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# Synthesis, identification, antibacterial, and dyeing applications of complexes of hexadentate ( $N_4O_2$ donor) Schiff base ligands derived from curcumin with some transition and non-transition metal cations

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**Abstract.** Schiff base ligand ( $H_2CANPT$ ) was prepared by two steps: first, by the condensation of curcumin with 4-amino antipyrin produces 4,4'-(((1E,3Z,5Z,6E)-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,6-diene-3,5-diylidene)bis(azanylylidene))bis(1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one) (CANP). Second, by the condensation of (CANP) with L-tyrosine produces 2,2'-(((3Z,3'Z)-(((1E,3Z,5Z,6E)-1,7-bis(4-hydroxy-3-methoxyphenyl)hepta-1,6-diene-3,5-diylidene)bis(azanylylidene))bis(1,5-dimethyl-2-phenyl-1,2-dihydro-3-H-pyrazole-4-yl-3-ylidene))bis(azanylylidene))bis(3-(4-hydroxyphenyl)propanoic acid) ( $H_2CANPT$ ). The resulted Schiff complexed as hexadentate coordinated with ( $N_4O_2$ ) atoms, then it was treated with some transition and non-transition metal ions, such as (Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Cd(II), Hg(II) chloride and Ag(I) as nitrate to synthesize complexes. All the prepared compounds were identified using FT-IR, UV-visible, elemental analysis (C.H.N),  $^1H$  and  $^{13}C$ -NMR, molar conductivity and magnetic susceptibility. Schiff base and its complexes were tested against two types of bacteria (*Staphylococcus aureus* and *Escherichia Coli*). Besides, they were tested as dyes on cotton fibres.

## 1. Introduction

Schiff bases are organic compounds carry azomethine (C=N) group, known for the first time by Hugo Schiff in 1864 [1,2]. Schiff bases were prepared by several methods, such as Reflux, Fusion, Microwave and Grading [3,4]. They have many applications in organic chemistry field [5]. Azomethine compounds and copper complexes are Schiff bases involved in the manufacturing of ink and dyes [6,7]. Schiff base ligands form colored complexes with many metal ions; thus, they are selective and sensitive reagents compounds for estimating metals [8,9]. Many derivatives of 4-amino antipyrine estimated in medical fields such as analgesic, anti-inflammatory, antimicrobial and anticancer activities [10,11]. Schiff bases complex of amino acids and metal ions play an important role in industries and in pharmaceutical and biological fields [12]. This study aimed to synthesize and identify the behaviour of Schiff bases that have four azomethine groups from curcumin, 4-amino antipyrine and L-Tyrosine amino acid, to test the efficient biological activity of the ligand and its complexes against two types of bacteria and finally, to investigate the usage of these Schiff bases and their complexes in dyeing process.



## 2. Experimental

### 2.1. Chemicals

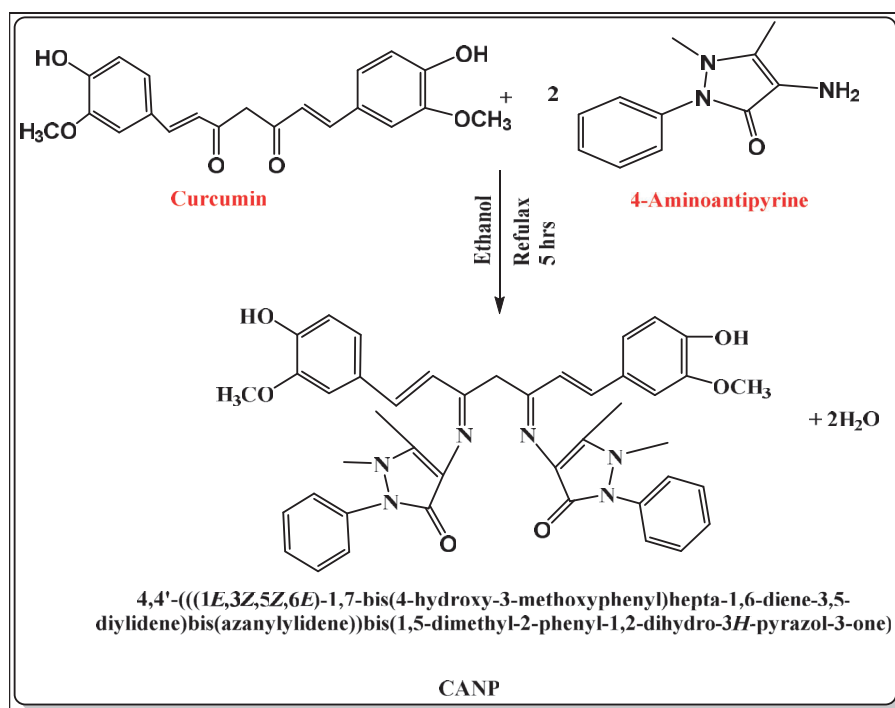
All chemical compounds used with no need to purification and they were purchased from (BDH) company.

### 2.2. Material and Methods

The melting point was determined by using (MPA160 Digi Melt) melting point apparatus. FT-IR spectra measurements were determined by Fourier transform infrared spectra ( $4000\text{--}400\text{ cm}^{-1}$ ) as KBr pellets on (Shimadzu FT-IR 8400S) spectrophotometer. Ultraviolet-visible (UV) spectra were recorded by using a solvent (DMSO) at  $1 \times 10^{-3}\text{ M}$  for the Schiff base (ligand) and its complexes by device of type (U.V 160A Shimadzu apparatus). Elemental analyses (C, H, N) were performed by (Eager300 for EA1112 Thermo Finnegan C.H.N.S 2400) elemental analyzer. The  $\Lambda_m$  measurements were recorded for complexes with at  $10^{-3}\text{ mol.L}^{-1}$  in dimethyl sulfoxide by using digital conductivity Series (Ino.Lab.720). Magnetic susceptibility of all the complexes was measured by (Balance Johnson Matthey).  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra were recorded using dimethyl sulfoxide (DMSO) - $d_6$  Solution (Inova 500).

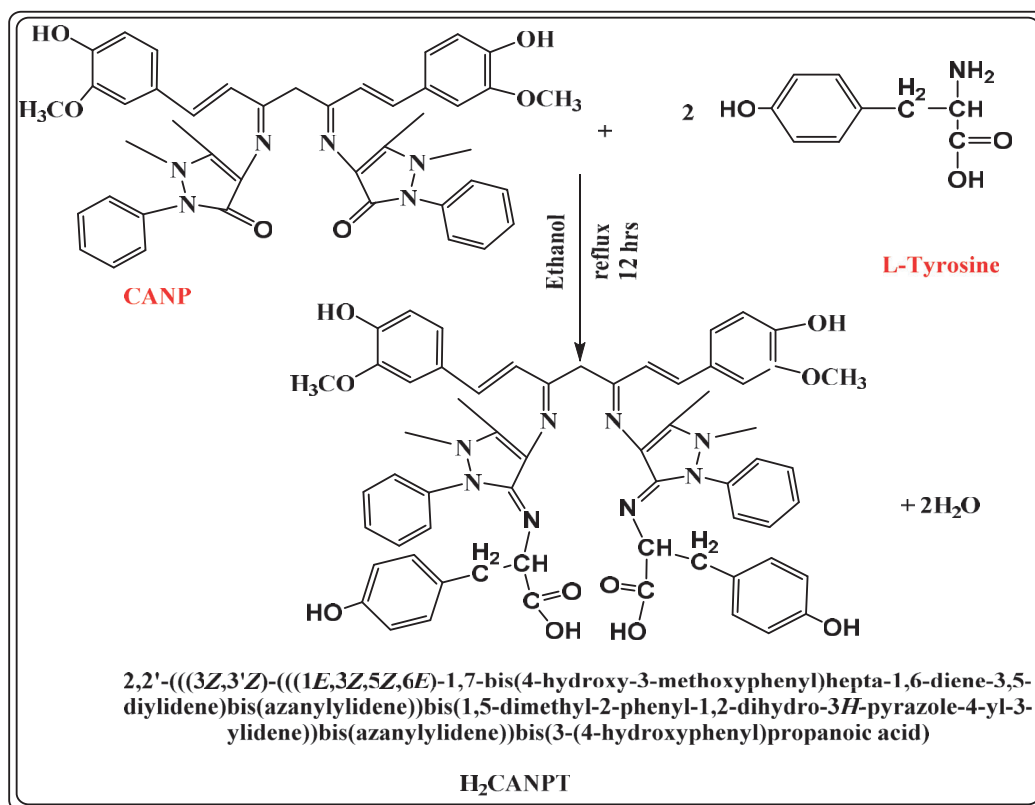
### 2.3. Synthesis of Schiff base ligand ( $H_2CANPT$ )

2.3.1. *Step I (CANP)*. A weight of 0.368 gm (1mmol) of curcumin was dissolved in 20 mL ethanol, 4 drops of glacial acetic acid were added and 406 gm (2 mmol) of 4-amino antipyrine dissolved in 20 mL of ethanol was gradually added. This mixture was refluxed with stirring at  $70\text{ }^\circ\text{C}$ , for 5 hours, The reaction was followed up by TLC technique. A yellow precipitate was separated and recrystallized from hot ethanol, as shown in scheme 1.



**Scheme 1.** A diagram of synthesis of Schiff base (CANP).

2.3.2. *Step II ligand (H<sub>2</sub>CANPT)*. A weight of 0.730 gm (1 mmol) of (CANP) was dissolved in 20 mL ethanol and mixed with 0.362 gm ( 2 mmol) of L-Tyrosine ( dissolved in 20 mL ethanol in a base medium). This mixed solution was refluxed with stirring at 70°C for 12 hours and the reaction followed up by TLC technique until a brown-yellow precipitate formed, then separated, washed several times with hot ethanol and finally recrystallizing from hot ethanol under room temperature. The yield: 78%. Elemental Analysis: Found (Calc.): C, 68.78(67.92); H, 5.68 (5.92); N, 10.52 (10.60); O, 15.02 , as shown in scheme 2.



**Scheme 2.** A schematic diagram for the synthesis of Schiff base (H<sub>2</sub>CANPT).

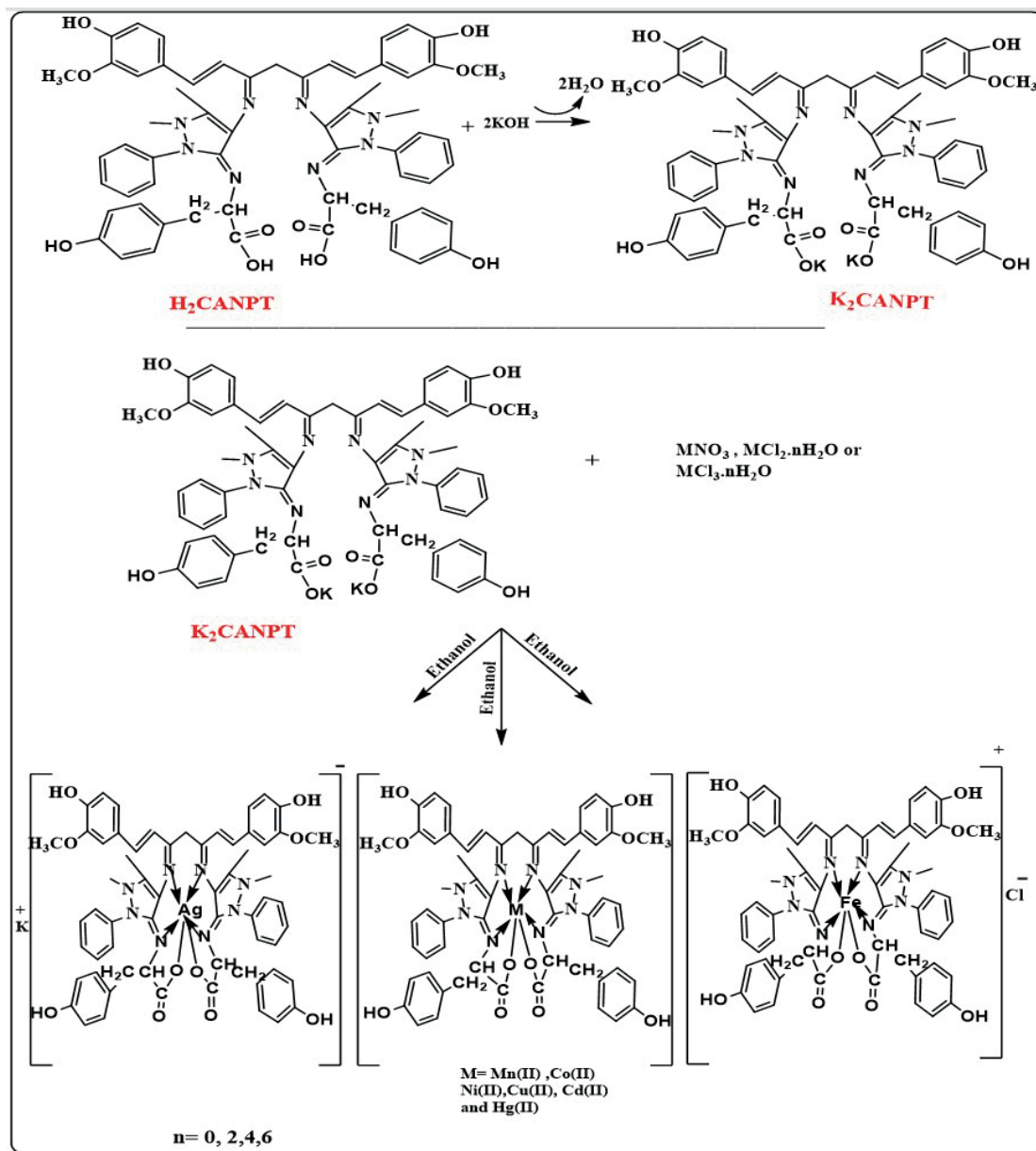
#### 2.4. Preparation of Schiff base ligand (H<sub>2</sub>CANPT) with metal complexes

A weight of 1.05 gm (1mmol) of the Schiff base (ligand) was dissolved in 20 mL ethanol and then 0.112 gm (2 mmol) KOH was added. The mixture was gradually added to (1 mmol) of MnCl<sub>2</sub>·4H<sub>2</sub>O, FeCl<sub>3</sub>, CoCl<sub>2</sub>·6H<sub>2</sub>O, NiCl<sub>2</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O, AgNO<sub>3</sub>, CdCl<sub>2</sub>·2H<sub>2</sub>O and HgCl<sub>2</sub> (dissolved in 10 mL ethanol) with constant stirring for 30 minutes. The resulted precipitates were separated, washed several times with a mixture of solvent (distilled water: ethanol 50%) and then recrystallized from hot ethanol. Scheme 3 showed the suggested geometry of the recrystallized structures.

### 3. Results and Discussion

Generally, all complexes were prepared by reacting to the respective metal salts with the Schiff base (H<sub>2</sub>CANPT) using 1:1 mole ratio (metal salts: H<sub>2</sub>CANPT). All complexes were intensively coloured solid compounds. The analytical data in table 1 agreed with the suggested formulas of 1:1 metal : (H<sub>2</sub>CANPT) molar ratio. The compounds were insoluble in water, but fairly soluble in some common solvents, such as ethanol, methanol, acetone, hydrochloric acid, dimethylformamide, chloroform and dimethyl sulfoxide. Most of the prepared compounds have a relatively high melting point and high

stability at room temperature. Table 1 shows some the physical and chemical properties. The molar conductance of  $1 \times 10^{-3}$  M of the complexes (dissolved in DMSO) in a range  $5.4$  to  $16 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  indicated that these complexes were nonelectrolytes; except Fe(III) and Ag(I) complexes that are electrolytes at  $32.2$  and  $34.2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , respectively [13].



**Scheme 3.** The proposed geometry structures of the Schiff base(H<sub>2</sub>CANPT) complexes.

**Table 1.** The physical and chemical properties of Schiff base and its complexes.

| Compounds molecular formula                                                                             | M.Wt    | M.P °C  | Color         | Yield% | $\Delta m$<br>$\Omega^{-1} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$ | Metal% (exp) |
|---------------------------------------------------------------------------------------------------------|---------|---------|---------------|--------|----------------------------------------------------------------------|--------------|
| H <sub>2</sub> CANPT<br>(Schiff base)<br>C <sub>61</sub> H <sub>60</sub> N <sub>8</sub> O <sub>10</sub> | 1065.20 | 118-120 | Brown-yellow  | 78     | -----                                                                | ----         |
| [Mn (CANPT)]<br>C <sub>61</sub> H <sub>58</sub> N <sub>8</sub> O <sub>10</sub> Mn                       | 1118.13 | 196-198 | Orange        | 78     | 16                                                                   | 4.91(4.99)   |
| [Fe(CANPT)] Cl<br>C <sub>61</sub> H <sub>58</sub> N <sub>8</sub> O <sub>10</sub> FeCl                   | 1154.54 | 162-163 | black         | 90     | 32.2                                                                 | 4.83(4.87)   |
| [Co(CANPT)]<br>C <sub>61</sub> H <sub>58</sub> N <sub>8</sub> O <sub>10</sub> Co                        | 1122.13 | 190-192 | Pale yellow   | 70     | 9.5                                                                  | 5.25(4.88)   |
| [Ni(CANPT)]<br>C <sub>61</sub> H <sub>58</sub> N <sub>8</sub> O <sub>10</sub> Ni                        | 1122.13 | 151-152 | Pale yellow   | 75     | 6.3                                                                  | 5.23(4.73)   |
| [Cu (CANPT)]<br>C <sub>61</sub> H <sub>58</sub> N <sub>8</sub> O <sub>10</sub> Cu                       | 1126.74 | 170-172 | Brown         | 84     | 10.4                                                                 | 5.63(5.63)   |
| K [Ag(CANPT)]<br>K C <sub>61</sub> H <sub>58</sub> N <sub>8</sub> O <sub>10</sub> Ag                    | 1210.15 | 190-192 | Deep brown    | 93     | 34.2                                                                 | 8.91(8.30)   |
| [Cd (CANPT) ]<br>C <sub>61</sub> H <sub>58</sub> N <sub>8</sub> O <sub>10</sub> Cd                      | 1175.41 | 216-217 | Brown         | 89     | 9.1                                                                  | 9.56(9.73)   |
| [Hg(CANPT)]<br>C <sub>61</sub> H <sub>58</sub> N <sub>8</sub> O <sub>10</sub> Hg                        | 1263.79 | 129-130 | Reddish brown | 88     | 5.4                                                                  | 15.87(15.60) |

### 3.1. FT-IR spectra

The synthesized ligand (Schiff base) and its complexes showed distinctive functional groups and bands, such as -OH (hydroxyl group), C=N(azomethine groups), COO-(carboxylic group) and metal bands (M-N, M-O), where the frequencies of absorbing changes were identified using FT-IR spectroscopy. Two strong bands at (3420 cm<sup>-1</sup>) and (1610-1631 cm<sup>-1</sup>) belong to -OH and C=N, respectively were observed [11,14]. The C=N band was detected in all complexes to be shifted to lower and higher frequencies according to the proportions, such as involvement in the process of coordination with metal ions through the nitrogen atom of (azomethine) band[15]. The asymmetric stretching of  $\nu_{as} \text{COO}^-$  was assigned at 1589 cm<sup>-1</sup> while the symmetric stretching  $\nu_s \text{COO}^-$  diagnosed at 1417cm<sup>-1</sup> [16,17]. The difference between frequencies  $\Delta \nu = (\nu_{asymmetric}(\text{COO}^-) - \nu_{symmetric}(\text{COO}^-))$  of free ligand was at 172 cm<sup>-1</sup>. When the ligand coordinated with a metal ion at its carboxyl group, the  $\Delta \nu$  observed between 213-259 cm<sup>-1</sup>, which supports the monodentate coordination nature of (COO<sup>-</sup>) carboxylate anion [16]. As well as, a band of  $\nu(\text{O-CH}_3)$  appeared at 1246 cm<sup>-1</sup> [18], but the band (1456 cm<sup>-1</sup>) shifted back to (C=C) aromatic [18]. New bands assigned at 574-586 cm<sup>-1</sup> and 416-445cm<sup>-1</sup> for stretching frequencies of M-O and M-N, respectively[12,14]. Table 2 includes the most important FT-IR data in this study.

### 3.2. UV-vis spectra

The electronic spectra of the ligand and its complexes were collected at  $1 \times 10^{-3}$  mol/L in DMSO at room temperature (table 3). The electronic spectrum of the Schiff base exhibited three bands. The first absorption band in UV-region appeared at 275 nm (36363 cm<sup>-1</sup>) which could be appointed to  $\pi - \pi^*$  of the benzene ring and double bonds in the ligand structure [12,18]. The second absorption band appeared at 344nm (29069 cm<sup>-1</sup>) could be appointed to the  $n - \pi^*$  transitions in azomethine (C=N) groups[12,14]. The third band at 422 nm (23696 cm<sup>-1</sup>) could be allotted to the  $n - \pi^*$  transitions, which possessed non-shared electronic pairs of groups (hydroxyl, amine, and methoxy) [15,18]. Herein,

shifting of the absorption bands to higher wavelength indicate a successful preparation of the complexes and the appearance of new bands could refer to (d-d) orbital transitions.

**Table 2.** The main FT-IR spectra ( $\text{cm}^{-1}$ ) of compounds under study.

| Compound             | $\nu$<br>O-H | $\nu$<br>C=N | $\nu$ as<br>COO | $\nu$ s<br>COO | $\Delta\nu$<br>as-s | $\nu$<br>M-O | $\nu$<br>M-N |
|----------------------|--------------|--------------|-----------------|----------------|---------------------|--------------|--------------|
| H <sub>2</sub> CANPT | 3420         | 1631<br>1610 | 1589            | 1417           | 172                 | -----        | -----        |
| [Mn(CANPT)]          | 3408         | 1612<br>1585 | 1570            | 1325           | 245                 | 580          | 422          |
| [Fe(CANPT)] Cl       | 3444         | 1612<br>1593 | 1565            | 1328           | 237                 | 574          | 430          |
| [Co(CANPT)]          | 3441         | 1629<br>1587 | 1568            | 1355           | 213                 | 586          | 418          |
| [Ni(CANPT)]          | 3402         | 1643<br>1633 | 1544            | 1321           | 223                 | 586          | 416          |
| [Cu(CANPT)]          | 3400         | 1643<br>1633 | 1554            | 1305           | 249                 | 586          | 418          |
| k[Ag(CANPT)]         | 3398         | 1643<br>1633 | 1564            | 1305           | 259                 | 586          | 445          |
| [Cd(CANPT)]          | 3442         | 1612<br>1587 | 1570            | 1328           | 242                 | 574          | 428          |
| [Hg(CANPT)]          | 3400         | 1625<br>1587 | 1548            | 1300           | 248                 | 586          | 418          |

Four bands of manganese ion complex [Mn(CANPT)] were observed at 276 nm ( $36231 \text{ cm}^{-1}$ ), 345nm ( $28985 \text{ cm}^{-1}$ ), 397nm ( $25188 \text{ cm}^{-1}$ ) and 817nm ( $12239 \text{ cm}^{-1}$ ), which could be addressed as ligand field (L.F), charge transfer (C.T) and  ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{G})$ , respectively [19]. The magnetic moment ( $\mu_{\text{eff}}$ ) of the Mn (II)  $d^5$  (Term  ${}^6\text{S}$ ) the complex was (5.19 B.M) corresponding to (five unpaired ) electrons, see table 3.

The spectrum of [Fe(CANPT)]Cl exhibited four transitions; the first two high intense bands at 280 nm ( $35714 \text{ cm}^{-1}$ ) and 431 nm ( $23201 \text{ m}^{-1}$ ) assigned to the ligand field (L.F ) and intra ligand charge transfer (INCT) ,respectively. The other two bands at 822 nm ( $12165 \text{ cm}^{-1}$ ) and 951 nm ( $10515 \text{ cm}^{-1}$ ) referred to  ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{1g}(\text{v}3)$  and  ${}^6\text{A}_{1g}(\text{S}) \rightarrow {}^4\text{T}_{2g}(\text{v}2)$  transitions respectively, that corresponded to their octahedral(O.h) geometry [20,21]. The spectrum of [Co(CANPT)] complex revealed four bands at 275nm ( $36363 \text{ cm}^{-1}$ ), 345 ( $28985 \text{ cm}^{-1}$ ) and 420nm ( $23809 \text{ cm}^{-1}$ ) assigned to (L.F) and (C.T) transitions, while d-d transition at 744 nm ( $13440 \text{ cm}^{-1}$ ) assigned to the  ${}^3\text{T}_{1g}(\text{F}) \rightarrow {}^3\text{A}_{2g}(\text{F}) \text{v}_3$  transition [22].

The solution spectrum of [Ni(CANPT)] complexes illustrated two intensive bands at 281 nm ( $35587 \text{ cm}^{-1}$ ) and 348nm ( $28735 \text{ cm}^{-1}$ ), which assigned to the ligand field and charge transfer ,respectively. Another band observed at 424nm ( $23584 \text{ cm}^{-1}$ ) assigned to  ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{1g}(\text{F})$  transition. The magnetic moment of the Ni(II)  $d^8$  (Term  ${}^3\text{F}$ ) complex (2.98 B.M) indicated a octahedral configuration of this complex [23,24].

The UV-visible spectrum of [Cu (CANPT)] was exhibited three bands. The first band was located in the ultraviolet region at 277 nm and related to the ligand filed and other three bands were appeared in the visible region at 346nm, 362nm related to Charge transfer. In addition, the value of ( $\mu_{\text{eff}}$ ) that had been measured for [Cu (CANPT)] complex (1.85 B.M) indicated a mononuclear octahedral geometry [25].

The UV-vis spectrum of k[Ag(CANPT)] showed two absorption bands; a band at 277 nm ( $36101 \text{ cm}^{-1}$ ) assigned to the exist of intra ligand, but a second band at 424 nm ( $23584 \text{ cm}^{-1}$ ) assigned to (C.T) transition type (M $\rightarrow$ L) [26,27]. The absorption has included electronic transitions for all other

complexes in (table 3) that supported by magnetic sensitivity values to reach the proposed geometric shapes.

**Table 3.** UV- visible outputs and magnetic moments of the H<sub>2</sub>CANPT and its complexes.

| Compound             | $\lambda$ max<br>nm | $\nu'$<br>cm <sup>-1</sup> | $\epsilon$ max<br>Mol <sup>-1</sup> ·L·cm <sup>-1</sup> | Assignments                                                                                  | $\mu_{\text{eff}}$<br>B.M | Geometric<br>shape |
|----------------------|---------------------|----------------------------|---------------------------------------------------------|----------------------------------------------------------------------------------------------|---------------------------|--------------------|
| H <sub>2</sub> CANPT | 275                 | 36363                      | 1851                                                    | $\pi \rightarrow \pi^*$                                                                      | ----                      | ---                |
|                      | 344                 | 29069                      | 2295                                                    | *n- $\pi$                                                                                    |                           |                    |
|                      | 422                 | 23696                      | 1511                                                    | *n- $\pi$                                                                                    |                           |                    |
| [Mn (CANPT)]         | 276                 | 36231                      | 2058                                                    | Ligand field                                                                                 | 5.19                      | O.h                |
|                      | 345                 | 28985                      | 1981                                                    | Charge transfer                                                                              |                           |                    |
|                      | 397                 | 25188                      | 1209                                                    | Charge transfer                                                                              |                           |                    |
| [Fe(CANPT)] Cl       | 817                 | 12239                      | 5                                                       | <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub> (G)                              | 5.72                      | O.h                |
|                      | 280                 | 35714                      | 760                                                     | Ligand field                                                                                 |                           |                    |
|                      | 431                 | 23201                      | 170                                                     | Charge transfer                                                                              |                           |                    |
|                      | 822                 | 12165                      | 5                                                       | <sup>6</sup> A <sub>1g</sub> ( <sup>S</sup> ) → <sup>4</sup> T <sub>1g</sub>                 |                           |                    |
| [Co(CANPT)]          | 951                 | 10515                      | 2                                                       | (v3)<br><sup>6</sup> A <sub>1g</sub> ( <sup>S</sup> )<br>→ <sup>4</sup> T <sub>2g</sub> (v2) | 4.46                      | O.h                |
|                      | 275                 | 36363                      | 1782                                                    | Ligand field                                                                                 |                           |                    |
|                      | 345                 | 28985                      | 2262                                                    | Charge transfer                                                                              |                           |                    |
|                      | 420                 | 23809                      | 1672                                                    | Charge transfer                                                                              |                           |                    |
|                      | 744                 | 13440                      | 21                                                      | <sup>4</sup> T <sub>1g</sub> (F)<br>→ <sup>4</sup> A <sub>2g</sub> (F)                       |                           |                    |
| [Ni(CANPT)]          | 281                 | 35587                      | 550                                                     | Ligand field                                                                                 | 2.98                      | O.h                |
|                      | 348                 | 28735                      | 627                                                     | Charge transfer                                                                              |                           |                    |
|                      | 424                 | 23584                      | 507                                                     | <sup>3</sup> A <sub>2g</sub> (F) →<br><sup>3</sup> T <sub>2g</sub> (F)                       |                           |                    |
| [Cu(CANPT)]          | 277                 | 36101                      | 1860                                                    | Ligand field                                                                                 | 1.85                      | O.h                |
|                      | 346                 | 28901                      | 1475                                                    | Charge transfer                                                                              |                           |                    |
|                      | 362                 | 27624                      | 934                                                     | Charge transfer                                                                              |                           |                    |
| k[Ag(CANPT)]         | 277                 | 36101                      | 1231                                                    | $\pi \rightarrow \pi^*$                                                                      | Dia.                      | O.h                |
|                      | 424                 | 23584                      | 1556                                                    | intra-ligand<br>*n- $\pi$                                                                    |                           |                    |
| [Cd(CANPT )]         | 276                 | 36231                      | 1755                                                    | $\pi \rightarrow \pi^*$                                                                      | Dia.                      | O.h                |
|                      | 345                 | 28985                      | 1969                                                    | *n- $\pi$                                                                                    |                           |                    |
|                      | 416                 | 24038                      | 1240                                                    | C.T                                                                                          |                           |                    |
| [Hg(CANPT)]          | 277                 | 36101                      | 1484                                                    | $\pi \rightarrow \pi^*$                                                                      | Dia.                      | O.h                |
|                      | 385                 | 25974                      | 968                                                     | *n- $\pi$                                                                                    |                           |                    |
|                      | 819                 | 12210                      | 1                                                       | C.T                                                                                          |                           |                    |

Dia = Diamagnetic      O.h = octahedral

### 3.3 . The <sup>1</sup>H and <sup>13</sup>C -NMR spectra of the ligand

The Schiff base ligand was dissolved in (DMSO) -d<sub>6</sub> solution to get spectra of <sup>1</sup>H and <sup>13</sup>C-NMR . Figure 1 showed the <sup>1</sup>H-NMR spectrum, of ligand (H<sub>2</sub>CANPT), a sharp peak at (12.32) ppm  $\delta$  was assigned to (-COOH) carboxyl groups , the (C-OH) phenol protons were observed at  $\delta$  (9.46 and,9.06) ppm[16,17]. Furthermore, multiple signals at range of 5.93-7.51 ppm were owned to the  $\delta$  (C-H) aromatic protons [28]. The  $\delta$  (-OCH<sub>3</sub>),  $\delta$  H (-CH) and  $\delta$  H (-CH<sub>2</sub>) protons have appeared at (3.83, 3.62 and 2.7, 2.95) ppm, respectively [22,29].



Figure 2 shows the structure of the Schiff base (ligand) by <sup>13</sup>C-NMR. Through the <sup>13</sup>C-NMR spectrum of H<sub>2</sub>CANPT was elucidated a peak at δ (159.73) ppm belong to the carbon atom (CH=N) azomethine groups [30,31]. A peak at 172.21 ppm indicated a carbon atom of δ (-COOH) carboxyl groups [32], then peaks at range (111.83-130.33) ppm were attained to an aromatic carbon, as well as, peaks at (135.6, 55.70, 21.3 and 9.92) ppm referred to δ (C-OH) phenol, δ (-OCH<sub>3</sub>), δ H (-CH<sub>2</sub>) and δ H (-CH), respectively [31,32]. The chemical shifts of <sup>1</sup>H and <sup>13</sup>C-NMR are listed and assigned in (table 4).

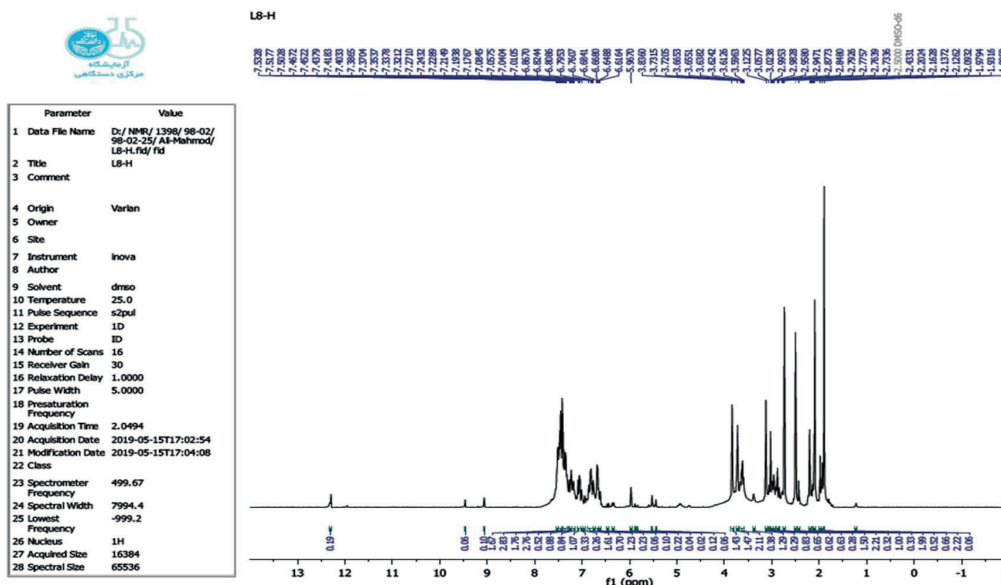


Figure 1. <sup>1</sup>H-NMR spectrum of H<sub>2</sub>CANPT.

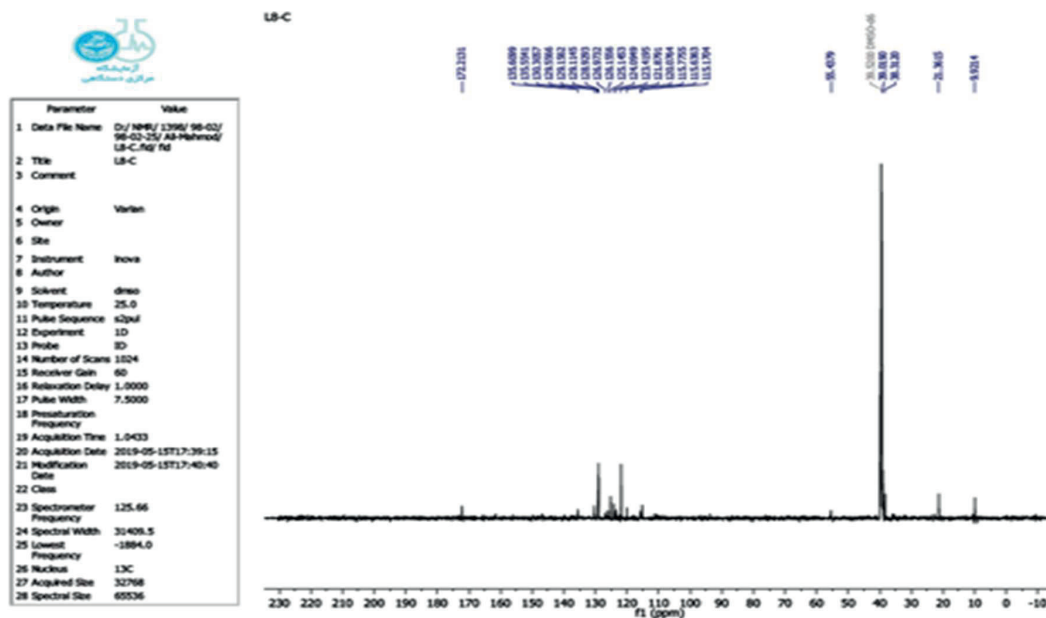


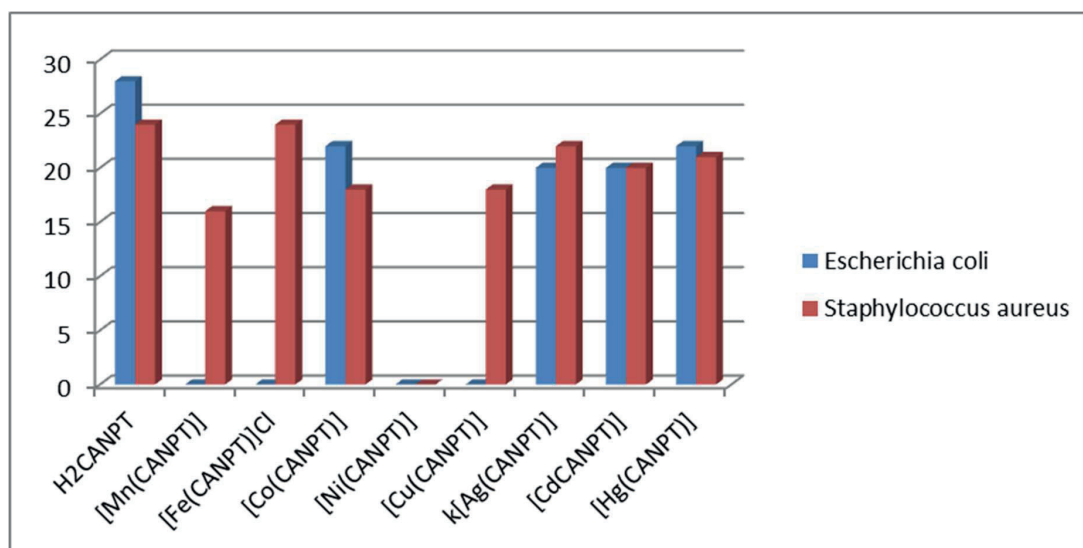
Figure 2. <sup>13</sup>C-NMR spectrum of H<sub>2</sub>CANPT.

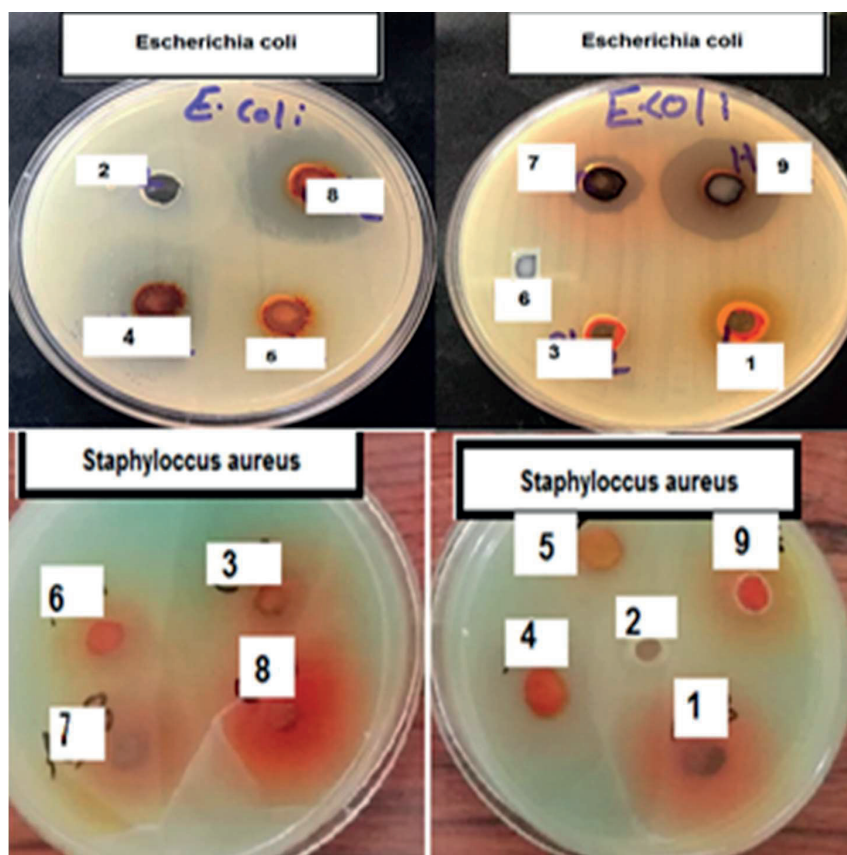
**Table 4.** Analysis of the  $^1\text{H}$  and  $^{13}\text{C}$  -NMR spectrum of  $\text{H}_2\text{CANPT}$ .

| Functional groups                 | $^1\text{H}$ -NMR $\delta$ (ppm) | $^{13}\text{C}$ -NMR $\delta$ (ppm) |
|-----------------------------------|----------------------------------|-------------------------------------|
| COOH) carboxyl(- $\delta$         | 12.32                            | 172.21                              |
| C-OH) phenol(- $\delta$           | 9.46, 9.06                       | 135.6                               |
| For $\delta$ (-C=N)               | -----                            | 159.73                              |
| $\delta$ (C-H) aromatic           | 5.93-7.51                        | 111.83-130.33                       |
| For $\delta$ (-OCH <sub>3</sub> ) | 3.83                             | 55.70                               |
| for $\delta$ (-CH)                | 3.62                             | 21.36                               |
| for $\delta$ (-CH <sub>2</sub> )  | 2.7, 2.95                        | 9.92                                |
| $\delta$ DMSO                     | 1.90-2.50                        | 39.58                               |

### 3.4. Biological studies

Antibacterial activities of the synthesized compounds were carried out by two bacterial strains of Gram-negative *Escherichia coli* and Gram-positive *Staphylococcus aureus* using the agar diffusion method [30]. The antibacterial activity of each compound was measured according to the diameter of the inhibition zone (IZ) in mm and compared with DMSO as a control or as a solvent when for a concentration  $1 \times 10^{-3}$  M [25]. *Escherichia coli*, and *Staphylococcus aureus* were selected here due to their known effects on a number of diseases; they have different resistance nature to the antibiotics and therapeutic chemicals [33,34]. The ligand and its complexes showed a very good zone of inhibition, except the nickel complex, which showed no efficacy for both types of bacteria. The order of the inhibition potential can be arranged as follows for both types of bacteria: *Escherichia coli* :  $\text{H}_2\text{CANPT} > \text{Co} > \text{Hg} > \text{Ag} > \text{Cd} > \text{Cu} = \text{Mn} = \text{Fe} = \text{Ni}$ ; *Staphylococcus aureus* :  $\text{H}_2\text{CANPT} = \text{Fe} > \text{Ag} > \text{Hg} > \text{Cd} > \text{Cu} = \text{Co} > \text{Mn} > \text{Ni}$ . The antibacterial activities of all the prepared compounds are included in figure 3 and image 1.

**Figure 3.** Antibacterial activity of compounds.

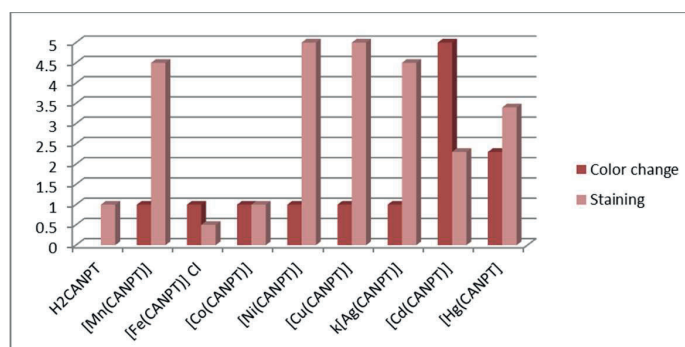


**Image 1.** Photograph of antibacterial activity of compounds: 1-  $H_2CANPT$ , 2-  $[Mn(CANPT)]$ , 3-  $[Fe(CANPT)]Cl$ , 4-  $[Co(CANPT)]$ , 5-  $[Ni(CANPT)]$ , 6-  $[Cu(CANPT)]$ , 7-  $k[Ag(CANPT)]$ , 8-  $[Cd(CANPT)]$ , 9-  $Hg(CANPT)$ .

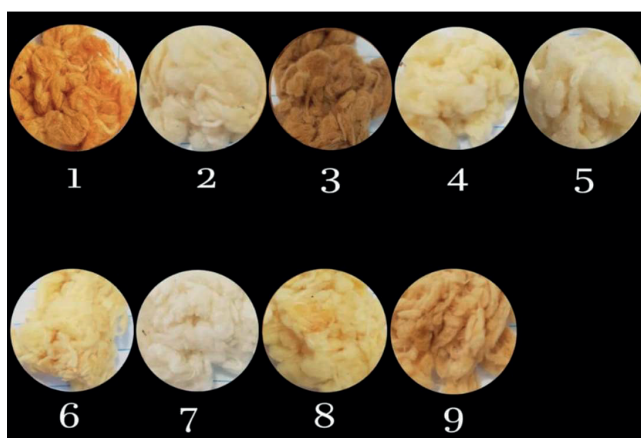
### 3.5. In dyes

Schiff base and their complexes can participate in the dyeing process [35]. The presence of some ions of exist transitional elements promotes positive properties in the dyeing technique [36]. Some azomethine complexes such as cobalt and chromium used in the dyeing process because of their obvious pigments that give constant colors for food packages, wool and leather [37]. This species of dyes based on many methods depending on the chemical structure, the chromophore system and other systems [38].

**3.5.1. Dyeing procedure.** The dyeing process was conducted according to the optimized provision which was tested approving to ISO 105- C10 method [39]: (1) Preparation of dyeing solution: The ligand and its complexes were dissolved in ethanoic aqueous solution and soaked in a dyeing bath with mordant (alum or sodium carbonate), then some drops of (NaOH) solution was added. (2) Dyeing after treatment: The cotton fibers was delivered in the mixture which was prepared in the step 1, then heated to 50 °C for 20 minutes with continuous stirring until getting a homogenous dye. It was extracted from the mixture, then washed with cold water and left to dry. (3) The cotton was separated from the mixture, washed with water and left to dry. (4) The washing fastness was examined with 5 g/L (soap liquid) at 40 °C for 30 minutes. After washing tests for dyeing cotton fibers, some samples showed good results as explained in image 2 and table 5 for manganese, nickel, copper, silver, cadmium, and mercury complexes, while the results of ligand complexes and other ions were weak.



**Figure 4.** The zone of inhibition in mm of (H<sub>2</sub>CANPT) Schiff base and its complexes.



**Image 2.** Shapes of cotton fibers dyeing to Schiff base and complexes; 1-H<sub>2</sub>CANPT, 2- [Mn(CANPT)], 3- [Fe(CANPT)]Cl, 4-[Co(CANPT)], 5-[Ni(CANPT)], 6-[Cu(CANPT)], 7-k[Ag(CANPT)], 8-[Cd(CANPT)], 9-[Hg(CANPT)].

**Table 5.** The results of the colorfastness rating of the cotton fabric.

| Compounds            | Color change | Staining |
|----------------------|--------------|----------|
| H <sub>2</sub> CANPT | 1            | 1        |
| [Mn(CANPT)]          | 1            | 4.5      |
| [Fe(CANPT)]Cl        | 1            | 0.5      |
| [Co(CANPT)]          | 1            | 1        |
| [Ni(CANPT)]          | 1            | 5        |
| [Cu(CANPT)]          | 1            | 5        |
| K[Ag(CANPT)]         | 5            | 4.5      |
| [Cd(CANPT)]          | 2.3          | 2.3      |
| [Hg(CANPT)]          | 2            | 3.4      |

\* Wash fastness; 5 = very good, 4-4.5 = good, 1-2 and 2-2.3 = poor

#### 4. Conclusion

Synthesis of Schiff base was done by two steps, the reacting of curcumin 1mmol with 4-aminantipyrine 2 mmol to produce compound (CANP) and reacting of (CANP) 1mmol with L-tyrosine (2 mmole) to produce Schiff base ligand (H<sub>2</sub>CANPT). It was performed as hexadentate coordinates by the atoms (N<sub>4</sub>O<sub>2</sub>). All complexes prepared to assume octahedral geometric shape based on the available data from the such as FT-IR, UV-Visible, micro elemental (C.H.N), <sup>13</sup>C,<sup>1</sup>H-NMR, molar conductivity, and magnetic susceptibility. Some of Schiff bases and their complexes were observed to have color stability when used in the dyeing process on fiber cotton. The prepared compounds had an acceptable inhibition in varying proportions when assessing their biological efficacy against two types of bacteria (*Staphylococcus aureus* and *Escherichia Coli*), except for nickel complex that was not recorded inhibition of two types of bacterial species, in addition to (Iron, manganese and copper) complexes toward *Escherichia Coli*.

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