# (E)-2-((1,7,7-Trimethylbicyclo [2.2.1]Heptan-2-Ylidene) Amino) Acetic Acid Compound and their Metal Complexes: Synthesis and Characterization

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#### **Abstract**

The reaction of camphor with glycine under the showing conditions yielded (E)-2-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)amino)acetic acid ligand . The complexes of Cu(II), Ni(II), Co(II), Zn(II) and Fe(II) with ligand have been obtained by the reaction between copper bromide, hydrate nickel chloride, hydrate cobalt chloride, zinc chloride, and iron bromide with ligand in 1:2 mole ratio. The free ligands and their metal complexes have been separated in the solid state. The spectroscopic data of the complexes recommend their 1:2 structures which are researched by elemental analysis (CHN) <sup>1</sup>H NMR and FT-IR spectroscopy. From the spectroscopic data proposed the octahedral structure for the all complexes.

**Keywords**: synthesis of Complexes, camphor, metal complexes, glycine, heptan-2-ylidene, octahedral structure.

#### I. INTRODUCTION

Condensing the carbonyl group with amino group having the general structure RR'-C=N-R". Where R, R' and R" are aliphatic or aromatic groups [1]. They are described by (-N=C-) bond which have organic applications, for example, antimicrobial [2, 3], antifungal [4] and anticancer [5]. Schiff bases are generally bidentate [6], tridentate [7], tetradentate [8] or polydentate [9]. They seem, by all accounts, to be of significance for an expansive scope of move metal catalyzed responses including lactide

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polymerization [10], epoxidation of olefins [11], hydroxylation [12] and hilter kilter ring opening of epoxides [13].

The chelating Schiff base ligands got from diamines and different carbonyl mixes, include a very striking class of mixes having an extensive variety of utilizations in catalytic [14], synthetic [15], analytical [16], clinical [17], and biochemical [18] ranges and they have impressive physiological activities [17].

A progression of Schiff base ligands were combined from camphor [19]. Schiff base-camphorsulfonyl amide legends combined[20]. The investigation of the way of cooperations amongst benefactor and acceptor in a charge exchange edifices has pulled in the consideration of both hypothetical and test [21, 22].

This project aims to prepare and characterize of the new compounds formed ligand produced by the reaction between camphor and amino acid (glycine) and a new complexes from this ligand with copper, iron, zinc, nickel and cobalt metal.

#### 2. EXPERIMENTAL

#### 2.1 Chemicals and Apparatus

Chemicals procured from Sigma-Aldrich, Fluka and BDH used without purification. Melting point was determined by using open capillary tube melting point apparatus MPS10 electrically. <sup>1</sup>H NMR spectra was recorded on Bruker 300 MHz spectrometers with TMS as an internal reference using DMSO-d<sub>6</sub> dissolvable. Infra-red spectra were recorded with KBr disks using a FTIR spectrophotometer Shimadzu display 8400 S in achieve 4000-400 cm<sup>-1</sup>. Fundamental examination for Carbon, Hydrogen and Nitrogen were performed by using an Euro vector EA 3000A elemental analysis (Italy).

#### 2.2 Synthesis of Schiff base:-

The following compound **(E)-2-((1,7,7-trimethylbicyclo [2.2.1] heptan-2-ylidene)amino)acetic acid** was prepared by the following general method: [23]

Camphor (20 mmol, 3.04 g) was dissolved in 20 ml of methanol and to this solution was added glycine (20 mmol, 1.5 g) in 20 ml of methanol and 2 ml from acetic acid [AcOH]. The reaction mixture obtained was refluxed for 9 h. Upon cooling, the white crystalline powder Schiff- base (*Scheme 1*) was collected by filtration, washed with methanol and dried. Finally, the Schiff base was recrystallized from hot methanol to give pure

white crystalline powder. yield 87%, m. p. 178- 179 °C. ligand 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 method: (1 mmol) Schiff-base were separately dissolved in 25 ml of methanol and mixed with NiCl<sub>2</sub>·6H<sub>2</sub>O, CoCl<sub>2</sub>·6H<sub>2</sub>O, CuBr<sub>2</sub>, ZnCl<sub>2</sub> or FeBr<sub>2</sub> (0.5 mmol) in methanol (25 mL) in mole ratio of 1:2. The mixture was stirred at room temperature for 4 h and the precipitated complex was then filtered off and dried under vacuum. Then, the precipitate was recrystallized from ethanol, and after one day, the complex was separated from the solvent and dried under a vacuum (*Scheme 2*). The exploratory and physical data of the complexes are recorded in *Table 1*.

Table -1: Physical and analytical data for complexes 1-5

| Comp.                 | color | Melting<br>point (C) |                  | Yield          |                |    |
|-----------------------|-------|----------------------|------------------|----------------|----------------|----|
|                       |       |                      | C                | Н              | N              | %  |
| Ligand (L)            | White | 178- 179             | 68.87<br>(68.63) | 9.15<br>(9.10) | 6.69<br>(6.31) | 87 |
| $Cu(L)_2(H_2O)_2$ [1] | Gray  | 233 – 234            | 55.85<br>(55.99) | 7.81<br>(7.33) | 5.43<br>(5.21) | 63 |
| $Fe(L)_2(H_2O)_2$ [2] | Red   | 215 – 216            | 56.70<br>(56.35) | 7.93<br>(7.51) | 5.51<br>(5.70) | 69 |
| $Zn(L)_2(H_2O)_2[3]$  | White | 243 – 244            | 55.65<br>(55.73) | 7.78<br>(7.45) | 5.41<br>(5.63) | 58 |
| $Ni(L)_2(H_2O)_2$ [4] | Green | 198 – 200            | 56.38<br>(56.22) | 7.89<br>(7.94) | 5.48<br>(5.44) | 71 |
| $Co(L)_2(H_2O)_2$ [5] | Gray  | 240 – 241            | 56.35<br>(56.78) | 7.88<br>(7.47) | 5.48<br>(5.91) | 79 |

<sup>&</sup>lt;sup>a</sup> calculated values are in parentheses

#### 3. Results and discussion:

The Schiff base [(E)- 2-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)amino)acetic acid] is shaped in great yield by the buildup of camphor (*structure 1*) with glycine happened in the 1:1 proportion as in structure 2 (*Scheme 1*).

### SCHEME 1. Preparative method for base [(E)-2-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)amino)acetic acid]

Schiff base is crystalline in nature and is dissolvable in common solvents. Reactions of (Cu-, Ni-, Zn-, Co-and Fe-halides) with [(E)- 2-((1,7,7-trimethylbicyclo[2.2.1]heptan-2-ylidene)amino)acetic acid] in 1:2 molar in ethanol are showed in Scheme 2. The results of elemental analysis (C, H, N) with molecular formula and the melting points are presented in *Table 1*. The results obtained have agreement with those processed for the proposed condition and the melting concentrations are sharp, The structures of the Schiff base and their complexes under survey are given underneath (*Scheme 2*). The structure of these Schiff bases is also confirmed by IR and <sup>1</sup>H NMR spectra, which will be discussed in a detailed manner

$$H_3$$
C

 $H_3$ C

 $H_4$ 

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

Where  $MX_2 xH_2O = NiCl_2 6H_2O$ ;  $CoCl_2 6H_2O$ ,  $CuBr_2$ ,  $ZnCl_2$  or  $FeBr_2$ 

#### **3.1** *Infrared Spectra* :

The IR spectra of ligand and their complexes are introduced in Table 2. The IR spectra of the ligands and complexes united are shows solid band showed up at range (2956-2960) cm<sup>-1</sup> by virtue of opening up aliphatic (C-H). [24, 25] The IR spectra of the structures are separated from the free ligand (L) with a specific extreme target to pick the coordination areas that might be joined into chelating. There is a guide beat in the spectra of the ligands, which was significant in satisfying this objective. The position and what's more, the powers of these apexes are relied on to change in the wake of chelating. New pinnacle is additionally prompt top, as M-N and M-O in chelating. This guide zenith is appeared in *Table 2*. Upon examination This band is moved to higher or chop down wave numbers in the structures, exhibiting the excitement of the azomethine nitrogen in coordination (M-N). [24, 25]A couple of medium power bundles shown up in the (424 - 437) cm<sup>-1</sup> region of the spectra are an immediate consequence of the extending of different (M—N). [24, 25] New social occasions are found in the spectra of the structures in the districts (491 - 516) cm<sup>-1</sup> which are alloted to v(M-O) creating vibrations for metal buildings. [24, 25] The IR spectra of the ligand and structures fused show two social occasions shown up at range (1043 - 1045) cm<sup>-1</sup> and (1618 -1681) cm<sup>-1</sup> because of widening aliphatic (C-N) and (C=N) solely. [24, 25] Figure (1-6) explain the IR spectra for ligand and it's complexes.

Table -2: IR Spectroscopic data for Ligand and compounds 1-5

| Ligand/<br>complexes IR<br>(cm <sup>-1</sup> ) | (C-H)<br>aliph. | C=O  | C=N  | C-N  | M-N | М-О | О-Н  |
|--|-----------------|------|------|------|-----|-----|------|
| Ligand (L)                                     | 2958            | 1739 | 1639 | 1045 | -   | -   | -    |
| $Cu(L)_2(H_2O)_2[1]$                           | 2958            | 1739 | 1618 | 1043 | 424 | 514 | 3327 |
| $Fe(L)_2(H_2O)_2[2]$                           | 2958            | 1739 | 1662 | 1045 | 433 | 516 | 3288 |
| $Zn(L)_2(H_2O)_2$ [3]                          | 2956            | 1743 | 1681 | 1043 | 437 | 491 | 3387 |
| $Ni(L)_2(H_2O)_2$ [4]                          | 2960            | 1739 | 1645 | 1045 | 437 | 491 | 3352 |
| $Co(L)_2(H_2O)_2$ [5]                          | 2958            | 1739 | 1624 | 1043 | 437 | 491 | 3248 |

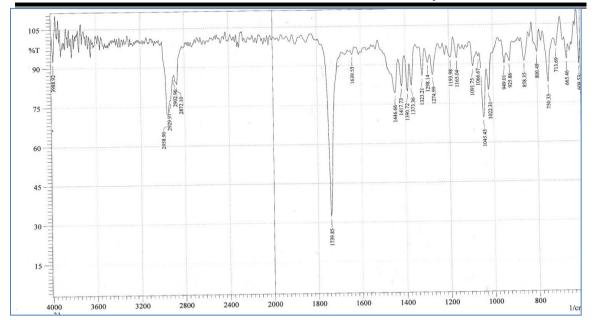


Figure (1): IR spectra for ligand

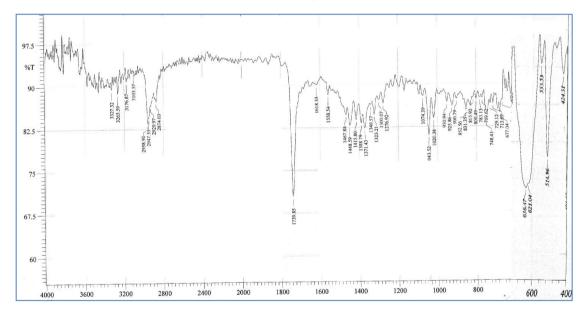


Figure (2): IR spectra for copper complex

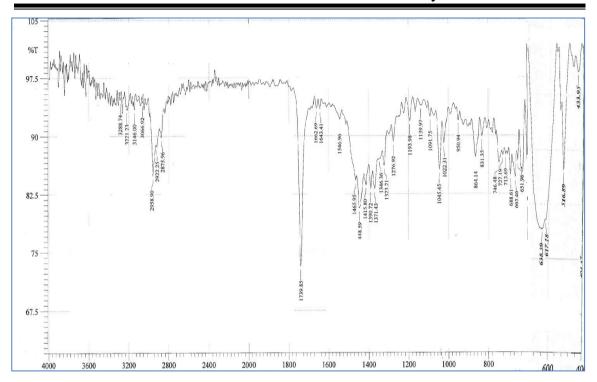


Figure (3): IR spectra for iron complex

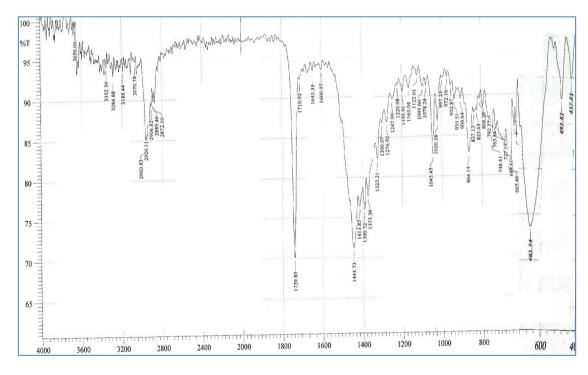


Figure (4): IR spectra for nickel complex

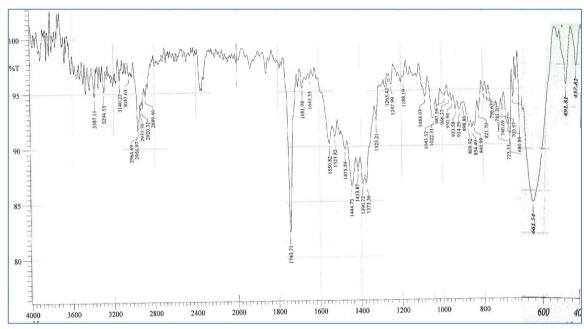


Figure (5): IR spectra for zinc complex

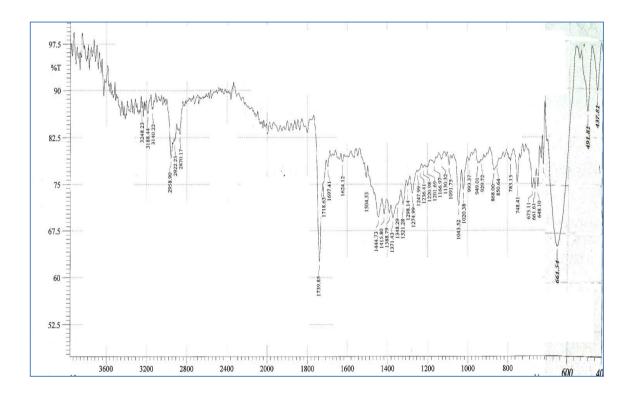


Figure (6): IR spectra for cobalt complex

In IR spectra of complexes is good and clear evidence to the occurrence of reaction. Therefore; from the IR spectra it is concluded that the Schiff base ligand behaves as a neutral bidentate ligand coordinated to the metal ion via azomethine N and deprotonated hydroxyl group. [24, 25] 3.2 <sup>1</sup>H NMR spectra

<sup>1</sup>H NMR data in deturated DMSO solution of the synthesized compounds are given in *Table 1*, The spectra of the complexes are examined in comparison with those of the parent Schiff base. The <sup>1</sup>H NMR spectra of the Schiff base obtained from camphor and glycine appeared signal at 9.83 ppm (singlet) due to proton OH (oxygen atom No. 15) in Figure (7) and The proton OH has disappeared in <sup>1</sup>H NMR spectra of complexes, showing that the OH proton is removed by chelation with the metal ion[24, 25]

Figure (7): the structure for ligand

Table -3: <sup>1</sup>H NMR Spectroscopic data for Ligand and compounds 1-5

| Ligand/ complexes                                      | Chemical shift (ppm)   |
|--|--|
| Ligand (L)   | 2.03 – 2.12 (m, 6H, 10, 11), 1.50 – 1.56 (m, 5H, 1, 7), 1.38 – 1.43 ( m, 2H, 8 ), 3.85 – 3.89 ( m, 2H, 5), 4.10 ( s, 2H, 13) and 9.83 ( s, 1H, 15) |
| Cu(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> [1] | 2.20 – 2.25 (m, 12H, 10, 11), 1.64 (d, 10H, 1, 7), 1.38 – 1.43 (m, 4H, 8), 3.33 – 3.45 (m, 2H, 5) and 5.26 – 5.37 (m, 4H, 13).                     |
| Fe(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> [2] | 2.10 – 2.33 (m, 12H, 10, 11), 1.94-1.98 (d, 10H, 1, 7), 1.38 – 1.43 (m, 4H, 8), 3.33 – 3.45 (m, 2H, 5) and 5.26 – 5.37 (m, 4H, 13).                |
| Zn(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> [3] | 2.10 – 2.25 (m, 12H, 10, 11), 1.98 (d, 10H, 1, 7), 1.38 – 1.43 (m, 4H, 8), 3.33 – 3.45 (m, 2H, 5) and 5.26 – 5.37 (m, 4H, 13).                     |
| Ni(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> [4] | 2.08 – 2.25 (m, 12H, 10, 11), 1.64 (d, 10H, 1, 7), 1.38 – 1.43 (m, 4H, 8), 3.33 – 3.45 (m, 2H, 5) and 5.26 – 5.37 (m, 4H, 13).                     |
| Co(L) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> [5] | 2.20 – 2.25 (m, 12H, 10, 11), 1.64 (d, 10H, 1, 7), 1.38 – 1.43 (<br>m, 4H, 8), 3.33 – 3.45 (m, 2H, 5) and 5.26 – 5.37 (m, 4H, 13).                 |

The spectra of the huge number of mixes display a multiple movement at the range 2.03 - 2.25 ppm (carbon atom No. 10 & 11) and 1.50 - 1.98 ppm (carbon atom No. 1 & 7) in light of the protons CH<sub>3</sub> of the ligand in Schiff base and it's structures. The multiple signals at 3.33 - 3.89 ppm (carbon atom No. 5) and 1.38 - 1.43 ppm (carbon atom No. 8) proposed the attribution of the proton of the seven proton for CH<sub>2</sub>- and CH- in ligand and fourteen proton in the complexes. [24, 25] Figure (8 – 13) explain the  $^1$ H NMR spectra for ligand and it's complexes.

#### **Conclusion:**

Another complexes have been set up by the reacting between schiff base as ligand bidntate with metal halide. Illustrative IR, <sup>1</sup>H NMR and elemental analysis (CHN) revealed a 1:2 mole proportion in which one of Schiff base. These complexes will be examined for their activity as antimicrobial, antifungal, anticancer and antipyretic properties.

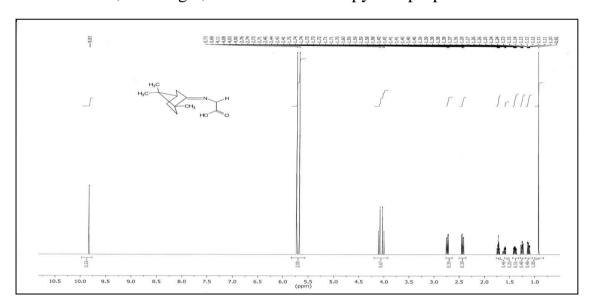


Figure (8): <sup>1</sup>H NMR spectra for ligand.

Figure (1): <sup>1</sup>H NMR spectra for ligand cu

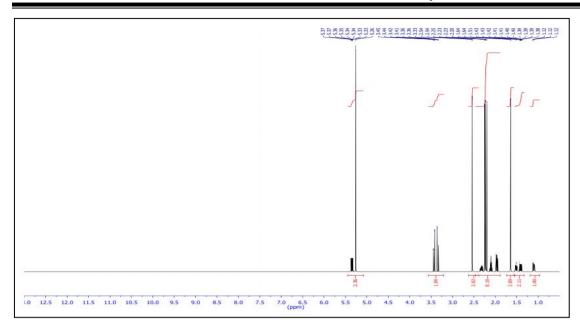


Figure (9): <sup>1</sup>H NMR spectra for copper complex

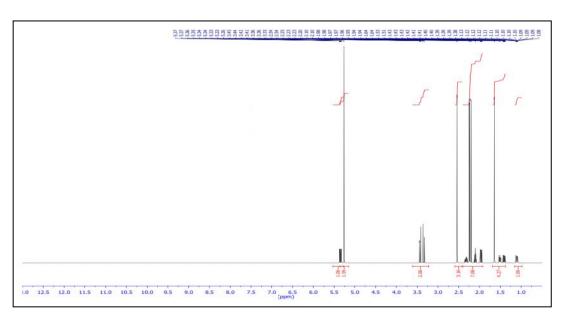


Figure (10): <sup>1</sup>H NMR spectra for zinc complex

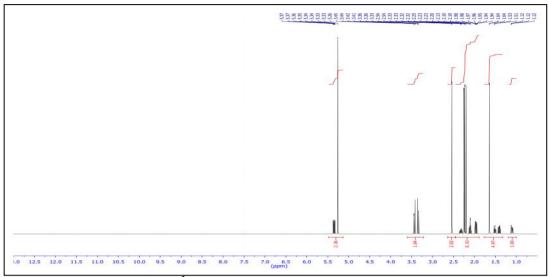


Figure (11): <sup>1</sup>H NMR spectra for iron complex

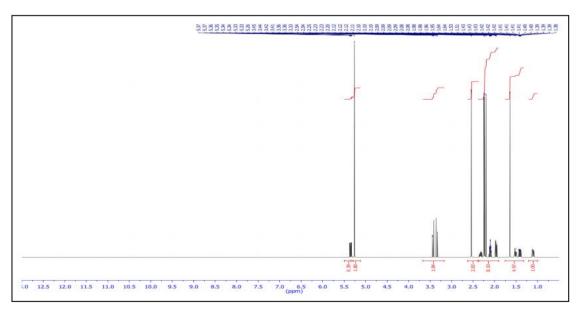


Figure (12): <sup>1</sup>H NMR spectra for nickel complex

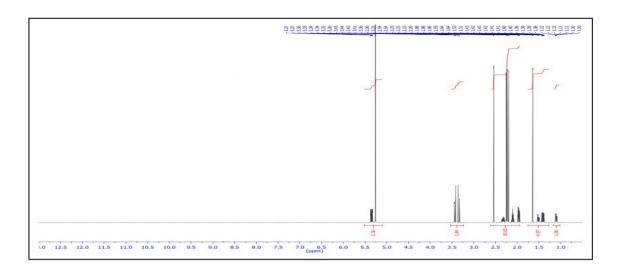


Figure (13): <sup>1</sup>H NMR spectra for cobalt complex

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مركب (E) -2-(E) ثلاثي مثيل ثنائي حلقي [1.2.2] هبتان -2يلدين)امينو)حامض الخليك ومعقداته الفلزية: تحضيرها وتشخيصها
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#### الخلاصة:

تفاعل الكافور مع الكلايسين تحت الظروف الموضحة لينتج ليكاند قاعدة شيف. الصيغ التركيبية للنحاس الثنائي والنيكل الثنائي والكوبلت الثنائي والزنك الثنائي والحديد الثنائي مع مركب قاعدة شيف قد تكونت بواسطة النفاعل بين بروميد النحاس وكلوريد النيكل المائي وكلوريد الكوبلت المائي وكلوريد الزنك وبروميد الحديد مع الليكاند بنسبة مولية 2:1. تركيب الليكاند الحر وتركيب معقداته قد عزل في الحالة الصلبة, البيانات الطيفية للصيغ اقترحت تكون المعقدات بنسبة 2:1 وفحصت بواسطة التحليل العنصري الدقيق للكربون والهيدروجين والنتروجين (CHN) وطيف الاشعة تحت الحمراء. من الدراسات الطيفية افترضنا ان شكل كل المعقدات هو ثماني السطوح كما موضحة في تفاصيل البحث.

الكلمات المفتاحية: تخليق معقدات, كافور, معقدات فلزية, كلايسين, هبتان-2-يلدين, تركيب ثماني السطوح