

Synthesis, characterization and extraction studies of N,N'' -bis[1-biphenyl-2-hydroxyimino-2-(4-acetylanilino)-1-ethylidene]-diamines and their homo- and heteronuclear copper(II) complexes

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Abstract. A new series of homo- and heteropolynuclear copper(II) complexes of N,N'' -bis[1-biphenyl-2-hydroxyimino-2-(4-acetylanilino)-1-ethylidene]-diamines have been prepared and characterized by different physical techniques. The starting point of the research was the reaction of chloroacetyl chloride with biphenyl in the presence of aluminum chloride. 4-Biphenylhydroximoyl chloride was obtained by reacting synthesized 4-(chloroacetyl)biphenyl with alkyl nitrite. Substituted 4-(alkylaminoisonitrosoacetyl)biphenyl (ketooxime) was prepared by reacting 4-biphenylhydroximoyl chloride with 4-aminoacetophenone in EtOH. Homodi-, homotrimeric and heterodimeric copper(II) perchlorate complexes of tetradentate Schiff bases which possess N_4 donor sets derived from the condensation of 4-(arylaminoisonitrosoacetyl)biphenyl and diamine derivatives were synthesized and characterized. Elemental analysis, FT-IR, ESR, molar conductivity, magnetic moment measurements and thermal analyses studies were utilized for the investigation of the complexes. The free ligands were also characterized by ^1H - and ^{13}C -NMR spectra. Elemental analyses, stoichiometric and spectroscopic data of the metal complexes indicated that the metal:ligand ratio of dinuclear copper(II) complexes were found to be 2 : 1 while this ratio was 3 : 2 in trinuclear copper(II) complexes and the metal complexes indicated that the metal ions are coordinated to the oxime and imine nitrogen atoms. The extraction abilities of the novel ligands were also evaluated in chloroform by using several transition metal picrates such as Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , Hg^{2+} . It has been observed that both ligands show a high affinity to Cu^{2+} ions.

Keywords. Schiff bases; oximes; metal complexes; extraction.

1. Introduction

The condensation of primary amines with carbonyl compounds yields Schiff bases¹ that are regarded as one of the most important group of chelators for facile preparations of new metal chelates. Schiff bases and oximes represent an important series of chelating agents and are now being widely used to synthesize mono-, di- or polynuclear transition metal complexes. In the past two decades, the synthesis, structure and properties of Schiff base complexes have stimulated much interest for their noteworthy contributions in single molecule-based magnetism, material science,² catalysis of many reactions like carbonylation, hydroformylation, reduction, oxidation, epoxidation and hydrolysis,³ etc. Different oximes and their metal complexes have shown notable bioactivity as chelat-

ing therapeutics, as drugs, as inhibitors of enzymes and as intermediates in the biosynthesis of nitrogen oxides.⁴ Also some oximes act as an important analytical reagents for the gravimetric and colorimetric determination of transition metals.⁵

The presence of copper(II) ion in these complexes has received wide interest in the fields of (i) the magneto-structural relationship and (ii) the characterization of active sites in multicopper proteins.⁶ Copper(II) complexes have a wide range of biological activity and some of these complexes have been known to be antitumour, antiviral, and anti-inflammatory agents. In addition, since copper(II) complexes especially with Schiff base and oxime ligands are models of physical and chemical behaviour of biological copper systems, considerable attention has been focused on these compounds.^{7–11} The copper(II) complex of 1,10-phenanthroline was the first synthetic transition metal complex effectively exhibiting nucleolytic activity.¹²

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Solvent extraction is one of the most versatile procedures among the separation techniques used for the removal and separation of metals. The development of selective extractants has expanded the use of solvent extraction for metal recovery and purification. Oximes and Schiff bases have been widely used as extractants for metal ions in solvent extraction.¹³

This study aims obtaining new coordinative compounds. Spectral characterization and thermal decomposition reactions serve as an important tools for the interpretation of structures of molecules of biological and analytical importance. Therefore, we report herein the synthesis, spectral characterization (infrared and ¹H, ¹³C NMR), magnetic susceptibility measurements, ESR and thermal studies of the homo- and heteropolynuclear copper(II) complexes of N, N'-bis[1-biphenyl-2-hydroxyimino-2-(4-acetylanilino)-1-ethylidene]-diethylenetriamine (H₂L¹) and N, N'-bis[1-biphenyl-2-hydroxyimino-2-(4-acetylanilino)-1-ethylidene]-1,3-propanediamine (H₂L²). We also investigate the possible utilization of these ligands in metal extractions from aqueous solutions into organic solvents.

2. Experimental

2.1 Physical measurements

All reagents were purchased from commercial sources and used as received. ¹H NMR and ¹³C NMR spectra of the ligands were recorded a from CDCl₃ solutions with TMS as internal standart at the Central Laboratory at METU-Ankara-Turkey. The IR spectra were recorded as KBr pellets on a Shimadzu IRPrestige-21 FT-IR Spectrophotometer. The thermogravimetric analysis (TG and DTG) of the complexes were measured on a Perkin Elmer Diamond TGA thermal analyser. The experiments were carried out in dynamic nitrogen atmosphere (20 mL min⁻¹) with a heating rate of 10°C min⁻¹ in temperature range 20–900°C using platinum crucibles. The X-band ESR spectra of the complexes were recorded at room temperature on a Bruker Elexsys E580 spectrometer. The stoichiometric analyses (C, H and N) of the ligand and the complexes were performed using LECO 932 CHNS analyzer. Metal contents (Mn, Co and Cu) were measured on Perkin Elmer Optima 5300 DV ICP-OES Spectrometer in solution prepared by decomposing the respective complex in hot concentrated HNO₃. UV-Vis spectra were obtained on a Perkin

Elmer λ 20 UV-Vis spectrometer. magnetic susceptibility measurements were carried out at room temperature in powder form on a Sherwood Scientific Magnetic Susceptibility Balance (Model MX1). The conductance measurements were carried out using an Optic Ivymen System conductivity meter. Melting point determinations were performed with a digital melting point instrument from electrothermal model IA 9100.

2.2 Synthesis of ligands [H₂L¹ (1) and H₂L² (6)]

1-(Biphenyl)-2-hydroxyimino-2-(4-acetylanilino)-1-ethanone (HL) were prepared according to previously published procedures.¹⁴

To an absolute ethanol solution (10 cm³) of 1-(biphenyl)-2-hydroxyimino-2-(4-acetylanilino)-1-ethanone (30 mmol, 10.75 g HL) was added diethylenetriamine (1.547 g, 15 mmol) and 1,3-propanediamine (1.112 g, 15 mmol) in absolute ethanol (10 cm³) respectively. The contents were stirred for 2 h at room temperature. The compound which precipitated was filtered off and washed several times with Et₂O and dried on P₂O₅.

2.3 Synthesis of complexes

Caution: Perchlorate salts of metal complexes are potentially explosive and should be handled in small quantities.

2.3a [Cu(H₂L¹)(H₂O)](ClO₄)₂ and [Cu(H₂L²)(H₂O)](ClO₄)₂: The copper(II) complexes were prepared in a similar manner.¹⁵ A solution of Cu(ClO₄)₂·6H₂O (370 mg, 1 mmol) in Me₂CO (25 cm³) was added to the ligand solution (1 mmol) in 30 cm³ of EtOH, and this mixture was refluxed with stirring for 1 h. After stripping off the excess solvent under reduced pressure, a crude oily product was obtained. The mononuclear copper(II) complexes were used without further purification.

2.3b [Cu(L¹)(H₂O)Cu(phen)₂](ClO₄)₂ (2) and [Cu(L²)(H₂O)Cu(phen)₂](ClO₄)₂ (7): The mononuclear copper complex (1 mmol) was added to Et₃N (101 mg, 1 mmol) in MeOH (25 cm³) and the mixture was stirred for 0.5 h. The solution of Cu(ClO₄)₂·6H₂O (370 mg, 1 mmol) in MeOH (10 cm³) and 1,10-phenanthroline monohydrate (397 mg, 2 mmol) in MeOH (10 cm³) was successively added to the resulting mixture, which was refluxed for 3 h.

imino-1-ethanone was prepared by reacting 4-(chloroacetyl) biphenyl with alkyl nitrite in the presence of dry HCl gas.¹⁷ 1-(Biphenyl)-2-hydroxyimino-2-(4-acetylanilino)-1-ethanone was prepared by reaction of 1-(biphenyl)-2-chloro-2-hydroxyimino-1-ethanone with 4-aminoacetophenone.¹⁴ N,N'' bis[1-biphenyl-2-hydroxyimino-2-(4-acetylanilino)-1-ethylidene]-diethylenetriamine (H_2L^1) and N,N' bis[1-biphenyl-2-hydroxyimino-2-(4-acetylanilino)-1-ethylidene]-1,3-propanediamine (H_2L^2) were originally synthesized by condensing of 1-(biphenyl)-2-hydroxyimino-2-(acetylanilino)-1-ethanone with diethylenetriamine and 1,3-propanediamine respectively.

Condensation of the 1-(biphenyl)-2-hydroxyimino-2-(4-acetylanilino)-1-ethanone with diamines readily gives rise to the corresponding imines, which were easily identified by their IR, elemental and thermal analysis, 1H and ^{13}C -NMR spectra, where replacement of the carbonyl by the imine group results in: (i) lowering of the energy of the $\nu(C=O)$ stretch in the IR spectrum and (ii) a shift to higher field of the $CH=N$ proton signal in the 1H -NMR spectrum.

The mono- (figure 1), homodi- (figure 2), homotri- (figure 3) and heterodinuclear Cu(II)-Mn(II) and Cu(II)-Co(II) complexes (figure 2) have been prepared by reaction of the ligand mixture in acetone with copper(II), manganese(II) or cobalt(II) salts. The complexes were obtained in powder form. All the complexes are stable at room temperature, are non-hygroscopic and insoluble in water, methanol and ethanol, but slightly soluble in chloroform, and

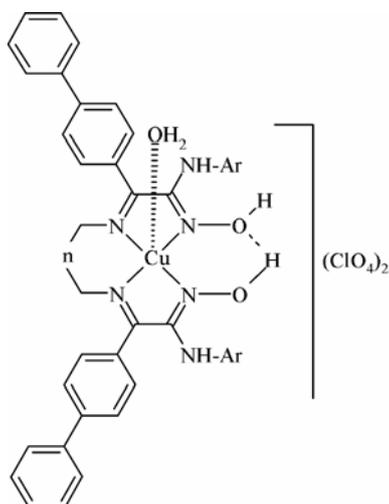


Figure 1. Mononuclear copper(II) complexes of H_2L^1 and H_2L^2 .

soluble in DMF and DMSO. Various attempts to obtain the single crystals of the complexes have so far been unsuccessful.

The melting points, yields, colours, magnetic susceptibility, molar conductivity values and elemental analyses of complexes and ligands are given in table 1. The results obtained are in good agreement with the suggested formulae and the melting points are sharp, indicating the purity of the prepared Schiff bases. The structure of the ligands (H_2L^1 and H_2L^2) is also confirmed by 1H -NMR, ^{13}C -NMR, FT-IR spectra and thermal analysis which will be discussed in a detailed manner, along with metal complexes, later.

3.1 NMR spectra

To understand the solution structure of the free Schiff base ligands, 1H - and ^{13}C -NMR spectra have been employed. The 1H - and ^{13}C -NMR spectra of the $CDCl_3$ solution of the ligands provided well-resolved signals, as expected. The chemical shifts, expressed in ppm downfield from tetramethylsilane, are given in tables 2 and 3.

1H -NMR spectrum of the ligands the deuterium exchangeable proton of the $=N-OH$ groups show a chemical shift in the 8.21 and 8.22 ppm as a singlet peak. All the multiplet signals in the 7.26–7.87 ppm range are assigned to the carbon atoms of the aromatic rings. The chemical shift values of the aromatic amine protons of H_2L^1 and H_2L^2 appeared at

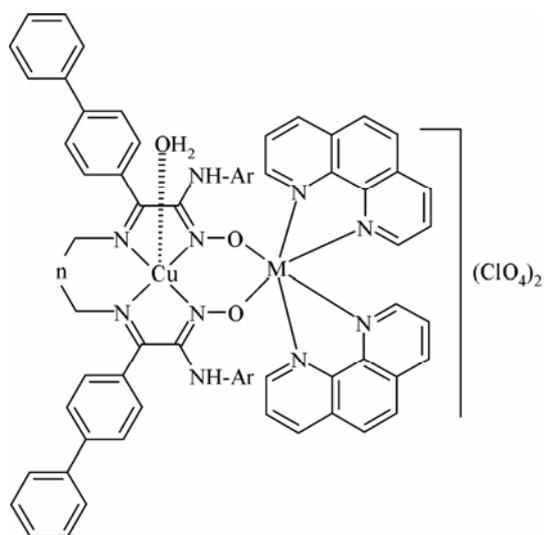


Figure 2. Homodinuclear Cu(II) and heterodinuclear Cu(II)-Mn(II) and Cu(II)-Co(II) complexes of H_2L^1 and H_2L^2 [M = Cu(II), Mn(II), Co(II)].

6.81 and 6.79 ppm as singlet, respectively. In the $^1\text{H-NMR}$ spectrum, the chemical shifts around 0.85–2.37 ppm can be attributed to the methylene group protons of the diethylenetriamine and 1,3-propanediamine. The other obtained values for $^1\text{H-NMR}$ chemical shifts of these compounds are given in table 2. These data are in good agreement with that previously reported for similar compounds.¹⁸ All the complexes are paramagnetic; therefore the $^1\text{H-NMR}$ spectra of the complexes could not be obtained.

The $^{13}\text{C-NMR}$ data and assignments of ligands are listed in table 3. The proton-decoupled $^{13}\text{C-NMR}$ spectrum of H_2L^1 and H_2L^2 displayed a single resonance at 186.72 and 186.13 ppm respectively which shows that the azomethine carbon atoms are equivalent, which also confirm the structure of ligands. The chemical shift observed at 147.48 and 147.46 ppm corresponds to oxime carbons. All the signals in the 117.09–146.67 ppm range are assigned to the carbon atoms of the aromatic rings. The chemical shift values of the carbonyl carbon atoms of H_2L^1 and H_2L^2 appeared at 196.21 and 196.72 ppm respectively. Addition signals observed at 27.38 and 27.34 ppm are attributable to the carbon atom of methyl group in the 4-aminoacetophenone. The chemical shifts for carbon atoms of methylene group were recorded between 12.43 and 56.83 ppm.

3.2 IR spectra

IR spectra is one of the most suitable techniques to give enough information to elucidate the nature of bonding of the ligand to the metal ion. The IR spectra of the free ligand and metal complexes were carried out in the range 4000–400 cm^{-1} (table 4).

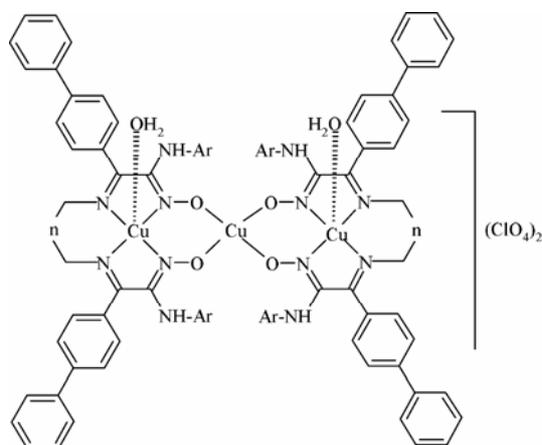


Figure 3. Homotrimeric Cu(II) complexes of H_2L^1 and H_2L^2 .

The IR spectra of the ligands show a broad band at 3292 cm^{-1} , which can be attributed to oxime OH groups. These bands disappeared in all complexes indicated that the oxime protons were separated upon complex formation and bonded to the metals. This is supported by the appearance of a new band in the region 526–493 cm^{-1} assigned to $\nu(\text{M-O})$.^{19,20} In addition, the N–O stretching vibrations for the Schiff base ligands were seen as medium-strong bands at 1359 and these vibrations in the complexes shift to upfield suggesting that the oxime groups are nitrogen coordinated. In the IR spectral data of the ligands, strong bands at 3358 and 3377 cm^{-1} belong to the $\nu(\text{N-H})$ vibration of the aromatic amine groups.

The spectra of H_2L^1 and H_2L^2 do not show absorptions characteristic of the C=O function owing to the formation of the C=N bond. A strong band observed in the 1672–1668 cm^{-1} and 1598–1597 cm^{-1} frequency ranges in the free ligands were assigned to the C=N stretch of the imine and oxime groups, respectively. The shift of $\nu(\text{C=N})$ vibration in all the complexes to a lower frequency suggests that coordination from imine and oxime nitrogen atoms. But when the complex is formed, two C=N bonds were distinguishable. The lower $\nu(\text{C=N})$ frequency also indicates stronger M–N bonding.^{21,22}

Coordination of the metal and the oximino or imino nitrogen in the copper(II) complexes are supported by the appearance of new bands at 435–418 cm^{-1} which are assigned to $\nu(\text{M-N})$.²³

A broad band observed in the IR spectrum of the copper(II) complexes in the 3585–3500 cm^{-1} region is attributed to the O–H stretch which confirms the presence of water molecules coordinated to the metal ion¹⁹. All of the perchlorate salts show a medium band near 1180–1176 cm^{-1} and a strong band at 1099–1089 cm^{-1} (antisymmetric stretch) and sharp band at 626–621 cm^{-1} (antisymmetric bend), indicative of uncoordinated perchlorate anions.^{24,25,26}

3.3 Molar conductance

The molar conductance of the complexes was an aid for proposing their formulas. Conductivity measurements were carried out in ca. 10^{-3} mol dm^{-3} *N,N*-dimethylformamide solutions at 20°C. The molar conductance values fall within the range 161–190 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ for all complexes. The molar conductances of the mono-, di- and trinuclear copper(II) complexes in DMF indicated that complexes of copper(II) containing perchlorate ions behave as 1 : 2 electrolytes.²⁷

Table 1. Physical properties and elemental analysis of the Schiff base ligands and their complexes.

Compds	Formula	m.p. (°C)	Yield (%)	Colour	μ_{eff} (BM)	Λ_{M} ^b	Calcd (found) %			
							C	H	N	Metal
(1)	C ₄₈ H ₄₅ N ₇ O ₄	143	87	Yellow	–	–	73.54 (73.48)	5.79 (5.65)	12.51 (12.42)	–
(2)	C ₇₂ H ₆₁ N ₁₁ O ₁₃ Cu ₂ Cl ₂	270 ^a	51	Black	1.83	166	58.18 (58.32)	4.14 (4.37)	10.37 (10.58)	8.55 Cu (8.63)
(3)	C ₇₂ H ₆₁ N ₁₁ O ₁₃ CuMnCl ₂	175 ^a	58	Brown	3.92	181	58.52 (58.40)	4.16 (4.24)	10.43 (10.36)	4.30 Cu (4.47) 3.72 Mn (3.85)
(4)	C ₇₂ H ₆₃ N ₁₁ O ₁₄ CuCoCl ₂	240 ^a	75	Green	2.12	178	58.36 (58.28)	4.15 (4.18)	10.40 (10.24)	4.29 Cu (4.42) 3.98 Co (3.75)
(5)	C ₉₆ H ₉₂ N ₁₄ O ₁₉ Cu ₃ Cl ₂	210 ^a	49	Brown	2.20	169	57.96 (57.81)	4.56 (4.67)	9.86 (9.75)	9.58 Cu (9.39)
(6)	C ₄₇ H ₄₂ N ₆ O ₄	135	75	Yellow	–	–	74.78 (74.52)	5.61 (5.79)	11.13 (11.28)	–
(7)	C ₇₁ H ₅₈ N ₁₀ O ₁₃ Cu ₂ Cl ₂	216 ^a	40	Green	1.94	190	58.52 (58.86)	4.01 (4.35)	9.61 (9.67)	8.72 Cu (8.94)
(8)	C ₇₁ H ₆₀ N ₁₀ O ₁₄ CuMnCl ₂	178 ^a	57	Brown	3.83	184	58.14 (58.37)	4.09 (4.28)	9.55 (9.67)	4.33 Cu (4.46) 3.74 Mn (3.83)
(9)	C ₇₁ H ₅₈ N ₁₀ O ₁₃ CuCoCl ₂	237 ^a	73	Green	2.10	186	58.70 (58.54)	4.02 (4.13)	9.64 (9.52)	4.37 Cu (4.52) 4.06 Co (4.17)
(10)	C ₉₄ H ₈₄ N ₁₂ O ₁₈ Cu ₃ Cl ₂	218 ^a	68	Brown	2.18	161	58.46 (58.63)	4.38 (4.16)	8.70 (8.94)	9.87 Cu (9.64)

^aDecomposition point. ^bMolar conductivity ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)

3.4 Magnetic and ESR studies

The magnetic moments of the complexes have been measured at room temperature and are listed in table 1. The magnetic susceptibility measurements show that the complexes are paramagnetic at ambient temperature.

The trinuclear complexes (5) and (10) have room temperature magnetic moments 2.20 and 2.18 B.M. while homodinuclear copper(II) complexes (2) and (7) have magnetic moments 1.83 and 1.94 B.M. which are somewhat lower than the spin only value of a single electron.²⁸

It is obvious that the di- and trinuclear copper(II) complexes possess antiferromagnetic properties at room temperature by a strong intramolecular antiferromagnetic spin exchange interaction as reported previously for di and trinuclear copper(II) complexes with oximato and oxamidato bridged ligands.^{29,30}

The magnetic moment values at room temperature for compounds [Cu(L¹)Mn(phen)₂], [Cu(L¹)Co(phen)₂], [Cu(L²)Mn(phen)₂] and [Cu(L²)Co(phen)₂] in the powder state are 3.92, 2.12, 3.83 and 2.10 respectively. Magnetic data show that manganese(II) and cobalt(II) which are in an octahedral environment adopts a high-spin configuration in the heterodinuclear copper(II) complexes.³¹

These results show that the axial coordination of perchlorate anion is not important to their magnetic behaviour.⁶

The X-band ESR spectra of heterodinuclear Cu(II)–Mn(II) (3) and homotrimeric Cu(II) complexes (10), in the solid state, were measured at room temperature. The ESR spectrum of the heterodinuclear copper(II)–manganese(II) complex (3) give a dissymmetric broad band around $g \approx 2.0$ in the low field region (3000 G) Compound (3) also gave an Cu-hyperfine structure, but this compound is indicating that the broadened ESR spectrum is due to the

Table 2. $^1\text{H-NMR}$ spectral data of the Schiff base ligands (in ppm).

Compds	O–H _(oxime)	C–H _(aromatic)	N–H	C–H _(aliphatic)
(1)	8.21 (s, 2H)	7.26–7.82 (m, 26H)	6.45 (s, 1H) 6.81 (s, 2H) (Ar–NH–)	2.49 (s, 6H) (Ar–CH ₃) 2.18 (t, 4H) 2.37 (t, 4H)
(6)	8.22 (s, 2H)	7.28–7.87 (m, 26H)	6.79 (s, 2H)	2.38 (s, 6H) (Ar–CH ₃) 0.85 (p, 2H) 1.28 (t, 4H)

Table 3. $^{13}\text{C-NMR}$ spectral data of the Schiff base ligands (in ppm).

Compds	C _(carbonyl)	C _(imine)	C _(oxime)	C _(aromatic)	C _(aliphatic)
(1)	196.21	186.72	147.48	117.71–146.21	27.38 (Ar–CH ₃) 47.82 56.78
(6)	196.72	186.13	147.46	117.09–146.67	27.34 (Ar–CH ₃) 12.43 56.83

intramolecular exchange coupled copper-manganese system.³² For copper(II) in the complex (3) $g_{\parallel} = 2.273$ and $g_{\perp} = 2.138$ showed distorted square-based pyramidal geometry, but Mn-hyperfine structure did not detected from the spectrum.

For compound (10) a well resolved signal is obtained with $g_{\parallel} = 2.274$ and $g_{\perp} = 2.081$. The fact that $g_{\parallel} > g_{\perp} > 2.00$ showed that the unpaired electron is in the $d_{x^2-y^2}$ orbital of copper(II) and the complex is a distorted square-based pyramidal geometry.³³ The hyperfine structure is well resolved for the complex. The spectrum of trinuclear copper complex, reveals four lines in the g_{\parallel} region which are assigned to the interaction of the paramagnetic electron with the Cu(II) nucleus ($I = 3/2$); however, the intensity pattern of the lines is complex.^{34,35} This indicates that spin-exchange interactions exist between the copper(II) ions.^{36,37} The ESR spectral features of these complexes indicate the presence of magnetically coupled copper(II) [$G = (g_{\parallel} - 2)/(g_{\perp} - 2)$] < 4.0 ($G = 3.38$) ions within trimer.^{36,38}

3.5 Thermal studies

Thermogravimetric (TG) and differential thermogravimetric (DTG) analyses for the ligands and metal complexes were carried out within the temperature range from ambient temperature up to 900°C. The thermal behaviour of the ligands and some of their complexes show good agreement with the formulae

suggested from the analytical data (table 1). The thermal behaviour of all the complexes was almost the same. Therefore, two ligands and only two of the complexes are discussed here in detail.

The ligands (1) and (6) are thermally decomposed in two successive degradation steps. The first step occurs which is reasonably accounted for the loss of two 4-acetylanilino, OH and CN groups. The second step occurs which corresponds to the loss of two biphenyl groups leaving R(CN)₂ as residue. Total loss of masses were found to be 84.50% (calc. = 84.24%) and 87.40% (calc. = 87.48%) for ligands (1) and (2), respectively.

The thermal decomposition of the complex (4) with the molecular formula [C₇₂H₆₃N₁₁O₁₄CuCoCl₂] takes place in three stages. In the first stage from 40 to 110°C one mole of hydrated H₂O molecule degrade, shown as one maximum in DTG curve at 55°C with a 1.20% mass loss (calc. = 1.26%). The second stage starts at 110°C and ends at 500°C, the corresponding mass loss 38.50% is due to the degradation of one H₂O, two perchlorate and two phenanthroline molecules, which is in agreement with the calculated value (calc. = 38.62%). The DTG curve shows three peaks at 245, 310 and 400°C for this stage. The third stage is related to the decomposition of the remaining part of the ligand molecule but decomposition did not finish at 900°C.

The complex (5) with the molecular formula [C₉₆H₉₂N₁₄O₁₉Cu₃Cl₂] is thermally decomposed in

Table 4. Significant bands in the IR spectra of the Schiff base ligands and their complexes.

Compds	$\nu(\text{O-H})$	$\nu(\text{N-H})$	$\nu(\text{C=N})_{\text{im}}$	$\nu(\text{C=N})_{\text{ox}}$	$\nu(\text{N-O})$	$\nu(\text{C-N})$	$\nu(\text{ClO}_4)$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
(1)	3292 <i>b</i>	3358 <i>m</i>	1672 <i>s</i>	1598 <i>s</i>	1359 <i>m</i>	1520 <i>m</i>	–	–	–
(2)	3500 <i>b</i>	3325 <i>w</i>	1668 <i>s</i>	1595 <i>s</i>	1417 <i>m</i>	1502 <i>s</i>	1099 <i>m</i> , 1180 <i>m</i> , 621 <i>w</i>	526 <i>w</i>	435 <i>w</i>
(3)	3527 <i>b</i>	3321 <i>w</i>	1658 <i>s</i>	1591 <i>s</i>	1421 <i>m</i>	1508 <i>s</i>	1091 <i>s</i> , 1178 <i>m</i> , 621 <i>w</i>	513 <i>w</i>	426 <i>w</i>
(4)	3585 <i>b</i>	3396 <i>m</i>	1658 <i>m</i>	1593 <i>m</i>	1427 <i>m</i>	1516 <i>m</i>	1095 <i>s</i> , 1176 <i>w</i> , 626 <i>w</i>	516 <i>w</i>	428 <i>w</i>
(5)	3523 <i>b</i>	3329 <i>m</i>	1668 <i>s</i>	1594 <i>s</i>	1409 <i>m</i>	1508 <i>s</i>	1099 <i>s</i> , 1178 <i>m</i> , 626 <i>w</i>	522 <i>w</i>	435 <i>w</i>
(6)	3292 <i>b</i>	3377 <i>w</i>	1668 <i>m</i>	1597 <i>s</i>	1359 <i>m</i>	1525 <i>m</i>	–	–	–
(7)	3533 <i>b</i>	3373 <i>m</i>	1629 <i>w</i>	1589 <i>m</i>	1433 <i>s</i>	1519 <i>s</i>	1097 <i>s</i> , 1176 <i>m</i> , 626 <i>s</i>	493 <i>w</i>	430 <i>w</i>
(8)	3547 <i>b</i>	3340 <i>w</i>	1653 <i>s</i>	1593 <i>s</i>	1419 <i>m</i>	1504 <i>s</i>	1093 <i>s</i> , 1176 <i>m</i> , 626 <i>w</i>	507 <i>w</i>	418 <i>w</i>
(9)	3578 <i>b</i>	3377 <i>m</i>	1654 <i>m</i>	1593 <i>m</i>	1426 <i>m</i>	1516 <i>m</i>	1089 <i>s</i> , 1180 <i>w</i> , 621 <i>w</i>	513 <i>w</i>	432 <i>w</i>
(10)	3537 <i>b</i>	3321 <i>m</i>	1666 <i>s</i>	1595 <i>s</i>	1413 <i>m</i>	1506 <i>s</i>	1095 <i>s</i> , 1180 <i>m</i> , 626 <i>w</i>	526 <i>w</i>	426 <i>w</i>

s, strong; *m*, medium; *w*, weak; *b*, broad

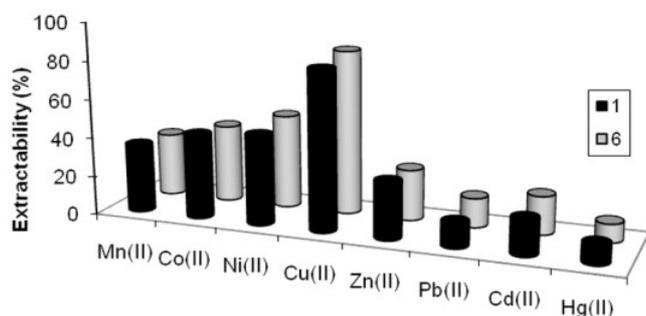


Figure 4. Extraction percentage of the metal picrates with ligands. (1 = H_2L^1 , 6 = H_2L^2), $\text{H}_2\text{O}/\text{CHCl}_3 = 10/10$ (v/v): $[\text{picric acid}] = 2 \times 10^{-5}$ M, $[\text{ligand}] = 1 \times 10^{-3}$ M, $[\text{metal nitrate}] = 1 \times 10^{-2}$ M, 298 K, 1 h contact time.

three successive steps too. The degradation of one mole of hydrated H_2O molecule takes place in the first stage between 35 and 115°C with a mass loss of 1.05% (calc. = 0.89%). The maximum rate of mass loss is indicated by the DTG peak at 50°C. The second step occurs within the temperature range 115–250°C with an estimated mass loss 28.55% (calc. = 28.76%), which is reasonably accounted for the loss of one H_2O , two perchlorate and two phenanthroline groups. The DTG curve gives a peak at 225°C. Again decomposition did not finish at 900°C. Therefore last decomposition residue did not determine.

3.6 Extraction ability of the H_2L^1 and H_2L^2

Extraction efficiencies of the Schiff base ligands H_2L^1 and H_2L^2 which contain oxime group have been carried out by the two-phase solvent extraction of transition metal picrates (Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , Hg^{2+}) into chloroform under neutral conditions. The results obtained using chloroform solutions of ligands to extract metal picrates from aqueous solution according to Pedersen's procedure.¹⁶ The equilibrium concentration of picrate in

aqueous phase was then determined spectrophotometrically.³⁹

As can be seen in figure 4 the extractability of transition metal picrates differs in $\text{Cu}^{2+} \gg \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+} > \text{Hg}^{2+}$ order. However, it is seen that ligands are selective for the Cu^{2+} cation, and that it does not show the same characteristic for all transition metal cations other than the Cu^{2+} cation. This result can be explained by the hard soft acid–base principle. The $-\text{C}=\text{N}-\text{OH}$ group is a soft base owing to its contribution to cation- π interaction; therefore, shows a high affinity toward soft acidic Cu^{2+} cation.^{40–44}

4. Conclusion

Elemental analyses, stoichiometric and spectroscopic data of the metal complexes indicated that in the dinuclear complexes, in which the first $\text{Cu}(\text{II})$ ion was complexed with nitrogen atoms of the oxime and imine groups, the second ion [$\text{Cu}(\text{II})$, $\text{Mn}(\text{II})$, $\text{Co}(\text{II})$] is ligated with dianionic oxygen atoms of the oxime groups and are linked to the 1,10-phenanthroline nitrogen atoms. The trinuclear copper(II) complex was formed by coordination of the third $\text{Cu}(\text{II})$ ion with dianionic oxygen atoms of each of two molecules of the mononuclear copper(II) complexes. Moreover, dinuclear complexes of the diimine-dioxime ligands have a 2:1, trinuclear complexes of the diimine-dioxime ligands have a 3:2 metal:ligand ratio. All complexes of these ligands have square pyramidal or octahedral structure except second copper(II) in the trinuclear complexes. The thermal analyses data of these chelates shows that the complexes were generally thermally decomposed in 2–3 successive decomposition steps. The results are in good agreement with the proposed structures for the obtained complexes. Additionally,

cation-binding abilities of the ligands were evaluated using a solvent extraction technique. Picrate was used as a counter anion for all compounds. The results of the liquid-liquid extraction study towards selected transition metals (Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , Hg^{2+}) presented in this work show that *N,N''-bis[1-biphenyl-2-hydroxyimino-2-(4-acetylanilino)-1-ethylidene]-diethylenetriamine* (H_2L^1) and *N,N''-bis[1-biphenyl-2-hydroxyimino-2-(4-acetylanilino)-1-ethylidene]-1,3-propanediamine* (H_2L^2) have strong affinity towards Cu^{2+} ion whereas the ligands are poor extractant for the other transition metals. This can make these ligands suitable selectively separating Cu^{2+} ion.

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