



Synthesis and characterization of new homo and heteronuclear Schiff base copper(II) complexes

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Abstract: This article describes the synthesis of isonitrosomethyl-p-tolyl ketone [HL] as the starting compound and then we prepared the new oxime ligand from the reactions of the amine materials with 1,2-diaminobenzene [H_2L^1]. (1E, 2E, 1'E, 2'E) - 3,3'-bis [(4-tolyl ketone) - (1,2 phenylene diimine)]. Acetaldehyde dioxime ligand was used to synthesize the metal complexes. The complexes were elucidated by FT-IR, elemental analysis, magnetic moment measurements, molar conductivity, mass spectra, and TGA studies. The free ligand was also described with its ^{13}C and 1H -NMR spectra. For complexes using spectroscopic and stoichiometric data of the complexes showed that metal:ligand ratio of mononuclear copper(II) complex was found to be 1:1 while this ratio was 2:1 in homo- and heterodinuclear copper(II) complex and 3:2 in the trinuclear copper(II) complex. All these data show us that the proposed structure is consistent with the obtained data.

Keywords: Schiff base, heteronuclear, trinuclear, nickel.

Submitted: June 30, 2017. **Accepted:** May 05, 2018.

Cite this: Topal T, Karapınar E. Synthesis and characterization of new homo and heteronuclear Schiff base copper(II) complexes. JOTCSA. 2018;5(2):785–802.

DOI: <http://dx.doi.org/10.18596/jotcsa.324878>.

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INTRODUCTION

Heteronuclear and homonuclear complexes especially nickel(II) and copper(II) compounds are of great interest in the last decades years chiefly because of the convenience of bioinorganic chemistry of nickel and copper and molecular magnetism (1-2). Important attention has been devoted to their correlations with the active sites of metalloproteinase including binuclear metallocenters and to the mimicking of the activity of such biomolecules. Important interest has been committed to their relation with the active sites of metalloproteinase and metalloenzymes having homodinuclear and heterodinuclear metallocenters and biomolecules (3-4). Moreover, because copper(II) and nickel(II) complexes especially with tetradentate oxime groups are models of chemical and physical behavior of biological metal system. Recently, biological studies of oxime ligands and metal complexes gained importance. In order to examine the features of DNA cleaving and combining, many studies have been conducted about characterization and developing new compounds modified with organic and inorganic substances for 30 years (5-13).

The importance of nickel and copper compounds is increasing day by day in the preparation and design of new magnetic materials and composites. Nickel- and copper-bridged structures are used for magnetic properties especially in space and medicine industry. (*E, E*)-dioxime-containing unsymmetrical ligands can form square pyramidal, octahedral and square planar complexes with cobalt(II), nickel(II), palladium(II) and copper(II) as central metal atoms (14). The pharmacological properties of the complexes obtained from our study have been observed but the results of this study have not been reported. Some researchers have synthesized containing *o*-phenylenediamine but the substances we synthesized were not found in the literature. Ligands and complexes were characterized by magnetic susceptibility, elemental analyses, molar conductivity, ¹H- and ¹³C-NMR, FT-IR, LC-MS and TG-DTG studies (15-21). The newly obtained materials provide new contributions especially in the literature and it is aimed to be used as a reference substance for use in various branches of science.

EXPERIMENTAL

IR spectra were performed in the 4000-400 cm⁻¹ on Perkin Elmer FTIR-Spectrometer Spectrum Two Model. Mass spectra were recorded on Agilent Micromass Quattro LC-MS/MS model spectrometer. ¹³C-NMR and ¹H-NMR data of the ligands were recorded from DMSO-d₆ solutions and on a Varian 400 MHz NMR Spectrometer Direct Drive Console Dell Precision 380 Model spectrometer. The molar conductance was measured with WTW Cond 7110. Elemental analyses (C, H and N) were recorded on a Thermo Finnigan Flash EA 1112 Model

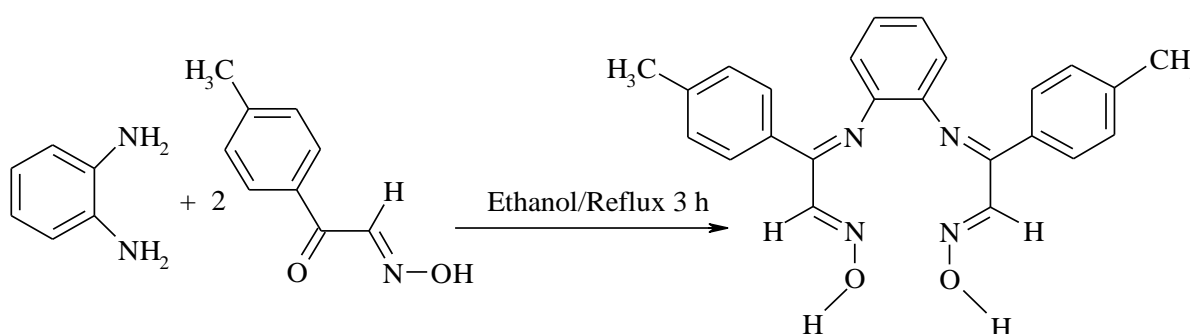
analyzer. Sherwood Scientific MX1 Model devices used at for Magnetic susceptibility measurements. The TGA thermograms were carried out 900-25 °C on a Perkin-Elmer Diamond TGA System; nitrogen flow and heating rate were 50 mL/min and 10 °C/min⁻¹.

Synthesis of the ligand

The preparation of isonitrosomethyl-p-tolyl ketone (HL) was described in the literature (22-24). Coated glass reactors were used in the synthesis of the experiments.

To an ethanolic solution (30 mL) of isonitrosomethyl-p-tolyl ketone (30 mmol, 4.8951 g HL in was added *o*-phenylenediamine (1.622 g, 15 mmol) in ethanol (15 ml) respectively (25-26) (H₂L¹) (**1**). This solution was heated and stirred for 3 h and monitored by thin layer chromatography (TLC) using ethyl acetate/n-hexane (1:5). The precipitates thus formed were filtered off with Et₂O and dried on P₂O₅.

Light Brown; Yield 81%. m.p.:101 °C. ¹H-NMR (400 MHz, DMSO-d₆, ppm): δ 9.31 (s, 2H, OH), 8.12 (s, 2H, H-C=N), 8.16-7.37 (m, 12H, Ar-H), 2,46 (s, 6H, Ar-CH₃). ¹³C-NMR (100 MHz, DMSO-d₆, ppm): δ=151.83 (C=N_(imine)), 143.26 (C=N_(oxime)), 141.38, (C_(aromatic)) 140.51, (C_(aromatic)) 133.94 (C_(aromatic)), 130.21 (C_(aromatic)), 129.89 (C_(aromatic)), 129.51 (C_(aromatic)), 129.31, 129.05, 127.42, (C_(aromatic)), 21.43 (Ar-CH₃). (MS-ESI): [M-2]⁺ =398.4 [C₂₄H₂₂N₄O₂, %27.3], 395.2 [C₂₄H₂₁N₄O₂, %100], 349.2 [C₂₃H₂₁N₃O, %7.8], 255.2 [C₁₅H₁₃N₃O, %6.9], 235.1 [C₁₅H₁₄N₂O, %31.5], 161.0 [C₉H₉N₂O, %2.8]. Elemental analysis: Anal.Calc.for C₂₂H₁₆Br₂N₄O₂: C, 72.34; H, 5.57; N, 14.06; Found C, 72.25; H, 5.19; N, 14.67%. IR (KBr) cm⁻¹: 3219 (OH), 1672 (C=N)_{imine}, 1607 (C=N)_{oxime}, 992 (=N-O); Structure of the ligands is given in Scheme 1.



Scheme 1: Synthesis of the H₂L¹ ligand.

Synthesis of the complexes

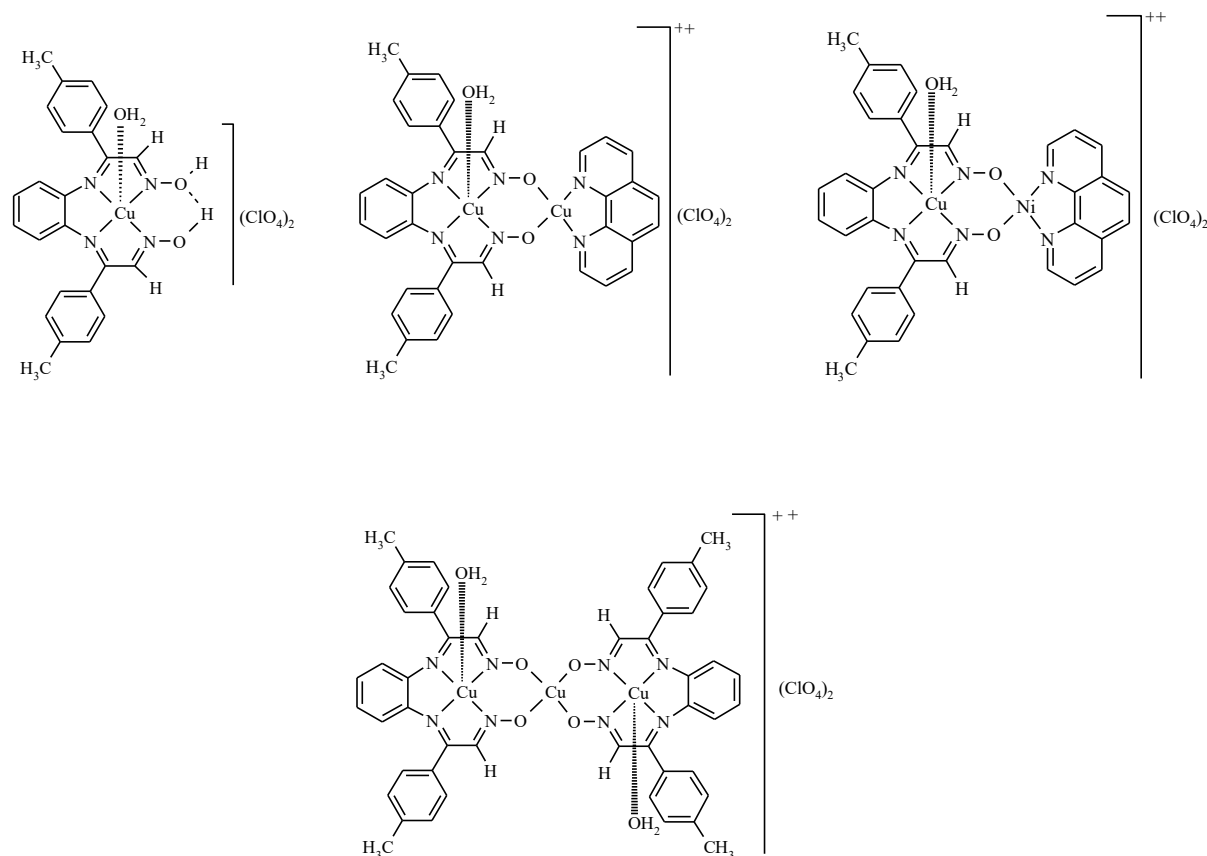
Caution: All perchlorate salts are potentially explosive so the readers are urged to be careful when using them.

$[\text{Cu}(\text{H}_2\text{L}^1)(\text{H}_2\text{O})](\text{ClO}_4)_2 \cdot (\text{H}_2\text{O})$ (**2**) : A solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (370 mg, 1 mmol) dissolved in acetone (10 ml), were added to a stirred solution of ligands (1 mmol) dissolved in 10 mL of acetone, and this mixture was refluxed with stirring for 1 h and monitored by thin layer chromatography (TLC) using ethyl acetate/n-hexane (1:5). The precipitated complexes were filtered off, washed with H_2O and dried over P_4O_{10} . Light green solid; Yield 43%. m.p.:249 °C. μ_{eff} B.M.=1.56. $\Lambda_{\text{M}}^{\text{b}}=325$. (MS-ESI): $[\text{M}-[(\text{ClO}_4)_2]]^+ = 498.0$ [$\text{C}_{24}\text{H}_{26}\text{CuN}_4\text{O}_4$, %19], 379.6 [$\text{C}_{24}\text{H}_{20}\text{N}_4\text{O}$, %27], 238.7 [$\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}$, %100], 216.8 [$\text{C}_{15}\text{H}_{13}\text{N}_2$, %63]. Elemental analysis: Anal. Calc. for $\text{C}_{24}\text{H}_{26}\text{Cl}_2\text{CuN}_4\text{O}_{12}$: C, 41.36; H, 3.76; N, 8.04; Cu, 9.12; Found C, 41.46; H, 3.59; N, 8.24; Cu, 9.35%. IR (KBr) cm^{-1} : 3516 (OH or H_2O), 2320 ($\text{O}\cdots\text{H}-\text{H}$), 1613 ($\text{C}=\text{N}$)_{imine}, 1592 ($\text{C}=\text{N}$)_{oxime}, 1428 ($=\text{N}-\text{O}$), 1091, 1046, 618 (ClO_4), 474 (M-N).

$[\text{Cu}(\text{H}_2\text{L}^1)(\text{H}_2\text{O})_2\text{Cu}(\text{phen})](\text{ClO}_4)_2 \cdot (\text{H}_2\text{O})$ (**3**) : A mixture of mononuclear copper(II) complex (1 mmol) and Et_3N (101 mg, 1 mmol) in MeOH (20 ml) was refluxed for 0.5 h. The solution of 1,10-phenanthroline monohydrate (198 mg, 1 mmol) in MeOH (10 ml) and $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (370 mg, 1 mmol) in MeOH (10 ml) was added to the resulting mixture, which was refluxed for 3 h and monitored by thin layer chromatography (TLC) using ethyl acetate/n-hexane (1:5). The precipitated complexes were filtered off, washed with H_2O and dried over P_4O_{10} . Dark Brown Solid; Yield 36%. m.p.:217 °C. μ_{eff} B.M.=1.94. $\Lambda_{\text{M}}^{\text{b}}=473$. (MS-ESI): 757.7 $[\text{M}-[(\text{ClO}_4)_2]+2]^+ = [\text{C}_{36}\text{H}_{34}\text{Cu}_2\text{N}_6\text{O}_5$, %2], 703.7 [$\text{C}_{36}\text{H}_{28}\text{Cu}_2\text{N}_6\text{O}_2$, %5], 523.5 [$\text{C}_{24}\text{H}_{20}\text{Cu}_2\text{N}_4\text{O}_2$, %100], 398.4 [$\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_2$, %22]. Elemental analysis: Anal. Calc. for $\text{C}_{36}\text{H}_{34}\text{Cl}_2\text{Cu}_2\text{N}_6\text{O}_{13}$ C, 45.20; H, 3.58; N, 8.78; Cu, 13.28; Found C, 45.34; H, 3.46; N, 8.59; Cu, 13.41%. IR (KBr) cm^{-1} : 3338 (OH or H_2O), 1610 ($\text{C}=\text{N}$)_{imine}, 1589 ($\text{C}=\text{N}$)_{oxime}, 1429 ($=\text{N}-\text{O}$), 1035, 618 (ClO_4), 557 (M-O), 475 (M-N).

$[\text{Cu}(\text{H}_2\text{L}^1)(\text{H}_2\text{O})_2\text{Ni}(\text{phen})](\text{ClO}_4)_2$ (**4**) : A mixture of mononuclear copper(II) complex (1 mmol) and Et_3N (101 mg, 1 mmol) in MeOH (20 ml) was refluxed for 0.5 h. The solution of 1,10-phenanthroline monohydrate (198 mg, 1 mmol) in MeOH (10 ml) and $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (366 mg, 1 mmol) in MeOH (10 ml) was added to the resulting mixture, which was refluxed for 5 h and monitored by thin layer chromatography (TLC) using ethyl acetate/n-hexane (1:5). The precipitated complexes were filtered off washed with H_2O and dried over P_4O_{10} . Dark Yellow Solid; Yield 48%. m.p.:229 °C. μ_{eff} B.M.=2.81. $\Lambda_{\text{M}}^{\text{b}}=369$. (MS-ESI): 734.9 $[\text{M}-[(\text{ClO}_4)_2]+1]^+ = [\text{C}_{36}\text{H}_{32}\text{CuNiN}_6\text{O}_4$, 2%], 698.8 [$\text{C}_{36}\text{H}_{28}\text{CuNiN}_6\text{O}_2$, 18%], 462.0 [$\text{C}_{24}\text{H}_{22}\text{CuN}_4\text{O}_2$ 100%], 253.2 [$\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}$, 56%]. Elemental analysis: Anal. Calc. for $\text{C}_{36}\text{H}_{32}\text{Cl}_2\text{CuNiN}_6\text{O}_{12}$ C, 46.30; H, 3.45; N, 9.00; Cu, 6.81; Ni, 6.29; Found C, 46.44; H, 3.39; N, 8.86; Cu, 6.70; Ni, 6.31%. IR (KBr) cm^{-1} : 3538 (OH or H_2O), 1611 ($\text{C}=\text{N}$)_{imine}, 1591 ($\text{C}=\text{N}$)_{oxime}, 1485 ($=\text{N}-\text{O}$), 1089, 1044, 617 (ClO_4), 553 (M-O), 479 (M-N).

[Cu₃(H₂L¹)₂(H₂O)₂](ClO₄)₂ (**5**) : Mononuclear copper complex (2 mmol), Cu(ClO₄)₂·6H₂O (370 mg, 1 mmol) and Et₃N (101 mg, 1 mmol) in MeOH (25 ml) was refluxed for 5 h and monitored by thin layer chromatography (TLC) using ethyl acetate/n-hexane (1:5). The precipitated complexes were filtered off washed with H₂O and dried over P₄O₁₀. Dark Yellow Solid; Yield 42%. m.p.:246 °C. μ_{eff} B.M.=2.13. $\Lambda_{\text{m}}^{\text{b}}$ =551. (MS-ESI): 1019.5 [M-[(ClO₄)₂]-4]⁺ = [C₄₈H₄₄Cu₃N₈O₆, 15%], 983.5 [C₄₈H₄₀Cu₃N₈O₄, 28%], 679.6 [C₂₉H₂₈Cu₂N₈O₄ 100%], 557.5 [C₂₄H₂₂Cu₂N₄O₂, 38%], 462.0 [C₂₄H₂₂CuN₄O₂, 37%]. Elemental analysis: Anal. Calc. for C₄₈H₄₄Cl₂Cu₃N₈O₁₄ C, 47.32; H, 3.64; N, 9.20; Cu, 15.65; Found C, 47.21; H, 3.55; N, 9.11; Cu, 15.80%. IR (KBr) cm⁻¹: 3581, 3548, 3510 (OH or H₂O), 1609 (C=N)_{imine}, 1576 (C=N)_{oxime}, 1485 (=N-O), 1101, 1040, 619 (ClO₄), 514 (M-O), 495 (M-N). The materials obtained were based on the studies in the literature.



Scheme 2: Structures for the mono, homo-heterodinuclear copper(II) and homotrimeric copper(II) complexes

RESULTS AND DISCUSSION

In this work, 4'-methylacetophenone was used as the starting substance. Isonitroso-p-methylacetophenone has been isolated through the nitrosation reaction between 4'-methylacetophenone with butylnitrite in sodium ethoxide medium. The new ligand was

synthesized as a result of isonitrosoacetophenone derivative reaction with aromatic amine (*o*-phenylenediamine) and four novel complexes were synthesized by the addition of metal salts of nickel(II) and copper(II) to the Schiff-based ligands. Study has shown that the obtained theoretical optimized structural parameters are in coherence with the experimental results.

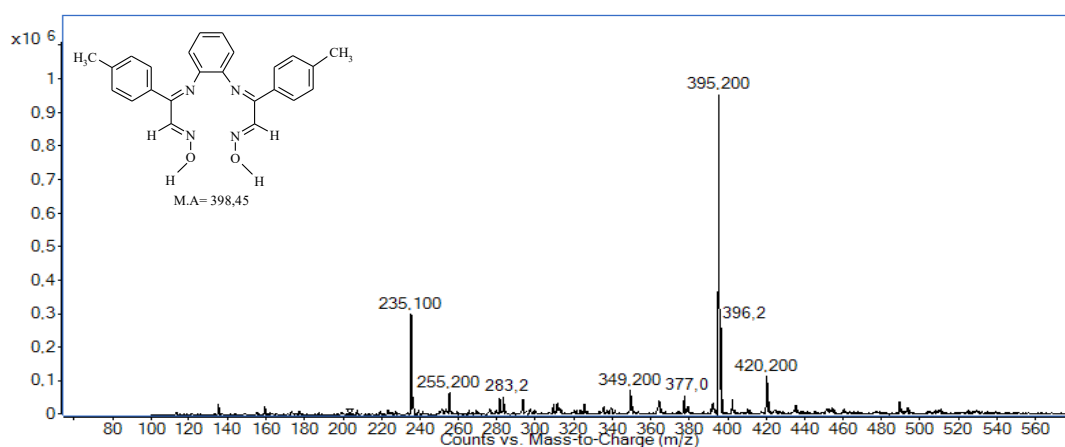
Condensation of the 4'-methylacetophenone with diamine was coordinated and identified by ^1H and ^{13}C -NMR spectra, elemental analysis, mass spectra, FT-IR and thermal analysis. This newly synthesized oxime ligand and its metal complexes are shown Scheme 2. In addition, ligand and its copper(II) and nickel(II) complexes were verified by elemental analysis, mass spectra, thermal analysis and FT-IR. All the complexes and ligand are durable at room temperature, are soluble in methanol, DMSO and ethanol, insoluble in hexane, diethyl ether and water and slightly soluble in acetone and dichloromethane. Single crystals were not obtained for complexes and the ligand.

The resulting complexes are highly colored, and durable in air. Spectroscopic techniques, elemental analyses, magnetic susceptibility, conductivity, and thermal techniques were applied to shed light into the complexes. The ligand and their metal complexes are in good agreement with the previous experimental studies. Mononuclear complexes have square bipyramidal geometric structure while homodinuclear and heterodinuclear complexes have not been stable geometric structure. Because homodinuclear complexes possess two copper(II) ions and heterodinuclear complexes one copper(II) and one nickel(II) ions, and different axial position of metal ions are effected geometrical structure. Homodinuclear and heterodinuclear copper(II) complex were found to have a 2:1 metal:ligand ratio. Due to trinuclear copper(II) complexes have three copper(II) ions and not to say solely one geometrical structure. Homotrimeric copper(II) complex were found to have a 3:2 metal:ligand ratio.

NMR spectra

All the ^1H -NMR and ^{13}C -NMR spectra of the tetradentate Schiff base types were recorded in DMSO- d_6 . ^1H -NMR spectrum of the ligand shifts observed at $\delta=9.31$ ppm was observed to the oxime group of the protons (N-OH) of the schiff base ligands H_2L^1 , as a singlet peak. All the multiplet signals of the ligand 8.16–7.37 ppm range were observed to the protons of the aromatic rings (27). The oxime proton signals (H-C=N) at $\delta=8.12$ ppm disappeared upon deuterium exchange of the H_2L^1 ligand. The spectrum of the H_2L^1 ligand observed at singlets 2.46 (6H) ppm of the aromatic amine of methylene group protons.

^{13}C -NMR spectrum of H_2L^1 observed a single peak at 151.83 ppm, respectively which showed that the (C=N) imine carbon atoms were equivalent, 143.26 ppm were observed to the (C=N) oxime carbon atoms of the ligands (27). All the signals in the 141.38–127.42 ppm range were assigned to the aromatic carbons of the ligand. In addition, signals were observed in the 21.43 ppm of the aromatic amine of the methylene group carbon (29-30). When the NMR spectra were evaluated, it was determined that they were compatible with previous studies. It is difficult to elucidate the structure solely on the basis of NMR spectroscopy, so the data should be supported by elemental analysis and mass spectral studies.



Scheme 3: The mass spectrum of $[(\text{H}_2\text{L}^1)]$ ligand

IR spectra

The IR spectra of the metal complexes and ligand were studied in the range 4000–400 cm^{-1} . The oxime peaks in general were determined as $\nu(\text{C}=\text{N})$, $\nu(\text{O}-\text{H})$, and $\nu(\text{N}-\text{O})$ (31). The FT-IR spectrum of the ligand showed (C=N) imine peak at 1672 cm^{-1} and (C=N) oxime at 1607 cm^{-1} absence of a (C=O) at around 1710-1700 cm^{-1} were observed of oxime ligand condensation. In the IR spectrum of ligand ($-\text{O}-\text{H}$) band of oxime group peak was showed at 3219 cm^{-1} . Coordinated water of the complexes was observed 3581-3338 cm^{-1} and which exhibit medium intense broad bands. FT-IR data confirmed the presence of coordinated water. (C=N) imine stretching vibrations for complexes at 1613–1609 cm^{-1} and (C=N) oxime stretching vibrations for complexes at 1592-1576 cm^{-1} . It was found that the (C=N) imine and (C=N) oxime bands in the complexes were changed by about 63-59 cm^{-1} , 31-15 cm^{-1} to the free ligand of H_2L^1 . Azomethine nitrogen also coordinated to the metal ion (38).

Results were supported by shifting N-O stretching vibrations to lower or higher frequencies than the ligands (32-35). In the FT-IR spectrum of the complexes (M-N) imino or oximino nitrogen atoms were observed as a new band 495–474 cm^{-1} (36) and oxygen atom of

oxime and the metal ions of the copper(II) complexes (M-O) showed a new band at 557–514 cm^{-1} (37). (H–O...H) intramolecular hydrogen bond was observed at 2320 cm^{-1} for mononuclear copper(II) complexes (39). All of the perchlorate salts showed a strong band 1101–1089 cm^{-1} and 1046–1035 cm^{-1} (antisymmetric stretch) and sharp band at 619–617 cm^{-1} (antisymmetric bend), which showed of uncoordinated perchlorate anions (40). Although the general spectroscopic peaks for oximes are (C = N), (O-H) and (N-O), perchlorate, (C=O) and (OH) ions also play an important role.

Thermal studies

The thermal studies of the ligand, one mononuclear, one homodinuclear, one heterodinuclear, and one trinuclear copper(II) complexes were discussed in this section. The data from the thermogravimetric analyses showed that the fragmentation of the complexes occurs in two or three steps and the ligand proceeds in two steps (41). The thermal behavior of the complexes and ligand are given in Table 1.

The ligand [$\text{C}_{24}\text{H}_{22}\text{N}_4\text{O}_2$] was thermally decomposed two degradation steps. The first step at range 92–186 °C with an estimated mass loss 7.97% (calculated mass loss = 8.53) which indicating the removal of two OH groups. The 2nd decomposition step within the temperature range 186–255 °C with an estimated mass loss 92.03% (calculated mass loss = 91.47%), due to the removal of four CN, Ar_{amine} , two 4'-methylacetophenone. At the end of the study there is no product left so total estimated mass loss was 100.00%.

The complex [$\text{C}_{24}\text{H}_{26}\text{Cl}_2\text{CuN}_4\text{O}_{12}$] showed three steps of decomposition at 35–82 °C with an estimated mass loss 2.39% leaving one hydrate H_2O group. (calculated mass loss = 2.58%). The second step within the temperature range 82–193 °C with an estimated mass loss 2.30% (calculated mass loss = 2.58%), which leaving coordination H_2O . The third and last step exhibited an estimated mass loss of 81.12% (calculated mass loss = 80.52%) within the temperature range 193–1000 °C due to the liberation of four CN, Ar_{amine} , two (ClO_4), and two 4'-methylacetophenone groups. The mass loss is continues, so final product was not determined.

The thermogram of the dimeric complex [$\text{C}_{36}\text{H}_{34}\text{Cl}_2\text{Cu}_2\text{N}_6\text{O}_{13}$] showed three steps of decomposition at 22–104 °C leaving one hydrate group. The DTG curve gave a peak at 62 °C. The 2nd decomposition step at within the temperature range 104–186 °C with an estimated mass loss 3.68% (calculated mass loss = 3.76%), ascribable to two hydrate molecules leaving coordination. The 3rd step 186–1000 °C with an estimated mass loss of %78.34 leaving four CN, Ar_{amine} , two (ClO_4), phenanthroline groups, two 4'-

methylacetophenone groups. Finally two CuO leaves the residue. (calculated mass loss = 77.74%). Total estimated mass loss was 100.00%.

The thermogram of the heterodinuclear complex $[C_{36}H_{32}Cl_2CuNiN_6O_{12}]$ showed three steps of decomposition at 29–94 °C with an estimated mass loss 0.9% which is reasonably accountable for the loss of moisture. The DTG curve gave a peak at 72 °C. The 2nd decomposition step at within the temperature range 94–196 °C with an estimated mass loss of 3.71% (calculated mass loss = 3.85%), meaning that two hydrate molecules leaving the coordination. The 3rd step indicates the removal of four CN, Ar_{amine}, two (ClO₄), phenanthroline groups, and two 4'-methylacetophenone groups. The mass loss is in continuation, so the final product was not determined.

The thermogram of the trinuclear complex **(5)** $[C_{48}H_{44}Cl_2Cu_3N_8O_{14}]$ was thermally decomposed in three decomposition steps. The first step at range 42–108 °C with an estimated mass loss of 0.85% which means the leaving of moisture. The 2nd decomposition step at range 108–205 °C with an estimated mass loss of 2.84% (calculated mass loss = 2.95%), which means that two hydrate molecules leaving the coordination. The 3rd step between 205-1000 °C with an estimated mass loss of leaving eight CN, two Ar_{amine}, two (ClO₄), and four 4'-methylacetophenone groups. Finally, three moles of CuO was found as residue. Total estimated mass loss was 100.00%.

Table 1. Thermoanalytical results (TG, DTG) of the ligands and their metal complexes

Comp.	TG range (°C)	DTA max.(°C)	Founded mass loss %	Calc. mass loss %	Assignment	Residue
(1)	92-186	96 (+)	7.97	8.53	Loss of two OH	-
	186-255	253 (+)	92.03	91.47	Loss of four CN, Ar _{amine} , two 4'-methylacetophenone	
(2)	35-82	79(+)	2.39	2.58	Loss of hydrate H ₂ O	Decomposition is in progress
	82-193	154(-)	2.30	2.58	Loss of coordination H ₂ O	
	193-1000	395(-) 625(-)	88.12	80.52	Loss of four CN, Ar _{amine} , two (ClO ₄ , two 4'-methylacetophenone	
(3)	22-104	62(+)	1.69	1.88	Loss of hydrate H ₂ O	2 CuO 16.29 (16.62)

	104-186	169(+)	3.68	3.76	Loss of coordination two H ₂ O	
	186-1000	376(-)	78.34	77.74	Loss of four CN, Ar _{amine} , two (ClO ₄), phenanthroline groups, two 4'-methylacetophenone	
(4)	29-94	72(+)	0.9	-	Loss of moisture	Decomposition is in progress
	94-196	156(+)	3.71	3.85	Loss of coordination two H ₂ O	
	196-1000	726(-)	86.68	79.40	Loss of four CN, Ar _{amine} , two (ClO ₄), phenanthroline groups, two 4'-methylacetophenone	
(5)	42-108	86(+)	0.85	-	Loss of moisture	3 CuO 20.19 (21.24)
	108-205	203(-)	2.84	2.95	Loss of coordination two H ₂ O	
	205-1000	670(-)	76.12	75.80	Loss of eight CN, two Ar _{amine} , two (ClO ₄), four 4'-methylacetophenone	

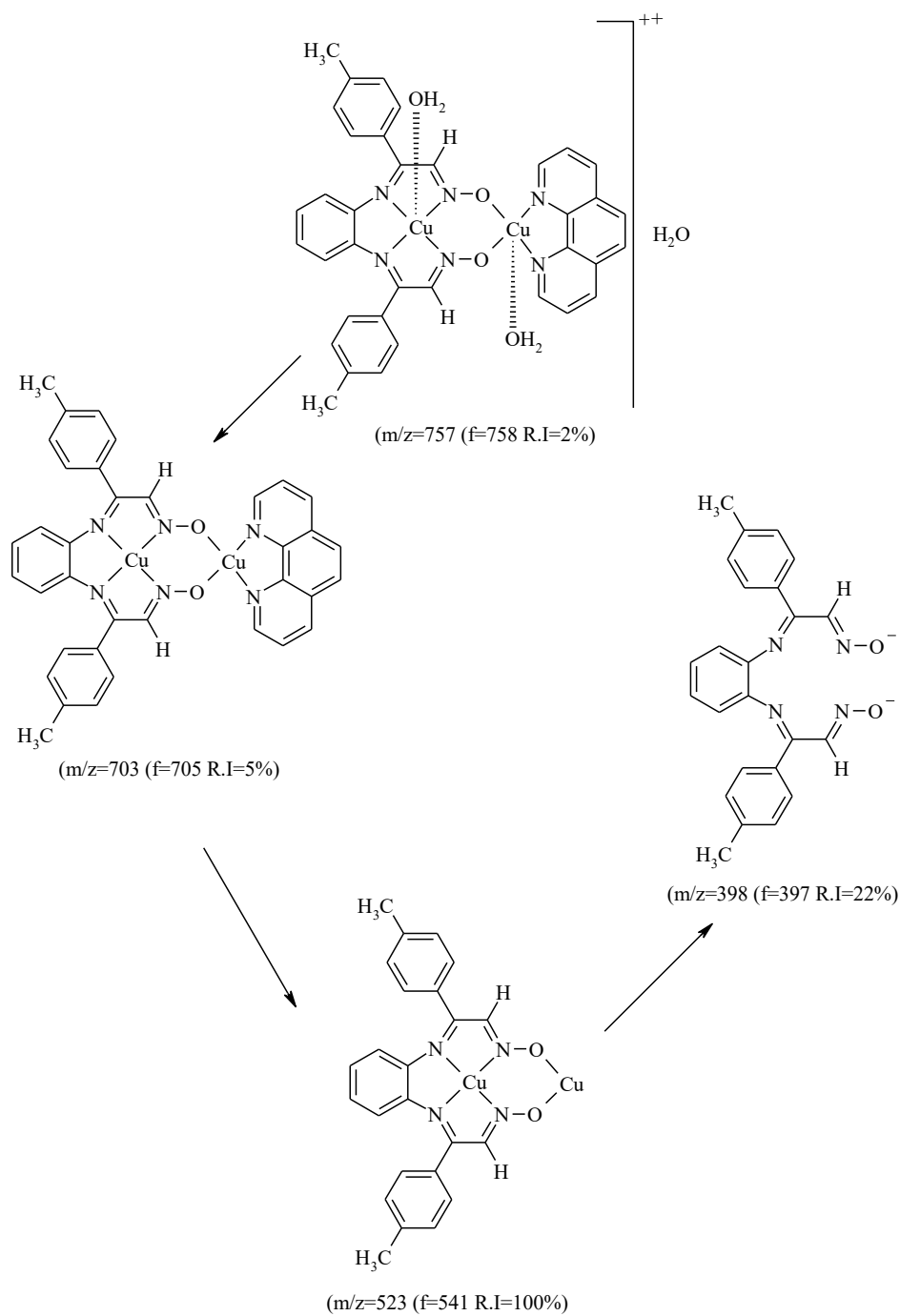
Molar conductance and magnetic susceptibility

2×10^{-5} mol/dm⁻³ methanolic solutions were used for conductivity measurements at 25 °C. For all the complexes, conductivity measurement data fall within between 325 and 551 Ω⁻¹ cm².mol⁻¹ and behaved as 1:2 electrolytes because of the fact that the complex includes perchlorate ions (42).

The magnetic moments measurements showed that complexes were paramagnetic. The magnetic moment data of the mononuclear copper(II) complex (2) 1.56 B.M. corresponding to one unpaired electron. The measured magnetic moments of the trinuclear complex (5) 2.13 B.M., homodinuclear complex (3) have magnetic moments 1.94 B.M., heterodinuclear complex (4) 2.81 B.M., which have strong intramolecular antiferromagnetic effected for the complexes (43-45). It was possible that a distorted tetragonal geometry was responsible for this kind of interaction (46).

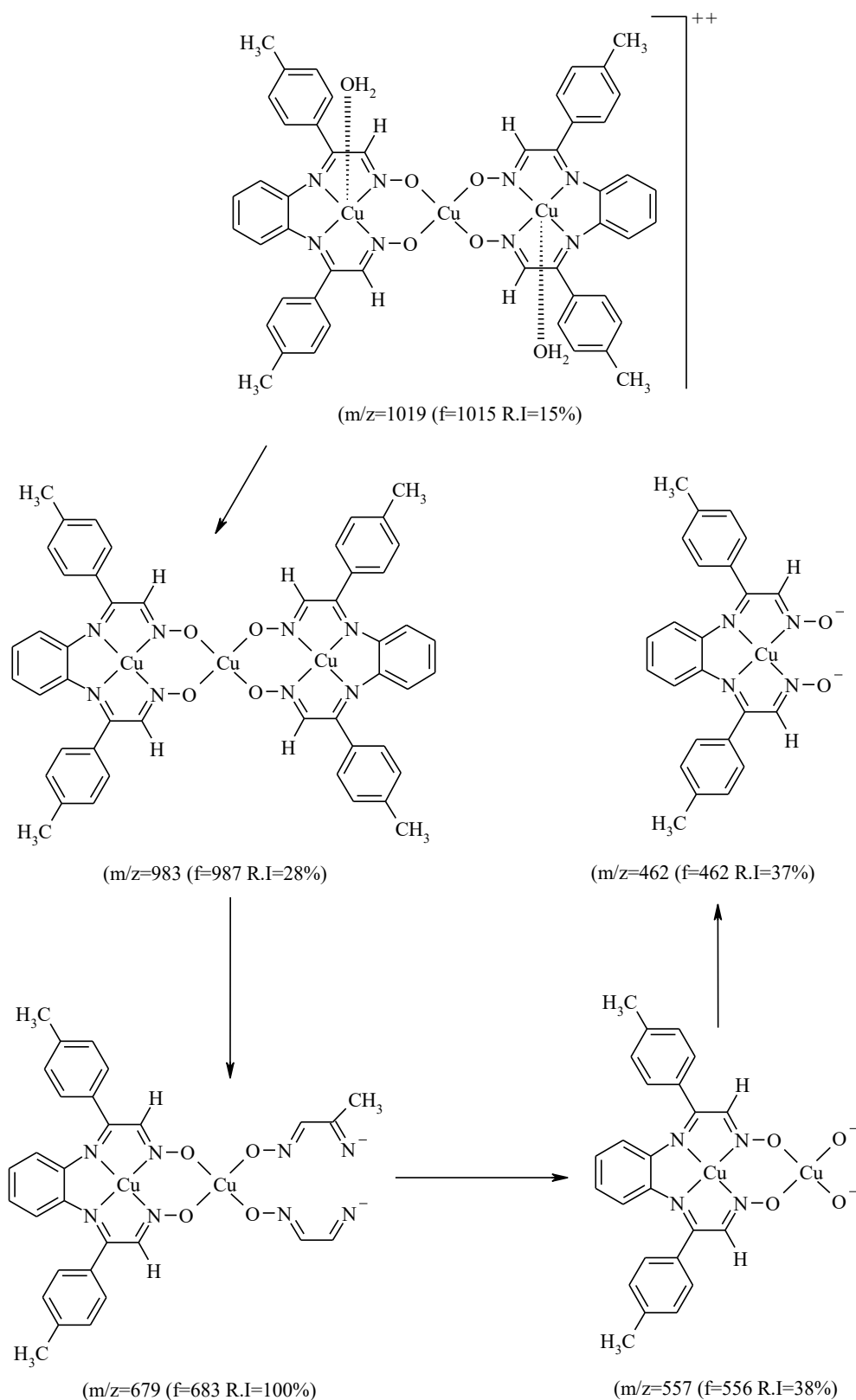
Mass spectra

The molecular ion peak of the H_2L^1 ligand was observed at 398.4 $[M-2]^+$ (1). The mononuclear copper(II) ion peak appeared at (m/z, ESI) 498.0 $[M-[(ClO_4)_2]]^+$ (2), at 757.7 $[M-[(ClO_4)_2]+2]^+$ for the homodinuclear copper(II) (3), at 734.9 $[M-[(ClO_4)_2]+1]^+$ for the heterodinuclear copper(II)-nickel(II) (4), at 1019.5 $[M-[(ClO_4)_2]-4]^+$ for the homotrinnuclear copper(II) (5) complex. According to the mass spectroscopy values, the proposed structure coincides with the experimental data obtained. Mass spectroscopy shows us the decomposition products of the compounds. There are two figures showing the fragmentation products. In mass spectra of the heterodinuclear Cu(II) complex m/z 734.9 $[Cu(H_2L^1)(H_2O)_2Ni(phen)]$ (Calcd. 734.90 amu) represents the molecular ion of the Cu(II) complex with 2% abundance. The other peaks (698, 462, 253) are attributed to fragmentation. In mass spectra of the mononuclear Cu(II) complex m/z 490.0 $[Cu(H_2L^1)(H_2O)](H_2O)$ (Calcd. 490.0 amu) represents the molecular ion of the Cu(II) complex with 19% abundance. The other peaks (379, 238, 216) were attributed to fragmentation. When fragmentation products are carefully evaluated, a cycle is contrary to the synthesized steps. Since mass spectrometer operates in negative mode, all the complexes perchlorate ions was not observed. Schemes 4 and 5 show that the proposed path of decomposition for the investigated homodinuclear and homotrinnuclear Cu(II) complexes (46).



R.I.=relative intensity of the peak, f =found value of m/z , m/z =ratio of mass to charge (calculated);.

Scheme 4. Mass fragmentation pattern of the $[\text{Cu}(\text{H}_2\text{L}^1)(\text{H}_2\text{O})_2\text{Cu}(\text{phen})](\text{H}_2\text{O})$ complex of dioxime.



R.I.=relative intensity of the peak, f=found value of m/z, m/z=ratio of mass to charge (calculated);.

Scheme 5. Mass fragmentation pattern of the $[Cu_3(H_2L^1)_2(H_2O)_2](ClO_4)_2$ complex of dioxime.

CONCLUSION

In this article, a new Schiff base ligand and its metal complexes were designed and synthesized. Spectroscopic and stoichiometric data were shown and discussed above. The metal ion in the mononuclear copper (II) complexes is covalently bound to the nitrogen atom in the oxime and imine groups and a square pyramidal geometric structure is considered. In the homodinuclear and heterodinuclear complexes, the first copper(II) metal atom forms a coordinate covalent bond with the nitrogen atom of the oxime and imine group, while the second metal ion linked with the oxygen atom of the oxime group via the 1,10-phenanthroline nitrogen atom. As there are 2 metal ions in the structure, it is not possible to propose a single geometry. The two mononuclear copper (II) compounds are linked by a coordinated covalent bond to form a homotrimeric compound, and it is not possible to mention any geometrical structure related to this structure. No single crystal analysis of the ligand and complexes could be made, but it was determined that elemental analysis, mass spectroscopy and magnetic moment data yielded the predicted structure and the results were in agreement. The thermal analyses data of ligand and complexes showed that generally thermally decomposed in 2-3 decomposition steps and the correlations between the founded and calculated mass were in good agreement.

ACKNOWLEDGEMENTS

This study has been supported by Pamukkale University (Grant Nos: 2013FBE041 and 2015HZL014)

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