Structures and properties of three new homobinuclear nanosized supramolecular copper coordination polymers derived from carboxylate type ligands and benzimidazole

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Three new homobinuclear nanosized supramolecular copper coordination polymers are hydrothermally synthesized by self-assembly reaction of L-tyrosine (Tyr), terephthalic acid (H\textsubscript{2}bdc), pyromellitic acid (H\textsubscript{4}btec) and benzimidazole (Hbzim) with copper chloride salt to generate with formula \([\text{[Cu}_2\text{(tyr)}_2\text{(bzim)}_2\text{(Cl)}_2\text{(H}_2\text{O)}_2]\text{]}_n\) \textsuperscript{1}, \([\text{[Cu}_2\text{(bdc)}_2\text{(bzim)}_2\text{(H}_2\text{O)}_6]\text{]}_n\text{.3H}_2\text{O}\text{]}_n\) \textsuperscript{2} and \([\text{[Cu}_2\text{(H}_2\text{btec})(\text{bzim})(\text{H}_2\text{O})_8].2\text{H}_2\text{O}\text{]}_n\) \textsuperscript{3}, which have been investigated by elemental analysis, molar conductivity and magnetic measurements, FT-IR and UV-Vis spectroscopy, (TGA/DTA) thermal analysis and X-ray powder diffraction(XRPD) analysis as well as MM2 theoretical calculations. The magnetic moment and electronic spectra of the complexes are certainly indicating the octahedral geometries. Thermal analysis of the complexes confirms the suggested structures and thermal stability. The results of the XRPD analysis and the average nanosized values of the complexes have nanosized supramolecular polymers in the triclinic system. The MM2 theoretical calculations are supported by the proposed structures.

Introduction

Supramolecular chemistry is one of the most promising areas of research in chemistry\cite{1, 2}, because of the wide variety of compounds structural topologies and their various applications as optic, electronic and magnetic devices or microporous materials and antimicrobial activity\cite{1-3}. The design and synthesis of supramolecular coordination polymeric networks have been receiving much attention recently, and the hydrogen bonding and \(\pi\)-\(\pi\)-stacking interactions are often employed in their construction, such rational design based on covalent or supramolecular contacts is a key part of self-assembly supramolecular chemistry\cite{4-6}. One synthetic strategy for the synthesis of the supramolecular coordination polymers is the controlled assembly of donor and acceptor building blocks\cite{7-9}. The Organic aromatic polycarboxylate ligands based on a variety of
carboxylate binding modes have been used to create coordination polymers of different dimensionality in this structurally rich system 1D polymeric chains, 2D polymeric sheets, and 3D polymeric networks with a variety of metal ions reported in the literature[10, 11]. Additionally, the assembly of organic aromatic polycarboxylate and the transition metal ions is highly influenced by the multitopic organic spacer ligands, careful selection of the pH value, solvent system, temperature, counter anions, and metal-to-ligand ratio as well as the coordination nature of the metal ions[12]. All these factors have a significant effect on the formation of desirable frameworks[13, 14]. The benzimidazole as a bidentate ligand is well-known that excellent building blocks in the construction and structural tuning of the resultant MOFs[15, 16]. The L-tyrosine is an amino acid that plays an important role in human life and its pharmacological importance[17, 18]. Supramolecular coordination polymers based on the mixed-ligand systems containing O-donor carboxylates and N-donor heterocyclic ligands have been obtained[19-22]. For example, Wang team have obtained two Co(II) coordination polymers [Co(bdc)(bib)(H2O)]n (1) and [Co(bdc)(bibp)]n (2), where H2bdc = 1,4-benzenedicarboxylic acid, bib = 1,4-bis(1-imidazolyl)benzene, and bibp = 4,4’-bis(imidazolyl)biphenyl[23]. H. Lin team, have reported four Cu(II) and Co(II) coordination polymers [Cu(L)(bdc)(H2O)]·3H2O (1), [Cu(L)(dnba)]2 (2), [Co(L)2(dnba)]2 (3), and [Co(L)(npiph)(H2O)]·H2O (4), where H2bdc =1,4-benzenedicarboxylic acid, Hdnba = 3,5-dinitrobenzoic acid, H2npiph =5-nitroisophthalic acid and L =N,N-di(3-pyridyl)sebacic diamide[24]. In our study, we focus on assembly reactions of the benzimidazole and copper (II) via hydrothermal synthetic methods with aromatic carboxylate ligands (L-tyr, H2bdc, H4btec) to form new homobinuclear nanosized supramolecular copper coordination polymer complexes and described by elemental analysis, molar conductivity, FT-IR and UV-Vis spectra, magnetic susceptibility, TGA/DTA and XRPD analysis as well as MM2 theoretical calculations to elucidate suggested structures as seen here later and influences the aromatic carboxylates, benzimidazole, and copper ion on the structures.

Experimental Section

Chemicals: All the chemicals were obtained from analytical reagent grade (BDH, Aldrich or Fluka).

Preparation of the polymer complexes: The complexes were synthesized by addition of L-tyrosine (0.362 g, 2 mmol / 10 ml) and terephthalic acid (0.332 g, 2 mmol / 10 ml) and pyromellitic acid (0.254 g, 1 mmol / 10 ml) dissolved in a minimum amount of water containing KOH (0.16 mmol / 20 ml) to benzimidazole (0.236 g, 2 mmol / 10 ml) in complexes 1-2 and (0.118 g, 1 mmol / 10 ml) in complex 3, with an aqueous solution of
appropriate CuCl₂. 2H₂O (0.34 g, 2 mmol / 10 ml) was added with constant stirring and refluxed for 30 min on magnetic stirrer at 25°C (pH= 6.5). The solid product was collected by vacuum filtration, washed several times with cold water, ethanol and anhydrous ether and dried over P₂O₅ in a desiccator vacuum for 24 hours.

**Molecular Mechanics (MM2) calculations:**
The potential energy of all systems in molecular mechanics is calculated using force fields[25]. The optimized geometry, steric energy, and MM2 calculated of the L–tyrosine, terephthalic acid and pyromellitic acid and their complexes were done using the CsChem3D Ultra program package[26].

**Physical measurements:** Stoichiometric analysis (C, H, N, S) was performed using AnalyischerFunktionstestVario El Fab-Nr.11982027 elemental analyzer. The IR spectra were recorded on a Shimadzu IR-470 spectrophotometer and the electronic spectra were obtained using a Shimadzu UV-2101 PC spectrophotometer. The Thermogravimetric analysis was carried out on a 2000 DuPont thermal analyzer at a heating rate of 10 °C min⁻¹. Magnetic moments were measured at room temperature using a magnetic susceptibility balance of type MSB-Auto. Molar susceptibilities were corrected for diamagnetism of the component atoms by the use of Pascal’s constants. The calibrate used to be Hg [Co (SCN)₄]. The X-ray crystallography data were collected using Oxford Gemini Diffractometer at 25°C and Cu-Kα radiation (λ=1.54 Å). The crystal structure was analyzed with the aid of computer software such as Peakfit and Chekcell programs[27, 28].

**Results and Discussion**

**Syntheses and description of the structures:**
The self-assembly reaction some carboxylates such as tyrosinate and terephthalate and pyromellitate with copper ion and benzimidazole to generate new homobinuclear nanosized supramolecular copper coordination polymer complexes are seen in Figures (1 and 2).

![Figure 1. The components of complexes](image)

Based on the physical properties, FT-IR data, UV–Vis data, thermal decomposition data, thermodynamic parameters, and TGA/DTA curves, the three suggested structures of the homobinuclear copper coordination complexes can be represented as follows in Figure (2).

![Complex 1](image)
The suggested structures of the prepared complexes.

In the suggested structures are seen in Figure (2), the complexes possess an octahedral geometry. In the structure complex 1, the benzimidazole gives a new type of coordination mode, it acts as bidentate bridge ligand to leading one-dimensional chain with copper (II) tyrosinate complex. In the structure complex 2 and 3, the H$_2$bdc and H$_4$btec ligands have an important influence on structures, attributed to differences in substituent groups positions of carboxylic groups and numbers of the carboxylic groups and positions copper ions. The suggested structures of the complexes exhibit may be supramolecular coordination polymer structures through hydrogen bonding interactions involving the constituent materials which enhance the stability of these complexes[29, 30]. The hydrogen bond affording the possibility of participation in intermolecular and/or intramolecular hydrogen bonding interactions. The hydrogen-bonding interactions, the first type is O-H..O hydrogen bonds in the presence of many uncoordinated water molecules are connected between the hydrogen atoms and carboxylate oxygen atoms in intramolecular, the second type is O...H-O hydrogen bonds exist of the coordinated water molecules are connected between the hydrogen atoms and carboxylate oxygen atoms intramolecular, the third type is O...H-O hydrogen bonds, inter-sheet maybe contacted are strengthened by π-π* interactions, and three hydrogen bond types are importing factor in the supramolecular assembly and stability of these complexes and also maybe act to hold the chains together within the 3D architecture[31-33].

**Conductivity measurement:** The coordination polymer complexes showed values at 13.78, 15.69 and 36.80 ohm$^{-1}$cm$^{-2}$ mol$^{-1}$ listed in Table 1, indicating non-electrolyte in DMSO[34]. These results are common with supramolecular polymers and coordination polymers, these complexes are insoluble in common solvents such as methanol, water, and acetonitrile but soluble in N,N-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).
Table 1. Physical properties of coordination polymer complexes

| Complexes | Color     | $\Lambda M$ ohm$^{-1}$ cm2mol$^{-1}$ | M.P ($^\circ$C) (Decomp.) | % Analysis, found (calced) |
|-----------|-----------|-------------------------------------|---------------------------|-----------------------------|
|           |           |                                     |                           | C%  | H%   | N%    | $\mu_{eff}$  |
|           |           |                                     |                           | (%) | (%)  | (%)   | (B.M)       |
| 1         | Dark -blue| 13.78                               | >320                      | 47.54 | 5.16 | 10.24 | 1.72        |
|           |           |                                     |                           | (46.15) | (4.37) | (10.95) |             |
| 2         | Dark - blue| 15.69                              | >320                      | 45.45 | 5.81 | 7.14  | 1.67        |
|           |           |                                     |                           | (44.82) | (6.12) | (6.33) |             |
| 3         | Dark -blue| 36.80                               | >360                      | 44.65 | 4.78 | 9.29  | 1.87        |
|           |           |                                     |                           | (43.67) | (4.28) | (8.49) |             |

IR spectra and mode of bonding:

From the FT-IR spectra, there are some bands appeared in the polymer complexes spectra which are attributed to M-O and M-N, these two bands confirm the complexes formation. The $\nu$(C=N) band of the benzimidazole occurs at 1470, 1480 and 1490 cm$^{-1}$[35]. In the free L-tyr ligand the bands of $\nu_{as}$(COO) and $\nu_{s}$(COO) located about 1612 and 1416 cm$^{-1}$, respectively, a notable shift to a lower frequency at 1605 and 1390 cm$^{-1}$, due to the $\nu_{as}$(COO) and $\nu_{s}$(COO), respectively, in the complex 1 as in Figure(3), the separation ($\Delta \nu$=215 cm$^{-1}$), indicates that the tyrosinate behaved as bidentate fashion[36].

Figure 3. FT-IR Spectrum of the copper polymer complex 1

In the FT-IR spectrum comparison of the free H2bdc ligand with complex 2, as in Figure(4). In the ligand, the band exhibit at 1680 cm$^{-1}$ is ascribed to $\nu_{as}$(COO) and 1420 cm$^{-1}$ is attributed to the $\nu_{s}$(COO), whereas these bands shifted to a lower frequency in the complex 2 at 1575 cm$^{-1}$ and 1380 cm$^{-1}$, respectively. In the complex 2, as in Figure(4), the separation $\Delta \nu$=195 cm$^{-1}$ typical indicates a monodentate fashion.[37, 38]
Figure 4. FT-IR Spectrum of the copper polymer complex 2
In the FT-IR spectrum comparison of the free H₄btec ligand with complex 3, as in Figure (5). The absence of any strong bands around 1720 cm⁻¹ indicates that all carboxylic groups are deprotonated. In the ligand, the bands of νₐs(COO) and νₐ(COO) exhibits at 1500 and 1380 cm⁻¹, respectively, these bands shifted to a higher frequency in the complex-3 at 1580 cm⁻¹ and 1390 cm⁻¹. In the complex 3, as in Figure(5), the separation (Δν = 190 cm⁻¹) value proved that the carboxylate group is coordinated to the copper ion in a monodentate fashion.[39-41]

The ν(O–H) stretching vibration of coordinated water for the complexes 2 and 3 are located at 2900 and 2900 cm⁻¹[42], whereas the ν(O–H) of the uncoordinated water of the complexes are assigned to the bands in the 3600, 3450 and 3400 cm⁻¹[43]. The most important bands which appeared in the 550, 520 and 540 due to ν(M–O) and 450, 480 and 450 cm⁻¹ due to ν(M–N), these bands confirm the complexes formation and represent further evidence for the coordination of the ligands through both nitrogen and oxygen atoms.

UV-Vis spectra and magnetic susceptibility measurement: The FT-IR spectra were recorded on a Shimadzu IR-470 The electronic spectra of the coordination polymer complexes were recorded in DMSO and in Figure (6). The third band for complexes appearing at 18466, 18726 and 18832 cm⁻¹, respectively, which may be assigned to the ²Eg→²T₂g transition indicating octahedral geometry around copper ion,[44] and showed magnetic properties with μeff values of 1.72, 1.67 and 1.87 B.M, respectively, listed in Table 1. The low values due to weak antiferromagnetic interaction because of the long distance between the two magnetic copper centers with homobinuclear complexes. The suggested structures of these complexes are shown in Figure (2).

Figure 5. FT-IR Spectrum of the copper polymer complex 3
Thermogravimetric analysis: The thermal stability of the coordination polymer complexes was investigated by TGA/DTA in the air flow in the Tables 2-4 and the structures are observed in the TGA/DTA spectra in Figures (7-9)[45].

Thermal decomposition: The thermal decomposition of the polymer complex 1 \([[[\text{Cu}_2\text{tyr}]_2(\text{bzim})_2(\text{Cl})_2(\text{H}_2\text{O})_2]]_n\), from 31-482°C listed in Table 2 and TGA/DTA spectra is shown in Figure (7), it decomposes in three steps, the initial weight loss occurring in the range 31–209°C, with the release of two coordinate water molecules (calc. 4.32 %, found 3.62 %) and it is connected with an activation energy of 36.49 kJ/mol. The DTG curve exhibits a peak at 50°C and an exothermic DTA curve gives a peak at 52°C. The second step of decomposition in the range 210-283°C (calc. 14.18 %, found 13.85 %) corresponds to the loss of the one bzim ligand and activation energy of 114.73 kJ/mol. The DTG curve exhibits midpoint at 249°C, which is associated with an exothermic DTA curve that gives a peak at 253°C. The third is composed of three overlapping steps of mass loss in the range 284–482°C (calc. 50.13 %, found 51.84 %) corresponds to the loss of the Tyr and bzim ligands from the anhydrous complex, a three DTG curve exhibits peaks at 289, 357 and 403°C and the exothermic DTA curve gives three peaks at 290, 358 and 405°C are observed. The corresponding activation energy amounts to 192.21 KJ/mol. After this, the complex decomposes continuously till 482 °C, the decomposition mechanisms proposed for the copper complex are summarized by equation 1:

**Figure 6.** UV-Vis spectrum of the copper polymer complexes


\[
\left[ \text{Cu}_2(\text{tyr})_2(bzim)_2(\text{Cl})_2(H_2O)_2 \right]_n \xrightarrow{31 - 209^\circ C} \left[ \text{Cu}_2(\text{tyr})_2(bzim)_2(\text{Cl})_2 \right]_n \xrightarrow{-2H_2O} \left[ \text{Cu}_2(\text{tyr})_2(bzim)_2(\text{Cl})_2 \right]_n \xrightarrow{210 - 283^\circ C} \left[ \text{Cu}_2(\text{tyr})_2(bzim)_2(\text{Cl})_2 \right]_n \xrightarrow{284 - 482^\circ C} \left[ \text{Cu}_2(\text{tyr})_2(bzim)_2(\text{Cl})_2 \right]_n \xrightarrow{-bzim + tyr} \left[ \text{Cu}_2(\text{tyr})_2(bzim)_2(\text{Cl})_2 \right]_n \xrightarrow{After 741^\circ C} \left[ \text{Cu}_2(\text{tyr})_2(bzim)_2(\text{Cl})_2 \right]_n \xrightarrow{Complex decomposes continuously} (1)
\]

Figure 7. TGA – DTA - DrTGA curves of complex 1

Table 2. Thermal decomposition data of complex 1

| Step | Temp. range(°C) | Weight loss (%) | Assignment | DTG (°C) | DTA (°C) |
|------|----------------|----------------|------------|----------|----------|
|      | Found          | Calc           |            |          |          |
| 1st  | 31–209         | 3.62- 4.32     | Loss of two coordinated water molecules | 50 | 52 |
| 2nd  | 210-283        | 14.85- 14.18   | Loss of the one bzim ligand             | 249 | 253 |
| 3rd  | 284–482        | 51.84 -50.13   | Loss of the tyr and bzim ligands        | 289, 357, 403 | 290, 358, 405 |

The thermal decomposition of the polymer complex [[Cu2(bdc)2(bzim)2(H2O)6].3H2O]n, from 31-748°C listed in the Table 3 and TGA/DTA spectra, is shown in Figure (8), the first is composed of two overlapping steps of mass loss occurring in the range 31-171°C, (calc. 6.29 %, found 5.87 %)with the elimination of three uncoordinated water molecules and the corresponding activation energy of 179.06KJ/mol, the DTG curve exhibits two peaks at 79 and 113°C and an endothermic DTA curve gives two peaks at 82 and 126°C. The second step is composed of three overlapping steps of mass loss in the range 172-308°C and (calc. 12.59 %, found 12.18 %) corresponds to the loss of the six-coordinate water molecules with an activation energy of 104.23 kJ/mol. A DTG curve exhibits three peaks at 135, 190 and 242°C and the exothermic DTA curve gives two peaks at 136 and 289°C and DTA curve gives peak an endothermic 191°C and exothermic, were observed. The third step is decomposed in the range 309-421°C (Calc. 33.14 %, found 32.77 %) corresponds to the loss of the bdc and bzim ligands, the computed activation energy amounts
to 160.51 kJ/mol. A DTG curve exhibits a peak at 385°C and the exothermic DTA curve gives a peak at 392°C, were observed. The fourth step is composed of two overlapping steps of mass loss in the range 422–748°C (calc. 33.14 %, found 32.54 %) indicates decomposition of the bdc and bzim ligands and activation energy amounts to 206.99 kJ/mol. The DTG curve exhibits two peaks at 476 and 529°C and exothermic two DTA curves give peaks at 475 and 535°C. The final product indicates that the residue is 2CuO (Calc. 18.54 %, found 16.74 %), the decomposition mechanisms proposed for copper complex 2 are summarized by equation 2:

\[
[Cu_2(bdc)_2(bzim)_2(Cl)_2(H_2O)_6 \cdot 3H_2O]_n \frac{31 - 308^\circ C}{9H_2O} \to [Cu_2(bdc)_2(bzim)_2] \frac{309 - 421^\circ C}{bdc + bzim} \\
\to [Cu_2(bdc)(bzim)] \frac{422 - 748^\circ C}{bdc + bzim} \to 2CuO + Decomposition products \ (2)
\]

The thermal decomposition of the polymer complex 3 \([Cu_2(H_2btec)(bzim)(H_2O)_6 \cdot 2H_2O]n\), from 28-747 °C listed in Table 4 and TGA/DTA spectra is shown in Figure (9), its decompose in four steps, the initial weight loss release of two uncoordinated water molecules (calc. 5.62 %,
found 5.56 %) in the range 28–80 °C, this step has an activation energy value of 58.63 kJ/mol. The DTG curve exhibits a peak at 54 °C and the endothermic DTA curve gives a peak at 66 °C. The second step is composed of three overlapping steps of mass loss (calc. 16.36 %, found 17.74 %), corresponds to the loss of the six coordinated water molecules in the range 81–257 °C, the DTG curve exhibits three peaks at 98, 132 and 232°C and an endothermic DTA curve gives three peaks at 102, 136 and 225°C, are observed. It is connected with an activation energy of 184.54 kJ/mol. The third step of decomposition in the range 258–456°C (calc. 20.12 %, found 19.55 %), corresponds to the loss of the one bzm ligand, a DTG curve exhibits a peak at 332°C and the exothermic DTA curve gives a peak at 297°C, are observed. The corresponding activation energy amounts to 113.81 KJ/mol. The fourth step is composed of three overlapping steps of mass loss (calc. 39.31 %, found 40.19 %) corresponds to the loss of the one btec ligand in the range 457–747 °C, a DTG curve exhibits three peaks at 550, 652 and 685°C and the endothermic DTA curve give peaks at 557 and 690°C, exothermic DTA peak 660°C, are observed. The corresponding activation energy amounts to 322.43KJ/mol. The final product indicates that the residue is 2CuO (calc. 24.68 %, found 22.5 %), the decomposition mechanisms proposed for copper complex 3 are summarized by equation 3:

\[
[Cu_2(btec)(bzm)(H_2O)_6 \cdot 2H_2O]_n \rightarrow [Cu_2(btec)(bzm)]^{28 - 257°C} \rightarrow [Cu_2(btec)]^{258 - 456°C} \rightarrow \frac{457 - 747°C}{btec} \rightarrow 2CuO + \text{Decomposition products} \quad (3)
\]

Table 4. Thermal decomposition data of complex 3

| Step | Temp. Range (°C) | Weight loss (%) | Assignment | DTG (°C) | DTA (°C) |
|------|------------------|-----------------|------------|----------|----------|
|      |                  | Found    Calc   |            |          |          |
| 1st  | 28-80            | 5.56 – 5.62    | Loss of two uncoordinated water molecules | 54       | 66       |
| 2nd  | 81–257           | 17.74 – 16.36  | Loss of six coordinate water molecules | 98, 132, 232 | 102, 136, 225 |
| 3rd  | 258–456          | 19.55 – 20.12  | Loss of the one bzm ligand | 332      | 297      |
| 4th  | 457–747          | 40.19 – 39.31  | Loss of the btec ligand | 550, 652, 685 | 557, 660, 690 |
Figure 9. TGA-DTA-DrTGA curves of the polymer complex-3

Kinetic analysis: The order of the reaction (n), activation energy (E) and the pre-exponential factor (Z) of the different stages of thermal decomposition reactions for the first dehydration step have been evaluated from the TGA curve by using Coats–Redfern equations 4 and 5 and Horowitz-Metzger equations 6 and 7. [46-48]

The plot of

$$\ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{(1 - n)} \right] = \frac{M}{T} + B$$

for \( n \neq 1 \) \hspace{1cm} (4)

or

$$\ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{(1 - n)} \right] = \ln \left[ \frac{ZRT_s^2}{\Phi E} \right] - \frac{E}{RT_s} + \frac{E \theta}{RT_s^2}$$

for \( n \neq 1 \) \hspace{1cm} (5)

where \( \alpha \) is the fraction of material decomposed, \( n \) is the order of the decomposition reaction and \( M=E/R \) and \( B=ZR/\Phi E \); \( E, R, Z \) and \( \Phi \) are the activation energy, gas constant, pre-exponential factor and heating rate, respectively. The plot of

$$\ln \left[ \frac{1 - (1 - \alpha)^{1-n}}{(1 - n)} \right] = \ln \left[ \frac{ZRT_s^2}{\Phi E} \right] - \frac{E}{RT_s} + \frac{E \theta}{RT_s^2}$$

for \( n \neq 1 \) \hspace{1cm} (6)

$$\ln \frac{E}{RT_s} = \ln \frac{Z}{\Phi} - \frac{E}{RT_s}$$

for \( n \neq 1 \) \hspace{1cm} (7)

where \( \theta=T-T_s \), \( T_s \) is the temperature at the peak of DTG. The change in the activation enthalpy \( \Delta H \), activation entropy \( \Delta S \) and the free energy of activation \( \Delta G \) were calculated and listed in Tables 5 and 6. The negative value of entropy also indicates that the activated complexes have a more ordered and more rigid structure than the reactants or intermediates.

| Comp. | Step | \( n \) | \( r \) | \( \Delta E \) | \( Z \) | \( \Delta H \) | \( -\Delta S \) | \( \Delta G \) |
|-------|------|--------|--------|----------|------|---------|---------|--------|
|       | 1st  | 1.00   | -0.99944 | 36.49 | 3.04 x10⁵ | 32.74 | 0.15172 | 101.34 |
|       | 2nd  | 0.00   | -0.99941 | 114.73 | 2.44 x10⁴ | 110.39 | 0.2695 | 251.21 |
|       | 3rd  | 0.00   | -0.99983 | 192.21 | 2.46 x10⁵ | 186.96 | 0.34766 | 406.17 |
|       | 1st  | 2.00   | -0.99998 | 179.06 | 7.12 x10⁻¹⁷ | 176.35 | 0.563075 | 359.73 |
|       | 2nd  | 2.00   | -0.98250 | 104.23 | 3.38 x10⁻² | 100.38 | 0.285043 | 232.35 |
|       | 3rd  | 2.00   | -0.99935 | 160.51 | 2.23 x10⁶ | 156.23 | 0.36595 | 344.68 |
|       | 4th  | 2.00   | -0.99749 | 206.99 | 4.25 x10⁶ | 201.52 | 0.36263 | 440.14 |
|       | 1st  | 2.00   | -0.97756 | 58.63 | 6.43283 | 55.91 | 0.23851 | 133.84 |
|       | 2nd  | 2.00   | -0.9802 | 184.54 | 3.6 x10⁶ | 181.46 | 0.55068 | 385.80 |
|       | 3rd  | 2.00   | -0.97752 | 113.81 | 9.19404 | 108.77 | 0.24068 | 254.7 |
|       | 4th  | 2.00   | -0.99112 | 322.43 | 1.07 x10⁹ | 315.59 | 0.43338 | 672.27 |
Table 6. Kinetic and thermodynamic parameters of the complexes in dynamic air atmosphere (Horowitz-Metzger)

| Comp. | Step | n   | r    | ΔE       | Z          | ΔH   | -ΔS | ΔG    |
|-------|------|-----|------|----------|------------|------|-----|-------|
| 1     | 1st  | 1.00| 0.99991 | 43.21 | 4.42 x10⁴ | 39.45 | 0.15943 | 111.54 |
|       | 2nd  | 0.00| -0.99592 | 123.52 | 6.36x10¹¹ | 119.18 | 0.02360 | 131.49 |
|       | 3rd  | 0.00| -0.99546 | 202.39 | 1.6x10¹⁶ | 197.15 | 0.05908 | 234.41 |
| 2     | 1st  | 2.00| 0.999998 | 184.69 | 4.57x10²⁷ | 181.76 | 0.28320 | 281.64 |
|       | 2nd  | 2.00| 0.983927 | 111.84 | 3.6x10¹² | 107.99 | 0.00820 | 111.79 |
|       | 3rd  | 2.00| 0.99925 | 169.05 | 1.29x10¹⁷ | 164.77 | 0.07812 | 205.01 |
|       | 4th  | 2.00| 0.99749 | 217.89 | 1.12x10¹⁷ | 212.42 | 0.07492 | 261.72 |
| 3     | 1st  | 0.00| 0.981663 | 64.23 | 6.66x10⁹ | 61.52 | 0.0576 | 80.34 |
|       | 2nd  | 2.00| 0.98114 | 190.51 | 9.74x10²⁶ | 187.42 | 0.26993 | 287.58 |
|       | 3rd  | 2.00| 0.99667 | 126.08 | 2.55x10¹⁰ | 121.04 | 0.05156 | 152.30 |
|       | 4th  | 2.00| 0.99172 | 336.12 | 1.08x10²¹ | 329.28 | 0.14931 | 452.17 |

The large negative entropy of activation and high free energy of activation denote a slow reaction and consequently stable complexes[49]. The high values of the activation energies, reflect the thermal stability of the complexes[50, 51]. The values of ΔG increase for the subsequent decomposition steps reflects that the rate of removal of the subsequent ligand will be lower than that of the preceding ligand due to the structural rigidity of the remaining copper polymer complex after the expulsion of one ligand and more ligand removal will require more energy for its rearrangement before undergoing any compositional change[44, 52, 53]. Based on the information gained from the above results, the suggested structures of these complexes can be seen in Figure (2).

**X-ray powder diffraction:** The X-ray powder diffraction patterns of the three copper coordination polymer complexes are shown in Figure (10). There are many computer codes that have been used to analyze the X-ray line profile. We have used the residual-peak fitting (PeakFit) software. This program helps to detect, separate, quantify hidden peaks that standard instrumentation misses and background correction. PeakFit also includes different nonlinear spectral application line shapes. There are three AutoFit peaks options offered by PeakFit software[27]. We have selected one of these options. In this option, the hidden peaks are detected by the "sharpening" achieved by deconvolving a Gaussian instrument response to the raw data. The baseline is also fitted with a Gaussian deconvolution procedure. The fitting procedure also ensures a good convergence factor.

We have used the standard cell parameters for the three complexes[54] as starting values for “CHEKCELL” program to identify the Bragg reflections. CHEKCELL program is a powder Indexing software. The crystal lattice parameters were computed with the aid of the computer program Chekcell[28].
The unit cell parameters of the complexes are given in Table 7.

**Table 7. Unit cell parameters of the copper polymer complexes**

| Parameters            | Comp.1 | Comp.2 | Comp.3 |
|-----------------------|--------|--------|--------|
| Crystal system        | Triclinic | p1    |
| Space group           |         |        |
| \( a \) (Å)           | 10.010 | 9.432  | 9.453  |
| \( b \) (Å)           | 14.971 | 12.726 | 12.709 |
| \( c \) (Å)           | 21.875 | 17.575 | 17.578 |
| \( \alpha \) (°)      | 90.58  | 90.18  | 90.17  |
| \( \beta \) (°)       | 109.12 | 99.93  | 100.03 |
| \( \gamma \) (°)      | 90.05  | 90.17  | 90.26  |
| Volume of unit cell \((Å)^3\) | 3097.14 | 2077.87 | 2079.82 |

**Nanosized analysis:** From the indexed data, the unit cell parameters which calculated and recorded in Table (7). Furthermore, using the diffraction data, the mean crystallite sizes of the complexes, \( D \), were determined according to the Scherer equation: \( D = \frac{0.9\lambda}{(\beta\cos\theta)} \), where \( \lambda \) is X-ray wavelength (1.54056 Å), \( \theta \) is Bragg diffraction angle, and \( \beta \) is the full width at half maximum of the diffraction peak[55]. The average crystallite sizes of the three complexes were found to be 72.27 nm, 111.54 nm and 194.39 nm. The values indicate that complexes 2 and 3 are more crystalline than that complex 1. The Figure (10) show the crystalline nature of the three copper polymer complexes and the peak sharpness in the XRD patterns indicates the existence of the nanosized supramolecular polymers.

**Molecular modeling studies:** In order to get finer structural details of polymer complexes, we have optimized and MM2 calculated the
molecular structure of complexes[25]. Therefore, we could obtain the optimized geometry for each complex by competing for the minimum steric energy and the theoretical physical parameters, such as bond lengths and bond angles using the Chem3D Ultra program package. The optimized structures of these complexes in Figure (11) were some selected calculated parameters in the coordination sphere in Tables 8-10. In these complexes, coordination by chelation involving the various modes of oxygen, nitrogen and chloride are possible. The results reveal the presence of an octahedral geometry in the complexes. The reveals minimum steric energies values studied of four ligands and their complexes (7.75 kcal/mol for L-tyrosine, 20.63 kcal/mol for terephthalic acid, 80.9592 kcal/mol for pyromellitic acid and 9.62 kcal/mol for benzimidazole, 199.32 kcal/mol for complex 1, 223.83 kcal/mol for complex 2 and 230.32 kcal/mol for complex 3). MM2 calculated of complexes is in good agreement with proposed compositions of the complexes based on elemental analysis.

Conclusions

Based on the above analysis and spectroscopic evidence, magnetic data and MM2 theoretical studies, we hydrothermally synthesized of the new nanosized homobinuclear coordination polymer complexes and have octahedral geometry. From the FT-IR spectra of the complexes are completely deprotonated in these ligands proves very clearly that the complexes
are supramolecular coordination polymers. The suggested structures of complexes reveal that the carboxylates, benzimidazole, and copper ion have an influence on the structures. The FT-IR spectra of the complexes are completely deprotonated in these ligands proves very clearly that the complexes are supramolecular coordination polymers. Thermogravimetric analysis of the complexes showed thermal stability and suggested structures. In addition, the first step towards H$_2$O release is important in the TGA/DTA thermal analysis of the investigated of these complexes and it is usually regarded as participating in extensive structure hydrogen bonding because it is an important factor in the stabilization of lattice and supramolecular assemblies. The XRD patterns and average particle size values indicated the crystalline nature of the complexes and confirm the existence of the nanosized supramolecular polymers. The MM2 calculations were performed to obtain the theoretical information on the structures which was confirmed by the experimental results.

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