

Research Article

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

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A series of new di-, tri-, and tetranuclear Co(II) and Cu(II) complexes of three new diSchiff base ligands were synthesized by two different methods. The first method involved the synthesis of the three ligands from condensation reaction of 3,4-dihydroxybenzaldehyde ($L'H_2$) with ethylenediamine (en), o-phenylenediamine (o-PD), or 4,5-dimethyl-1,2-phenylenediamine (DMPD) in a mole ratio of 2:1 followed by the reaction of the resulting Schiff bases ligands with Cu(II) or Co(II) ions in the presence of 2,2'-bipyridyl (L) to form the di- and trinuclear metal complexes. The second method involved the condensation of the copper complex $LCu(II)L'$ (L = 2,2'-bipyridyl, L' = 4-formylbenzene-1,2-bis(olate)) with en, o-PD, or DMPD in a mole ratio of 2:1, respectively, followed by reaction with $CuCl_2$ or $Cu(ClO_4)_2$ to form di-, tri-, and tetranuclear copper (II) complexes, respectively. The structures of the ligands and metal complexes were characterized by elemental analyses, NMR, and FTIR spectra. The geometries of metal complexes were suggested according to elemental analysis, electronic spectra, thermal analyses, atomic absorption, and magnetic moments and conductivity measurements.

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

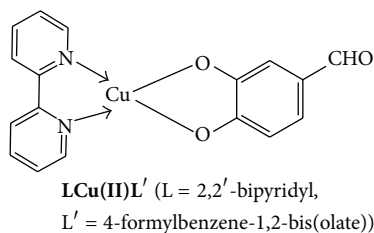


FIGURE 1

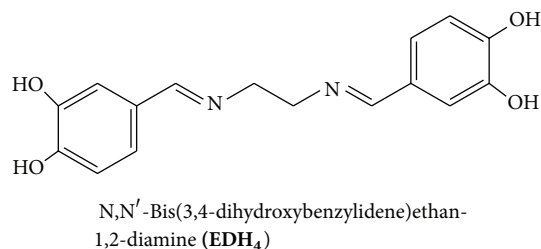


FIGURE 2

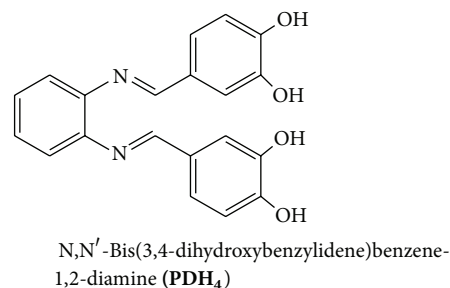


FIGURE 3

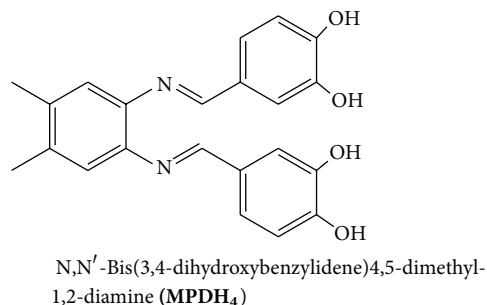


FIGURE 4

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)ethan-1,2-diamine (**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.

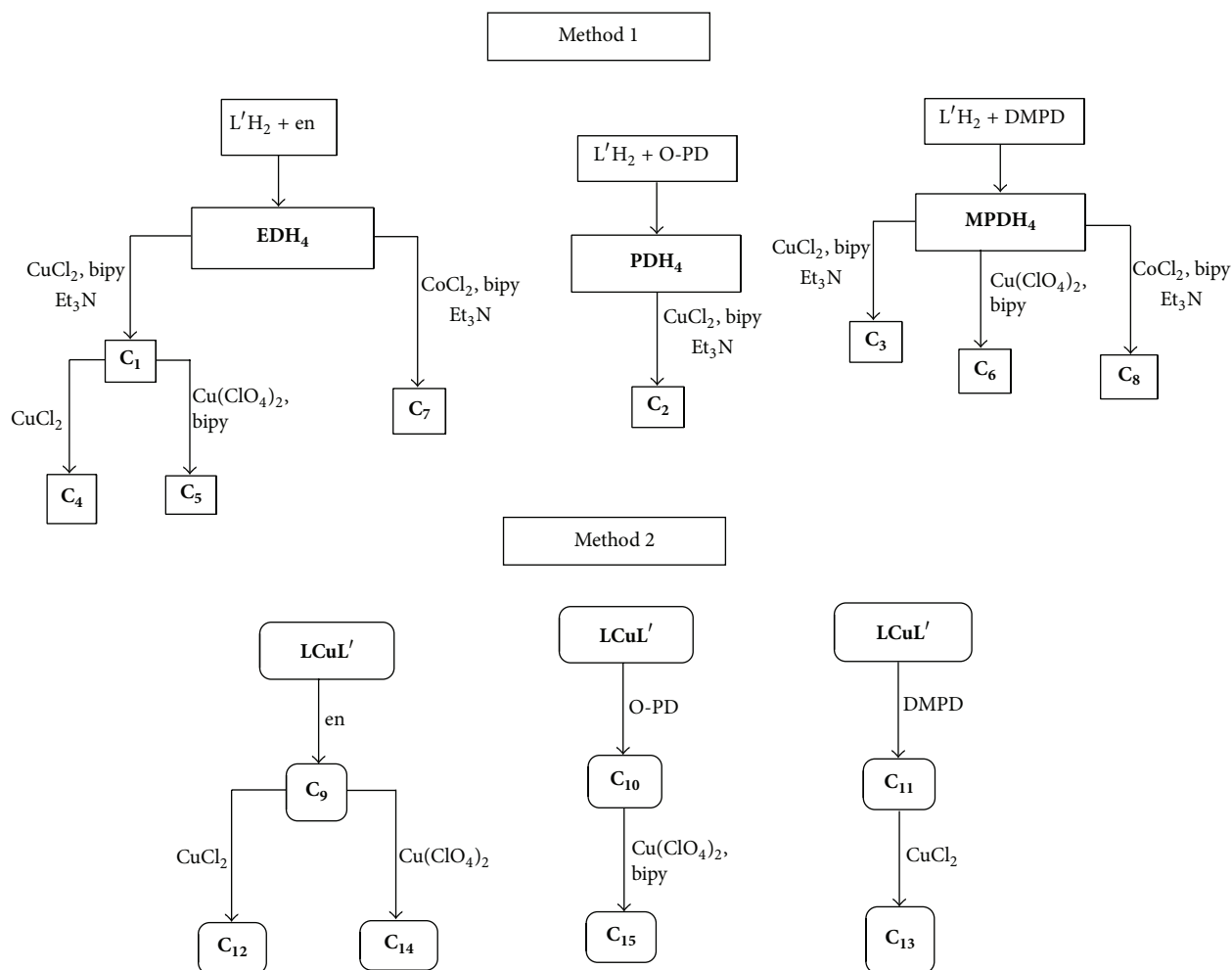
The structures of the prepared compounds were elucidated depending on elemental analyses, Uv-vis, NMR, and FTIR spectra as well as, thermal analyses, atomic absorption,

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.F.B 600-010f 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 CsI 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 (μ_{eff} B.M) for the prepared complexes was measured at room temperature by using Bruker Magnet B.M-6.



SCHEME 1: The synthesis routes of the studied metal complexes by two different methods.

2.2. Preparation Methods

2.2.1. Method 1

Synthesis of Schiff Bases EDH_4 , PDH_4 , and $MPDH_4$: 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 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 (C_1 , C_2) and Tetranuclear (C_3) Copper Bis(bipyridyl) Schiff Base Complexes. Dinuclear copper complexes C_1 and C_2 were prepared as follows: to a stirred ethanolic solution of Schiff bases (0.05 g) (0.166 and 0.143 mmol for EDH_4 and PDH_4 , resp.) $CuCl_2 \cdot 2H_2O$

(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 (NEt_3) (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. C_3 was prepared by treating an ethanolic solution of $MPDH_4$ (0.050 g, 0.132 mmol) with a solution mixture of excess $CuCl_2 \cdot 2H_2O$ (0.100 g, 0.586 mmol), 2,2'-bipyridyl (0.0414 g, 0.265 mmol), and NEt_3 (0.0537 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 (C_4). To an ethanol solution of C_1 (0.05 g, 0.06 mmol) $CuCl_2 \cdot 2H_2O$ (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

TABLE I: The physical properties and analytical data for Schiff bases and their metal complexes.

Symbol	Color	(m.p.) °C	Yield %	CHN % analysis found (Calc.)			M % found (Calc.)	Cl % found (Calc.)
				C %	H %	N %		
EDH₄	Yellow	210 dec.	67.07	65.04 (64.00)	5.77 (5.33)	9.78 (9.33)	—	—
PDH₄·4H₂O	Dark brown	240	30.03	57.78 (57.14)	3.84 (4.28)	7.32 (6.66)	—	—
MPDH₄·MeOH	Pale yellow	222	56.82	67.50 (67.60)	6.24 (5.88)	7.72 (6.86)	—	—
C₁	Brown	>280	68.92	53.29 (53.52)	4.31 (4.46)	10.39 (10.40)	16.05 (15.74)	—
C₂	Dark brown	>280	37.55	52.77 (53.65)	4.46 (4.51)	8.92 (9.38)	14.95 (14.20)	—
C₃	Brown	>280	62.24	46.00 (45.89)	3.79 (3.09)	8.25 (7.64)	23.79 (23.14)	12.57 (12.93)
C₄	Dark brown	>280	67.53	44.67 (44.18)	3.78 (4.09)	7.80 (8.59)	19.92 (19.50)	7.47 (7.26)
C₅	Dark brown	>280	76.95	47.77 (47.84)	3.90 (3.12)	10.14 (9.71)	16.00 (16.52)	5.55 (6.15)
C₆	Dark brown	>280	63.57	46.23 (46.65)	3.82 (3.88)	9.13 (8.37)	14.98 (14.25)	5.82 (5.31)
C₇	Dark brown	>280	26.10	37.78 (37.70)	4.22 (4.04)	6.85 (7.29)	20.85 (20.44)	12.11 (12.32)
C₈	Dark green	>280	26.68	55.44 (55.20)	5.32 (4.99)	9.90 (9.99)	13.74 (14.02)	6.03 (5.63)
C₉	Dark brown	>280	68.06	59.50 (58.76)	4.55 (3.81)	11.73 (11.42)	17.93 (17.28)	—
C₁₀	Dark brown	>280	86.26	59.38 (59.91)	4.15 (3.74)	9.61 (10.48)	16.54 (16.22)	—
C₁₁	Brown	>280	77.00	58.39 (58.26)	4.12 (4.39)	8.92 (9.71)	15.22 (14.69)	—
C₁₂	Dark brown	>280	52.56	36.24 (37.04)	4.02 (3.43)	7.9 (7.20)	22.42 (21.79)	11.59 (12.17)
C₁₃	Brown	>280	57.05	45.80 (46.25)	4.12 (4.40)	8.33 (7.70)	16.47 (17.49)	7.08 (6.51)
C₁₄	Reddish brown	>280	93.03	51.24 (50.64)	3.90 (4.52)	10.53 (10.20)	15.23 (14.54)	5.14 (5.41)
C₁₅	Brown	>280	65.50	45.18 (45.81)	3.96 (3.66)	7.93 (8.55)	13.91 (14.55)	6.05 (6.07)

brown precipitate was formed. The product was filtered off, washed with ethanol, and vacuum dried.

Synthesis of Trinuclear Copper Tris(bipyridyl) Complexes of EDH₄ (C₅) and MPDH₄ (C₆). To a hot solution of **C₁** (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 (**C₅**) 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 **MPDH₄** (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 MPDH₄ (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, 0.1664 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 **MPDH₄** (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 [11] with modification. A solution of CuCl₂·2H₂O (0.1234 g, 0.724 mmol) in ethanol was added to an ethanolic mixture 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, C₁₀, and C₁₁. 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	ν_{OH}	$\nu_{\text{C-H}}$	$\nu_{\text{C=N}}$ imine	$\nu_{\text{C=N}}$ bipy.	ν_{ClO_4} ionic (Coord.)	ν H_2O lattice (Coord.)	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{M-Cl}}$
EDH₄	3263	2839	1651 1608	—	—	—	—	—	—
PDH₄·4H₂O	3253	2750	1631 1604	—	—	3448–3417	—	—	—
MPDH₄·MeOH	3251	2985	1670	—	—	—	—	—	—
C₁	—	2860 2760	1654 1608	1519	—	(3150, 767, 651)	420	370	—
C₂	—	2950	1640 1610	1500	—	3400 (3250, 775, 660)	460	350	—
C₃	—	2900	1658 1604	1570	—	3444	474	385	297 ^a 254 ^b
C₄	—	2800 2750	1643 1604	1543	—	(3356, 771, 729)	470	385	340 ^a
C₅	—	2819 2746	1651 1608	1570	1111, 1083, 1037	—	470	333	—
C₆	—	2950 2800	1660 1610	1570	(1093, 1040)	3580 (3240, 750, 675)	550	341	—
C₇	—	2750	1653 1610	1580	—	3750 (3300, 770, 650)	490	405	312 ^a 241 ^b
C₈	—	2980 2870	1640 1610	1560	—	(3240, 775, 655)	560	395	325 ^a 270 ^b
C₉	—	2951 2839	1655	1573	—	—	478	358	—
C₁₀	—	2980	1630	1590	—	3550	490	400	—
C₁₁	—	2823 2754	1651 1608	1570	—	3456	489	389	—
C₁₂	—	2950 2800	1645 1600	1550	—	3700 (3250, 690, 640)	450	322	304 ^a 250 ^b
C₁₃	—	2960 2850	1660 1610	1550	—	(3300, 770, 640)	560	343	—
C₁₄	—	2750	1639 1604	1570	1103, 1050	—	459	393	—
C₁₅	—	2800	1620	1550	(1091, 1050)	3600 (3380, 771, 740)	510	400	—

^aTerminal; ^bbridged.

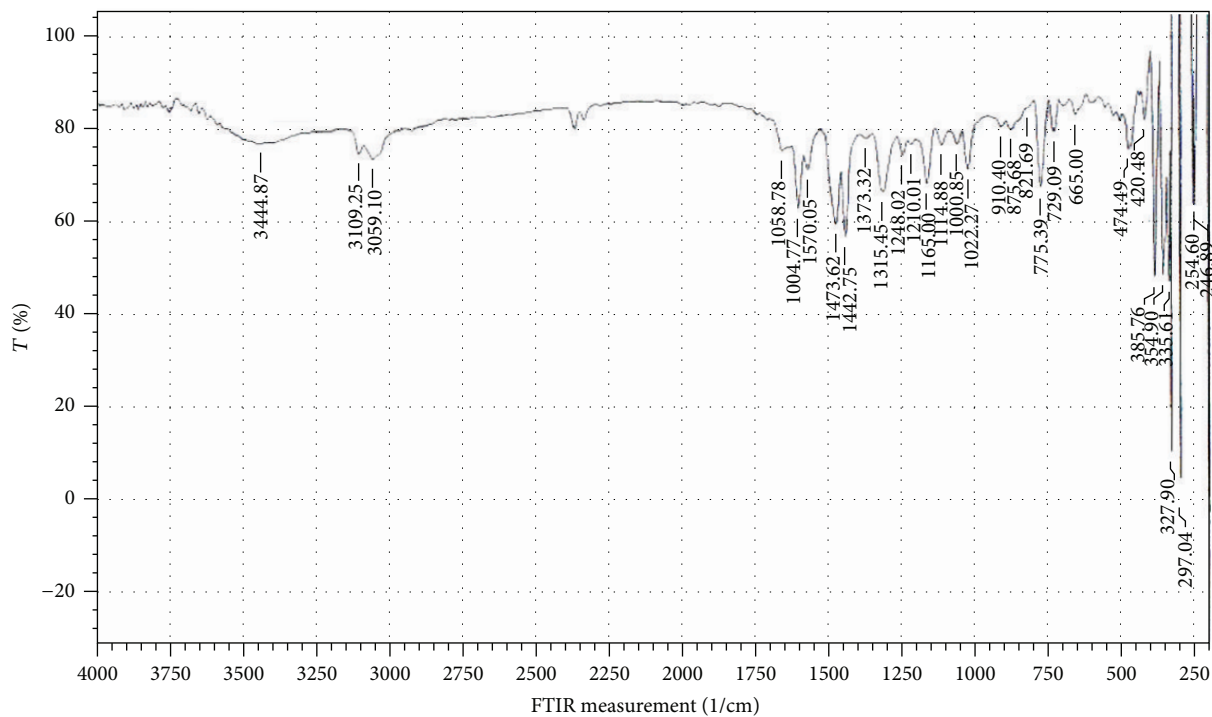
Synthesis of Trinuclear Copper Bis(bipyridyl) Schiff Base Complexes C₁₂ and C₁₃. To a solution of **C₉** and **C₁₁** (0.0441 and 0.0519 g, resp., 0.06 mmol) in hot ethanol $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.0115 g, 0.06 mmol) was added in a minimum amount of ethanol with stirring for 1 h. The colors of solutions changed to brown and precipitation of products took place. The mixtures were heated under reflux for 4 h and the products were filtered off, washed with ethanol, and vacuum dried.

Synthesis of Trinuclear Copper Tris(bipyridyl) Schiff Base Complexes C₁₄ and C₁₅. A solution mixture of 2,2'-bipyridyl (0.0093 g, 0.06 mmol) and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.0222 g, 0.06 mmol) in ethanol was added to a solution of **C₉** and **C₁₀** (0.0441 and 0.0536 g, resp., 0.06 mmol) in hot ethanol with stirring for 1 h until the formation of precipitates was observed. The mixtures were then heated under reflux for 4 h

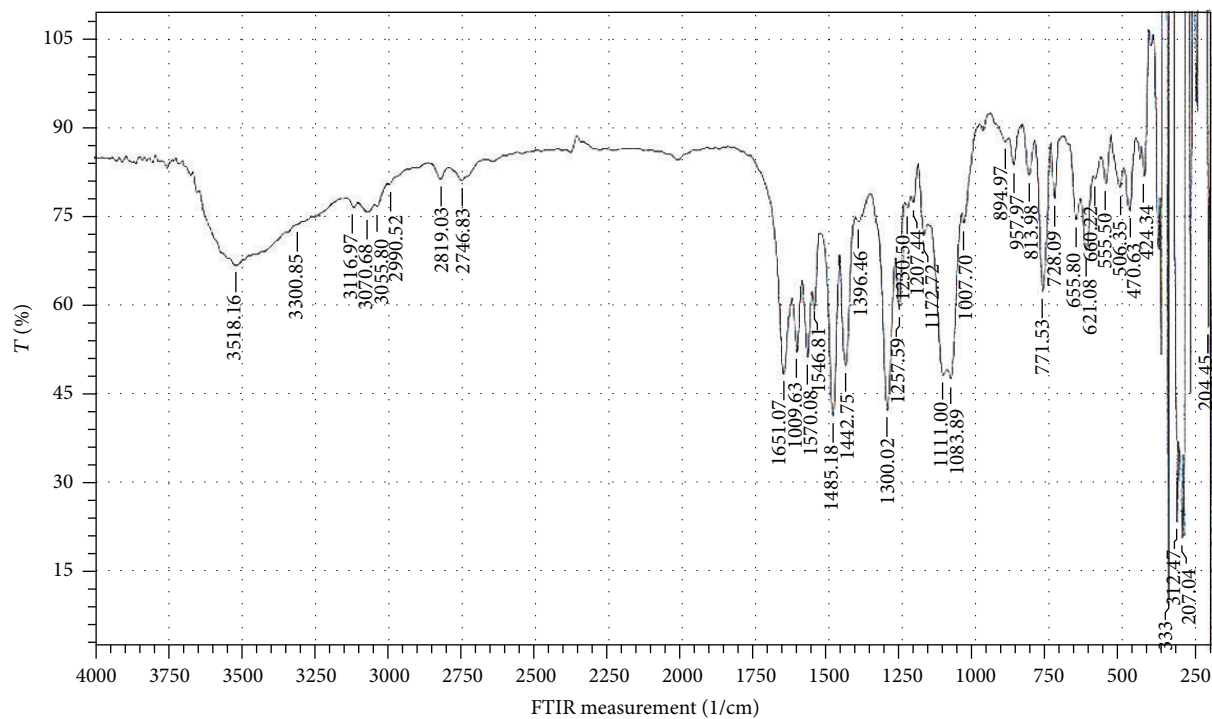
and the products were filtered off, washed with hot ethanol, and vacuum dried.

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 ($\text{L}'\text{H}_2$) 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 LCuL' . 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.



(a)

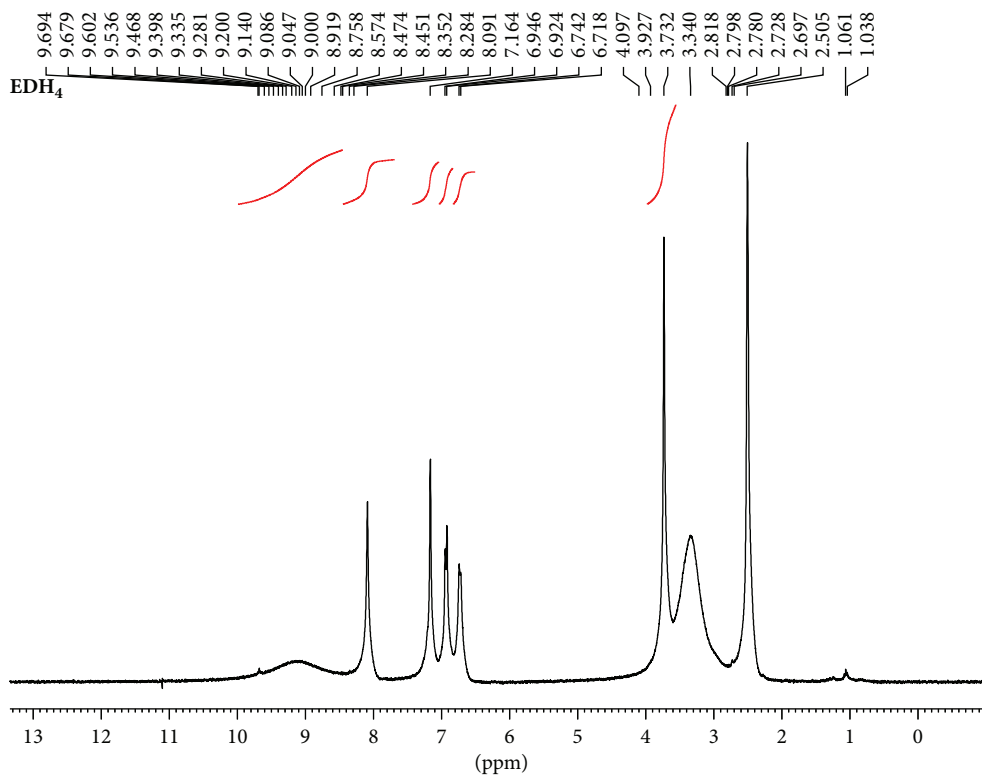


(b)

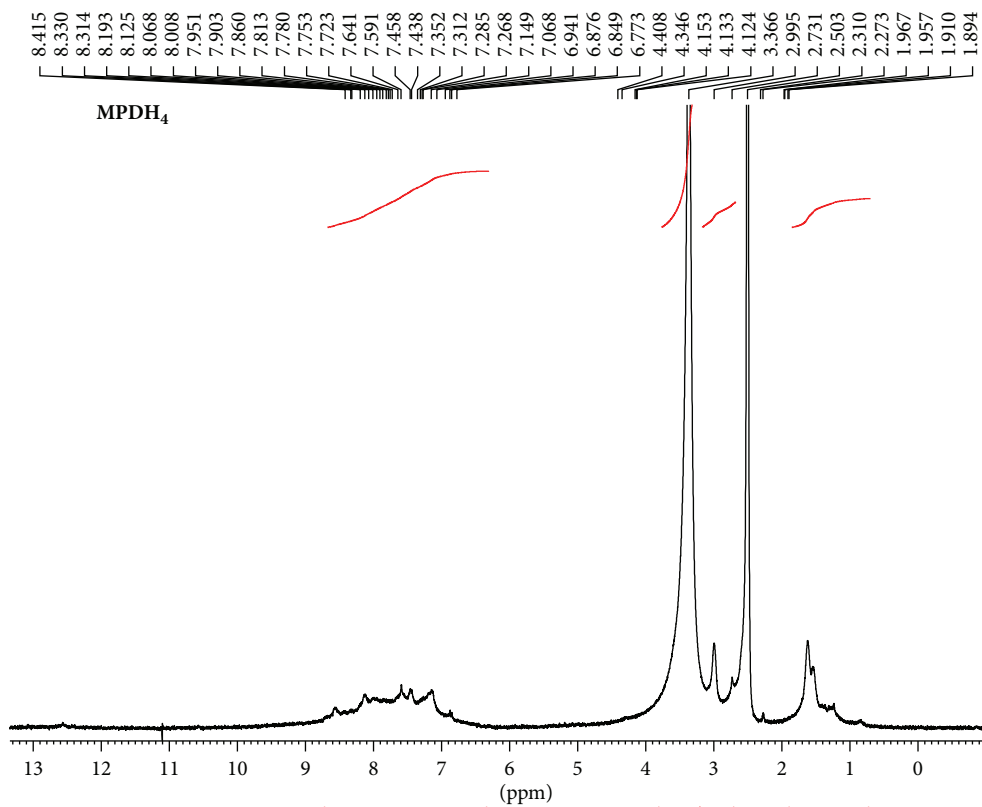
FIGURE 5: FTIR spectra of (a) C_3 and (b) C_5 .

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



(a)



(b)

FIGURE 6: ¹H NMR spectra of diSchiff base ligands EDH₄ and MPDH₄.

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

EDH_4		PDH_4	
Chemical shift δ (ppm)	Assignments	Chemical shifts δ (ppm)	Assignments
(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_2O
(3–3.5, 2H, b)	Protons of H_2O (in DMSO)	(2.5, 6H, s)	Protons of DMSO
(2.5, 6H, s)	Protons of DMSO		
MPDH_4		C_{11} complex	
Chemical shifts δ (ppm)	Assignments	Chemical shifts δ (ppm)	Assignments
(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 of benzene rings and bipyridyl
(6.9–7.6, 10, m)	Aromatic protons	(3.2, 6H, m)	Protons of H_2O
(3.0–3.6, 2H, m)	Protons of H_2O	(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 EDH_4 and MPDH_4 in DMSO.

Compound	Chemical shifts δ (ppm)	Assignments
EDH_4	60.99	Carbon of CH_2
	113.6–161.2	Aromatic carbons
	167.2	Carbon of $\text{HC}=\text{N}$
MPDH_4	19.8, 20.1	Carbon of methyl group
	110.8–146.8	Aromatic carbons
	150.6, 152.7	Carbon of $\text{HC}=\text{N}$

as conductivity and magnetic susceptibility measurements of metal complexes. All complexes were noncrystalline which made it difficult to obtain their single crystal structures.

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 band in the wavenumber region $3251\text{--}3263\text{ cm}^{-1}$ 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, 11]. The spectrum of the mixed ligand copper (II) complex precursor CuLL' displayed strong absorption bands at 1660 and 1540 cm^{-1} assigned to the stretching vibrations of the $\text{C}=\text{O}$ and $\text{C}=\text{N}$ 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 $\text{Cu}-\text{O}$ and $\text{Cu}-\text{N}$ bonds, respectively [3, 5].

The strong bands observed at $1631\text{--}1670\text{ cm}^{-1}$ 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 ($\nu\text{C}=\text{N}$) [2–5]. These bands were shifted

to lower frequency in all complexes (except C_1 , C_2 , C_9 , C_{10} , and C_{11}) indicating the coordination of the Schiff bases with the metal ions through the azomethine nitrogens [5]. All complexes exhibited strong bands at wavenumber range $1500\text{--}1590\text{ cm}^{-1}$ attributed to $\nu_{\text{C}=\text{N}}$ 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 (ν_{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 $3400\text{--}3750\text{ cm}^{-1}$ in the spectra of PDH_4 , C_2 , C_3 , C_6 , C_7 , C_{10} , C_{11} , C_{12} , and C_{15} were attributed to vibrational modes of lattice H_2O [15], while the bands which appeared at $3100\text{--}3380\text{ cm}^{-1}$ and $621\text{--}775\text{ cm}^{-1}$ in the spectra of C_1 , C_2 , C_4 , C_6 , C_7 , C_8 , C_{12} , C_{13} , and C_{15} were due to coordinated H_2O [15]. The spectrum of MPDH_4 exhibited a strong band in the range $3552\text{--}3421\text{ cm}^{-1}$ and another band at $1195\text{--}1161\text{ cm}^{-1}$ 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). Figure 5 shows representative FTIR spectra of C_3 and C_5 prepared by method 1 from MPDH_4 and EDH_4 , respectively.

3.4. ^1H NMR and ^{13}C NMR Spectra. The ^1H NMR spectra of diSchiff bases and the binuclear bis(bipyridyl) copper complex of 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 $\delta = 8.5\text{--}9.9$ ppm attributed to phenolic hydroxyl protons [3, 4, 16] as is demonstrated by the spectra of EDH_4 and 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

TABLE 5: Electronic spectra, magnetic moments, and molar conductivity data of Schiff bases and their metal complexes.

Symbol	Band positions (cm ⁻¹)	Assignment	μ_{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
	20833	$n \rightarrow \pi^*$		
MPDH ₄	33333	$\pi \rightarrow \pi^*$	—	0.0007
	27777	$n \rightarrow \pi^*$		
C ₁	32362, 29154	Intraligand $\pi \rightarrow \pi^*$		0.022
	23255	C.T	0.386 oh	
	15431	${}^2B_{1g} \rightarrow {}^2B_{2g}$		
	13513	${}^2B_{1g} \rightarrow {}^2A_{1g}$		
C ₂	33444	Intraligand $\pi \rightarrow \pi^*$		
	26315	C.T	0.514 oh	
	18868	${}^2B_{1g} \rightarrow {}^2B_{2g}$		
	33333	Intraligand $\pi \rightarrow \pi^*$		
C ₃	25641	C.T		
	15625	${}^2B_{1g} \rightarrow {}^2B_{2g}$	1.260 Sq.	
	12658	${}^2B_{1g} \rightarrow {}^2A_{1g}$		
	37735, 34843	Intraligand $\pi \rightarrow \pi^*$		
C ₄	27247	C.T		
	23148	${}^2B_{1g} \rightarrow {}^2E_g$	1.023 oh	
	10989	${}^2B_{1g} \rightarrow {}^2A_{1g}$		
	34013, 27247	Intraligand $\pi \rightarrow \pi^*$		
C ₅	23313	C.T		
	16025	${}^2B_{1g} \rightarrow {}^2B_{2g}$	1.061 Sq.	
	34129, 28571	Intraligand $\pi \rightarrow \pi^*$		
	25974	C.T		
C ₆	22883	${}^2B_{1g} \rightarrow {}^2E_g$		
	10460	${}^2B_{1g} \rightarrow {}^2A_{1g}$	0.810 oh	
	36363, 33333	Intraligand $\pi \rightarrow \pi^*$		
	31250	C.T		
C ₇	26178	C.T		
	15731	${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$	0.200 oh	
	10504	${}^4T_{1g} \rightarrow {}^4A_{2g}$		
	7083 cal.	${}^4T_{1g} \rightarrow {}^4T_{2g}$		
C ₈	34843, 33003	Intraligand $\pi \rightarrow \pi^*$		
	28248	C.T	1.092 Sq.	
	15983.	${}^4T_{1g} \rightarrow {}^4T_{1g}(P)$		
	9900	${}^4T_{1g} \rightarrow {}^4A_{2g}$		
C ₉	6456 cal.	${}^4T_{1g} \rightarrow {}^4T_{2g}$		
	36363, 27247	Intraligand $\pi \rightarrow \pi^*$	2.017 Sq.	
	23310	C.T		
	19920	${}^2B_{1g} \rightarrow {}^2E_g$		
C ₁₁	15313	${}^2B_{1g} \rightarrow {}^2B_{2g}$		
	10298	${}^2B_{1g} \rightarrow {}^2A_{1g}$	1.023 oh	
	29585	Intraligand $\pi \rightarrow \pi^*$		
	26041	C.T		
C ₁₂	21739	${}^2B_{1g} \rightarrow {}^2E_g$		
	15873	${}^2B_{1g} \rightarrow {}^2B_{2g}$	1.023 oh	
	36496, 32894	Intraligand $\pi \rightarrow \pi^*$		
C ₁₂	27624	C.T		
	22935	${}^2B_{1g} \rightarrow {}^2E_g$	1.023 oh	
	10482	${}^2B_{1g} \rightarrow {}^2A_{1g}$		

TABLE 5: Continued.

Symbol	Band positions (cm ⁻¹)	Assignment	μ_{eff} (B.M)	Molar conductivity S·mol ⁻¹ ·cm ² in DMF
C ₁₃	33333, 29239	Intraligand $\pi \rightarrow \pi^*$	0.440	163
	27027	C.T		
	22472	${}^2B_{1g} \rightarrow {}^2E_g$		
C ₁₄	34013, 29154	Intraligand $\pi \rightarrow \pi^*$	1.89 Sq.	158
	27027	C.T		
	18833.	${}^2B_{1g} \rightarrow {}^2B_{2g}$		
C ₁₅	29325	Intraligand $\pi \rightarrow \pi^*$	1.783 oh	0.023
	27397	C.T		
	22727	${}^2B_{1g} \rightarrow {}^2E_g$		

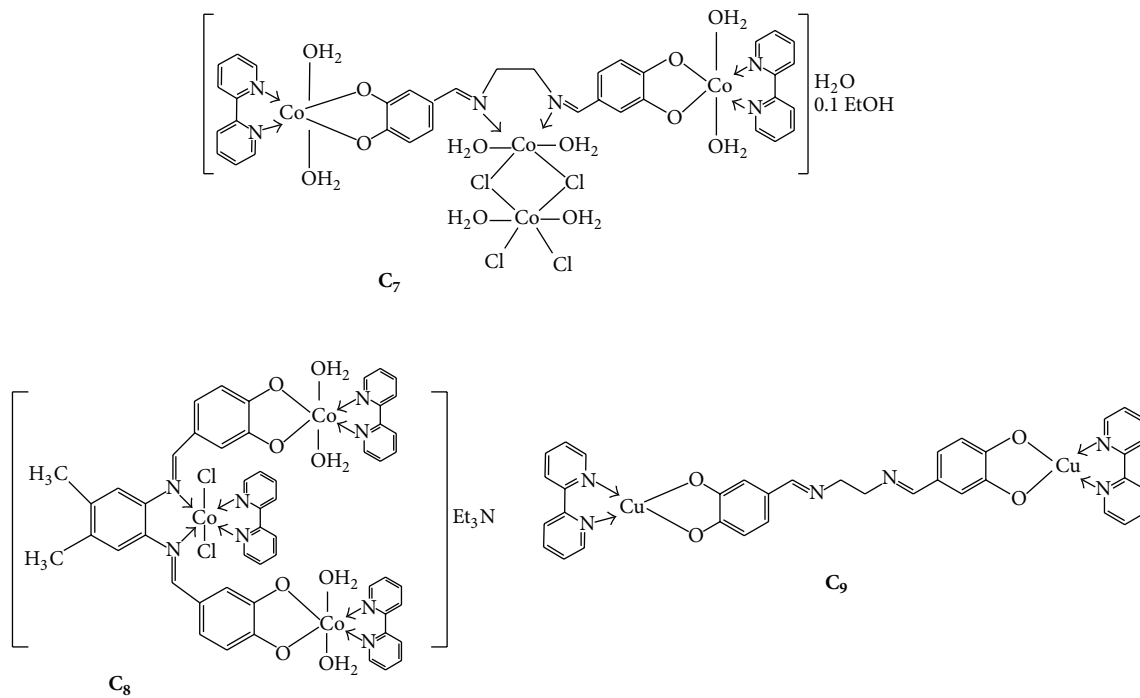
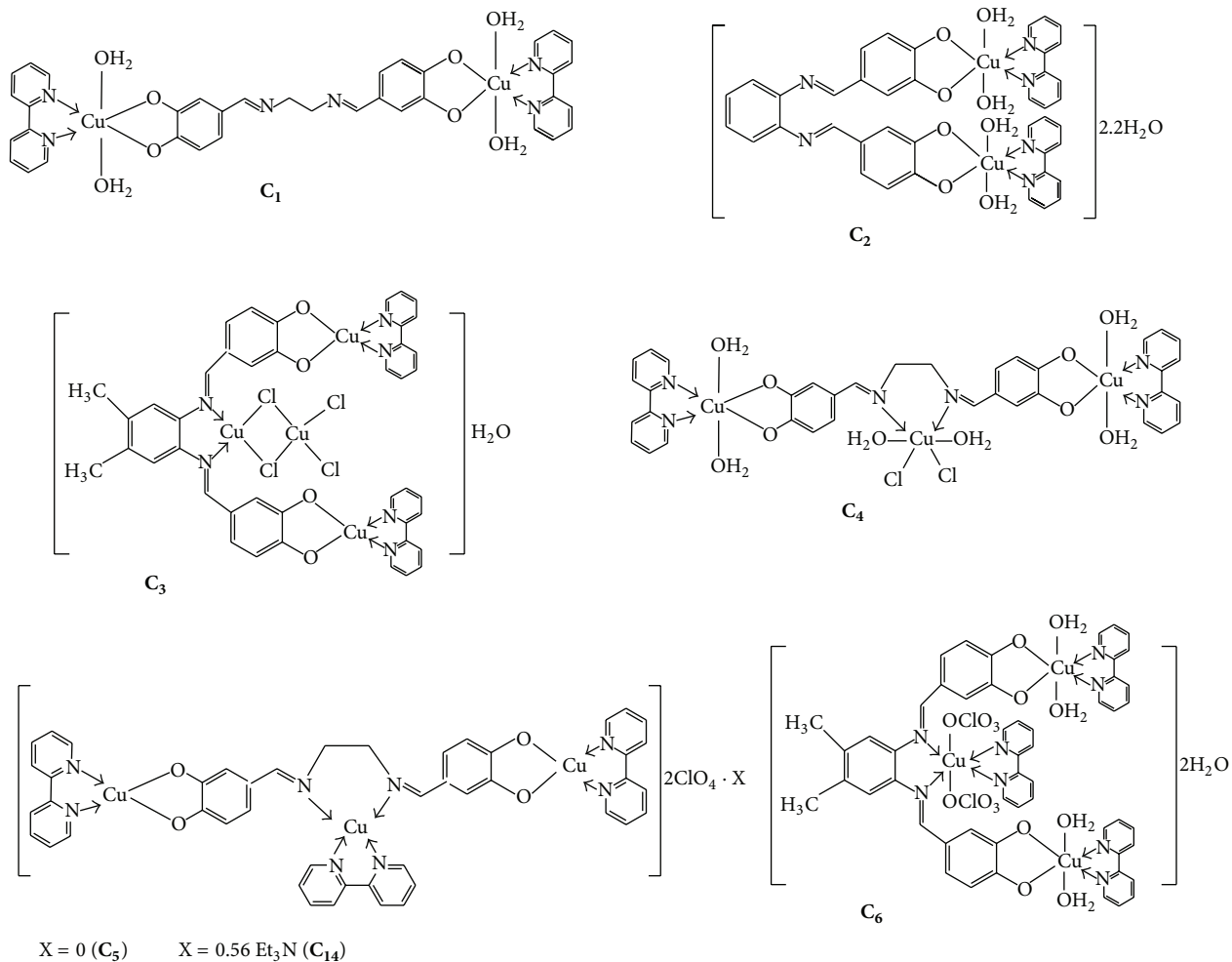
by ¹H NMR spectra of Schiff bases in the range $\delta = 7.9$ – 8.7 ppm were attributed to chemical shifts of the azomethine protons (HC=N) [3, 4, 16, 17]. The spectrum of C₁₁ exhibited the absence of the signals related to OH protons and the appearance of the azomethine proton signals downfield which 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 ¹³C NMR of EDH₄ and MPDH₄ 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 (CH₂) and at 19.8 and 20.1 (CH₃) 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].

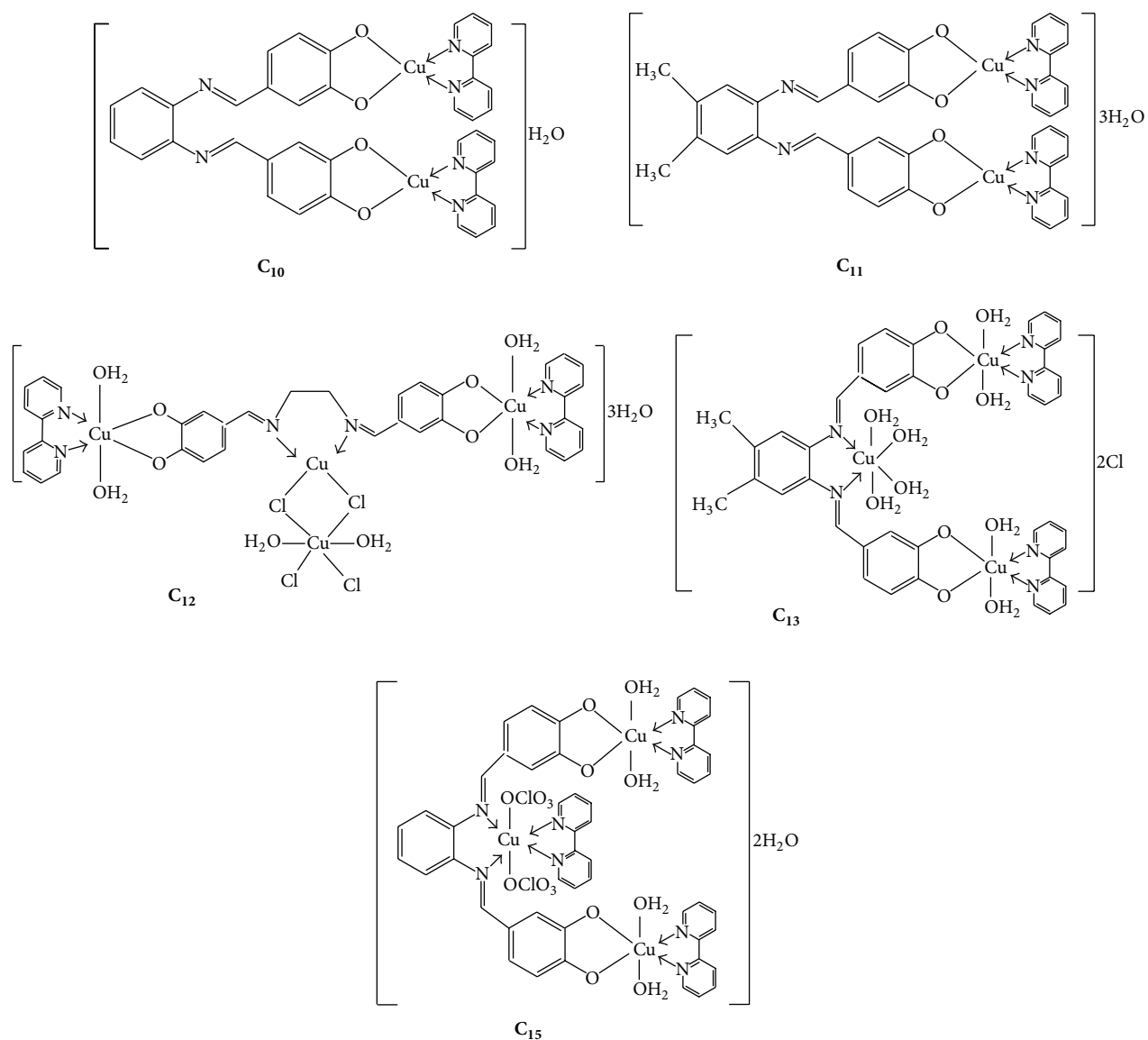
3.5. Electronic Spectra Conductivity and Magnetic Susceptibility Measurements. The results of electronic spectra of the ligands and their metal complexes in DMF are described in Table 5. The three ligands exhibited high intensity bands which appeared at wavenumber region 33333–24390 cm⁻¹ and low intensity 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 (C₃, C₅, C₉, C₁₀, C₁₁, and C₁₄) displayed bands in the regions 12970–10298 cm⁻¹, 18833–15313 cm⁻¹, and 21739–19920 cm⁻¹ assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$, and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively, of square planar Cu(II) complexes [23–27] while the spectra of the copper complexes (C₁, C₂, C₄, C₆, C₁₂, C₁₃, and C₁₅) 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 (C₇ and C₈) exhibited two bands observed at 15731 and 15983 cm⁻¹,

respectively, which were assigned to ${}^4T_{1g} \rightarrow {}^4T_{1g}$ (P) (ν_3) and at 10504 and 9900 cm⁻¹, respectively, corresponding to the transition ${}^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2) of octahedral Co(II) complexes [23]. The energies of ν_1 (${}^4T_{1g} \rightarrow {}^4T_{2g}$) as well as the values of the spectral parameters Dq/B' , B' , $10Dq$, and nephelauxetic ratio β for the Co(II) complexes C₇ (7083 cm⁻¹, 0.9, 787 cm⁻¹, 7080 cm⁻¹, and 0.811, resp.), and C₈ (6456 cm⁻¹, 0.7, 807 cm⁻¹, 5740 cm⁻¹, and 0.831, resp.), were calculated by applying the band ratio ν_3/ν_2 on Tanabe-Sugano diagram of d⁷ complexes. The values of β indicate a covalent bonding character of both complexes [23]. Conductivity measurements in DMF showed nonelectrolytic nature for all compounds (Table 3) 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 (μ_{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 μ_{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 C₁₂ 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



SCHEME 2: Continued.



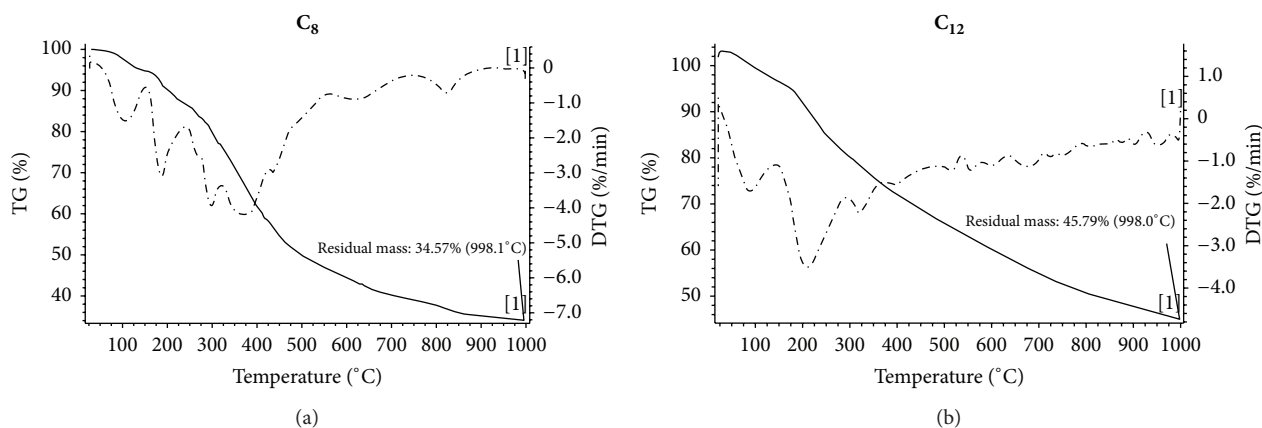
SCHEME 2: Suggested stereochemical structures of the synthesized diSchiff base complexes.

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 CuLL' with the diamines in a 2:1 ratio, respectively, as was confirmed by the NMR spectrum of 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.

FIGURE 7: TG and DTG thermographs of C_8 and C_{12} .TABLE 6: Thermal decomposition of the copper complexes (C_8 and C_{12}).

C_8 stable phase [MPD(Co ₃ (bipy) ₃ (H ₂ O) ₄ Cl ₂) Et ₃ N] M.wt = 1260.7	Temp. range of decomp. °C	Weight % loss found (calc.)
↓ 0.45Et ₃ N + Cl + 2H ₂ O	78–211	9.00 (9.28)
↓ 0.55Et ₃ N + 2H ₂ O	212–423	6.80 (7.26)
↓ 2CH ₃ + 2bipy + C ₆ H ₂	424–661	32.4 (33.43)
↓ Cl + bipy + HCN	662–998	17.23 (17.33)
C ₇ H ₄ NO ₂ Co ₂ + C ₆ H ₄ O ₂ Co (residue)	—	34.57 (33.13)
C_{12} stable phase [ED(Cu ₄ (bipy) ₂ (H ₂ O) ₆ Cl ₄) 3H ₂ O] M.wt = 1166.16	Temp. range of decomp. °C	Weight % loss found (calc.)
↓ 4H ₂ O	73–261	5.80 (6.17)
↓ 5H ₂ O + C ₂ H ₄	262–365	10.20 (10.11)
↓ C ₅ H ₄ N + bipy	366–542	20.00 (19.46)
↓ 4Cl	543–761	11.8 (12.13)
↓ C ₅ H ₄ N	762–998	6.4 (6.68)
C ₁₄ H ₈ N ₂ O ₄ Cu ₄ (residue)	—	45.79 (44.76)

Conflict of Interests

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

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