Research Article

Preparation and Characterization of Di-, Tri-, and Tetranuclear Schiff Base Complexes Derived from Diamines and 3,4-Dihydroxybenzaldehyde

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1. Introduction

Multinuclear transition metal complexes have become a central theme of current research because of their potentially useful properties. They are involved in some notable catalytic processes. Their important use for modelling the metal active sites of metalloproteins and their recent applications in the area of nanoscale materials have drawn the focal point of attraction of modern chemists towards the synthesis and characterization of such metal complexes [1]. A number of dinuclear complexes from various types of ligand systems have been prepared and examined in terms of their oxygen uptake or redox processes of oxygen, their catalytic activity, and their antibacterial and antifungal activities [2–4]. One of the synthetic strategies to prepare polynuclear transition metal complexes is the use of simple metal ion complexes which have the appropriate functionality to act as ligands for another metal ion [1]. There is currently a great deal of interest in the synthesis and characterization of polynuclear cobalt, nickel, and copper complexes due to their wide-ranging potential applications such as catalysts, electron transfer mediators in dye-sensitized solar cells, antiviral agents, and molecular nanomagnets [5]. Trinuclear cobalt complexes draw their speciality from their use as catalysts in epoxidation of olefins and in the autoxidation of hydrocarbons [1]. The presence of copper (II) ion in polynuclear complexes has received a wide interest in the fields of (i) the magnetostructural relationship, (ii) the characterization of active sites in multicopper proteins [5], and (iii) biological activity such as antitumor, antiviral, and anti-inflammatory [5]. Schiff bases derived from 3,4-dihydroxybenzaldehyde [3, 4] and diamines like ethylene diamine [5], 2,6-diaminopyridine [2], and 1,4-diaminobenzene [3, 4] represent an important series of chelating agents that have been used to synthesize mono-, di-, or polynuclear transition metal complexes [3–5] in which copper (II) complexes in particular represent models of physical and chemical behavior of biological copper systems that mimic copper metalloproteins such as hemocyanin.
and tyrosinase [2, 5]. Much attention has been paid to the synthesis and properties of molecules containing the copper (II) complex of 1,10-phenanthroline and 2,2’-bipyridyl units [2, 5–8] which are useful for applications in several fields.

For example, a π-conjugated polymer bearing 2,2’-bipyridyl units was found to serve as a unique electrically conducting polymer complex with transition metals such as Ru, Ni, and Fe [6–8]. Nickel (II) mixed ligand complexes involving an aromatic Schiff base and 1,10-phenanthroline showed higher cytotoxic activity than those of the individual ligands [7]. The copper (II) complex of 1,10-phenanthroline was the first synthetic transition metal complex effectively exhibiting nucleolytic activity [5]. In this work, we study for the first time the synthesis of di- and trinuclear copper (II) and cobalt(II) complexes as synthetic models for multicenter active sites of biological systems by following two methods. The first method (method 1) involves the reaction of metal salts with each of the following three new diSchiff base ligands: N,N’-bis(3,4-dihydroxybenzylidene)ethanediamine (EDH4) (Figure 2), N,N’-bis(3,4-dihydroxybenzylidene)benzene-1,2-diamine (PDH4) (Figure 3), and N,N’-bis(3,4-dihydroxybenzylidene)-4,5-dimethyl-1,2-diamine (MPDH4) (Figure 4) prepared from the condensation reaction of 3,4-dihydroxybenzaldehyde with ethylenediamine (en), o-phenylenediamine (o-PD), or 4,5-dimethyl-1,2-phenylenediamine (DMPD), respectively. The second method (method 2) involves the condensation reaction of mononuclear copper (II) mixed ligand complex of 3,4-dihydroxybenzaldehyde and 2,2’-bipyridyl (LCu(II)L’) (Figure 1) (L = 2,2’-bipyridyl, L’ = 4-formylbenzene-1,2-bis(olate)) with (en), o-PD, or DMPD followed by further reaction with the metal salts to form the tri- and tetrahomonuclear metal complexes.

The structures of the prepared compounds were elucidated depending on elemental analyses, UV-vis, NMR, and FTIR spectra as well as thermal analyses, atomic absorption, conductivity measurements, and magnetic susceptibility of metal complexes.

2. Experimental

2.1. Materials and Methods. All chemicals were of reagent grade and were used as received except o-phenylenediamine and ethanol which were purified and dried as reported previously [9, 10]. Melting points (uncorrected) were determined on Gallenkamp M.EB 600–010 melting point apparatus.

The elemental analyses were performed on Eurovector EA 3000A. 1HNMR and 13CNMR were carried out by using Bruker UltraShield 300 MHz NMR spectrophotometer. FTIR spectra were recorded as KBr and CaI discs using Shimadzu FTIR-8400S, Fourier Transform Infrared spectrophotometer. The electronic spectra were recorded in DMF on Shimadzu UV-visible-160 Spectrophotometer. Thermal analyses (TG & DTG) were carried out under nitrogen atmosphere by using Netzsch Sat 409 PG/PC at a heating rate of 20° C/min under nitrogen atmosphere over a temperature range of 25–1000° C. The metal contents of the complexes were determined by atomic absorption technique using Varian-AA 775 Atomic Absorption spectrophotometer. Electrical conductivity measurements for complexes (10−3 M) in DMF at room temperature were carried out by using Hunts Capacitors Trade Mark British made conductivity meter. Magnetic moment (μeff B.M) for the prepared complexes was measured at room temperature by using Bruker Magnet B.M-6.
2.2. Preparation Methods

2.2.1. Method 1

Synthesis of Schiff Bases EDH₄, PDH₄, and MPDH₄: General Procedure. To a solution of diamine (0.0217, 0.0391, and 0.0493 g for en, O-PD, and DMPD, resp., 0.362 mmol) in a minimum amount of absolute ethanol (en, O-PD) or methanol (DMPD) containing 2 drops of piperidine as an ethanolic solution of 3,4-dihydroxybenzaldehyde (0.1 g, 0.724 mmol) was added. Precipitation took place immediately giving yellow, brown, and orange-yellow products, respectively. The mixtures were heated under reflux with continuous stirring for 1 h, 1 h, and 1.5 h, respectively, to allow for complete precipitation. The products were filtered, washed with ethanol, methanol, and ether, and vacuum dried.

Synthesis of Binuclear (C₁, C₂) and Tetranuclear (C₃) Copper Bis(bipyridyl) Schiff Base Complexes. Dinuclear copper complexes C₁ and C₂ were prepared as follows: to a stirred ethanolic solution of Schiff bases (0.05 g) (0.166 and 0.143 mmol for EDH₄ and PDH₄, resp.) CuCl₂•2H₂O (0.0567 and 0.0489 g, 0.332 and 0.286 mmol, resp.), 2,2’-bipyridyl (0.0519 and 0.0448 g, 0.332 and 0.287 mmol, resp.), and triethylamine (NEt₃) (0.0673 and 0.0580 g, 0.665 and 0.574 mmol, resp.) were added in a minimum amount of ethanol. Precipitation took place immediately. Reflux was continued for 4 h with continuous stirring. The products were filtered off, washed with ethanol, and vacuum dried. C₃ was prepared by treating an ethanolic solution of MPDH₄ (0.050 g, 0.132 mmol) with a solution mixture of excess CuCl₂•2H₂O (0.100 g, 0.586 mmol), 2,2’-bipyridyl (0.0414 g, 0.265 mmol), and NEt₃ (0.0507 g, 0.531 mmol) in ethanol. The mixture was heated under reflux for 4 h. A brown precipitate was formed. The product was filtered off, washed several times with hot ethanol, and vacuum dried.

Synthesis of a Trinuclear Copper Bis(bipyridyl) Schiff Base Complex (C₄). To an ethanol solution of C₁ (0.05 g, 0.06 mmol) CuCl₂•2H₂O (0.0115 g, 0.06 mmol) dissolved in a minimum amount of ethanol was added with continuous stirring for 1 h during which the color of solution changed to dark brown. The mixture was heated under reflux for 4 h. A
brown precipitate was formed. The product was filtered off, washed with ethanol, and vacuum dried.

**Synthesis of Trinuclear Copper Tris(bipyridyl) Complexes of EDH₄ (C₃) and MDPH₄ (C₆).** To a hot solution of C₇ (0.05 g, 0.06 mmol) in hot ethanol Cu(ClO₄)₂·6H₂O (0.0222 g, 0.06 mmol) and 2,2'-bipyridyl (0.0093 g, 0.06 mmol) in ethanol were added with continuous stirring for 1 h followed by heating under reflux for 4 h to allow for complete precipitation. The resulting product (C₃) was filtered off, washed with hot ethanol, and vacuum dried. C₆ was prepared by adding a solution of Cu(ClO₄)₂·6H₂O (0.0678 g), 2,2'-bipyridyl (0.0285 g) (0.183 mmol each), and NEt₃ (0.0246 g, 0.244 mmol) in ethanol to MDPH₄ (0.0229 g, 0.061 mmol) dissolved in a minimum amount of ethanol. A dark brown precipitate started to appear. The mixture was heated under reflux for 3-4 h for complete precipitation. The product was filtered, washed with hot ethanol, and vacuum dried.

**Synthesis of Tetra- and Trinuclear Cobalt Bis- and Tris(bipyridyl) Complexes of EDH₄ and MDPH₄ (C₇ and C₈).** C₇ was prepared as follows: a solution of 2,2'-bipyridyl (0.0517 g, 0.332 mmol) and NEt₃ (0.0672 g, 0.665 mmol) in a minimum amount of ethanol was added to a solution of EDH₄ (0.0499 g, 0.166 mmol) in warm ethanol with continuous stirring. Then a solution of CoCl₂·6H₂O (0.1592 g, 0.669 mmol) in ethanol was added. The color of solution was changed from blue to brown. The reaction mixture was then heated under reflux for 4 h. A brown precipitate was formed. The product was filtered, washed with hot ethanol, and vacuum dried. The preparation and purification of C₈ (dark green) was carried out in the same manner, but the quantities of the reactants were MDPH₄ (0.0625 g, 0.1664 mmol), 2,2'-bipyridyl (0.0778 g, 0.4992 mmol), CoCl₂·6H₂O (0.1187 g, 0.499 mmol), and NEt₃ (0.0672 g, 0.665 mmol) and the color of solution after the addition of the cobalt salt was changed from yellow to green.

2.2.2. Method 2. In this method the metal complexes were prepared from condensation reaction of the Cu(II) complex precursor (LCuL) (L = 2,2'-bipyridyl, L' = 4-formylbenzene-1,2-bis(olate)) with the diamines followed by the reaction with the metal salts to form tri- and tetranuclear complexes.

**Synthesis of LCuL'.** This complex was prepared by following a previously published method [III] with modification. A solution of CuCl₂·2H₂O (0.0124 g, 0.0724 mmol) in ethanol was added to an ethanol solution of 3,4-dihydroxybenzaldehyde (0.1 g, 0.724 mmol), 2,2'-bipyridyl (0.1130 g, 0.724 mmol), and triethylamine (0.1465 g, 1.448 mmol). The reaction mixture was stirred for 20 min. at room temperature during which a brown precipitate was formed. The mixture was heated under reflux for 2 h and the resulting product was separated by filtration, washed with hot ethanol, and dried under vacuum. The product was characterized by elemental analysis and the FTIR spectral analysis.

**Synthesis of Binuclear Copper Bis(bipyridyl) Schiff Base Complexes C₉, C₈b, and C₁₁b.** An ethanol solution of diamine (en, O-PD, and DMPD, 0.0140, 0.0151, and 0.0191 g, resp., 0.14 mmol) was added to a solution of LCuL' (0.1 g, 0.28 mmol) in hot ethanol with stirring for 30 min. The mixture was then heated under reflux for 3 h to allow for complete precipitation. The products were filtered off, washed with ethanol and ether, and vacuum dried.
Table 2: Significant bands in the FTIR spectra (cm\(^{-1}\)) for Schiff bases and their metal complexes.

| Symbol | \(\nu_{\text{OH}}\) | \(\nu_{\text{C-H}}\) | \(\nu_{\text{C-N}}\) imine | \(\nu_{\text{C=N}}\) bipy. | \(\nu_{\text{ClO}_4}\) ionic (Coord.) | \(\nu_{\text{H}_2\text{O}}\) lattice (Coord.) | \(\nu_{\text{M-O}}\) | \(\nu_{\text{M-N}}\) | \(\nu_{\text{M-Cl}}\) |
|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| EDH\(_4\) | 3263 | 2839 | 1651 | — | — | — | — | — | — |
| PDH\(_4\)\(\cdot\)4\(\text{H}_2\text{O}\) | 3253 | 2750 | 1651 | — | — | 3448–3417 | — | — | — |
| MPDH\(_4\)\(\cdot\)MeOH | 3251 | 2985 | 1670 | — | — | — | — | — | — |
| C\(_1\) | — | 2860 | 1654 | 1519 | — | (3150, 767, 651) | 420 | 370 | — |
| C\(_2\) | — | 2950 | 1640 | 1500 | — | 3400 (3250, 775, 660) | 460 | 350 | — |
| C\(_3\) | — | 2900 | 1658 | 1570 | — | 3444 | 474 | 385 | 297\(^a\) |
| C\(_4\) | — | 2800 | 1643 | 1543 | — | (3356, 771, 729) | 470 | 385 | 340\(^a\) |
| C\(_5\) | — | 2819 | 1651 | 1570 | — | 3444 | 474 | 385 | 297\(^a\) |
| C\(_6\) | — | 2950 | 1660 | 1570 | (1093, 1040) | 3580 (3240, 750, 675) | 550 | 341 | — |
| C\(_7\) | — | 2750 | 1653 | 1580 | — | 3750 (3300, 770, 650) | 490 | 405 | 312\(^a\) |
| C\(_8\) | — | 2980 | 1640 | 1560 | — | (3240, 775, 655) | 560 | 395 | 325\(^b\) |
| C\(_9\) | — | 2951 | 1655 | 1573 | — | — | 478 | 358 | — |
| C\(_10\) | — | 2980 | 1630 | 1590 | — | 3550 | 490 | 400 | — |
| C\(_11\) | — | 2823 | 1651 | 1570 | — | 3456 | 489 | 389 | — |
| C\(_12\) | — | 2950 | 1645 | 1550 | — | 3700 (3250, 690, 640) | 450 | 322 | 304\(^a\) |
| C\(_13\) | — | 2800 | 1600 | 1550 | — | (3300, 770, 640) | 560 | 343 | 250\(^b\) |
| C\(_14\) | — | 2750 | 1639 | 1570 | 1103, 1050 | — | 459 | 393 | — |
| C\(_15\) | — | 2800 | 1620 | 1550 | (1091, 1050) | 3600 (3380, 771, 740) | 510 | 400 | — |

\(^a\)Terminal; \(^b\)bridged.

3. Results and Discussion

3.1. Synthesis. The synthesis routes for the metal complexes by the two methods are illustrated in Scheme 1. Method 1 involves the condensation reaction of the diamines with two molecules of 3,4-dihydroxybenzaldehyde (L\(^{\text{H}}\)) to form the diSchiff bases as a first step for the formation of metal complexes. In the second method the condensation reaction occurs between the diamine molecule and two molecules of the mixed ligand copper complex precursor L\(\text{Cu}L\). Although the last method is simpler than the first method to avoid side reactions, the copper complex precursor is slightly soluble in cold ethanol and therefore reaction with this complex required heating in large amount of solvent.
3.2. Physical Properties. The physical properties and results obtained from elemental analyses of the prepared compounds are described in Table 1. The analytical data are quite agreeable with calculated values with few exceptions which were attributed to incomplete combustion of the compounds. The molecular formula of the prepared compounds has been suggested according to the aforementioned data together with those obtained from spectral and thermal analyses as well.
Figure 6: $^1$H NMR spectra of diSchiff base ligands EDH$_4$ and MPDH$_4$. 
3.3. Infrared Spectra. The important vibrational modes of IR spectra for the free Schiff bases and their metal complexes are described in Table 2. The spectra of the free ligands displayed strong to moderate absorption bands in the wavenumber region 3251–3263 cm\(^{-1}\) which were assigned to intramolecular hydrogen bonding of the two adjacent OH groups [12]. These bands were absent in the spectra of all metal complexes which indicates that the phenolic oxygen atoms were bonded to the metal ions [3–5, II]. The spectrum of the mixed ligand copper (II) complex precursor \(\text{CuL}^2\) displayed strong absorption bands at 1660 and 1540 cm\(^{-1}\) assigned to the stretching vibrations of the C=O and C=N groups of L\(^+\) and L moieties, respectively [11, 13]. The low intensity bands observed at lower wavenumber region at 440 and 345 cm\(^{-1}\) were assignable to stretching vibrations of Cu–O and Cu–N bonds, respectively [3, 5].

The strong bands observed at 1631–1670 cm\(^{-1}\) and 1604, 1608 cm\(^{-1}\) in the spectra of the free Schiff bases were assigned to the asymmetric symmetric stretching vibration of the azomethine group (\(\nu_{C\equiv N}\)) [2–5]. These bands were shifted to lower frequency in all complexes (except \(C_9\), \(C_{10}\), \(C_{19}\), and \(C_{10}\)) indicating the coordination of the Schiff bases with the metal ions through the azomethine nitrogens [5]. All complexes exhibited strong bands at wavenumber range 1500–1590 cm\(^{-1}\) attributed to \(\nu_{C=N}\) of coordinated bipyridyl ligand [14]. The spectra of the complexes \(C_5\), \(C_6\), \(C_{14}\), and \(C_{15}\) exhibited strong bands assigned to the stretching vibrational modes of ClO\(^4\) anion (\(\nu_{\text{ClO}_4}\)) which behaved as monodentate ligand in \(C_6\) and \(C_{15}\) complexes [15] and as a free ion in \(C_5\) and \(C_{14}\) complexes [15]. The bands appeared at 3400–3750 cm\(^{-1}\) in the spectra of \(C_4\), \(C_2\), \(C_{13}\), \(C_9\), \(C_{10}\), \(C_{11}\), \(C_{12}\), and \(C_{13}\) were attributed to vibrational modes of lattice \(H_2O\) [15], while the bands which appeared at 3100–3380 cm\(^{-1}\) and 621–775 cm\(^{-1}\) in the spectra of \(C_2\), \(C_{12}\), \(C_{14}\), \(C_9\), \(C_{10}\), \(C_{11}\), \(C_{12}\), and \(C_{13}\) were due to coordinated \(H_2O\) [15].

The spectrum of \(\text{MPDH}_4\) exhibited a strong band in the range 3552–3421 cm\(^{-1}\) and another band at 1195–1161 cm\(^{-1}\) attributed to OH and C–O stretching vibrations of methanol embedded in the crystal lattice of the ligand [13, 15]. Further bands which appeared at lower frequencies in the spectra of metal complexes were assigned to M–O, M–N and M–Cl stretching vibrations (Table 2).

3.4. \(^1\)H NMR and \(^{13}\)C NMR Spectra. The \(^1\)H NMR spectra of diSchiff bases and the binuclear bis(bipyridyl) copper complex of \(\text{MPDH}_4\) (\(C_{11}\)) were recorded in DMSO and the chemical shifts and peak assignments are given in Table 3. The spectra of the Schiff base ligands showed a broad peak in the range \(\delta = 8.5–9.9\) ppm attributed to phenolic hydroxyl protons [3, 4, 16] as is demonstrated by the spectra of \(\text{EDH}_4\) and \(\text{MPDH}_4\) shown in Figure 6.

The absence of this peak in the spectrum of complex \(C_{11}\) (Table 3) confirms the involvement of deprotonated hydroxyls in chelation to the metal ion [16, 17]. The peaks displayed

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### Table 3: \(^1\)H NMR data of the three Schiff base ligands and the Cu(II) complex \(C_{11}\) in DMSO.

| Compound | Chemical shifts (ppm) | Assignments | Chemical shifts (ppm) | Assignments |
|----------|-----------------------|-------------|-----------------------|-------------|
| \(\text{EDH}_4\) | (8.8–9.9, 4H, b)      | Protons of OH | (9.60–9.75, 4H, b)    | Protons of OH |
|           | (8.1, 2H, s)         | Protons of azomethine | (8.7–7.9, 2H, b)     | Protons of azomethine |
|           | (6.7–7.4, 6H, m)     | Aromatic protons | (6.5–7.9, 10H, b)    | Aromatic protons |
|           | (3.9, 4H, s)         | Protons of NCH\(_2\) | (3–3.5, 8H, b)       | Protons of H\(_2\)O |
|           | (3–3.5, 2H, b)       | Protons of H\(_2\)O (in DMSO) | (2.5, 6H, s)    | Protons of DMSO |
|           | (2.5, 6H, s)         | Protons of DMSO |                        |              |
| \(\text{MPDH}_4\) | (8.5–8.68, 4H, b)    | Protons of OH | (10.1–10.98, 2H, b)  | Protons of azomethine |
|           | (8.0–8.28, 2H, b)    | Protons of azomethine | (6.7–7.5, 24H, b)   | Aromatic protons |
|           | (6.9–7.6, 10, m)     | Aromatic protons | (3.2, 6H, m)         | Protons of H\(_2\)O |
|           | (3.0–3.6, 2H, m)     | Protons of H\(_2\)O | (2.4–2.8, 6H, m)    | Protons of DMSO |
|           | (2.5, 6H, s)         | Protons of DMSO | (0.97–1.85, 6H, b)   | Protons of CH\(_3\) |
|           | (1.5–1.7, 6H, m)     | Protons of CH\(_3\) |                        |              |

### Table 4: Chemical shifts (ppm) for \(^{13}\)C NMR of Schiff bases \(\text{EDH}_4\) and \(\text{MPDH}_4\) in DMSO.

| Compound | Chemical shifts (ppm) | Assignments |
|----------|-----------------------|-------------|
| \(\text{EDH}_4\) | 60.99 | Carbon of CH\(_3\) |
|           | 113.6–161.2 | Aromatic carbons |
|           | 167.2 | Carbon of HC=N |
| \(\text{MPDH}_4\) | 19.8, 20.1 | Carbon of methyl group |
|           | 110.8–146.8 | Aromatic carbons |
|           | 150.6, 152.7 | Carbon of HC=N |

as conductivity and magnetic susceptibility measurements of metal complexes. All complexes were noncrystalline which made it difficult to obtain their single crystal structures.
Table 5: Electronic spectra, magnetic moments, and molar conductivity data of Schiff bases and their metal complexes.

| Symbol | Band positions (cm\(^{-1}\)) | Assignment | \(\mu_{\text{eff}}\) (B.M) | Molar conductivity S·mol\(^{-1}\)·cm\(^{2}\) in DMF |
|--------|-----------------------------|------------|-----------------------------|----------------------------------|
| EDH\(_4\) | 33222, 24691 | \(\pi \rightarrow \pi^*\) | — | 0.0018 |
| PDH\(_4\) | 33222, 27777 | \(\pi \rightarrow \pi^*\) | — | 0.011 |
| MPDH\(_4\) | 20833 | \(n \rightarrow \pi^*\) | — | 0.0007 |
| C\(_1\) | 33333 | Intraligand \(\pi \rightarrow \pi^*\) | | |
| C\(_2\) | 26315 | Intraligand \(\pi \rightarrow \pi^*\) | 0.386 oh | 0.022 |
| C\(_3\) | 25641 | Intraligand \(\pi \rightarrow \pi^*\) | 1.260 Sq. | 0.093 |
| C\(_4\) | 34013, 27247 | Intraligand \(\pi \rightarrow \pi^*\) | 0.514 oh | 0.251 |
| C\(_5\) | 23313 | Intraligand \(\pi \rightarrow \pi^*\) | 1.061 Sq. | 149 |
| C\(_6\) | 25974 | Intraligand \(\pi \rightarrow \pi^*\) | 0.810 oh | 0.114 |
| C\(_7\) | 31250 | Intraligand \(\pi \rightarrow \pi^*\) | 2.440 oh | 0.043 |
| C\(_8\) | 26178 | Intraligand \(\pi \rightarrow \pi^*\) | 0.005 |
| C\(_9\) | 15731 | Intraligand \(\pi \rightarrow \pi^*\) | 0.273 |
| C\(_10\) | 10504 | Intraligand \(\pi \rightarrow \pi^*\) | 0.0002 |
| C\(_11\) | 7083 cal. | Intraligand \(\pi \rightarrow \pi^*\) | 0.005 |
| C\(_12\) | 36496, 32894 | Intraligand \(\pi \rightarrow \pi^*\) | 0.013 |
by $^1$H NMR spectra of Schiff bases in the range $\delta = 7.9$–8.7 ppm were attributed to chemical shifts of the azomethine protons (HC=N) [3, 4, 16, 17]. The spectrum of C11 exhibited the absence of the signals related to OH protons and the appearance of the azomethine proton signals downfield which confirms the formation of the metal complex [16, 17].

Signals of aromatic and aliphatic protons were observed in the chemical shift ranges 6.5–7.9 and 1.5–3.9 ppm, respectively [13]. Chemical shifts for $^1$C NMR of EDH$_4$ and MPDH$_4$ in DMSO are described in Table 4. The signals assigned to the chemical shifts of methylene and methyl groups for the two ligands, respectively, were observed at 60.99 (CH$_2$) and at 19.8 and 20.1 (CH$_3$) ppm [18], while the signals of aromatic carbons were located at 113.6–161.2 and 110.8–146.8 ppm, respectively [18, 19]. The signals observed at 167.2 and 150.6–152.7 ppm, respectively, were attributed to the chemical shifts of azomethine carbons which confirms the formation of the Schiff bases [20–22].

### 3.5. Electronic Spectra Conductivity and Magnetic Susceptibility Measurements

The results of electronic spectra of the ligands and their metal complexes in DMF are described in Table 5. The three ligands exhibited high intensity bands which appeared at wavenumber region 33333–24390 cm$^{-1}$ and low intensity bands at 27777–20833 cm$^{-1}$ which were assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions, respectively [13]. The spectra of metal complexes exhibited hypsochromic shifts of the ligand $\pi \rightarrow \pi^*$ band which refers to complex formation with the metal ions [18]. The spectra of complexes exhibited additional medium intensity bands in the near UV to visible region at 28248–23255 cm$^{-1}$ which were attributed to charge transfer transitions [23]. The copper complexes (C4, C5, C6, C7, C8, and C17) displayed bands in the regions 12970–10298 cm$^{-1}$, 18833–15313 cm$^{-1}$, and 21739–19920 cm$^{-1}$ assigned to $^2$B$_{1g} \rightarrow ^2$A$_{1g}$, $^2$B$_{1g} \rightarrow ^2$B$_{2g}$, and $^2$B$_{1g} \rightarrow ^2$E$_g$ transitions, respectively, of square planar Cu(II) complexes [23–27] while the spectra of the copper complexes (C4, C5, C6, C7, C8, and C17) displayed bands in the regions 13513–10460, 18868–15431, and 23148–22472 which were attributed to the transitions of tetragonally distorted octahedral Cu(II) complexes [23–25]. The two cobalt complexes (C9 and C13) exhibited two bands observed at 15731 and 15983 cm$^{-1}$, respectively, which were assigned to $^4$T$_{2g} \rightarrow ^4$T$_{2g}$ (P) ($\nu_2$) and at 10504 and 9900 cm$^{-1}$, respectively, corresponding to the transition $^4$T$_{2g} \rightarrow ^4$A$_{2g}$ ($\nu_2$) of octahedral Co(II) complexes [23]. The energies of $\nu_1$ ($^4$T$_{2g} \rightarrow ^4$T$_{2g}$) as well as the values of the spectral parameters Dq/B, B', 10Dq, and nephelauxetic ratio $\beta$ for the Co(II) complexes C9 (7083 cm$^{-1}$, 0.9, 787 cm$^{-1}$, 7080 cm$^{-1}$, and 0.811, resp.), and C13 (6456 cm$^{-1}$, 0.7, 807 cm$^{-1}$, 5740 cm$^{-1}$, and 0.831, resp.), were calculated by applying the band ratio $\nu_1/\nu_2$ on Tanabe-Sugano diagram of $d^7$ complexes. The values of $\beta$ indicate a covalent bonding character of both complexes [23]. Conductivity measurements in DMF showed nonelectrolytic nature for all compounds (Table 5) except C5, C13, and C14 which were electrolytes with ionic ratio (1:2) [28]. Magnetic susceptibility measurements at room temperature showed that the magnetic moment ($\mu_{eff}$) of the Cu(II) complex precursor CuLL$^+$ (1.69 B.M) agrees with square planar geometry of the complex [11, 23]. The values of $\mu_{eff}$ of the other complexes were less than those expected for copper and cobalt ions which imply that the di- and trinuclear copper (II) and cobalt (II) complexes possess antiferromagnetic properties by a strong intramolecular antiferromagnetic spin exchange interaction [5]. According to the aforementioned results in addition to elemental analysis and FTIR and NMR spectra the stereochemical structures of the studied complexes were suggested as is illustrated in Scheme 2.

### 3.6. Thermal Analysis

Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses for the two complexes C8 and C13 are shown in Figure 7. The decomposition temperature and the weight losses are described in Table 6. The loss of solvent molecules embedded in the crystal lattice of the complexes as well as uncoordinated ligand groups took place at the first stage at temperature range 78–180°C with peak temperatures at 100 and 98°C, respectively, as is indicated by the DTG curves of the two complexes (Figure 7). The successive loss of coordinated water molecules occurred in the second and third stages at peak temperatures 195, 300 and 210, 325°C, respectively. The loss of bipyridyl and chloride ligands took place at temperature range 400–900°C. The DTG curve of C8 showed three peaks at 412, 620, and 822°C for this stage. The high percentage of the remaining

### Table 5: Continued.

| Symbol | Band positions (cm$^{-1}$) | Assignment | $\mu_{eff}$ (B.M) | Molar conductivity S mol$^{-1}$ cm$^2$ in DMF |
|--------|---------------------------|------------|-----------------|---------------------------------------------|
| C13    | 33333, 29239              | Intraligand $\pi \rightarrow \pi^*$ | 0.440 | 163 |
| C14    | 27027                     | C.T        | 1.89 Sq.        | 158 |
| C15    | 27397                     | C.T        | 1.783 oh        | 0.023 |
|        | 22272                     | $^2$B$_{1g} \rightarrow ^2$E$_g$ |      |      |
Scheme 2: Continued.

$X = 0 \ (C_3) \quad X = 0.56 \ \text{Et}_3\text{N} \ (C_{14})$
residues at 1000°C indicates that the two complexes are very stable and require a higher temperature range for complete decomposition which is quite common for polynuclear metal complexes [5].

4. Conclusions

The bi-, tri-, and tetranuclear bis- and tris(bipyridyl) copper (II) and cobalt (II) mixed ligand complexes of three diSchiff base ligands derived from 3,4-dihydroxybenzaldehyde and three diamines in a stoichiometric ratio of 2:1 were successfully synthesized by two different methods. The structures of the ligands were confirmed by elemental and spectral analysis. Coordination of the metal ions to form trinuclear and tetranuclear complexes took place through the two imino nitrogens and phenolic dianionic oxygen atoms of each ligand molecule as was indicated by FTIR spectra. The formation of binuclear diSchiff base copper bis(bipyridyl) complexes was achieved by reacting the mononuclear copper (II) mixed ligand complex \( \text{CuLL} \) with the diamines in a 2:1 ratio, respectively, as was confirmed by the NMR spectrum of \( \text{C}_{11} \) while trinuclear bis- and tris(bipyridyl) and tetranuclear complexes of the three ligands were achieved by reacting the synthesized Schiff bases with the copper salts in the presence of 2,2'-bipyridyl. The complexes exhibited low values of magnetic moments which made them a good synthetic model for intramolecular antiferromagnetic spin exchange interaction of biological systems. In the future work the enzyme like and metalloprotein activities of these complexes and their biological activities will be studied in detail.
Table 6: Thermal decomposition of the copper complexes (C₈ and C₁₂).

| Complex                  | Temp. range of decomp. °C | Weight % loss found (calc.) |
|--------------------------|---------------------------|----------------------------|
| C₈ stable phase          |                           |                            |
| [MPD(C₈)(bipy)₂(H₂O)₄Cl₂] Et₄N |                           |                            |
| M.wt = 1260.7            |                           |                            |
| ↓ 0.45Et₂N + Cl + 2H₂O   | 78–211                    | 9.00 (9.28)                |
| ↓ 0.55Et₂N + 2H₂O        | 212–423                   | 6.80 (7.26)                |
| ↓ 2CH₃ + 2bipy + CoCl₂   | 424–661                   | 32.4 (33.43)               |
| ↓ Cl + bipy + HCN        | 662–998                   | 17.23 (17.33)              |
| C₈H₄NO₂Co₂ + C₈H₆O₂Co   | —                         | 34.57 (33.13)              |
| (residue)                |                           |                            |
| C₁₂ stable phase         |                           |                            |
| [ED(C₁₂)(bipy)₂(H₂O)₃Cl₃] |                           |                            |
| M.wt = 1166.16           |                           |                            |
| ↓ 4H₂O                   | 73–261                    | 5.80 (6.17)                |
| ↓ 5H₂O + C₈H₄            | 262–365                   | 10.20 (10.11)              |
| ↓ C₈H₄N + bipy           | 366–542                   | 20.00 (19.46)              |
| ↓ 4Cl                    | 543–761                   | 11.8 (12.13)               |
| ↓ C₈H₄N                 | 762–998                   | 6.4 (6.68)                 |
| C₁₂H₈N₂O₄Cu₄ (residue)   | —                         | 45.79 (44.76)              |

Figure 7: TG and DTG thermographs of C₈ and C₁₂.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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