



# Novel homo- and hetero-nuclear copper(II) complexes of tetradentate Schiff bases: Synthesis, characterization, solvent-extraction and catalase-like activity studies

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## ARTICLE INFO

### Article history:

Received 13 April 2008

Received in revised form 4 July 2008

Accepted 16 July 2008

Available online 24 July 2008

### Keywords:

Schiff base

Oxime

Solvent extraction

Catalytic activity

Polynuclear complex

## ABSTRACT

Twelve homo- and hetero-nuclear copper(II) complexes of tetradentate Schiff base ligands containing N<sub>4</sub> donor sets have been prepared by employing several steps. The characterization and nature of bonding of the complexes have been deduced from elemental analysis, FT-IR, molar conductivity, magnetic moment measurements and thermal analysis. The three Schiff base ligands were further identified using <sup>1</sup>H and <sup>13</sup>C NMR spectra. All copper(II) complexes are 1:2 electrolytes as shown by their molar conductivities ( $\Lambda_M$ ) in DMF and paramagnetic. The subnormal magnetic moment values of the di- and tri-nuclear complexes explained by a very strong anti-ferromagnetic interaction. The extraction ability of the ligands has been examined by the liquid–liquid extraction of selected transition metal (Mn<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Cd<sup>2+</sup>, Hg<sup>2+</sup>) cations. The ligands show strong binding ability toward copper(II) ion. Furthermore the homo- and hetero-nuclear copper(II) complexes were each tested for their ability to catalyse the disproportionation of hydrogen peroxide in the presence of the added base imidazole.

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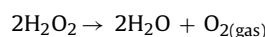
## 1. Introduction

Investigation on metal organic complexes represents one of the most active areas of material science and chemical research. Major advances have been made in these materials due to their interesting properties and potential in various applications, e.g., electrical conductivity, magnetism, hostguest chemistry, ion exchange, catalysis, nonlinear optics, etc. [1–3]. Synthesis of new Schiff bases and their metal complexes still the aim of many recent investigations. Schiff bases have played an important role in the development of coordination chemistry as they readily form stable complexes with most of the transition metals. They show interesting properties, e.g., their ability to reversibly bind oxygen [4], catalytic activity in hydrogenation of olefins [5] and transfer of an amino group [6], photochromic properties [7], and complexing ability towards toxic metals [8].

The process of solvent extraction is one of the most versatile procedures used for the removal, separation and concentration of metallic species, broadening its applications in the recycling of resources in the field of metallurgy and waste water treatment as demand increases for the development of new approaches to resolve the various problems presented. Some transition met-

als such as copper, cobalt and cadmium are both vital and toxic for many biological systems [9,10]. Thus, the determination of trace amounts of these metals are becoming increasingly important because of the increased interest in environmental pollution. For this purpose, many oxime derivatives have been synthesized and their extraction properties investigated by solvent extraction [11–15]. There are many processes, such as solvent extraction, ion exchange, adsorption and complexing that can be used for the removal of metals from wastewaters. Solvent extraction, ion exchange and activated carbon adsorption are the most commonly used processes for this purpose [16].

Hydrogen peroxide is a by-product of aerobic respiration; nevertheless in the presence of reductive metals [Fe(II) or Cu(I)], it can be converted to hydroxyl radicals whose deleterious effects on cell components is well documented [17,18]. Therefore, all living cells have devised a sophisticated machinery to suppress or at least control H<sub>2</sub>O<sub>2</sub> production. The catalase enzymes which are able to disproportionate H<sub>2</sub>O<sub>2</sub> into less harmful dioxygen and water are an important part of this machinery. The enzyme catalase catalyzes the rapid decomposition of hydrogen peroxide by the following reaction:



Several studies have been carried out on Mn complexes to act as catalase-like [19,20] and a variety of copper(II) complexes have been used in the treatment of many diseases, including cancer

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[21,22]. It has been suggested that the anticancer activity of these complexes may be based on their ability to inhibit DNA synthesis or on the possible scavenging of the superoxide anion [21].

Herein we have reported the synthesis and characterization of three novel Schiff bases and their homo- and hetero-polynuclear copper(II) complexes. We have also investigated the effectiveness of three imine–oxime derivatives in transferring the transition metals ( $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ) from the aqueous phase into the organic phase. In addition the reactivity of the complexes for  $\text{H}_2\text{O}_2$  disproportionation, as a functional model for Mn-CAT has been investigated.

## 2. Experimental

### 2.1. Physical measurements

All the reagents and solvents were of reagent-grade quality and purchased from commercial suppliers.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AVANCE 300 MHz spectrometer in  $\text{DMSO}-d_6$ , and chemical shifts are reported ( $\delta$ ) relative to  $\text{Me}_4\text{Si}$  as internal standard. The IR spectra were recorded on a Shimadzu IRPrestige-21 FT-IR Spectrophotometer as KBr pellets. Elemental analyses and metal contents of these compounds were determined by a LECO 932 CHNS analyzer and a PerkinElmer Optima 5300 DV ICP-OES Spectrometer. The thermogravimetric analysis and differential thermogravimetric (TG and DTG) of the complexes were measured on a PerkinElmer Diamond TGA thermal analyzer. The experiments were carried out in dynamic nitrogen atmosphere ( $20\text{ cm}^3\text{ min}^{-1}$ ) with a heating rate of  $10^\circ\text{C min}^{-1}$  in temperature range  $20\text{--}900^\circ\text{C}$  using platinum crucibles. Melting points were measured on an Electrothermal model IA 9100. The UV–vis measurements were recorded on a PerkinElmer  $\lambda$  20 UV–vis Spectrometer. Room temperature magnetic susceptibility measurements were done on a Sherwood Scientific Magnetic Susceptibility Balance (Model MX1). The conductance measurements were carried out using an Optic Ivymen System conductivity meter.

### 2.2. Synthesis of ligands [ $\text{H}_2\text{L}^1$ (**1**), $\text{H}_2\text{L}^2$ (**6**) and $\text{H}_2\text{L}^3$ (**11**)]

1-(Biphenyl)-2-hydroxyimino-2-(4-chloroanilino)-1-ethanone  $\text{HL}^1$ , 1-(biphenyl)-2-hydroxyimino-2-(4-methylanilino)-1-ethanone  $\text{HL}^2$  and 1-(biphenyl)-2-hydroxyimino-2-(pyrrolidino)-1-ethanone  $\text{HL}^3$  were prepared in a similar manner according to the reported procedure [23].

To an absolute ethanol solution ( $10\text{ cm}^3$ ) of  $\text{HL}^1$ ,  $\text{HL}^2$  or  $\text{HL}^3$  ( $30\text{ mmol}$ ) was added 1,3-propanediamine ( $1, 112\text{ g}, 15\text{ mmol}$ ) in absolute ethanol ( $10\text{ cm}^3$ ), respectively. The contents were stirred for 2 h at room temperature. The compound which precipitated was filtered off and washed several times with  $\text{Et}_2\text{O}$  and dried on  $\text{P}_2\text{O}_5$ .

### 2.3. Synthesis of complexes

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

#### 2.3.1. $[\text{Cu}(\text{H}_2\text{L}^1)(\text{H}_2\text{O})](\text{ClO}_4)_2$ , $[\text{Cu}(\text{H}_2\text{L}^2)(\text{H}_2\text{O})](\text{ClO}_4)_2$ and $[\text{Cu}(\text{H}_2\text{L}^3)(\text{H}_2\text{O})](\text{ClO}_4)_2$

The copper(II) complexes were prepared in a similar manner [24]. A solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $370\text{ mg}, 1\text{ mmol}$ ) in  $\text{Me}_2\text{CO}$  ( $25\text{ cm}^3$ ) was added to the ligand solution ( $1\text{ mmol}$ ) in  $30\text{ cm}^3$  of  $\text{EtOH}$ , 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.

#### 2.3.2. $[\text{Cu}(\text{L}^1)(\text{H}_2\text{O})\text{Cu}(\text{phen})_2](\text{ClO}_4)_2$ (**2**), $[\text{Cu}(\text{L}^2)(\text{H}_2\text{O})\text{Cu}(\text{phen})_2](\text{ClO}_4)_2$ (**7**), and $[\text{Cu}(\text{L}^3)(\text{H}_2\text{O})\text{Cu}(\text{phen})_2](\text{ClO}_4)_2$ (**12**)

The mononuclear copper complex ( $1\text{ mmol}$ ) was added to  $\text{Et}_3\text{N}$  ( $101\text{ mg}, 1\text{ mmol}$ ) in  $\text{MeOH}$  ( $25\text{ cm}^3$ ) and the mixture was stirred for 0.5 h. The solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $370\text{ mg}, 1\text{ mmol}$ ) in  $\text{MeOH}$  ( $10\text{ cm}^3$ ) and 1,10-phenanthroline monohydrate ( $397\text{ mg}, 2\text{ mmol}$ ) in  $\text{MeOH}$  ( $10\text{ cm}^3$ ) was successively added to the resulting mixture, which was refluxed for 3 h. The product was filtered-off, washed with  $\text{H}_2\text{O}$ ,  $\text{MeOH}$  and  $\text{Et}_2\text{O}$  and dried over  $\text{P}_4\text{O}_{10}$ .

#### 2.3.3. $[\text{Cu}(\text{L}^1)(\text{H}_2\text{O})\text{Mn}(\text{phen})_2](\text{ClO}_4)_2$ (**3**), $[\text{Cu}(\text{L}^2)(\text{H}_2\text{O})\text{Mn}(\text{phen})_2](\text{ClO}_4)_2$ (**8**) and $[\text{Cu}(\text{L}^3)(\text{H}_2\text{O})\text{Mn}(\text{phen})_2](\text{ClO}_4)_2$ (**13**)

The mononuclear copper complex ( $1\text{ mmol}$ ) was mixed with  $\text{Et}_3\text{N}$  ( $101\text{ mg}, 1\text{ mmol}$ ) in  $\text{MeOH}$  ( $20\text{ cm}^3$ ) and stirred for 0.5 h. The solution of  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  ( $268\text{ mg}, 1\text{ mmol}$ ) in  $\text{MeOH}$  ( $10\text{ cm}^3$ ) and 1,10-phenanthroline monohydrate ( $397\text{ mg}, 2\text{ mmol}$ ) in  $\text{MeOH}$  ( $10\text{ cm}^3$ ) were successively added to the resulting solution. A stoichiometric amount of  $\text{NaClO}_4$  ( $123\text{ mg}, 1\text{ mmol}$ ) was then added to the resulting mixture which was refluxed for 3 h. The product was filtered off, washed with  $\text{H}_2\text{O}$ ,  $\text{MeOH}$  and  $\text{Et}_2\text{O}$  and dried over  $\text{P}_4\text{O}_{10}$ .

#### 2.3.4. $[\text{Cu}(\text{L}^1)(\text{H}_2\text{O})\text{Co}(\text{phen})_2](\text{ClO}_4)_2$ (**4**), $[\text{Cu}(\text{L}^2)(\text{H}_2\text{O})\text{Co}(\text{phen})_2](\text{ClO}_4)_2$ (**9**) and $[\text{Cu}(\text{L}^3)(\text{H}_2\text{O})\text{Co}(\text{phen})_2](\text{ClO}_4)_2$ (**14**)

The mononuclear copper complex ( $1\text{ mmol}$ ) was mixed with  $\text{Et}_3\text{N}$  ( $101\text{ mg}, 1\text{ mmol}$ ) in  $\text{MeOH}$  ( $20\text{ cm}^3$ ) and stirred for 0.5 h. The solutions of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  ( $249\text{ mg}, 1\text{ mmol}$ ) in  $\text{MeOH}$  ( $10\text{ cm}^3$ ) and 1,10-phenanthroline monohydrate ( $397\text{ mg}, 2\text{ mmol}$ ) in  $\text{MeOH}$  ( $10\text{ cm}^3$ ) were successively added to the resulting solution. A stoichiometric amount of  $\text{NaClO}_4$  ( $123\text{ mg}, 1\text{ mmol}$ ) was then added to the resulting mixture which was refluxed for 5 h. The product was filtered off, washed with  $\text{H}_2\text{O}$ ,  $\text{MeOH}$  and  $\text{Et}_2\text{O}$  and dried over  $\text{P}_4\text{O}_{10}$ .

#### 2.3.5. $[\text{Cu}_3(\text{L}^1)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (**5**), $[\text{Cu}_3(\text{L}^2)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (**10**) and $[\text{Cu}_3(\text{L}^3)_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ (**15**)

A mixture of mononuclear copper complex ( $2\text{ mmol}$ ),  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  ( $370\text{ mg}, 1\text{ mmol}$ ) and  $\text{Et}_3\text{N}$  ( $202\text{ mg}, 2\text{ mmol}$ ) in  $\text{Me}_2\text{CO}$  ( $25\text{ cm}^3$ ) was refluxed for 2 h. The resulting solution was filtered while hot and concentrated slowly. As the solution cooled a powder product precipitated. It was isolated with vacuum filtration, washed with  $\text{Et}_2\text{O}$  and dried over  $\text{P}_4\text{O}_{10}$ .

### 2.4. Solvent extraction

The extraction properties of the Schiff base ligands (**1**, **6** and **11**) were investigated under liquid–liquid phase and neutral conditions using transition metal picrates ( $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ) as substrates and measuring by UV–vis measurements the amounts of metal picrate in the aqueous phase before and after treatment with the compounds. About  $10\text{ cm}^3$  of  $2 \times 10^{-5}\text{ M}$  aqueous picrate solution and  $10\text{ cm}^3$  of  $1 \times 10^{-3}\text{ M}$  solution of ligand in  $\text{CH}_2\text{Cl}_2$  were vigorously agitated in a stoppered plastic tube with a mechanical shaker for 2 min, then magnetically stirred in a thermostated water bath at  $25^\circ\text{C}$  for 1 h, and finally left standing for an additional 30 min. The concentration of the picrate ion remaining in the aqueous phase was then determined spectrophotometrically. Blank experiments showed that no picrate extraction occurred in the absence of ligand. Transition metal picrates were prepared by successive addition of a  $1 \times 10^{-2}\text{ M}$  metal nitrate solution to  $2 \times 10^{-5}\text{ M}$  aqueous picric acid solution and shaken at  $25^\circ\text{C}$  for 1 h. This metal picrates ( $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ )

were measured by UV–vis using maximum wavelength 352 nm. For each combination of host and metal picrate, the picrate extraction was conducted on three different samples and the average value of percent picrate extracted, with a standard deviation, was calculated. In the absence of host, a blank experiment, no metal ion picrate extraction was detected. The extractability was calculated by using the equation below:

$$\text{Extractability (\%)} = \left( \frac{A_0 - A}{A_0} \right) \times 100$$

where  $A_0$  is the absorbance in the absence of ligand.  $A$  denotes the absorbance in the aqueous phase after extraction.

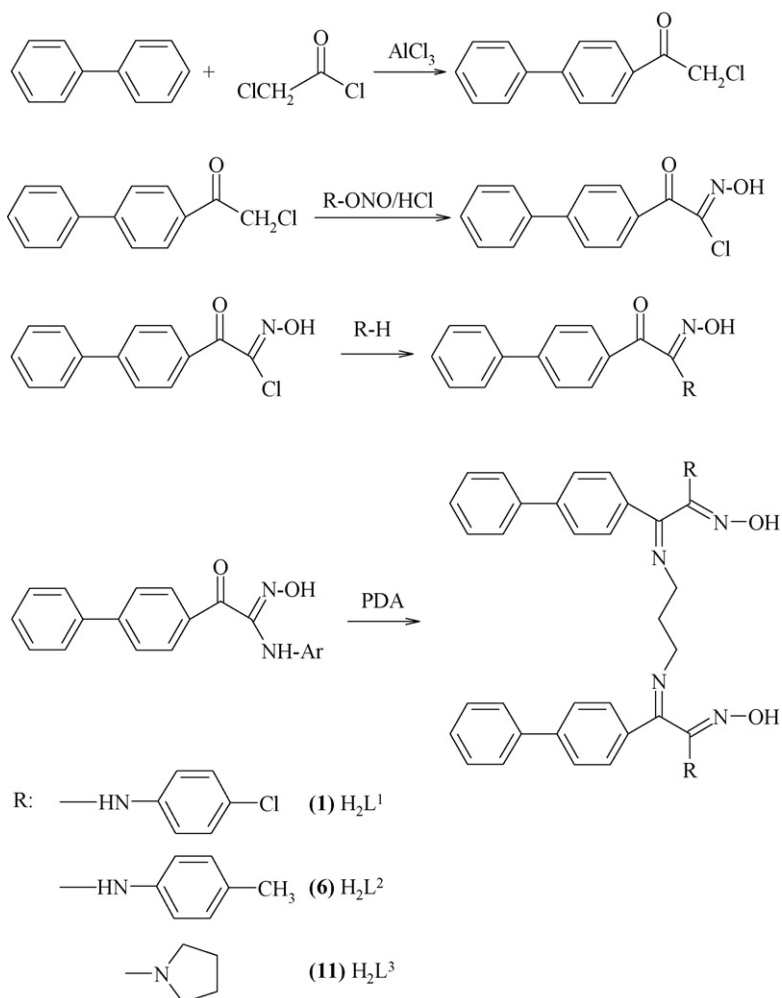
### 2.5. Catalase-like activity studies

Volumetric measurements of evolved dioxygen during the reactions of the heterodi-nuclear copper(II)–manganese(II) complexes with  $\text{H}_2\text{O}_2$  were carried out as follows: a 50  $\text{cm}^3$  three-necked round-bottom flask containing a solution of the complexes (0.005 mmol solid sample) in DMF (10  $\text{cm}^3$ ) was placed in a water bath (25 °C). One of the necks was connected to a burette and the others were stoppered by a rubber septum. While the solution was stirring,  $\text{H}_2\text{O}_2$  (1.33 mmol, 0.150  $\text{cm}^3$ ) was injected into it through the rubber septum using a microsyringe. Volumes of evolved dioxygen were measured at 1 min time intervals by volumetry. In

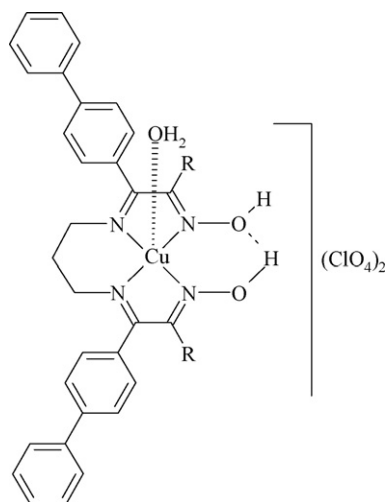
cases where imidazole (50 mg) was added this was introduced into the reaction vessel before the addition of  $\text{H}_2\text{O}_2$  (in the absence of the imidazole the complexes were either inactive or very weak catalysts for this reaction). The initial rates observed were expressed as  $\text{mol Ms}^{-1}$  by taking the volume of the solution (15  $\text{cm}^3$ ) into account and were calculated from the maximum slope of curve describing evolution of  $\text{O}_2$  versus time.

### 3. Results and discussion

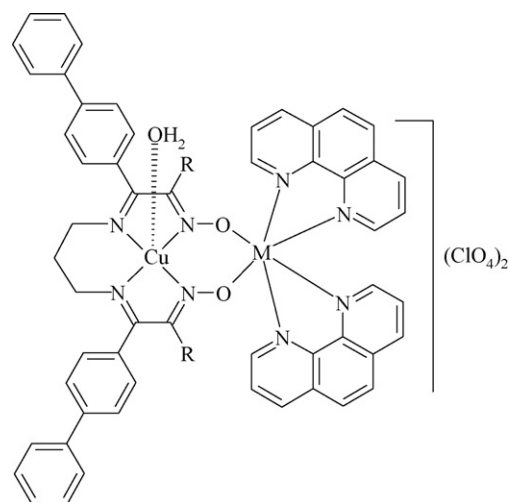
Scheme 1 shows the synthetic methodology followed for preparing imine–oxime ligands  $\text{H}_2\text{L}^1$ ,  $\text{H}_2\text{L}^2$  and  $\text{H}_2\text{L}^3$ . Firstly 4-chloroacetyl biphenyl was synthesized according to the literature from chloroacetyl chloride and biphenyl in the presence of  $\text{AlCl}_3$  as catalyst in a Friedel–Crafts reaction [25]. 1-(Biphenyl)-2-chloro-2-hydroxyimino-1-ethanone was prepared by reacting 4-(chloroacetyl) biphenyl with alkyl nitride in the presence of dry  $\text{HCl}$  gas [25]. 1-(Biphenyl)-2-hydroxyimino-2-(4-chloroanilino)-1-ethanone  $\text{HL}^1$ , 1-(biphenyl)-2-hydroxyimino-2-(4-methylanilino)-1-ethanone  $\text{HL}^2$  and 1-(biphenyl)-2-hydroxyimino-2-(pyrrolidino)-1-ethanone  $\text{HL}^3$  were prepared by reaction of 1-(biphenyl)-2-chloro-2-hydroxyimino-1-ethanone with 4-chloroaniline, 4-methylaniline and pyrrolidine, respectively [23].  $N,N'$ -Bis[1-biphenyl-2-hydroxyimino-2-(4-chloroanilino)-1-ethylidene]-1,3-propanediamine,  $\text{H}_2\text{L}^1$ ,  $N,N'$ -bis



Scheme 1. Synthetic route for the synthesis of ligands ( $\text{H}_2\text{L}^1$ ,  $\text{H}_2\text{L}^2$  and  $\text{H}_2\text{L}^3$ ).



**Fig. 1.** Structural scheme of the mononuclear copper(II) complexes of  $H_2L^1$ ,  $H_2L^2$  and  $H_2L^3$ .



**Fig. 2.** Structural scheme of the homodi-nuclear Cu(II), heterodi-nuclear Cu(II)–Mn(II) and Cu(II)–Co(II) complexes of  $H_2L^1$ ,  $H_2L^2$  and  $H_2L^3$ .

[1-biphenyl-2-hydroxyimino-2-(4-methylanilino)-1-ethylidene]-1,3-propanediamine  $H_2L^2$  and  $N,N'$ -bis[1-biphenyl-2-hydroxyimino-2-(pyrrolidino)-1-ethylidene]-1,3-propanediamine  $H_2L^3$ , were originally synthesized by condensing of 1,3-propanediamine with  $HL^1$ ,  $HL^2$  and  $HL^3$ , respectively.

The mono- (Fig. 1), homodi- (Fig. 2), homotri- (Fig. 3) and heterodi-nuclear Cu(II)–Mn(II) and Cu(II)–Co(II) complexes (Fig. 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 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 sus-

ceptibility, molar conductivity values and elemental analyses of complexes and ligands are summarized in Table 1. According to the results of the elemental analyses, 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.

### 3.1. NMR spectra

All the  $^1H$  NMR and  $^{13}C$  NMR spectra of the imino–oxime derivatives were taken in  $CDCl_3$ . The chemical shifts observed at  $\delta = 8.17$ , 8.14 and 8.45 ppm are assigned to the proton of the oxime group ( $=N-OH$ ) of the ligands  $H_2L^1$ ,  $H_2L^2$  and  $H_2L^3$ , respectively as a singlet peak. The peaks observed at range 7.14–7.85 ppm are assignable to the protons of the aromatic rings as multiplet peaks. The protons

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

Compounds	Formula	mp ( $^{\circ}C$ )	Yield (%)	Colour	$\mu_{eff}$ (B.M.)	$\Lambda_M^b$	Calculated (found) %			
							C	H	N	Metal
(1)	$[C_{43}H_{36}N_6O_2Cl_2]$	198	96	Yellow	–	–	69.82 (69.95)	4.91 (4.73)	11.36 (11.38)	–
(2)	$[C_{67}H_{52}N_{10}O_{11}Cu_2Cl_4]$	204 <sup>a</sup>	53	Brown	1.85	154	55.80 (55.71)	3.63 (3.54)	9.71 (9.86)	Cu 8.81 (8.64)
(3)	$[C_{67}H_{52}N_{10}O_{11}CuMnCl_4]$	250 <sup>a</sup>	46	Brown	3.50	168	56.14 (56.38)	3.66 (3.51)	9.56 (9.77)	Cu 4.43 (4.56) Mn 3.83 (3.96)
(4)	$[C_{67}H_{52}N_{10}O_{11}CuCoCl_4]$	233 <sup>a</sup>	47	Green	2.79	186	55.98 (55.74)	3.65 (3.57)	9.74 (9.83)	Cu 4.42 (4.23) Co 4.10 (4.25)
(5)	$[C_{86}H_{72}N_{12}O_{14}Cu_3Cl_6]$	138 <sup>a</sup>	61	Brown	1.97	171	54.34 (54.58)	3.82 (3.68)	8.84 (8.71)	Cu 10.03 (10.37)
(6)	$[C_{45}H_{42}N_6O_2]$	178	91	Yellow	–	–	77.34 (77.52)	6.06 (6.24)	12.03 (12.18)	–
(7)	$[C_{69}H_{58}N_{10}O_{11}Cu_2Cl_2]$	198 <sup>a</sup>	69	Green	1.78	164	59.14 (59.45)	4.17 (4.36)	10.00 (10.26)	Cu 9.07 (9.28)
(8)	$[C_{69}H_{58}N_{10}O_{11}CuMnCl_2]$	> 300	43	Brown	3.63	183	59.51 (59.67)	4.20 (4.39)	10.06 (10.02)	Cu 4.56 (4.63) Mn 3.94 (3.76)
(9)	$[C_{69}H_{58}N_{10}O_{11}CuCoCl_2]$	245 <sup>a</sup>	56	Brown	3.14	152	59.34 (59.59)	4.19 (4.36)	10.03 (10.36)	Cu 4.55 (4.69) Co 4.22 (4.25)
(10)	$[C_{90}H_{84}N_{12}O_{14}Cu_3Cl_2]$	187 <sup>a</sup>	47	Green	1.98	167	59.42 (59.51)	4.65 (4.41)	9.24 (9.47)	Cu 10.48 (10.27)
(11)	$[C_{39}H_{42}N_6O_2]$	78	52	Yellow	–	–	74.73 (74.96)	6.75 (6.76)	13.41 (13.58)	–
(12)	$[C_{63}H_{58}N_{10}O_{11}Cu_2Cl_2]$	221 <sup>a</sup>	65	Green	1.82	173	56.93 (56.68)	4.40 (4.27)	10.54 (10.46)	Cu 9.56 (9.74)
(13)	$[C_{63}H_{58}N_{10}O_{11}CuMnCl_2]$	182 <sup>a</sup>	45	Green	3.42	178	57.30 (57.47)	4.43 (4.58)	10.61 (10.79)	Cu 4.81 (4.96) Mn 4.16 (4.28)
(14)	$[C_{63}H_{60}N_{10}O_{12}CuCoCl_2]$	209 <sup>a</sup>	67	Yellow	3.38	186	56.36 (56.10)	4.50 (4.26)	10.43 (10.57)	Cu 4.73 (4.56) Co 4.39 (4.52)
(15)	$[C_{78}H_{86}N_{12}O_{15}Cu_3Cl_2]$	215 <sup>a</sup>	72	Green	1.98	164	55.33 (55.51)	5.12 (5.32)	9.93 (9.74)	Cu 11.26 (11.41)

<sup>a</sup> Decomposition point.

<sup>b</sup> Molar conductivity ( $\Omega^{-1} cm^2 mol^{-1}$ ).

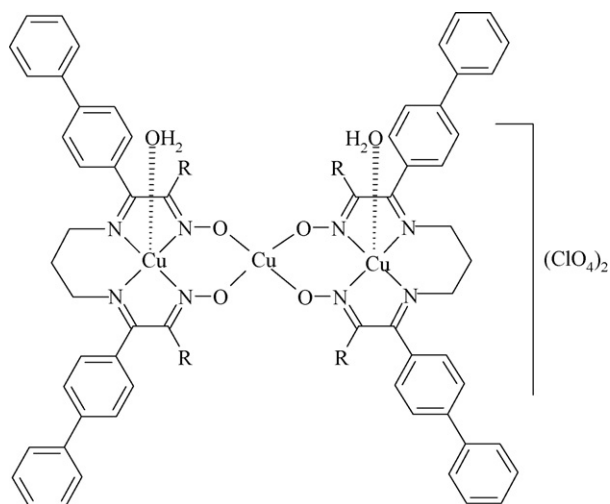


Fig. 3. Structural scheme of the homotri-nuclear Cu(II) complexes of  $H_2L^1$ ,  $H_2L^2$  and  $H_2L^3$ .

of the aromatic amine groups for  $H_2L^1$  and  $H_2L^2$  were observed at 6.80 and 6.78 ppm as singlets, respectively. The other obtained values for  $^1H$  NMR chemical shifts of these compounds are given in Table 2.

The  $^{13}C$  NMR data and assignments of ligands are listed in Table 3. The proton-decoupled  $^{13}C$  NMR spectrum of  $H_2L^1$ ,  $H_2L^2$  and  $H_2L^3$  displayed a single resonance at 186.27, 186.51 and 172.04 ppm, respectively which shows that the azomethine carbon atoms are equivalent, which also confirm the structure of ligands. All the signals in the 145.37–149.10 ppm range are assigned to the oxime carbons of the ligands. The chemical shifts for the carbon atoms of the aromatic rings were recorded between 119.88 and 146.65 ppm. Addition signals observed in the 11.96 and 57.83 ppm ranges are attributable to the carbon atoms of methylene group. These data are in good agreement with that previously reported for similar compounds [24,26,27]. The  $^1H$  NMR and  $^{13}C$  NMR spectra could not be taken for the copper(II) complexes due to its paramagnetic nature.

### 3.2. IR spectra

The characteristic vibrational frequencies have been identified by comparing the spectra of the complexes with their free ligands. The important IR spectral data of the free ligands and their homo- and hetero-polynuclear copper(II) complexes are presented in Table 4.

The IR spectrum of the ligands show  $\nu(C=N)$  peak at 1660–1667  $cm^{-1}$  and the absence of a  $\nu(C=O)$  peak at around

1700  $cm^{-1}$  is indicative of Schiff base condensation. The copper(II) complexes exhibit medium intense broad bands centered at 3502–3593  $cm^{-1}$  assigned to coordinated water [28]. The compounds were heated thermally at 100–130  $^{\circ}C$  and their IR spectra exhibit absence of the band at ca. 3502–3593  $cm^{-1}$ . This indirectly confirms the presence of coordinated water. The IR spectra of all complexes show  $\nu(C=N)$  bands at 1639–1654  $cm^{-1}$  [28] and it is found that the  $\nu(C=N)$  bands in the complexes are shifted by about 7–25  $cm^{-1}$  to lower energy regions compared to that of the free ligands  $H_2L^1$ ,  $H_2L^2$  and  $H_2L^3$ . This phenomenon appears to be due to the coordinated of azomethine nitrogen to the metal ion.

The O–H vibrations of the oxime groups disappeared in the IR spectra of the complexes indicated that the oxime protons were separated upon complex formation and bonded to the metals. This result is supported by shifting N–O vibrations to lower or higher frequencies than the free ligands [24,29]. Coordination of the metal and the oximino or imino nitrogen in the copper(II) complexes are supported by the appearance of new bands at 418–428  $cm^{-1}$  which are assigned to  $\nu(M-N)$  [30]. The IR spectra of the copper(II) complexes show a new band at 507–532  $cm^{-1}$  due to M–O bond resulting from the interaction between the oxygen atom of oxime and the metal ions [31]. In the IR spectral data of the  $H_2L^1$  and  $H_2L^2$ , strong bands at 3379 and 3377  $cm^{-1}$  belong to the  $\nu(N-H)$  vibration of the aromatic amine groups. All of the perchlorate salts show a medium band near 1145–1190  $cm^{-1}$  and a strong band at 1083–1109  $cm^{-1}$  (antisymmetric stretch) and sharp band at 621–626  $cm^{-1}$  (antisymmetric bend), indicative of uncoordinated perchlorate anions [32–34].

### 3.3. Molar conductance

Conductivity measurements were carried out in ca.  $10^{-3}$  mol  $dm^{-3}$  *N,N*-dimethylformamide solutions at 25  $^{\circ}C$ . The room temperature molar conductivity values of the complexes are given in Table 1. The molar conductance values for the perchlorate complexes are in the range characteristic of 1:2 electrolytes for all complexes [35].

### 3.4. Magnetic moment studies

As is known, magnetic susceptibility measurements provide information regarding the structure of the complexes. Magnetic susceptibility was determined using a magnetic susceptibility balance. The magnetic moment data of the solid-state complexes at room temperature are reported in Table 1. The magnetic susceptibility measurements show that the complexes are paramagnetic at ambient temperature.

The magnetic moment values of the homodi-nuclear copper(II) complexes are in the region of 1.78–1.85 B.M. while those of the homotri-nuclear copper(II) complexes are in the region of 1.97–1.98

Table 2  
 $^1H$  NMR spectral data of the Schiff base ligands (in ppm)

Compounds	O–H <sub>(oxime)</sub>	C–H <sub>(aromatic)</sub>	N–H	C–H <sub>(aliphatic)</sub>
(1)	8.17 (s,2H)	7.16–7.72 (m,26H)	6.80 (s,2H)	0.87 (p,2H) 1.32 (t,4H)
(6)	8.14 (s,2H)	7.14–7.73 (m,26H)	6.78 (s,2H)	2.23 (s,6H) (Ar–CH <sub>3</sub> ) 0.85 (p,2H) 1.29 (t,4H)
(11)	8.45 (s,2H)	7.31–7.85 (m,18H)	–	1.87 (m,8H) (pyrrolidine) 3.49 (m, 8H) (pyrrolidine) 1.41 (p,2H) 3.66 (t,4H)

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

Compounds	C <sub>(imine)</sub>	C <sub>(oxime)</sub>	C <sub>(aromatic)</sub>	C <sub>(aliphatic)</sub>
(1)	186.27	148.13	121.49–146.65	12.24 53.76
(6)	186.51	149.10	119.88–146.54	20.72 (Ar–CH <sub>3</sub> ) 11.96 57.83
(11)	172.04	145.37	124.48–143.85	23.82 (pyrrolidine) 47.96 (pyrrolidine) 14.35 52.97

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

Compounds	$\nu(\text{O-H})$	$\nu(\text{N-H})$	$\nu(\text{C=N})_{\text{im}}$	$\nu(\text{C=N})_{\text{ox}}$	$\nu(\text{N-O})$	$\nu(\text{C-N})$	$\nu(\text{ClO}_4)$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
(1)	3219b	3379m	1664s	1600s	1379m	1516s	–	–	–
(2)	3519b	3331m	1654s	1598s	1404m	1487s	1089s, 1188w 626w	526w	418w
(3)	3516b	3389s	1639s	1568s	1401m	1483m	1086s, 1146m 621w	513w	418w
(4)	3560b	3377w	1645w	1597w	1427m	1517m	1083s, 1167w 626w	513w	422w
(5)	3509b	3334m	1654m	1598s	1409m	1487s	1089s, 1190m 626w	532w	418w
(6)	3234b	3377m	1667s	1601s	1375m	1517s	–	–	–
(7)	3508b	3317m	1649s	1600s	1398m	1516s	1109s, 1145w 626w	522w	419w
(8)	3509b	3367w	1654w	1592w	1424s	1515s	1096s, 1146w 626s	513s	418w
(9)	3576b	3397w	1646w	1593m	1431m	1521m	1089s, 1161w 626w	516w	418w
(10)	3502b	3334m	1654s	1598s	1406s	1506s	1109s, 1188w 626w	513w	418w
(11)	3201b	–	1660w	1606s	1450s	1483m	–	–	–
(12)	3548b	–	1653w	1595s	1429m	1516m	1095s, 1180w 626w	507w	418w
(13)	3556b	–	1649w	1585m	1427s	1517s	1093s, 1153m 626m	513w	428w
(14)	3593b	–	1649w	1597m	1427m	1516m	1095s, 1166m 626w	507w	428w
(15)	3547b	–	1649w	1593s	1406m	1496w	1097s, 1180w 626w	509w	420w

s:strong, m:medium, w:weak, b:broad.

B.M. The magnetic moment values found for the homodi- and trinuclear copper(II) complexes are not consistent with the expected spin-only magnetic moment of an  $S = 1/2$ , Cu(II)  $d^9$  system. These low values are due to magnetic interaction between copper metal centers.

The observed magnetic moment values of the complexes are 3.42–3.63 for heterodinuclear copper(II)–manganese(II) and 2.79–3.38 for heterodinuclear copper(II)–cobalt(II). 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 [36].

As seen from Table 1 the homodi-, homotri- and heterodinuclear copper(II) complexes have subnormal magnetic moment values. The strong antiferromagnetic coupling that was found for the homo- and hetero-polynuclear copper(II) complexes are explained by the good superexchange properties of the oximate or oxamidato groups. These results show that the axial coordination of perchlorate anion is not important to their magnetic behaviour [37].

### 3.5. Thermal studies

The thermal behaviours of all the complexes were almost the same. Therefore, three ligands, one dinuclear and one trinuclear copper(II) of the complexes are discussed here in detail. TG and DTG analyses for the ligands and metal complexes were carried out within the temperature range from ambient temperature up to 900 °C. The correlations between the different

decomposition steps of the compounds with the corresponding weight losses are discussed in terms of the proposed formula of the compounds. The thermal behaviour of the ligands and their complexes are summarized in Table 5. The results show good agreement with the formulae suggested from the analytical data (Table 1).

The ligand (1) with the molecular formula  $[\text{C}_{43}\text{H}_{36}\text{N}_6\text{O}_2\text{Cl}_2]$  is thermally decomposed only one successive decomposition step. The estimated mass loss of 87.50% (calculated mass loss = 87.28%) within the temperature range 180–650 °C may be attributed to the loss of two 4-chloroanilino, OH, CN and biphenyl groups.

The thermal decomposition of the ligand (6) with the molecular formula  $[\text{C}_{45}\text{H}_{42}\text{N}_6\text{O}_2]$  proceeds with one degradation step. The step occurs within the temperature range 170–475 °C with an estimated mass loss 86.10% (calculated mass loss = 86.53) which is reasonably accounted for the loss of two 4-methylanilino, OH, CN and biphenyl groups.

The thermal decomposition of the other ligand (11) with the molecular formula  $[\text{C}_{39}\text{H}_{42}\text{N}_6\text{O}_2]$  proceeds with three main degradation steps. The first step occurs within the temperature range 80–190 °C with an estimated mass loss 54.10% (calculated mass loss = 54.31%) which is reasonably accounted for the loss of two OH and biphenyl groups. The second step occurs within the temperature range 190–365 °C with an estimated mass loss 30.90% (calculated mass loss = 30.67%), which is reasonably accounted for the loss of two pyrrolidino and CN groups.

The third estimated mass loss of 8.50% (calculated mass loss = 8.30%) within the temperature range 365–520 °C could be

**Table 5**  
Thermoanalytical results (TG, DTG) of the Schiff base ligands and some of their metal complexes

Compounds	TG range (°C)	DTG <sub>max</sub> (°C)	Estimated (calculated) %		Assignment	Residue
			Mass loss	Total mass loss		
(1)	180–650	200, 255 325	87.50 (87.28)	87.50 (87.28)	Loss of two 4-chloroanilino, two OH, two CN and two biphenyl groups	R(CN) <sub>2</sub>
(6)	170–475	180, 255 310	86.10 (86.53)	86.10 (86.53)	Loss of two 4-methylanilino, two OH, two CN and two biphenyl groups	R(CN) <sub>2</sub>
(11)	80–190	155	54.10 (54.31)		Loss of two OH and two biphenyl groups	
	190–365	290	30.90 (30.67)		Loss of two pyrrolidino and two CN groups	
	365–520	405	8.50 (8.30)	93.50 (93.28)	Loss of two CN groups	R
(14)	40–110	45, 80	1.60 (1.34)		Loss of one H <sub>2</sub> O group	
	110–330	180, 210, 320	28.70 (28.20)		Loss of one H <sub>2</sub> O and two phenanthroline groups	
	330				Loss of two biphenyl groups	Decomposition is in progress
(15)	40–110	40	1.40 (1.06)		Loss of one H <sub>2</sub> O group	
	110–350	215, 290	50.40 (50.03)		Loss of two H <sub>2</sub> O, two perchlorate and four biphenyl groups	
	350				Loss of four pyrrolidino groups	Decomposition is in progress

attributed to the liberation of two CN groups. Total estimated mass loss is 93.50% (calculated mass loss = 93.28%).

The complex **(14)** with the molecular formula  $[C_{63}H_{60}N_{10}O_{12}CuCoCl_2]$  is thermally decomposed in three decomposition steps. The first stage of decomposition within the temperature range 40–110 °C with an estimated mass loss 1.60% (calculated mass loss = 1.34%), which is attributed to the loss of one hydrated water molecule. The second estimated mass loss of 28.70% (calculated mass loss = 28.20%) within the temperature range 110–330 °C corresponding to the liberation of one coordinated  $H_2O$  and two phenanthroline groups.

In the temperature range 330–900 °C, the mass loss is in progress. It is due to the decomposition did not complete, final product did not determine.

The thermal decomposition of the complex **(15)** with the molecular formula  $[C_{78}H_{86}N_{12}O_{15}Cu_3Cl_2]$  also proceeds with three main degradation steps. The first estimated mass loss of 1.40% (calculated mass loss = 1.06%) within the temperature range 40–110 °C could be attributed to the liberation of one  $H_2O$  group. The DTG curve gives a peak at 40 °C. The second step occurs within the temperature range 110–350 °C with an estimated mass loss 50.40% (calculated mass loss = 50.03%), which is reasonably accounted for loss of two  $H_2O$ , perchlorate and four biphenyl groups. The last step probably accounted for the decomposition of remaining part of the ligand molecule. But decomposition did not finish at 900 °C. Therefore, last decomposition residue did not determine.

### 3.6. Extraction ability of the $H_2L^1$ , $H_2L^2$ and $H_2L^3$

The extraction efficiencies of ligands  $H_2L^1$ ,  $H_2L^2$  and  $H_2L^3$  containing  $N_4$  donor set toward transition metal ions ( $Mn^{2+}$ ,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Pb^{2+}$ ,  $Cd^{2+}$ ,  $Hg^{2+}$ ) were determined by the picrate extraction method developed by Pedersen [38]. Solvent extraction of aqueous metal cation into water saturated organic hosts' solutions, were performed at 25 °C. An aqueous solution containing metal picrate was extracted with the host solution (dichloromethane), and the data are expressed as percentages of the cation extracted (%E) by the ligand, as given in Table 6 and represented in Fig. 4.

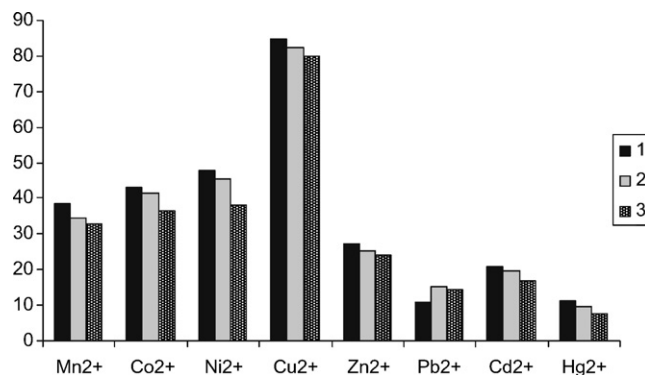
The extraction ability of  $H_2L^1$ ,  $H_2L^2$  and  $H_2L^3$  varies as  $Cu^{2+} \gg Ni^{2+} > Co^{2+} > Mn^{2+} > Zn^{2+} > Cd^{2+} > Pb^{2+} > Hg^{2+}$ . On the other hand it is clear from the Table 6 that the complexation ability of  $H_2L^1$ ,  $H_2L^2$  and  $H_2L^3$  toward  $Cu^{2+}$  is much higher and all ligands are excellent extractants for  $Cu^{2+}$  ion. The presence in the ligand of soft donor nitrogen groups, which show high affinity to transition metals, causes the increase in the extraction ability of this ligand. The effectiveness in transferring transition metals by the synthesized compound indicates that a cation– $\pi$  electron interaction is operative since the metal is bounded by the opposite N, N or N, O sites of this compound [39]. The presence of oxime groups ( $-C=N-OH$ ) indicate that the oxime groups play an important role in the extraction process [40].

**Table 6**  
Extraction of metal picrates with ligands<sup>a</sup>

Compounds	Percent of metal picrate extracted (%) <sup>b</sup>							
	$Mn^{2+}$	$Co^{2+}$	$Ni^{2+}$	$Cu^{2+}$	$Zn^{2+}$	$Pb^{2+}$	$Cd^{2+}$	$Hg^{2+}$
<b>(1)</b>	38.70	43.08	47.82	84.69	27.51	10.68	20.75	11.26
<b>(6)</b>	34.36	41.34	45.23	82.18	25.48	15.17	19.84	9.55
<b>(11)</b>	32.85	36.70	38.15	80.12	24.29	14.42	16.68	7.68

<sup>a</sup>  $H_2O/CH_2Cl_2 = 10/10$  v/v; [picric acid] =  $2 \times 10^{-5}$  M, [ligand] =  $1 \times 10^{-3}$  M, [metal nitrate] =  $1 \times 10^{-2}$  M, 298 K, 1 h contact time.

<sup>b</sup> Average and standard deviation for three independent measurements.



**Fig. 4.** Extraction percentages of the metal picrates with ligands (ligands: 1 =  $H_2L^1$ , 2 =  $H_2L^2$ , 3 =  $H_2L^3$ )  $H_2O/CH_2Cl_2 = 10/10$  v/v; [picric acid] =  $2.10^{-5}$  M, [ligand] =  $1 \times 10^{-3}$  M, [metal nitrate] =  $1 \times 10^{-2}$  M, 298 K, 1 h contact time.

### 3.7. Catalase-like activity

The catalytic activity of the polynuclear copper(II) complexes towards the disproportionation of hydrogen peroxide was investigated in the presence of the base imidazole (in the absence of the imidazole the complexes were either inactive or very weak catalysts for this reaction). It should be noted that imidazole itself causes only a very slight disproportionation of the peroxide. This may demonstrate the importance of the heterocyclic bases that are known to exist in the vicinity of the active sites of the manganoenzymes [41]. The catalytic activity of the heterodinuclear copper(II)–manganese(II) complexes were tested by measuring the dioxygen evolution with a complex (supported): $H_2O_2$  ratio of 1:500. This condition was found to be optimal in a controlled reaction process. All the complexes display catalytic ability for the disproportionation of  $H_2O_2$  but significantly, the activities of the complexes **(3)**, **(8)** and **(13)** are relatively higher than the other complexes. For this reason the reactivities of these three complexes toward  $H_2O_2$  are given in this study. The course of  $O_2$  evolution by the complexes **(3)**, **(8)** and **(13)** in DMF at room temperature is shown in Fig. 5. The evolution profile suggests the involvement of a fast catalytic process occurring at the initial stage followed by a short slow period process to finish the reaction. Previous investigation indicated that dicopper(II) [42] complexes are active in  $H_2O_2$  dismutation.

In the catalytic process the electron transfer only occurs between the Cu(II) and Cu(II) ions in the dimer structure. However, when the second coordinate metal ion was Mn(II), the reactivity was greatly enhanced. The main reason is that  $Mn_2(II)$  complexes are also good candidates for  $H_2O_2$  dismutation. Gao et al. supposed that the inter-molecular Mn(II)–Mn(II), Cu(II)–Mn(II) and Cu(II)–Cu(II) coupling are all possibly active centers in the CuMn system [43]. Furthermore, the presence of the bidentate chelating nitrogen donor ligand phenanthroline in the coordination sphere of the metal significantly enhances the ability of the manganese to disproportionate  $H_2O_2$  [44].

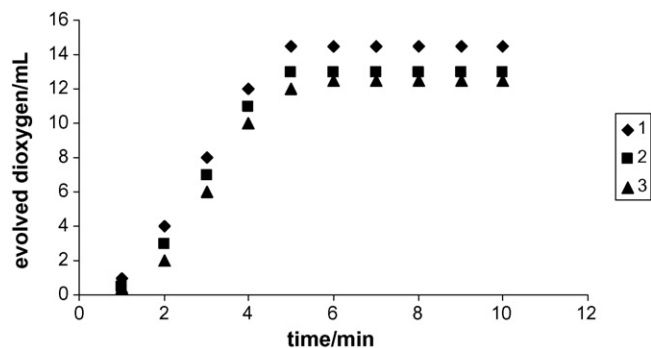


Fig. 5. Time courses of dioxigen evolution in the disproportionation of  $\text{H}_2\text{O}_2$  by heterodinuclear copper(II) complexes in DMF [complex] = 0.005 mmol,  $[\text{H}_2\text{O}_2] = 1.33$  mmol, 298 K, [complex (3)] = (◆), [complex (8)] = (■), [complex (13)] = (▲).

#### 4. Conclusion

The design and synthesis of three Schiff base ligands and their use in preparing homo- and hetero-polynuclear copper(II) complexes have been demonstrated in this report.

From the elemental analyses, stoichiometric and spectroscopic studies discussed above, the ligands have been shown to act as a tetradentate which coordinates through the nitrogen atoms of the oxime and imine groups. In the dinuclear complexes, in which the first copper(II) ion was complexed with nitrogen atoms of the oxime and imine groups in a square pyramidal coordination geometry, the second copper(II) ion is ligated with dianionic oxygen atoms of the oxime groups and are linked to the 1,10-phenanthroline nitrogen atoms. However, the trinuclear  $\text{Cu}(\text{II})$  complexes were formed by the coordination of the third  $\text{Cu}(\text{II})$  ions with dianionic oxygen atoms of each of the two molecules of the mononuclear copper(II) complexes. The proposed structures of these complexes are shown in Figs. 1–3. Furthermore liquid-liquid extraction of some transition metal ions ( $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ) with  $\text{H}_2\text{L}^1$ ,  $\text{H}_2\text{L}^2$ ,  $\text{H}_2\text{L}^3$  have been examined. All ligands are good extractant for copper(II) and can be used for copper recovery.

The catalytic activity of the heterodinuclear copper(II)–manganese(II) complexes were investigated for the disproportionation of hydrogen peroxide. In DMF solution, these materials display effective catalytic activity towards the disproportionation of  $\text{H}_2\text{O}_2$ . It was proposed that any residual hydrogen peroxide formed during industrial processes can be decomposed prior to disposal through the application of immobilized transition metal complexes.

#### Acknowledgement

Financial support from to the Research Fund of Süleyman Demirel University, Turkey (961-D-04) is gratefully acknowledged.

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