as a part of an extensive variety of natural exercises, including anti-infection , hostile to proliferative, calming, and antipyretic properties.

IV. REFERENCES

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تحضير وتشخيص قاعدة شيف -[(2S)-3-phenyl-2-((E)-((1S)-1,7,7 trimethylbicyclo[2.2.1]heptan-2-ylidene)amino)propanoic acid] ومعقداتها الفلزية

نهى حسين السعداوي

فرع الكيمياء الصيدلانية, كلية الصيدلة, جامعة ذي قار, ذي قار, العراق

الخلاصة:

فوعل الكافور مع الحامض الاميني فنيل الانين تحت ظروف معينة وتكون قاعدة شيف كليكاند. المعقدات تكونت من تفاعل (بروميد النحاس الثنائي, كلوريد النيكل الثنائي سداسي جزيئات الماء, كلوريد الكوبلت الثنائي سداسي جزيئات الماء وبروميد الحديد الثنائي) مع الليكاند (قاعدة شيف) في نسبة مولية 2:1. الليكاند ومعقداته جميعها كانت في الحالة الصلبة. الدراسات الطيفية للمعقدات اقترحت تكونها بنسبة مولية 2:1 وهذه الدراسات مثل التحليل العنصري الدقيق CHN والاشعة تحت الحمراء FT-IR والرنين النووي المغناطيسي للبروتون ^{1}H NMR وافترضت الدراسات في بحثنا هذا ان كل المعقدات بهيئة ثمانية السطوح والنتائج والتحاليل موضحة في متن البحث.

الكلمات المفتاحية: معقدات, معقدات فلزية, فنيل الانين, كافور, هبتان-2-يليدين.