

## Preparation, Spectroscopic Characterization, Thermal Stability and XRD of Some New Metal Chelates with Aceclofenac in Presence of 1,10-Phenanthroline

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**I**N THIS study, mixed ligand complexes derived from aceclofenac (Acecl) as primary ligand and 1,10-phenanthroline (Phen) as secondary ligand have been prepared and characterized by conventional techniques including elemental analyses, infrared, electronic spectra, <sup>1</sup>H NMR and XRD. The infrared spectral data showed that the chelation behavior of the ligands towards Ni(II), Cu(II), Zn(II), Zr(IV) and La(III) transition metal ions through oxygen of ketone, carboxylic group of aceclofenac and nitrogen atoms of 1,10-phenanthroline. Thermal analyses showed that the chelates lose water molecules of hydration initially and subsequently expel anionic part and organic ligands in continuous steps leaving metal or metal oxide as a final product. XRD analysis of the compounds showed that, Acecl, Phen and their metal complexes display crystalline peaks.

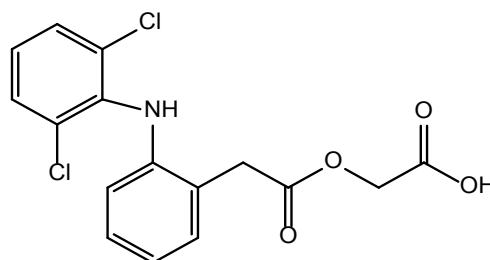
**Keywords:** Aceclofenac, Phen, Infrared spectral, XRD.

### Introduction

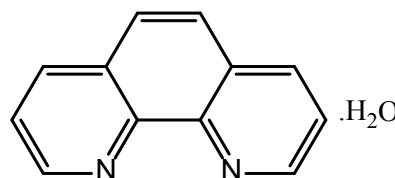
Aceclofenac is a non-steroidal anti-inflammatory drug (NSAID) whose efficacy is offset by significant incidence of gastrointestinal ulceration which is a major side effect of most of the NSAIDs (Scheme 1). This ulceration is associated in part with the presence of carboxylic acid functionality in its structure. This functionality which is commonly found in the NSAIDs is unionized in the highly acidic environment of the stomach. As a result, these agents are more lipophilic in nature and may pass into the cells of the gastric mucosa. The intracellular pH of these cells is more basic than that of the stomach lumen and the NSAID becomes ionized. This results in back flow of protons from the lumen into these cells with concomitant cellular damage. This type of damage can be prevented if the carboxylic acid function could be eliminated from these agents. However, this functional group is a mandatory requirement for the anti-inflammatory activity [1-3].

Phen (Scheme 2) is a heterocyclic organic compound. It is a white solid that is soluble in

organic solvents and may be prepared by two successive Skraup reactions of glycerol with o-phenylenediamine, catalyzed by sulfuric acid and an oxidizing agent, traditionally aqueous arsenic acidomnitrobenzene. Dehydration of glycerol



Scheme 1. Structure of aceclofenac (Acecl).



Scheme 2. The structure of 1, 10-phenanthroline monohydrate (Phen).

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gives acrolein which condenses with the amine followed by cyclization.

1, 10-phenanthroline is an attractive ligand due to its ability to act as strong binder for double-stranded DNA and facilitate the hydrogen atom abstraction from the sugar unit [4]. 1,10-Phenanthroline (Phen) has been examined as a corrosion inhibitor for mild steel in 1 N H<sub>2</sub>SO<sub>4</sub> acid solution by weight-loss and gasometric methods [5].

## Experimental

### Materials and Methods

#### Chemicals

All chemicals used for preparation of the complexes were of analytical reagent grade, commercially available from different sources and used without further purification. Aceclofenac used in this study was purchased from Obour Pharmaceutical Industrial Company. 1,10-phenanthroline monohydrate, acetone, NaOH, ZrO(NO<sub>3</sub>)<sub>2</sub> (99.9%), Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O, Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O and LaCl<sub>3</sub>·7H<sub>2</sub>O from Aldrich Chemical Co. All the chemicals and solvents were used as purchased without further purification. CHN analysis was carried on a Perkin Elmer CHN 2400. The percentages of the metal ions were determined gravimetrically by transforming the solid products into metal ion. The percentages of the metal ions were also estimated using an atomic absorption spectrometer. The spectrometer model was PYE-UNICAM SP 1900 and fitted with the corresponding lamp. IR spectra were recorded on FT-IR 460 PLUS (KBr discs) in the range from 4000-400 cm<sup>-1</sup>. <sup>1</sup>H NMR spectra were recorded on a Bruker 300 MHz NMR Spectrometer using tetramethylsilane (TMS) as the internal standard, chemical shifts are expressed in δ (ppm) and DMSO-*d*<sub>6</sub> was used as the solvent. Absorbance measurements were conducted on a double beam spectrophotometer (T80 UV/Vis) with wavelength range 190 nm ~ 1100 nm, spectral bandwidth of 2 nm. Magnetic measurements were carried out on a Sherwood scientific magnetic balance using Gouy balance using Hg[Co(SCN)<sub>4</sub>] as calibrate. All melting points are uncorrected and were determined on a Gallen Kamp electric melting point apparatus. Molar conductivities of the solutions of the ligand and metal complexes in DMSO with concentrations of 1×10<sup>-3</sup> M were measured on CONSORT K410.

#### Synthesis



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complex was prepared by adding 1mmol (0.2195 g) of zinc(II) acetate dihydrate in 20 ml acetone drop-wise to a stirred suspended solution 1mmol (0.353 g) of Acecl with 1mmol (0.056 g) KOH and 1mmol (0.198 g) Phen in 50 ml acetone. The reaction mixture was refluxed for 8 h. The dark red precipitate was filtered off, washed several times with acetone until the filtrate becomes clear and dried under vacuum over anhydrous CaCl<sub>2</sub>. The blue, pale green, white pink and pale pink [Cu(Acecl)(Phen)(H<sub>2</sub>O)<sub>2</sub>](CH<sub>3</sub>COO)<sub>2</sub>·6H<sub>2</sub>O, [Ni(Acecl)(Phen)(H<sub>2</sub>O)<sub>2</sub>](CH<sub>3</sub>COO)<sub>2</sub>·3H<sub>2</sub>O, [La(Acecl)(Phen)(H<sub>2</sub>O)<sub>2</sub>]Cl<sub>3</sub>·9H<sub>2</sub>O and [ZrO(Acecl)(Phen)(H<sub>2</sub>O)](NO<sub>3</sub>)<sub>2</sub>·9H<sub>2</sub>O were prepared in a similar manner described above by using acetone as a solvent and Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O, Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, LaCl<sub>3</sub>·7H<sub>2</sub>O and ZrO(NO<sub>3</sub>)<sub>2</sub> in 1:1:1:1 molar ratio.

## Results and Discussion

New mononuclear complexes of Ni(II), Cu(II), Zn(II), Zr(IV) and La(III) ions with Acecl in presence of Phen were synthesized. Analytical data indicated that the complexes formed with 1:1 stoichiometry. The results of physical properties of the prepared complexes along with their elemental analysis are collected in Table 1. The complexes are stable in air and soluble in most common organic solvents. The molar conductance in DMF (10<sup>-3</sup>M) at room temperature reveals the electrolytic nature of the metal complexes. Qualitative reactions also agree well with the molar conductance data which revealed the presence of chloride, nitrate and acetate ions as counter ions. The magnetic moment values of Ni(II) and Cu(II) complexes at room temperature are 3.2 and 2.25 B.M., respectively, which will consistence with octahedral geometry around Ni(II) and Cu(II) [6].

#### FT-IR absorption spectra

The significant infrared bands of the organic ligands (Acecl and Phen) and its metal complexes (Fig. 1) are listed in Table 8 and the following features can be pointed out: The medium strong intensity band due to ν(OH) group appear in the spectra of the free Acecl at 3316 cm<sup>-1</sup>. For metal complexes spectra the peak found at 3395-3445 cm<sup>-1</sup> were assigned to ν(OH) of water molecules. In the infrared spectra of Acecl and Phen, the bands at 1770, 1717 and 1586 cm<sup>-1</sup>, were assigned to the ν(COO)<sup>-</sup>, ν(C=O)<sub>ketone</sub> and ν(C=N) vibration frequencies [7,8]. In complexes the band due to ν(COO)<sup>-</sup> disappeared, while

$\nu(\text{C}=\text{O})_{\text{ketone}}$  was shifted to higher wavenumbers by 18-20  $\text{cm}^{-1}$  upon complexation denoting its coordination to metal ions. The  $\nu(\text{C}=\text{N})$  of Phen was shifted to lower values (46-76  $\text{cm}^{-1}$ ). The new bands appear in the region 1595-1575  $\text{cm}^{-1}$  can be assigned to the asymmetric stretching vibration ( $\nu_{\text{as}}$ ) of the ligated carboxylato group and the symmetric vibration occurs in the region 1340-1377  $\text{cm}^{-1}$ . The values of  $\Delta\nu$  for our complexes are higher than 200  $\text{cm}^{-1}$  indicating a monodentate coordination mode of the carboxylato group [9-12]. The coordination of the oxygen and nitrogen atoms of the ligands

was supported by the appearance of new bands were observed at 656, 528, 477  $\text{cm}^{-1}$  for Ni(II), 721, 662  $\text{cm}^{-1}$  for Cu(II), 657, 573, 529  $\text{cm}^{-1}$  for Zn(II), 660, 618, 570, 510  $\text{cm}^{-1}$  for Zr(IV) and 659, 634, 604, 570, 507, 474 for La(III) can be assigned to  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{N})$  respectively, confirming the coordination of both oxygen and nitrogen atoms to metal center [13]. The proposed structures for complexes are represented in Scheme 3. The data given in Table 8 show that  $\nu(\text{Zr}=\text{O})$  is a medium band at 840  $\text{cm}^{-1}$ .

**TABLE 1. Elemental analysis and physico-analytical data for aceclofenac (Acecl), 1,10-phenanthroline monohydrate (Phen) and their metal complexes.**

| Compounds<br>M.Wt. (M.F.)   | Yield<br>% | Mp/<br>°C | Color         | Found (Calcd.) (%) |                |                  |                  |                | $\Lambda$<br>S $\text{cm}^2$<br>$\text{mol}^{-1}$ | $\mu_{\text{eff}}$<br>(B.M.) |
|---|------------|-----------|---------------|--------------------|----------------|------------------|------------------|----------------|---|------------------------------|
|   |            |           |               | C                  | H              | N                | M                | Cl             |   |                              |
| Acecl<br>389.4 (C <sub>18</sub> H <sub>20</sub> FN <sub>5</sub> O <sub>4</sub> )  | -          | 150       | White         | 55.45<br>(55.47)   | 5.12<br>(5.14) | 17.95<br>(17.98) | -                | -              | 20.5  | -                            |
| Phen<br>198.2 (C <sub>12</sub> H <sub>10</sub> N <sub>2</sub> O)  | -          | 100       | White         | 72.70<br>(72.72)   | 5.08<br>(5.09) | 14.12<br>(14.13) | -                | -              | 5.0   | -                            |
| [Ni(Acecl)(Phen)(H <sub>2</sub> O) <sub>2</sub> ]<br>CH <sub>3</sub> COO.3H <sub>2</sub> O<br>775.69 (NiC <sub>32</sub> H <sub>40</sub> FN <sub>7</sub> O <sub>11</sub> )                 | 78.08      | 145       | Pale<br>green | 49.48<br>(49.50)   | 5.13<br>(5.16) | 12.60<br>(12.63) | 7.56<br>(7.57)   | -              | 85.20   | 3.2                          |
| [Cu(Acecl)(Phen)(H <sub>2</sub> O) <sub>2</sub> ]<br>CH <sub>3</sub> COO.6H <sub>2</sub> O<br>834.54 (CuC <sub>32</sub> H <sub>46</sub> FN <sub>7</sub> O <sub>14</sub> )                 | 80.04      | 114       | Blue          | 46.00<br>(46.01)   | 5.49<br>(5.51) | 11.71<br>(11.74) | 7.60<br>(7.61)   | -              | 80.80   | 2.25                         |
| [Zn(Acecl)(Phen)(H <sub>2</sub> O) <sub>2</sub> ]<br>CH <sub>3</sub> COO.3H <sub>2</sub> O<br>782.4 (ZnC <sub>32</sub> H <sub>40</sub> FN <sub>7</sub> O <sub>11</sub> )                  | 72.53      | 110       | Dark<br>red   | 48.05<br>(49.08)   | 5.09<br>(5.11) | 12.50<br>(12.53) | 8.33<br>(8.36)   | -              | 83.40   | -                            |
| [ZrO(Acecl)(Phen)(H <sub>2</sub> O)]<br>NO <sub>3</sub> .9H <sub>2</sub> O<br>917.22 (ZrC <sub>30</sub> H <sub>47</sub> FN <sub>8</sub> O <sub>18</sub> )                                 | 89.35      | 150       | Pale<br>pink  | 39.22<br>(39.25)   | 5.10<br>(5.12) | 12.19<br>(12.21) | 9.94<br>(9.95)   | -              | 90.10   | -                            |
| [La(Acecl)(Phen)(H <sub>2</sub> O) <sub>2</sub> ]<br>Cl <sub>2</sub> .9H <sub>2</sub> O<br>975.79<br>(LaC <sub>30</sub> H <sub>49</sub> FN <sub>7</sub> O <sub>16</sub> Cl <sub>2</sub> ) | 76.11      | 105       | White<br>pink | 36.87<br>(36.89)   | 5.00<br>(5.02) | 10.02<br>(10.04) | 14.23<br>(14.24) | 7.25<br>(7.27) | 165.40  | -                            |

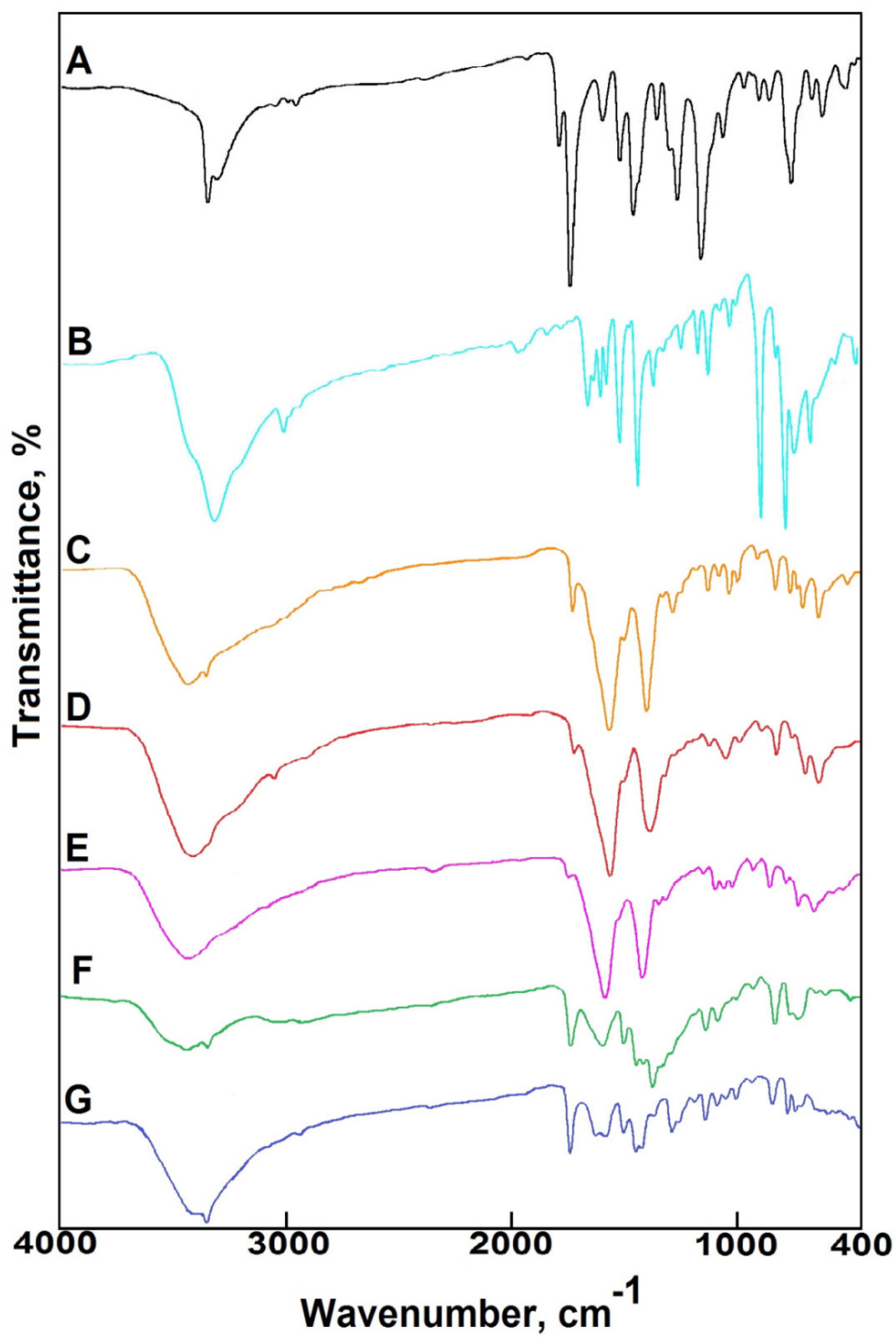
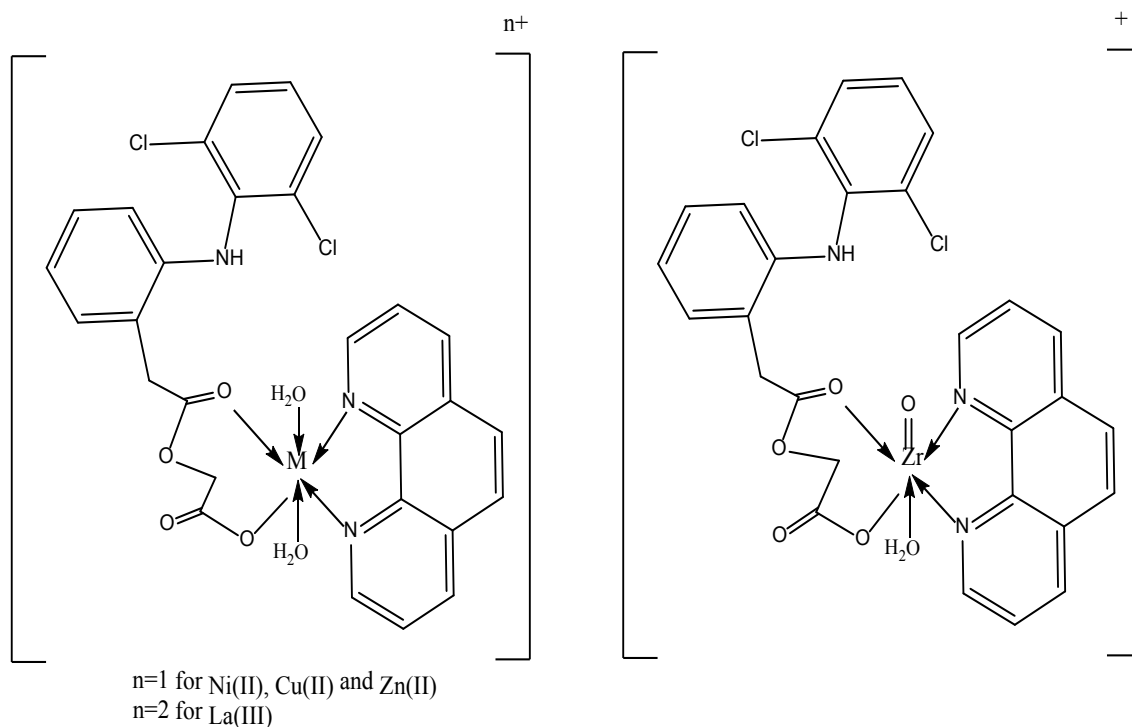


Fig. 1. Infrared spectra for (A)  $\text{AcceCl}$ , (B)  $\text{Phen}$ , (C)  $[\text{Ni}(\text{Acce})(\text{Phen})(\text{H}_2\text{O})_2]\text{CH}_3\text{COO}\cdot 3\text{H}_2\text{O}$ , (D)  $[\text{Cu}(\text{Acce})(\text{Phen})(\text{H}_2\text{O})_2]\text{CH}_3\text{COO}\cdot 6\text{H}_2\text{O}$ , (E)  $[\text{Zn}(\text{Acce})(\text{Phen})(\text{H}_2\text{O})_2]\text{CH}_3\text{COO}\cdot 3\text{H}_2\text{O}$ , (F)  $[\text{ZrO}(\text{Acce})(\text{Phen})(\text{H}_2\text{O})_2]\text{NO}_3\cdot 9\text{H}_2\text{O}$  and (G)  $[\text{La}(\text{Acce})(\text{Phen})(\text{H}_2\text{O})_2]\text{Cl}_2\cdot 9\text{H}_2\text{O}$ .



Scheme 3. The coordination mode of Ni(II), Cu(II) and Zn(II), Zr(IV) and La(III) with Acecl and Phen.

TABLE 2. Selected infrared absorption frequencies ( $\text{cm}^{-1}$ ) of Acecl, Phen and their metal complexes.

| Compounds  | $\nu(\text{O-H});$<br>$\text{H}_2\text{O};$<br>$\text{COOH}$ | $\nu(\text{C=O});$<br>$\text{COOH}$ | $\nu(\text{C=O})$ | $\nu_{\text{as}}(\text{COO}^-)$ | $\nu(\text{C=N})$ | $\nu_s(\text{COO}^-)$ | $\nu$<br>(Zr=O) | $\nu(\text{M-O})$ and<br>$\nu(\text{M-N})$    |
|--|--|-------------------------------------|-------------------|---------------------------------|-------------------|-----------------------|-----------------|---|
| Aceclofenac  | 3316ms   | 1770m                               | 1717vs            | -                               | -                 | -                     | -               | -   |
| Phen   | 3380mbr  | -                                   | -                 | -                               | 1586ms            | -                     | -               | -   |
| [Ni(Acecl)<br>(Phen)( $\text{H}_2\text{O}$ ) <sub>2</sub> ]<br>$\text{CH}_3\text{COO} \cdot 3\text{H}_2\text{O}$ | 3432mbr  |                                     | 1737m             | 1575s                           | 1513vw            | 1342vw                | -               | 656m, 528vw,<br>477vw                         |
| [Cu(Acecl)<br>(Phen)( $\text{H}_2\text{O}$ ) <sub>2</sub> ]<br>$\text{CH}_3\text{COO} \cdot 6\text{H}_2\text{O}$ | 3421mbr  |                                     | 1737w             | 1581s                           | 1521vw            | 1341vw                | -               | 721w, 662m                                    |
| [Zn(Acecl)<br>(Phen)( $\text{H}_2\text{O}$ ) <sub>2</sub> ]<br>$\text{CH}_3\text{COO} \cdot 3\text{H}_2\text{O}$ | 3427mbr  |                                     | 1736vw            | 1577vs                          | 1520sh            | 1340w                 | -               | 657w, 573vw,<br>529vw                         |
| [ZrO(Acecl)<br>(Phen)( $\text{H}_2\text{O}$ )]<br>$\text{NO}_3 \cdot 9\text{H}_2\text{O}$                        | 3445mbr  |                                     | 1735ms            | 1595ms                          | 1511ms            | 1377s                 | 840ms           | 660vw, 618vw,<br>570vw, 510vw                 |
| [La(Acecl)(Phen)<br>( $\text{H}_2\text{O}$ ) <sub>2</sub> ] $\text{Cl}_2 \cdot 9\text{H}_2\text{O}$              | 3395mbr  |                                     | 1736ms            | 1585m                           | 1510w             | 1366w                 | -               | 659vw, 634vw,<br>604vw, 570vw,<br>507w, 474vw |

Keys: s=strong, w=weak, m=medium, br=broad, v=stretching.

*UV-Vis. spectra*

In order to get information about the hybridization and configuration of the complexes, the electronic spectra of the complexes were measured. UV-Visible spectral data of the free Acecl, Phen ligands and their complexes were recorded from 200 to 800 nm as shown in Fig. 2. The absorption spectra of the free Acecl exhibited high intensity bands at 225, 240 nm and 266, 278 nm (Table 3) which may be assigned to  $\pi-\pi^*$  and  $n-\pi^*$  transitions, respectively [14,15]. Also, Phen shows bands at 243 nm and 273, 350 nm which may be assigned to  $\pi-\pi^*$  and  $n-\pi^*$  transitions, respectively. The shift of the absorption bands to higher or lower and appearance of new bands for the complexes is attributed to complexation

of mixed ligand. Also the complexes of Ni(II), Cu(II), Zn(II), Zr(IV) and La(III) show new bands in the range 393-426 nm, which may be assigned to ligand-metal charge transfer [16-19]. The electronic spectrum of the binuclear nickel(II) complex showed two bands, the first band occurs at 565 nm which is corresponding to the  ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$  electronic transition. The other band occurs at 615 nm which is corresponding to the  ${}^3A_{2g} \rightarrow {}^3T_{1g}(F)$  electronic transition. The two transitions are consistent with an octahedral geometry of the complex [20,21]. The d-d transition absorption spectra for Cu(II) complex shows one absorption band at 620 nm which are assigned to  ${}^2B_1 \longrightarrow {}^2E_g$  transitions in favor of octahedral geometry [22].

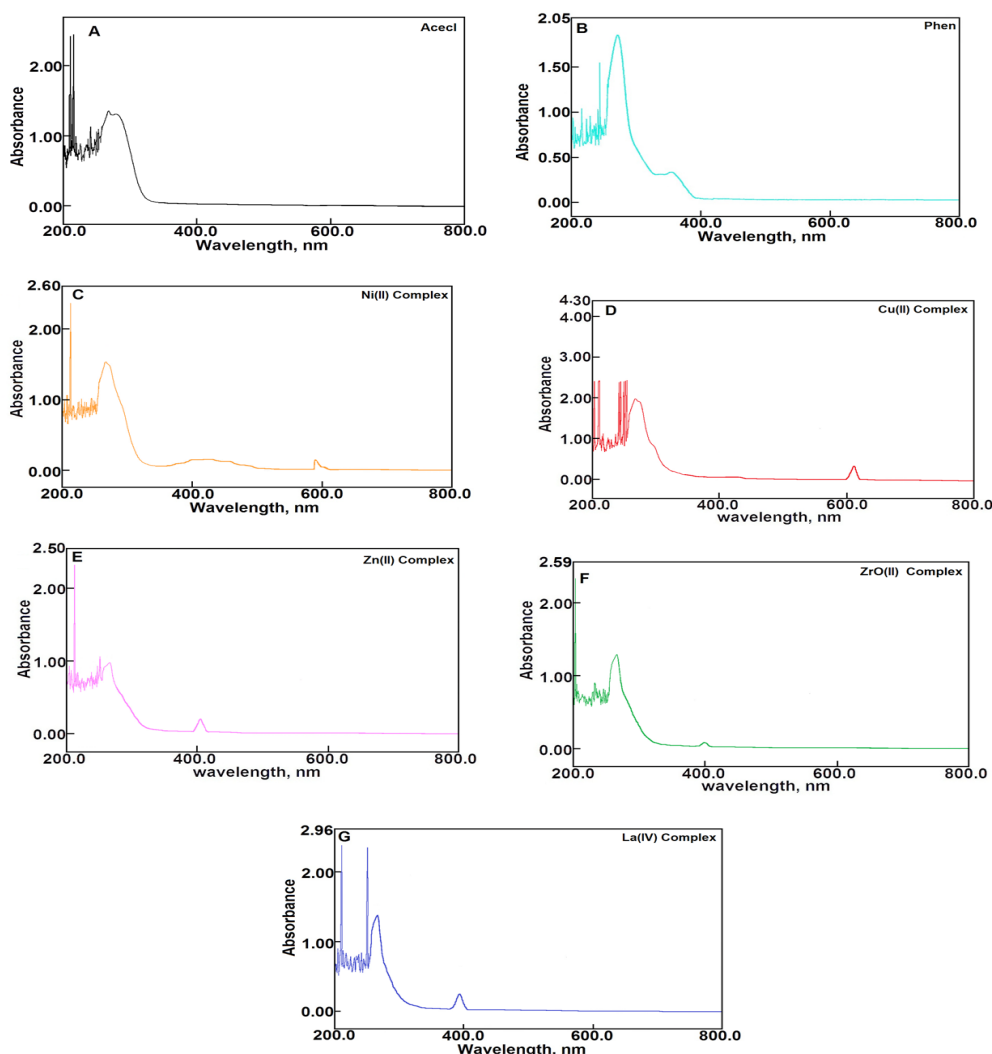


Fig. 2. Electronic absorption spectra for (A) Acecl, (B) Phen, (C)  $[\text{Ni}(\text{Acec})(\text{Phen})(\text{H}_2\text{O})_2]\text{CH}_3\text{COO}\cdot 3\text{H}_2\text{O}$ , (D)  $[\text{Cu}(\text{Acec})(\text{Phen})(\text{H}_2\text{O})_2]\text{CH}_3\text{COO}\cdot 6\text{H}_2\text{O}$ , (E)  $[\text{Zn}(\text{Acec})(\text{Phen})(\text{H}_2\text{O})_2]\text{CH}_3\text{COO}\cdot 3\text{H}_2\text{O}$ , (F)  $[\text{ZrO}(\text{Acec})(\text{Phen})(\text{H}_2\text{O})_2]\text{NO}_3\cdot 9\text{H}_2\text{O}$  and (G)  $[\text{La}(\text{Acec})(\text{Phen})(\text{H}_2\text{O})_2]\text{Cl}_2\cdot 9\text{H}_2\text{O}$ .

TABLE 3. UV-Vis. spectra of Acecl, Phen, Ni(II), Cu(II), Zn(II), Zr(IV) and La(III) complexes.

| Assignments (nm)             | Acecl      | Phen       | Mixed ligand complex with |        |        |        |            |
|------------------------------|------------|------------|---------------------------|--------|--------|--------|------------|
|                              |            |            | Ni(II)                    | Cu(II) | Zn(II) | Zr(IV) | La(III)    |
| $\pi-\pi^*$ transitions      | 225<br>240 | 243        | 245                       | 250    | 238    | 230    | 233<br>250 |
| $n-\pi^*$ transitions        | 266<br>278 | 273<br>350 | 267                       | 267    | 265    | 265    | 265        |
| Ligand-metal charge transfer | -          | -          | 426                       | 420    | 402    | 400    | 393        |
| d-d transition               | -          | -          | 565<br>615                | 620    | -      | -      | -          |

*<sup>1</sup>H NMR spectra*

Proof of the bonding type of the ligands is also confirmed by comparing the <sup>1</sup>H NMR spectra of the ligands in normal DMSO-*d*<sub>6</sub>, at room temperature deuterated solvent and their complexes. The chemical shifts of the various types of protons in the <sup>1</sup>H NMR spectra of the ligands and their complexes are given in Table 4. In the aromatic region, a few doublets and in few cases some overlapping doublets/multiplets are observed in the range  $\delta \sim 6.21$ - $9.24$  ppm due to the protons of benzene ring. Another singlet corresponding to one proton for Acecl is observed at 13.11 and 2.51 ppm. It can be assigned either to OH of carboxylic group or NH. The signal of OH disappeared in all metal complexes. The <sup>1</sup>H NMR spectra for all complexes exhibit new signal in the range 3.79-3.93 ppm, due to presence of water molecules in the complexes [23-25]. On comparing Acecl with its complexes, all signals of the free ligand are present in spectra of the complexes with some shifts from binding of the ligand to the metal (Fig. 3).

*X-ray diffraction*

The powder XRD patterns of Acecl, Phen, Ni(II), Cu(II), Zn(II), Zr(IV) and La(III) complexes were recorded over  $2\theta$  in the range scale (10-70) as shown in Fig. 4. The diffraction of Acecl, shows four sharp diffraction peaks at about  $2\theta$  [d value  $\text{\AA}^\circ$ ] = 25.96 [3.43], 22.25 [3.99], 19.43 [4.57] and 17.52 [5.06]. The diffraction of Phen, shows three sharp diffraction peaks at about  $2\theta$  [d value  $\text{\AA}^\circ$ ] = 19.87 [4.47], 22.43 [3.96] and 17.22 [5.15].

The diffractogram of Ni(II) complex indicated main peaks at  $2\theta$  [d value  $\text{\AA}^\circ$ ] = 15.99[5.54], 32.20[2.78], 26.01[3.43] and 15.66[5.66]. The XRD patterns of Cu(II) complex exhibited sharp peaks corresponding to  $2\theta$  [d value  $\text{\AA}^\circ$ ] = 8.08[10.93], 24.17[3.68], 10.77[8.22], 15.97[5.55], 11.50[7.70] and 32.39[2.76]. The x-ray powder diffraction for Zn(II) complex give six sharp peaks at  $2\theta$  [d value  $\text{\AA}^\circ$ ] = 11.88[7.45], 10.65[8.31], 25.95[3.43], 32.64[2.74], 27.02[3.30] and 21.38[4.16]. The diffraction of Zr(IV) complex give five sharp peaks at  $2\theta$  [d value  $\text{\AA}^\circ$ ] = 25.80[3.45], 10.61[8.34], 9.13[9.69], 15.36[5.77] and 21.31[4.17]. The XRD patterns of La(III) complex give five peaks at  $2\theta$  [d value  $\text{\AA}^\circ$ ] = 28.39[3.14], 12.18[7.27], 25.97[3.43], 16.50[5.37] and 23.88[3.73]. The mean crystallite sizes, estimated using Scherrer equation [26-28], are shown in Table 5. The data in this table clarify that, Acecl, Phen and their metal complexes display crystalline peaks.

**Conclusion**

Acetoclofenac (Acecl) in presence of 1,10-phenanthroline monohydrate (Phen) reacts with Ni(II), Cu(II), Zn(II), Zr(IV) and La(III) in acetone to form solid complexes by 1:1:1:1 molar ratios (metal: Acecl: Phen: KOH). These complexes characterized by elemental analyses, IR, UV-Vis., <sup>1</sup>H NMR spectra, XRD diffraction, molar conductance and magnetic susceptibility. The infrared spectra indicated that Acecl ligand is bound to metal ions via ketone oxygen and one carboxylate oxygen, where chelation occurs also through pyridyl nitrogen of Phen.

TABLE 4.  $^1\text{H}$  NMR values (ppm) and tentative assignments for (A) Acecl, (B) Phen, (C)  $[\text{Ni}(\text{Acec})(\text{Phen})(\text{H}_2\text{O})_2]\text{CH}_3\text{COO}\cdot 3\text{H}_2\text{O}$ , (D)  $[\text{Cu}(\text{Acec})(\text{Phen})(\text{H}_2\text{O})_2]\text{CH}_3\text{COO}\cdot 6\text{H}_2\text{O}$ , (E)  $[\text{Zn}(\text{Acec})(\text{Phen})(\text{H}_2\text{O})_2]\text{CH}_3\text{COO}\cdot 3\text{H}_2\text{O}$ , (F)  $[\text{ZrO}(\text{Acec})(\text{Phen})(\text{H}_2\text{O})]\text{NO}_3\cdot 9\text{H}_2\text{O}$  and (G)  $[\text{La}(\text{Acec})(\text{Phen})(\text{H}_2\text{O})_2]\text{Cl}_2\cdot 9\text{H}_2\text{O}$ .

| A          | B         | C         | D         | E         | F         | G         | Assignments                                   |
|------------|-----------|-----------|-----------|-----------|-----------|-----------|---|
| 2.50, 2.51 | -         | 2.51      | 2.51      | 1.75-2.52 | 1.92-2.51 | 1.91-2.51 | $\delta\text{H}$ , -NH                        |
| 3.37-4.65  | -         | 3.32-3.64 | 3.17-3.65 | 3.18-3.65 | 3.40-3.65 | 3.40-3.62 | $\delta\text{H}$ , -CH <sub>2</sub> aliphatic |
| -          | -         | 3.80-3.88 | 3.81      | 3.82      | 3.82-3.90 | 3.79-3.93 | $\delta\text{H}$ , H <sub>2</sub> O           |
| 6.27-7.54  | 7.26-8.81 | 6.24-7.72 | 6.24-7.54 | 6.25-9.13 | 6.25-9.12 | 6.21-9.24 | $\delta\text{H}$ , -CH aromatic               |
| 13.11      | -         | -         | -         | -         | -         | -         | $\delta\text{H}$ , -COOH                      |

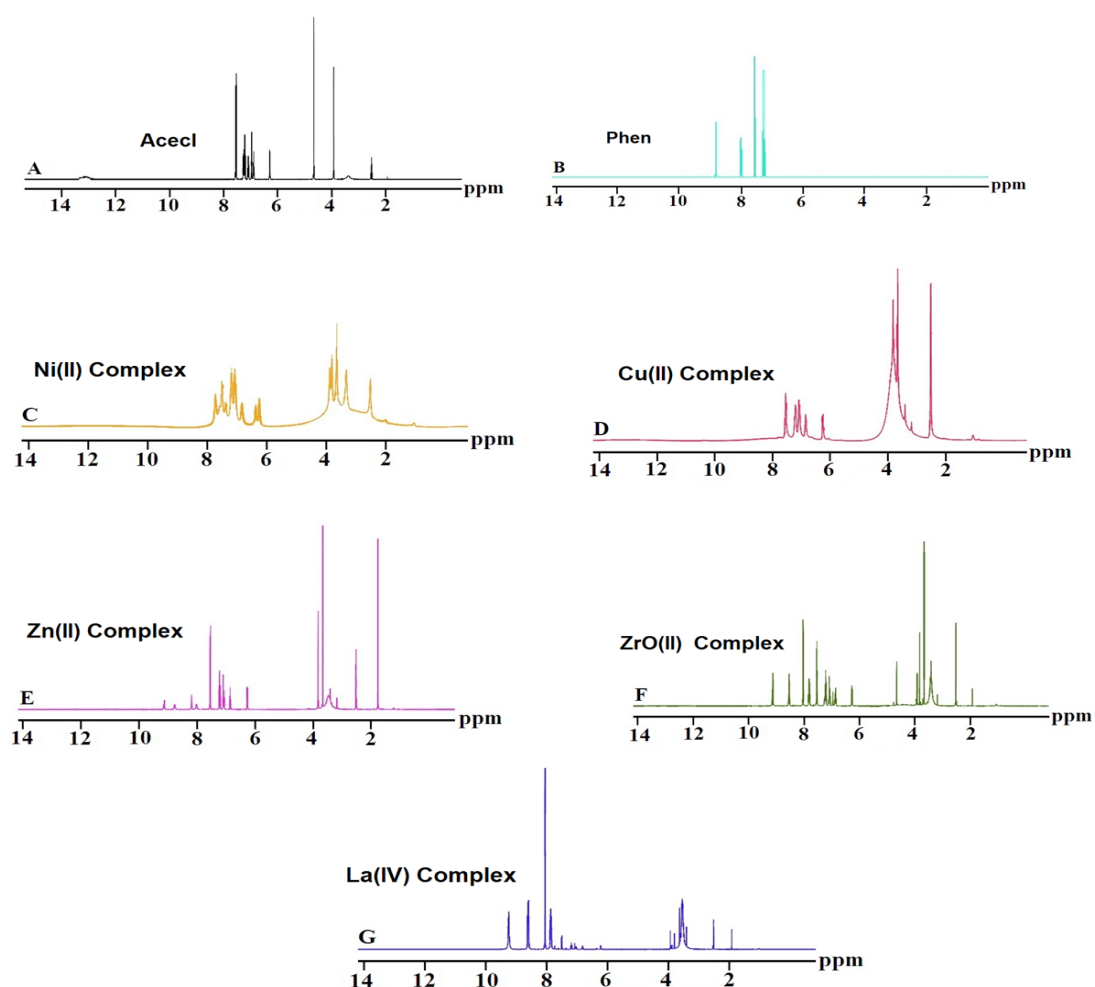


Fig. 3.  $^1\text{H}$  NMR spectra for (A) Acecl, (B) Phen, (C)  $[\text{Ni}(\text{Acec})(\text{Phen})(\text{H}_2\text{O})_2]\text{CH}_3\text{COO}\cdot 3\text{H}_2\text{O}$ , (D)  $[\text{Cu}(\text{Acec})(\text{Phen})(\text{H}_2\text{O})_2]\text{CH}_3\text{COO}\cdot 6\text{H}_2\text{O}$ , (E)  $[\text{Zn}(\text{Acec})(\text{Phen})(\text{H}_2\text{O})_2]\text{CH}_3\text{COO}\cdot 3\text{H}_2\text{O}$ , (F)  $[\text{ZrO}(\text{Acec})(\text{Phen})(\text{H}_2\text{O})]\text{NO}_3\cdot 9\text{H}_2\text{O}$  and (G)  $[\text{La}(\text{Acec})(\text{Phen})(\text{H}_2\text{O})_2]\text{Cl}_2\cdot 9\text{H}_2\text{O}$ .



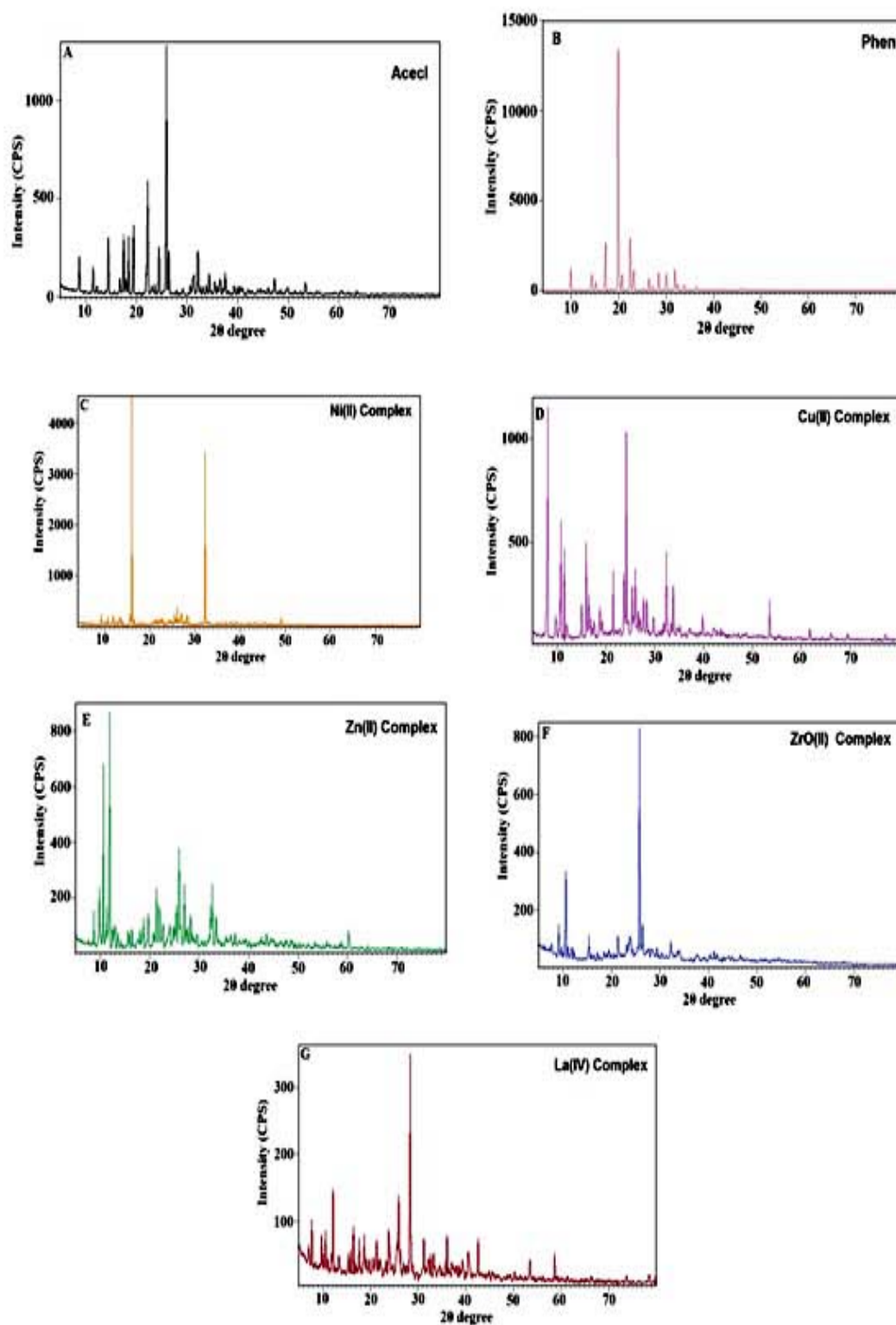


Fig. 4. Powder XRD pattern for (A) Acecl, (B) Phen, (C)  $[\text{Ni}(\text{Acecl})(\text{Phen})(\text{H}_2\text{O})_2]\text{CH}_3\text{COO}\cdot 3\text{H}_2\text{O}$ , (D)  $[\text{Cu}(\text{Acecl})(\text{Phen})(\text{H}_2\text{O})_2]\text{CH}_3\text{COO}\cdot 6\text{H}_2\text{O}$ , (E)  $[\text{Zn}(\text{Acecl})(\text{Phen})(\text{H}_2\text{O})_2]\text{CH}_3\text{COO}\cdot 3\text{H}_2\text{O}$ , (F)  $[\text{ZrO}(\text{Acecl})(\text{Phen})(\text{H}_2\text{O})]\text{NO}_3\cdot 9\text{H}_2\text{O}$  and (G)  $[\text{La}(\text{Acecl})(\text{Phen})(\text{H}_2\text{O})_2]\text{Cl}_2\cdot 9\text{H}_2\text{O}$ .

**TABLE 5.** The average crystallite size of Acecl, Phen and thier complexes estimated from XRD pattern.

| Compounds  | 2 $\theta$ (°) | d value (Å°) | Relative intensity (%) | Full width at half maximum (FWHM) <sup>a</sup> | Average crystallite size (nm) |
|--|----------------|--------------|------------------------|--|-------------------------------|
| Acecl  | 25.96          | 3.43         | 100                    | 0.074  | 37.59                         |
| Phen   | 19.87          | 4.47         | 100                    | 0.217  | 38.93                         |
| [Ni(Acecl)(Phen)(H <sub>2</sub> O) <sub>2</sub> ]CH <sub>3</sub> COO.3H <sub>2</sub> O | 15.99          | 5.54         | 100                    | 0.186  | 60.06                         |
| [Cu(Acecl)(Phen)(H <sub>2</sub> O) <sub>2</sub> ]CH <sub>3</sub> COO.6H <sub>2</sub> O | 8.09           | 10.93        | 100                    | 0.151  | 117.85                        |
| [Zn(Acecl)(Phen)(H <sub>2</sub> O) <sub>2</sub> ]CH <sub>3</sub> COO.3H <sub>2</sub> O | 11.88          | 7.45         | 100                    | 0.115  | 16.61                         |
| [ZrO(Acecl)(Phen)(H <sub>2</sub> O)]NO <sub>3</sub> .9H <sub>2</sub> O                 | 25.80          | 3.45         | 100                    | 0.065  | 37.81                         |
| [La(Acecl)(Phen)(H <sub>2</sub> O) <sub>2</sub> ]Cl <sub>2</sub> .9H <sub>2</sub> O    | 28.39          | 3.14         | 100                    | 0.092  | 34.55                         |

<sup>a</sup>The maximum diffraction patterns according to the highest value of intensity.

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## تخليق وتحليل طيفي وحراري وحيود الأشعة السينية لبعض المتراكبات الجديدة الناتجة من تفاعل الاسكلوفيناك في وجود ١٠,١ فينانثورلين

صديق عطية صديق<sup>١</sup>، سها فهيم محمد السيد<sup>١</sup> و نهاد راشد غالب<sup>٢</sup>  
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يهدف هذا البحث الى تحضير خمسة متراكبات لعقار الاسكلوفيناك في وجود ١٠,١ فينانثورلين احدى ماء التبلور يتفاعل مع بعض العناصر الإنتقالية مثل النيكل الثنائي، النحاس الثنائي، الزنك الثنائي، الزركونيوم الرباعي و اللانثانوم الرباعي بنسبة ١:١:١ (الاسكلوفيناك: ١٠,١ فينانثورلين: أيون معدني) في وجود وسط قاعدي مثل هيدروكسيد البوتاسيوم. وقد أفردت الدراسات الطيفية أن الاسكلوفيناك قد تتفاعل كثنائي العطاء من خلال ذرة الأكسجين لمجموعة الكيتون وإحدى ذرتي الأكسجين لمجموعة الكربوكسيل. وأيضاً ١٠,١ فينانثورلين يتفاعل كثنائي العطاء من خلال ذرتي النتروجين لحلقتي البيريدن.