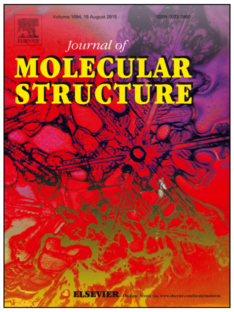


Dinuclear Cu(II) complexes of compartmental Schiff base ligands formed from unsymmetrical tripodal amines of varying arm lengths: Crystal structure of $[Cu_2L^1](ClO_4)_2$ and theoretical studies

Hassan Keypour, Maryam Shayesteh, Majid Rezaeivala, Koray Sayin

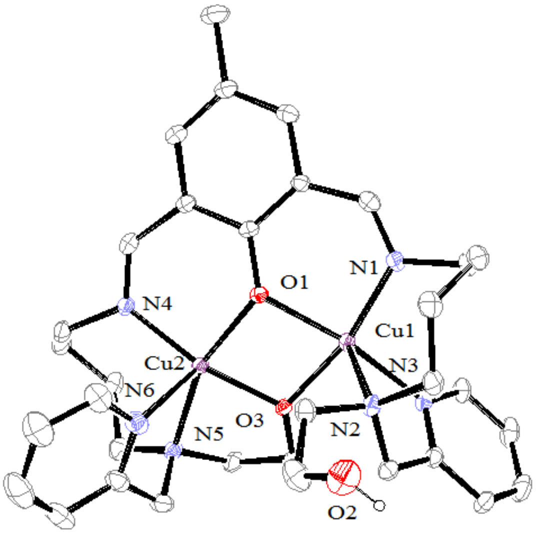
PII: S0022-2860(16)30098-9
DOI: 10.1016/j.molstruc.2016.02.004
Reference: MOLSTR 22213

To appear in: *Journal of Molecular Structure*

Received Date: 18 October 2015
Revised Date: 29 January 2016
Accepted Date: 2 February 2016

Please cite this article as: H. Keypour, M. Shayesteh, M. Rezaeivala, K. Sayin, Dinuclear Cu(II) complexes of compartmental Schiff base ligands formed from unsymmetrical tripodal amines of varying arm lengths: Crystal structure of $[Cu_2L^1](ClO_4)_2$ and theoretical studies, *Journal of Molecular Structure* (2016), doi: 10.1016/j.molstruc.2016.02.004.

Graphical Abstract pictogram



Dinuclear Cu(II) complexes of compartmental Schiff base ligands formed from unsymmetrical tripodal amines of varying arm lengths: Crystal structure of $[Cu_2L^1](ClO_4)_2$ and theoretical studies

Hassan Keypour[a,]*, Maryam Shayesteh[a], Majid Rezaeivala[b], Koray Sayin [C]

[a] *Faculty of Chemistry, Bu-Ali Sina University, Hamedan 65174, Iran*

[b] *Department of Chemical Engineering, Hamedan University of Technology, Hamedan 65155, Iran*

[C] *Department of Chemistry, Institute of Science, Cumhuriyet University, Sivas 58140, Turkey*

ABSTRACT

Three new dinuclear copper complexes were synthesized *via* condensation reaction of three new unsymmetrical *N*-capped tripodal amines and 2,6-diformyl-4-methylphenol, in the presence of copper(II) perchlorate. The solid-state structure of the dinuclear complex, $[Cu_2L^1](ClO_4)_2$, has been determined by X-ray crystallography, showing that the Cu^{II} centers have distorted square-pyramidal geometry with N_3O_2 coordination. The copper (II) ions are bridged by phenolic and hydroxyalkyl groups when in both cases, deprotonation of the hydrogen atoms of the OH groups occurs. The distance between the copper atoms is 3.062 A˚. This compound consists of the dication $[Cu_2L^1]^{2+}$ and two ClO_4^- anions in which one of ClO_4- groups has a week interaction with one of the Cu atoms. All complexes were characterized by a variety of physico-chemical techniques such as elemental analyses, IR, mass spectra, conductivity measurements and electronic spectral studies. Computational investigation of mentioned binuclear Cu(II) complexes was done by using M062X method with LANL2DZ basis set in vacuo.

Keywords: Binuclear Cu complexes; Compartmental Schiff base ligands; Unsymmetrical tripodal amines; X-ray crystal structure; Theoretical studies.

1. Introduction

In recent years, the chemistry of multinuclear metal compounds has received much attention due to their relevance to the multimetal active sites of various metallo-proteins and metallo-enzymes [1, 2]. Among them, the synthesis and characterization of polynuclear Cu(II) compounds have attracted amazing interest over the past decades due to their numerous biological activities. These complexes have potential application as models for the active sites of important biological systems [3, 4]. Moreover, considerable interest has been placed to the interaction of copper(II) complexes with DNA [5-9] due to their significance in the development of new therapeutic agents in medicine. Much effort has been devoted to the synthesis of new multinuclear copper complexes for a better understanding of the various properties of these complexes in bioinorganic chemistry [10], medicine [11] and catalysis [12]. Also, binuclear copper (II) complexes are of interest as models to investigate intramolecular magnetic-exchange interactions between two metal centers in different structural motifs, viz. the ‘‘paddle-wheel’’ di-copper(II) tetracarboxylates, symmetrically dibridged hydroxo or alkoxo species, and asymmetrically di-bridged complexes with a (l-hydroxo/alkoxo)(l-carb-oxylato)dicopper(II) core [13-22]. Dicopper (II) complexes are also of importance as precursors in the chemistry of supramolecular and discrete molecular high-nuclearity copper (II) complexes [23-32]. There has been growing interest in using bridging ligands in the synthesis of di- and multinuclear metal complexes. Ligands which contain potentially bridging phenoxo or hydroxo oxygen and nitrogen donor atoms have been widely used in the synthesis of multinuclear copper complexes [33–35]. Among the binuclear copper (II) complexes, bis-l-alkoxo, -hydroxo or -phenoxo bridged binuclear copper(II) complexes have great deal of importance in terms of correlating structure and magnetic properties [36–42]. However, bridged binuclear Cu(II) complexes have considerable interest as they provide examples of the simplest case of magnetic interaction including only two unpaired electrons [43,44]. The present study demonstrates the synthesis and characterization of new double asymmetric-bridged copper (II) complexes which were obtained by using H_2L^1, H_2L^2 and H_2L^3 compartmental Schiff-base ligands. These complexes were characterised by elemental analysis, IR, conductance measurements, UV-Vis, Mass spectra and in the case of $[Cu_2\mathbf{L^1}](ClO_4)_2$ with single crystal X-ray diffraction analysis. The molecular structure of the title molecule is illustrated in Fig. 1. It is a new binuclear Schiff base copper (II) complex, with the Cu(II) ion having a N_3O_2 square pyramidal geometry. Computational studies of relevant Cu(II) complexes were performed by using restricted M062X method. Optimized structures, IR spectrum, frontier molecular orbitals (FMOs) of Cu(II) complexes are investigated in detail. Additionally, nonlinear optical (NLO) properties of Cu(II) complexes are examined by using total static dipole moment (μ), the average linear polarizability (α), the anisotropy of polarizability ($\Delta\alpha$) and first hyperpolarizability (β), energy of the highest occupied molecular orbital (E_{HOMO}) and energy gap between the LUMO and HOMO ($E_{LUMO-HOMO}$).

2. Experimental

2.1. General remarks

Pyridine-2-carbaldehyde, 2-aminoethanol, 3-aminopropan-1-ol, *N*-(3-bromopropyl)phthalimide, *N*-(4-bromobutyl)phthalimide and metal salt were obtained from Aldrich and used without further purification. 2,6-diformyl-4-methylphenol was synthesised according to the literature procedure [45]. All other chemicals and solvents were of reagent grade and used as received.

2.2. Caution

Whilst no problems were encountered in the course of this work, perchlorate mixtures are potentially explosive and should therefore be handled with appropriate care.

2.3. Physical measurements

Infrared spectra were obtained between 4000-400 cm^{-1} on a Bruker Alpha FT-ATR IR spectrometer with a diamond anvil Alpha-P module and also KBr pellets on a BIO-RAD FTS-40A spectrophotometer. UV-vis spectra were recorded on a Jasco V550 spectrophotometer. Conductance measurements were performed using a Hanna HI 8820 conductivity meter. ESI mass spectra were recorded at the University of Otago on a Bruker MicrOTOFQ spectrometer. Standard microanalysis for all complexes was carried out by a Perkin–Elmer, CHNS/O elemental analyzer model 2400. ^{1}H and ^{13}C NMR spectra were taken in $CDCl_3$ on a Jeol 90 MHz spectrometer using $Si(CH_3)_4$ as an internal standard. Crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether vapor into a mixture of methanol and acetonitrile. Crystal data and structure refinement are given in Table 1. Single crystal X-ray crystallographic data were collected at 293 K for $[Cu_2L^1](ClO_4)_2$ (λ = 0.71073) on a Bruker SMART CCD area diffractometer. All data were corrected for Lorentz and polarization effects. Empirical absorption corrections were also applied for the crystal structure obtained [46]. Complex scattering factors were taken from the program package SHELXTL [47]. The structure was solved by direct methods which revealed the position of all non-hydrogen atoms. The structure was refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non hydrogen atoms. The hydrogen atoms were located in their calculated positions and refined using a riding model.

2.4. Computational method

Numerical calculations and computational processes were done by using GaussView 5.0.8 [48], Gaussian 09 RevD.01 package program [49] and ChemBioDraw Ultra Version (13.0.0.3015) [50]. M062X is one of the hybrid density functional theory methods [51]. In calculations, LANL2DZ basis set was used for its effective core potential [52-54]. All calculations were made in vacuo. Imaginary frequency was not obtained in whole calculations.

Fig.1 here

2.5 Synthesis

*2.5.1. General synthesis of unsymmetrical tripodal amines (**1**, **2** and **3**).*

2-Aminoethanol (1.22 g, 20 mmol) or 3-aminopropan-1-ol (1.50 g, 20 mmol) dissolved in dry EtOH (100 mL) was added dropwise to a solution of pyridine-2-carbaldehyde (2.14 g, 20 mmol) dissolved in dry EtOH (100 mL) over a period of 2h, separately. The mixture was refluxed under stirring for 12 h. Solid sodium borohydride (3.02 g, 80 mmol) was then added slowly and the reaction mixture was stirred for a further 12 h before it was filtered. The filtrate volume was reduced to 20 mL by rotary evaporation. Water (50 mL) was added and the products were extracted with chloroform (3×50 mL). The combined extracts were dried over magnesium sulfate, filtered, and then taken to dryness by rotary evaporation. The resulting brown oil (1.52 g, 10 mmole, **l'** (starting with 2-aminoethanol) or 1.66 g, 10 mmole, **2'** (starting with 3-aminopropanol) was dissolved in acetonitrile (70 mL), solid K_2CO_3 (2.07 g, 15 mmol) was added, and the mixture was brought to reflux before a solution of *N*-(4-bromobutyl)phthalimide (2.81 g, 10 mmole) was added dropwise to **l'**, or *N*-(3-bromopropyl)phthalimide (2.67 g, 10 mmole) or *N*-(4-bromobutyl)phthalimide (2.81 g, 10 mmole) in acetonitrile (70 mL) to **2'**. The mixture was refluxed for 48 h and then filtered hot. The filtrate was reduced to dryness by rotary evaporation. The brown oil residue was boiled under reflux for 12 h in aqueous HCl (25%, 100 mL) and then evaporated to a small volume (ca. 25 mL) under vacuum and cooled in a refrigerator for several hours. The resulting solid was filtered off and discarded, and the filtrate was evaporated to dryness under vacuum. Water (50 mL) was added to the resulting brown residue and the pH adjusted to 12 with sodium hydroxide before extracting with chloroform (3×50 mL). The combined extract was dried over magnesium sulfate, filtered and the chloroform was removed from the filtrate by rotary evaporation to leave the products, **1, 2** and **3**, as brown oils.

*2.5.1.1. Synthesis of 2-((4-aminobutyl)(pyridin-2-ylmethyl)amino)ethanol (**1**)*

Yield: 1.34 g (60%). Anal. Calc. for $C_{12}H_{21}N_3O$ (MW: 223.17): C, 64.54; H, 9.48; N, 18.82. Found: 64.35; H, 9.25; N, 19.10%. IR (Nujol mull, cm^{-1}) 3354, 3272 ν (NH_2), 1591 ν $(C=N)_{py}$. ^1H NMR ($CDCl_3$, ppm) δ = 1.36-1.55 (m, 4H); 2.15-2.48 (b, 3H), 2.54-2.63 (m, 4H) 2.71 (t, 2H); 3.58 (t, 2H); 3.78 (s, 2H); 7.14–7.17 (m, 1H); 7.28-7.31 (m, 1H); 7.64 (td, 1H); 8.52 (d, 1H). ^{13}C NMR ($CDCl_3$, ppm) δ = 24.0; 29.2; 40.4; 54.1; 56.1; 58.7; 59.69; 121.3, 122.5; 135.9; 148.3; 159.2.

*2.5.1.2. Synthesis of 3-((3-aminopropyl)(pyridin-2-ylmethyl)amino)propan-1-ol (**2**)*

Yield: 1.92 g (86%). Anal. Calc. for $C_{12}H_{21}N_3O$ (MW: 223.31): C, 64.54; H, 9.48; N, 18.82. Found: 64.20; H, 9.65; N, 18.90%. IR (Nujol mull, cm^{-1}) 3352, 3271 ν (NH_2), 1591 ν $(C=N)_{py}$. ^1H NMR ($CDCl_3$, ppm) δ = 1.5 (m, 4H); 2.3-2.5 (m, 6H); 3.5 (s, 4H); 4.4 (s, 3H); 6.9–7.5 (m, 3H); 8.3 (d, 1H). ^{13}C NMR ($CDCl_3$, ppm) δ = 25.9; 28.6; 39.2; 50.7; 51.8; 59.0; 59.7; 121.5, 122.5; 136.1; 148.2; 158.4.

*2.5.1.3. Synthesis of 3-((4-aminobutyl)(pyridin-2-ylmethyl)amino)propan-1-ol (**3**)*

Yield: 1.73 g (73%). Anal. Calc. for $C_{13}H_{23}N_3O$ (MW: 237.18): C, 65.79; H, 9.77; N, 17.70. Found: 65.10; H, 9.45; N, 17.20%. IR (Nujol mull, cm^{-1}) 3360, 3288 ν (NH_2) 1591 ν $(C=N)_{py}$. ^1H NMR ($CDCl_3$, ppm) δ = 1.3-1.5 (m, 6H); 2.3-2.5 (m, 6H); 3.5 (s, 4H); 4.5 (s, 3H); 6.9–7.5 (m, 3H); 8.3 (s, 1H). ^{13}C NMR ($CDCl_3$, ppm) δ = 23.5; 28.6; 29.6; 40.3; 51.6; 53.2; 59.4; 60.7, 121.2; 122.4; 135.8; 148.0, 158.7.

2.5.2. General synthesis of the complexes

A solution of 0.5 mmol of dialdehyde (0.082 g, 0.5 mmol) in methanol (50 ml) and 7 drops of triethyl amine were added dropwise to a refluxing solution of $Cu(ClO_4)_2.6H_2O$ (0.368 g, 1 mmol) and the appropriate amine, **1** (0.224 g, 1 mmol) or **2** (0.224 g, 1 mmol) or **3** (0.238 g, 1 mmol) in the same solvent (50 mL). After being refluxed for 12 h, the solution was concentrated in a rotary evaporator at room temperature to ca. 5–10 mL. A small volume of diethyl ether was added slowly, producing powdery precipitate. The powdery Cu(II) products were filtered off, washed with cold diethyl ether and dried under vacuum. Crystalline or powdery compounds were obtained by slow diffusion of diethyl ether vapor into a solution of these compounds in methanol or mixture of methanol and acetonitrile, as detailed below.

2.5.2.1. Synthesis of the $[Cu_2L^1](ClO_4)_2$

Recrystallisation of the initial solid from mixture of CH_3OH and MeCN in a 1:1 ratio *via* slow vapour diffusion of Et_2O yields green crystals (0.348g, 75%). Anal. Calc. for $C_{34}H_{48}Cl_2Cu_2N_6O_{12}$: C, 43.87; H, 5.20; N, 9.03. Found: C, 43.79; H, 5.05; N, 8.97%. IR (KBr, cm^{-1}) 1638 and 1628 ν$(C=N)_{imi}$; 1609 ν$(C=N)_{py}$; 1096, 623 ν(ClO_4). ESI-MS (MeOH, m/z^+):

799.16 [Cu_2**L^1**+2H](ClO_4)$^+$. Λ_m (CH_3CN): 290 Ω^{-1} cm^2 mol^{-1} (220–300 Ω^{-1} cm^2 mol^{-1} for a 2:1 conductor in MeCN) [55]. UV-Vis. {λ_{max}, nm (ε_{max}, M^{-1} cm^{-1})} in CH_3CN: 262 (21480), 372 (4730), 648 (146).

2.5.2.2. Synthesis of the [Cu_2L^2](ClO_4)$_2$

Recrystallisation of the initial solid from CH_3OH *via* slow vapour diffusion of Et_2O yields green powder (0.305 g, 68 %). Anal. Calc. for $C_{33.5}H_{46}Cl_2Cu_2N_6O_{11.5}$: C, 43.99; H, 5.07; N, 9.19. Found: C, 43.64; H, 5.24; N, 9.03%. IR (KBr, cm^{-1}) 1638 and 1629 ν(C=N)$_{imi}$; 1611 ν(C=N)$_{py}$; 1094, 623 ν(ClO_4). ESI-MS (MeOH, m/z$^+$): 799.16 [Cu_2**L^2**+2H](ClO_4)$^+$. Λ_m (CH_3CN) = 303 Ω^{-1} cm^2 mol^{-1} (220–300 Ω^{-1} cm^2 mol^{-1} for a 2:1 conductor in MeCN) [55]. UV–Vis. {λ_{max}, nm (ε_{max}, M^{-1} cm^{-1})} in CH_3CN: 265 (22210), 377 (4130), 622 (187).

2.5.2.3. Synthesis of the [Cu_2L^3](ClO_4)$_2$

Recrystallisation of the initial solid from mixture of CH_3OH and MeCN in a 1:1 ratio *via* slow vapour diffusion of Et_2O yields green powder (0.328 g, 71 %). Anal. Calc. for $C_{35}H_{48}Cl_2Cu_2N_6O_{11}$: C,45.36; H, 5.22; N, 9.07. Found: C, 45.27; H, 5.28; N, 8.92%. IR (KBr, cm^{-1}) 1638 and 1629 ν(C=N)$_{imi}$; 1612 ν(C=N)$_{py}$; 1092, 624 ν(ClO_4). ESI-MS (MeOH, m/z$^+$): 827.18 [Cu_2**L^3**+2H](ClO_4)$^+$, 725.23[Cu_2**L^3**+H]$^+$. Λ_m (CH_3CN) = 296 Ω^{-1} cm^2 mol^{-1} (220–300 Ω^{-1} cm^2 mol^{-1} for a 2:1 conductor in MeCN) [55]. UV–Vis. {λ_{max}, nm (ε_{max}, M^{-1} cm^{-1})} in CH_3CN: 263 (17930), 401(4020), 643 (125).

3. Results and discussion

Three new unsymmetrical tripodal amines, 2-((4-aminobutyl)(pyridin-2-ylmethyl)amino)ethanol (**1**), 3-((3-aminopropyl)(pyridin-2-ylmethyl)amino)propan-1-ol **(2)** and

3-((4-aminobutyl)(pyridin-2-ylmethyl)amino)propan-1-ol **(3)**, were prepared in good yields (to see the spectra refer to Fig. S1–S9, ESI†).

Subsequently, one- pot reactions of amines **1-3** with 2,6-diformyl-4-methylphenol in the presence of cooper perchlorate were employed to generate new dinuclear Cu(II) complexes of Schiff-base ligands $H_2\mathbf{L}^{\mathbf{1\text{-}3}}$ (Figure 1). Recrystallisation of the powders obtained from the reaction mixtures as detailed in the experimental section, by vapour diffusion of diethyl ether, yields powders, or in one case single crystal $[Cu_2\mathbf{L}^{\mathbf{1}}](ClO_4)_2$, which are dinuclear complexes (see next sections).

3.1. Infrared spectroscopy

The infrared spectra of all these complexes show two bands, at ca. 1628-1629 and 1638 cm^{-1}, attributable to the asymmetric imine groups, and no bands due to ν(C=O) vibrations. Medium to strong bands at ca. 1609–1612 and 1446–1449 cm^{-1} are present in all cases, and correspond to the two highest energy ring vibrations of the coordinated pyridine [56, 57]. Absorptions attributable to the perchlorate ions are seen at approximately 1092–1096 and 623–624 cm^{-1}. Lack of splitting suggests that they are not coordinated (to see the spectra refer to Fig. S10–S12, ESI†).

3.2. Mass spectrometry

The positive ion electrospray mass spectra of all complexes (to see the spectra refer to Fig. S13–S15, ESI†) show a common peak, the fragment $[Cu_2\mathbf{L}^{\mathbf{1\text{-}3}}+2H](ClO_4)^+$ which is associated with the loss of the ClO_4 anion. The mass spectra of these complexes indicate that these complexes are dinuclear.

3.3. UV-Vis spectra

Although the UV-Vis spectra of complexes with polydentate Schiff base ligands are not generally good indicators of geometry, they may help to support it.

The UV-Vis spectra of the dinuclear Cu(II) complexes, in CH_3CN solution , exhibit a broad low-intensity absorption band occurring in the range 622 nm < λ_{max} < 648 nm with 125 M^{-1} cm^{-1} < ε < 187 M^{-1} cm^{-1}. This is assigned to a d–d transition and is typical for five-coordinate copper(II) complexes with square pyramidal or distorted square pyramidal geometries, which generally exhibit a band in the 550-660 nm range ($dxz, dyz \rightarrow dx^2\text{-}y^2$) [58-66]. In addition, a few absorption bands are found in the range 262–401 nm for all Cu(II) complexes, due to either charge transfer or π– π^* transitions [61, 63, 67-69].

3.4. Molar conductivity measurements

The electrolytic nature of the dinuclear metal complexes can be predicted from the molar conductance values. The molar conductivity values in MeCN for all dinuclear Cu(II) complexes are in the literature range for a 2:1 electrolyte in CH_3CN (220-300 Ω^{-1} cm^2 mol^{-1}) [55].

3.5. Crystal structure of $[Cu_2L^1](ClO_4)_2$

Green single crystals of $[Cu_2\mathbf{L^1}](ClO_4)_2$ suitable to be studied by X-ray diffraction were obtained by slow diffusion of diethyl ether into a solution of the complex in mixture of CH_3OH and MeCN. It is crystallised in the monoclinic crystal system and $P2_1/n$ space group. The molecular structure , the selected bond lengths and bond angles relating to the coordination environment of the metal and also bond lengths related to similar compounds are given in Figure 2 and Table 2, respectively [56, 61, 70-81]. The X-ray crystal structure of this complex consists of $[Cu_2\mathbf{L^1}]^{2+}$ cation and two perchlorate anion. The charge distribution was assigned based on the presence of only two ClO_4^- anions which make the complex a dication with a dideprotonated ligand $[\mathbf{L^1}]^{2-}$. The structure is a dinuclear, comprising two Cu(II) centers. Each Cu atom is coordinated by two different bridged oxygen atoms related to phenoxy and hydroxyalkyl groups and three imino, amine and pyridine nitrogen atoms. Each of phenoxy and hydroxyalkyl oxygen atoms bridges the two copper atoms. Cu(1) and Cu(2) atoms lie in an N_3O_2 coordination environment which takes the form of a distorted square pyramidal. The coordination geometry around the copper centers is best described by the use of the τ-criterion [78], which indicates that the coordination geometry in $[Cu_2\mathbf{L^1}]^{2+}$ is only slightly distorted ($\tau = 0.018$ Cu(1) and $\tau = 0.121$ Cu(2)) from square-pyramidal. For Cu(l), the pyridine nitrogen N(3), imino nitrogen N(1), phenoxy oxygen O(1) and deprotonated hydroxyalkyl oxygen atom O(3) occupy equatorial positions, and the tertiary nitrogen N(2) occupies axial position. For Cu(2), the amino nitrogen N(5), imino nitrogen N(4), phenoxy O(1) and hydroxyalkyl O(3) oxygen atoms occupy equatorial positions and one pyridine nitrogen atom N(6) occupies axial position. The phenoxy oxygen atom O(1) and deprotonated hydroxyalkyl oxygen atom O(3) bridge the two Cu(II) centers. The bond distances of Cu(1)-N and Cu(2)-N are in the range of 1.954-2.467 Å, being normal coordination bonds. The bridging oxygen atoms form asymmetric linkages to the Cu atoms with a range of $Cu–O_{phenoxy}$ and $Cu–O_{alkoxy}$ distances 1.988-2.003 and 1.902-1.925 Å respectively and $Cu(1)–O_{phenolate}–Cu(2)$ and $Cu(1)–O_{alkoxy}–Cu(2)$ bridging angles of 100.20 and 106.29, respectively. In this compound, one of the hydroxyalkyl arms (O2) of the ligand remains uncoordinated (Figure 2). The distance between Cu(l) and Cu(2) is 3.062 Å. This long distance between two Cu(II) centers suggests that there is no interaction between these two metal centers. In addition, in this complex one of the oxygen atoms related to one of the perchlorate groups (O_2p) has a very week interaction with Cu(1) atom. The tripodal ligand is capable of forming five, six and seven membered chelate rings incorporating the copper ion in $[Cu_2\mathbf{L^1}](ClO_4)_2$ complex. In this complex, both the N_{amine}-Cu-N_{py} angles and also N_{amine}-Cu2-$O_{hydroxyalkyl}$ angle are smaller than 90° [75.68-82.82°] for five membered chelate rings. The larger six- and seven-membered chelate rings lead to $O_{phenolic}$-Cu-N_{imine} and O_{amine}-Cu-N_{imine} angles, respectively, that are larger than 90° [91.55-105.32°] (Table 2).

Fig 2. here

Table 2 here

3.6. Theoretical studies

3.6.1. Fully optimization of copper(II) complexes

Mentioned copper (II) complexes are optimized at M062X/LANL2DZ level in vacuo. Optimized structures of $[Cu_2L^1]^{2+}$ **(1)**, $[Cu_2L^2]^{2+}$ **(2)** and $[Cu_2L^3]^{2+}$ **(3)** are represented in Figs. 3, 4 and 5, respectively. Structural parameters of these complexes are given in Table 3.

Figs 3-5 here

Table 3 here

Experimental and calculated structural parameters of $[Cu_2L^1]^{2+}$ complex ions are subjected to correlation analyses. Distribution graphs are plotted and regression coefficients are calculated from this graph. Distribution graph and its regression coefficient are represented in Fig. 6.

Fig. 6. Here

According to Fig. 6, there are some differences between experimental and calculated structural parameters but they are mainly similar to each other. Therefore, regression coefficient is calculated as 0.908 from distribution graph. It shows that there is an agreement between experimental and calculated structures of $[Cu_2L^1]^{2+}$. As a result, complex structures of $[Cu_2L^2]^{2+}$ and $[Cu_2L^3]^{2+}$ are as shown in Figs. 4 and 5.

Vibrational spectra of mentioned copper complexes are calculated at the same level of theory. Some selected harmonic frequencies of mentioned complexes are given in Table 4.

Table 4. here

In Table 4, frequencies of mentioned complexes are harmonic while experimental frequencies are anharmonic frequencies. Therefore, there are some differences which are in acceptance limits.

3.6.2. Frontier molecular orbitals and NLO properties of Cu(II) complexes

Frontier molecular orbitals of copper(II) complexes and some quantum chemical descriptors which are energy gap ($E_{LUMO-HOMO}$), total static dipole moment (μ), the average linear polarizability (α), the anisotropy of polarizability (Δα) and first hyperpolarizability (β) are calculated by using Eqs. (1)-(5) [82, 83]:

$$E_{LUMO-HOMO} = E_{LUMO} - E_{HOMO} \tag{1}$$

$$\mu = \left(\mu_x{}^2 + \mu_y{}^2 + \mu_z{}^2\right)^{1/2} \tag{2}$$

$$a = \frac{1}{3}\left(a_{xx} + a_{yy} + a_{zz}\right) \tag{3}$$

$$\Delta a = \frac{1}{\sqrt{2}}\left[\left(a_{xx} - a_{yy}\right)^2 + \left(a_{yy} - a_{zz}\right)^2 + \left(a_{zz} - a_{xx}\right)^2 + 6a_{xz}{}^2 + 6a_{xy}{}^2 + 6a_{yz}{}^2\right]^{1/2} \tag{4}$$

$$\beta = \left[\left(\beta_{xxx} + \beta_{xyy} + \beta_{xzz}\right)^2 + \left(\beta_{yyy} + \beta_{yzz} + \beta_{yxx}\right)^2 + \left(\beta_{zzz} + \beta_{zxx} + \beta_{zyy}\right)^2\right]^{1/2} \tag{5}$$

Frontier molecular orbitals which are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and their energies are represented in Fig. 7.

Fig. 7. here

Mentioned quantum chemical descriptors are used to evaluate the non-linear optical (NLO) properties of mentioned complexes. These parameters are calculated and given in Table 5.

Non linear optical properties increase with the increase of total static dipole moment, the average linear polarizability, the anisotropy of polarizability, first hyperpolarizability, energy of HOMO and energy gap between LUMO and HOMO. Urea is selected as reference substance and mentioned parameters of urea are calculated with 6-31G(d,p) basis set. For urea, total static dipole moment, the average linear polarizability, the anisotropy of polarizability and first hyperpolarizability are taken from Ref. [82] as 1.671 Debye, 2.182 Å^3, 9.3119 Å^3 and 3.18x10^{-28} cm^5/esu, respectively [82]. According to Table 5, all values of each mentioned complexes are greater than their urea values. Therefore, NLO properties of mentioned complexes are better than those of urea. The general ranking of NLO properties should be as follows:

Complex **(3)** > Complex **(2)** > Complex **(1)** (according to μ, α and E_{HOMO})

Complex **(1)** > Complex **(3)** > Complex **(2)** (according to $\Delta\alpha$)

Complex **(2)** > Complex **(3)** > Complex **(1)** (according to β)

As can be seen from above rankings, complex **(3)** is mainly the best candidate for NLO aplication.

Table 5 here

4. Conclusion

We report the successful synthesis of a series of new unsymmetrical tripodal amines, and then three new unsymmetrical Schiff-base ligands from them, isolated as three new dinuclear Cu complexes by condensation of amines (**1-3**) with 2,6-diformyl-4-methylphenol in the presence of Cu(II) metal ion. X-ray crystal structure determinations of [Cu_2**L^1**]$(ClO_4)_2$ revealed them to be dinuclear. In this complex, there is a distorted square pyramidal environment around the central ions. Each Cu atom is coordinated by two different bridged oxygen atoms related to phenoxy and deprotonated hydroxyalkyl groups and three imino, amine and pyridine nitrogen atoms. Each of phenoxy and hydroxyalkyl oxygen atoms bridges the two copper atoms. Cu(1) and Cu(2) atoms lie in an N_3O_2 coordination environment. In this compound, one of the hydroxyalkyl arms (O_2) of the ligand remains uncoordinated. Also, copper (II) complexes were investigated by computational chemistry methods. Relevant complexes were optimized at M062X/LANL2DZ level in vacuo. IR spectrum, FMO and NLO properties of relevant complexes were examined at the same level of theory.

Supplementary material

Crystallographic data for the crystal structure analyses has been deposited with the Cambridge Crystallographic Data Centre, CCDC no. (1412483), for $[Cu_2\mathbf{L^1}](ClO_4)_2$. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; mail:deposit@ccdc.cam.ac.uk).

Acknowledgements

We are grateful to the Faculty of Chemistry of Bu-Ali Sina University, Ministry of Science, Research and Technology of Iran, the University of Otago and the MacDiarmid Institute for Advanced Materials and Nanotechnology for financial support (PhD scholarship for SD), and Professor Sally Brooker for hosting MS for a 6-month research visit. Also, we are grateful of the office of scientific research projects of Cumhuriyet University (Project No.: F-429) for financial supports. The numerical calculations reported in this paper are performed at TUBITAK ULAKBIM, High Performance and Grid Computing Center (TRUBA Resources).

References

[1] K. J. Waldron, J.C. Rutherford, D. Ford, N.J. Robinson, Nature 460 (2009) 823.

[2] K. Wieghardt, Angew. Chem., Int. Ed. Engl. 28 (1989) 1153.

[3] Y. Zhang, L. Zhang, L. Liu, J. Guo, D. Wu, G. Xu, X. Wang, D. Jia, Inorg. Chim. Acta 363 (2010) 289.

[4] L. Jia, P. Jiang, J. Xu, Z. Hao, X. Xu, L. Chen, J. Wu, N. Tang, Q. Wang, J.J. Vittal, Inorg. Chim. Acta 363 (2010) 855.

[5] S. Chowdhury, P. Mal, C. Basu, H. Stoeckli-Evans, S. Mukherjee, Polyhedron 28 (2009) 3863.

[6] K.E. Erkkila, D.T. Odom, J.K. Barton, Chem. Rev. 99 (1999) 2777.

[7] C. Liu, M. Wang, T. Zhang, H. Sun, Coord. Chem. Rev. 248 (2004) 147.

[8] U. Chaveerach, A. Meenongwa, Y. Trongpanich, C. Soikum, P. Chaveerach, Polyhedron 29 (2010) 731.

[9] A.K. Patra, M. Nethaji, A.R. Chakravarty, J. Inorg. Biochem. 101 (2007) 233.

[10] R.M. Kretzer, R.A. Ghiladi, E.L. Lebeau, H.-C. Liang, K.D. Karlin, Inorg. Chem. 42 (2003) 3016.

[11] C. Marzano, M. Pellei, D. Colavito, S. Alidori, G.G. Lobbia, V. Gandin, F. Tisato, C. Santini, J. Med. Chem. 49 (2006) 7317.

[12] G.S. Siluvai, B. Vargheese, N.N. Murthy, Inorg. Chim. Acta 375 (2011) 93.

[13] (a) M. Kato, Y. Muto, Coord. Chem. Rev. 92 (1988) 45; (b) M. Melnik, Coord. Chem. Rev. 42 (1982) 259; (c) R.J. Doedens, Prog. Inorg. Chem. 21 (1976) 209.

[14] (a) W.E. Hatfield, Comments Inorg. Chem. 1 (1981) 105; (b) D.J. Hodgson, Prog. Inorg. Chem 19 (1975) 173; (c) V.H. Crawford, H.W. Richardson, J.R. Wasson, D.J. Hodg-son, W.E. Hatfield, Inorg. Chem. 15 (1976) 2107.

[15] (a) O. Kahn, Angew. Chem., Int. Ed. Engl. 24 (1985) 834; (b) O. Kahn, Comments Inorg. Chem. 3 (1984) 105.

[16] P.J. Hey, J.C. Thibeault, R. Hoffmann, J. Am. Chem. Soc. 97 (1975) 4884.

[17] W. Mazurek, B.J. Kennedy, K.S. Murray, M.J. O Connor, J.R. Rodgers, M.R. Snow, A.G. Wedd, P.R. Zwack, Inorg. Chem. 24 (1985) 3258.

[18] (a) Y. Nishida, M. Takeuchi, K. Takahashi, S. Kida, Chem. Lett. (1982) 1815; (b) Y. Nishida, M. Takeuchi, K. Takahashi, S. Kida, Chem. Lett. (1985) 631.

[19] Y. Nishida, S. Kida, J. Chem. Soc., Dalton Trans. (1986) 2633.

[20] M. Handa, N. Koga, S. Kida, Bull. Chem. Soc. Jpn. 61 (1988) 3853.

[21] (a) K. Geetha, M. Nethaji, N.Y. Vasanthacharya, A.R. Chakrav-arty, J. Coord. Chem. 47 (1999) 77; (b) S. Meenakumari, S.K. Tiwari, A.R. Chakravarty, J. Chem. Soc., Dalton Trans. (1993) 2175; (c) K. Geetha, M. Nethaji, A.R. Chakravarty, N.Y. Vasantha-charya, Inorg. Chem. 35 (1996) 7666.

[22] (a) T.N. Sorrell, C.J. O Connor, D.P. Anderson, J.H. Reibenspies, J. Am. Chem. Soc. 107 (1985) 4199; (b) V. McKee, M. Zvagulis, J.V. Dagdigian, M.G. Patch, C.A. Reed, J. Am. Chem. Soc. 106 (1984) 4765.

[23] R.E.P. Winpenny, Adv. Inorg. Chem. 52 (2001) 1.

[24] S.P. Perlepes, E. Libby, W.E. Streib, K. Folting, G. Christou, Polyhedron 8 (1992) 923.

[25] (a) S.R. Batten, B.F. Hoskins, B. Moubaraki, K.S. Murray, R. Robson, Chem. Commun. (2000) 1095; (b) B. Graham, M.T.W. Hearn, P.C. Junk, C.M. Kepert, F.E. Mabbs, B. Moubaraki, K.S. Murray, L. Spiccia, Inorg. Chem. 40 (2001) 1536.

[26] M.-L. Tong, K.H. Lee, Y.-X. Tong, X.-M. Chen, T.C.W. Mak, Inorg. Chem. 39 (2000) 4666.

[27] (a) V. Tangoulis, C.P. Raptopoulou, S. Paschalidou, E.G. Bakalbassis, S.P. Perlepes, A. Terzis, Angew. Chem., Int. Ed. Engl. 36 (1997) 1083; (b) V. Tangoulis, C.P. Raptopoulou, A. Terzis, S. Paschalidou, S.P. Perlepes, E.G. Bakalbassis, Inorg. Chem. 36 (1997) 3996; (c) H.

Annetha, K. Panneerselvam, T.-F. Liao, T.-H. Lu, C.-S. Chung, J. Chem. Soc., Dalton Trans. (1999) 2869.

[28] A. Mukherjee, I. Rudra, M. Nethaji, S. Ramasesha, A.R. Chakravarty, Inorg. Chem. 42 (2003) 463.

[29] K. Geetha, M. Nethaji, A.R. Chakravarty, Inorg. Chem. 36 (1997) 6134.

[30] A. Mukherjee, M. Nethaji, A.R. Chakravarty, Angew. Chem. Int. Ed. 43 (2004) 87.

[31] A. Mukherjee, M. Nethaji, A.R. Chakravarty, Chem. Commun. (2003) 2978.

[32] A. Mukherjee, I. Rudra, S.G. Naik, S. Ramasesha, M. Nethaji, A.R. Chakravarty, Inorg. Chem. 42 (2003) 5660.

[33] R. Vafazadeh, B. Khaledi, A.C. Willis, M. Namazian, Polyhedron 30 (2011) 1815.

[34] S. Anbu, M. Kandaswamy, Polyhedron 30 (2011) 123.

[35] D. Venegas-Yazigia, D. Aravenab, E. Spodineb, E. Ruizd, S. Alvarez, Coord. Chem. Rev. 254 (2010) 2086.

[36] D. Gatteschi, O. Kahn, R.D. Willet, Magnetostructural Correlations in Exchange Coupled Systems, Reidel, Dordrecht, 1984.

[37] T.N. Doman, D.E. Williams, J.F. Banks, R.M. Buchanan, H.-R. Chang, R.J. Webb, D.N. Hendrickson, Inorg. Chem. 29 (1990) 1058.

[38] E. Kavlakoglu, A. Elmali, Y. Elerman, H. Fuess, Z. Naturforsch. 55b (2000) 561.

[39] V.H. Crawford, H.W. Richardson, J.R. Wasson, D.J. Hodgson, W.E. Hatfield, Inorg. Chem. 15 (1976) 2107.

[40] K. Liu, G. Liu, Z. Cao, M. Niu, Acta Cryst. E66 (2010) m78.

[41] P.K. Cougling, S.P. Lippard, J. Am. Chem. Soc. 103 (1981) 3228.

[42] A. Elmali, C.T. Zeyrek, Y. Elerman, J. Mol. Struct. 693 (2004) 225.

[43] M.S. Ray, G. Mukhopadhyay, M.G.B. Drew, T.-H. Lu, S. Chaudhuri, A. Ghosh, Inorg. Chem. Commun. 6 (2003) 961.

[44] E. Safaei, A. Wojtczak, E. Bill, H. Hamidi, Polyhedron 29 (2010) 2769.

[45] **A**nderson, A. A. and Geotzen, T., Syn. Comm. Vol. 30(17) (2000) 3227.

[46] G.M. Sheldrick, Sadabs, Program for empirical absorption correction of area detector data, University of Göttingen, Germany, 1996.

[47] SHELXTL version, an integrated system for solving and refining crystal structures from diffraction data (Revision 5.1), Bruker AXS LTD.

[48] GaussView, Version 5, Roy Dennington, Todd Keith, and John Millam, Semichem Inc., Shawnee Mission, KS, 2009.

[49] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[50] PerkinElmer, 2012. ChemBioDraw Ultra Version (13.0.0.3015), CambridgeSoft Waltham, MA, USA.

[51] Y. Zhao, D. G. Truhlar, Theor. Chem. Acc. 120 (2008) 215.

[52] P. J. Hay, W. R. Wadt, Ab initio effective core potentials for molecular calculations - potentials for the transition-metal atoms Sc to Hg, J. Chem. Phys. 82 (1985) 270.

[53] P. J. Hay, W. R. Wadt, Ab initio effective core potentials for molecular calculations - potentials for K to Au including the outermost core orbitals, J. Chem. Phys. 82 (1985) 299.

[54] W. R. Wadt, P. J. Hay, Ab initio effective core potentials for molecular calculations - potentials for main group elements Na to Bi, J. Chem. Phys. 82 (1985) 284.

[55] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.

[56] H. Keypour, A.H. Jamshidi, M. Rezaeivala, L. Valencia, Polyhedron 52 (2013) 872.

[57] M. Kalanithi, M. Rajarajan, P. Tharmaraj and C.D. Sheela, Spectrochim. Acta A 87 (2012) 155.

[58] G. A. McLachlan, G. D. Fallon, R. L. Martin and L. Spiccia, Inorg. Chem. 34 (1995) 254.

[59] S. J. Brudenell, L. Spiccia and E. R. T. Tiekink, Inorg. Chem. 35 (1996) 1974; A. B. P. Lever, Studies in physical and theoretical chemistry 33: Inorganic electronic spectroscopy, Elsevier, Amsterdam, 1997.

[60] B. Graham,M. T.W. Hearn, P. C. Junk, C. M. Kepert, F. E. Mabbs, B. Moubaraki,K. S.Murray and L. Spiccia, Inorg. Chem. 40 (2001) 1536.

[61] C. Ochs, F. E. Hahn and R. Fröhlich, Eur. J. Inorg. Chem. (2001) 2427.

[62] M. Du, Y-M. Guo, S-T. Chen, X-H. Bu and J. Ribas, Inorg. Chim. Acta 346 (2003) 207.

[63] S. Bhattacharyya, S.B. Kumar, S.K. Dutta, E.R.T. Tiekink and M. Chaudhury, Inorg. Chem. 35 (1996) 1967.

[64] B. Sarkar, M.S. Ray, Y.-Z. Li, Y. Song, A. Figuerola, E. Ruiz, J. Cirera, J. Cano and A. Ghosh, Chem. Eur. J. 13 (2007) 9297.

[65] B. Sarkar, S. Konar, C.J. Gomez-Garcia and A. Ghosh, Inorg. Chem. 47 (2008) 11611.

[66] B.J. Hathaway and A.A.G. Tomlinson, Coord. Chem. Rev. 5 (1970) 1.

[67] E. Colacio, J.M. Domı´nguez-Vera, M. Gazi, R. Kiveka¨s, J.M. Moreno and A. Pajunen, J. Chem. Soc., Dalton Trans. (2000) 505.

[68] (a) M.J. Scott, S.C. Lee and R.H. Holm, Inorg. Chem. 33 (1994) 4651.; (b) M.T. Gardner, G. Deinum, Y. Kim, G.T. Babcock, M.J. Scott and R.H. Holm, Inorg. Chem. 35 (1996) 6878.; (c) R.T. Conley, Infrared Spectroscopy, Allyn & Bacon Inc., Boston, 1966; (d) K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds; Part A and B, fifth ed., Wiley, New York, 1997.

[69] N. Mondal, D.K. Dey, S. Mitra and V. Gramlich, Polyhedron 20 (2001) 607.

[70] R.N. Patel, S.P. Rawat, M. Choudhary, V. P. Sondhiya, D. K. Patel, K.K. Shukla,D. K. Patel, Y. Singh and R. Pandey, Inorg. Chim. Acta 392 (2012) 283.

[71] P. Bhowmik, N. Aliaga-Alcalde, V. Gómez, M. Corbella, S. Chattopadhyay, Polyhedron 49 (2013) 269.

[72] F. Tuna, G. I. Pascu, J-P. Sutter, M. Andruh, S. Golhen, J. Guillevic, H. Pritzkow, Inorg. Chim. Acta 342 (2003) 131.

[73] A. Kumar Sharma and R. Mukherjee, Inorg. Chim. Acta 361 (2008) 2768.

[74] S. Sarkar, A. Mondal, J. Ribas, M.G.B. Drew, K. Pramanik, K. K. Rajak, Inorg. Chim. Acta 358 (2005) 641.

[75] E. V. Rybak-Akimova, A. Y. Nazarenko, L. Chen, P. W. Krieger, A. M. Herrera, V. V. Tarasov and P. D. Robinson, Inorg. Chim. Acta 324 (2001) 1.

[76] N. J. Lundin, I. G. Hamilton and A. G. Blackman, Polyhedron 23 (2004) 97.

[77] B. Sreenivasulu, M. Vetrichelvan, F. Zhao, S. Gao and J. J. Vittal, Eur. J. Inorg. Chem. (2005) 4635.

[78] Y. Yahsi and H. Kara, Inorg. Chim. Acta 397 (2013) 110.

[79] L. C. Nathan, J. E. Koehne, J. M. Gilmore, K. A. Hannibal, W. E. Dewhirst and T. D. Mai, Polyhedron 22 (2003) 887.

[80] A. Arbaoui, C. Redshaw, N. M. Sanchez-Ballester, M. R.J. Elsegood, D. L. Hughes, Inorg. Chim. Acta 365 (2011) 96.

[81] Z. Chu, W. Huang, Inorg. Chem. Commun. 11 (2008) 1166.

[82] K. Sayin, D. Karakaş, N. Karakuş, T.A. Sayin, Z. Zaim, S.E. Kariper, Polyhedron 90 (2015) 139.

[83] K. Sayin, D. Karakaş, Spectrochim. Acta A. 144 (2015) 176.

Figures

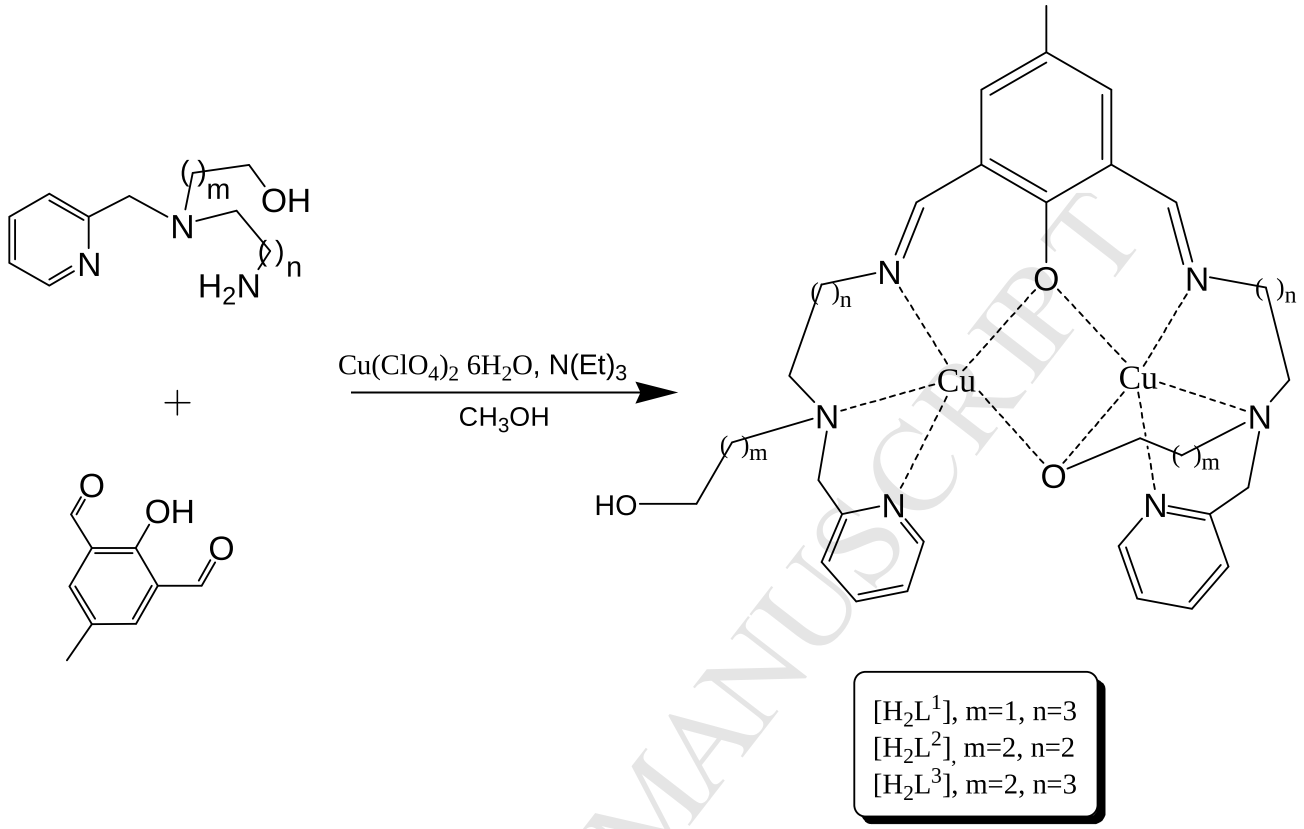


Figure 1.structural motifs for new complexes of the ligands highlighted in the box, $H_2\mathbf{L}^{\mathbf{1}}$, $H_2\mathbf{L}^{\mathbf{2}}$ and $H_2\mathbf{L}^{\mathbf{3}}$resulting from the condensation of 2,6-diformyl-4-methylphenol with the unsymmetrical triamines **1** (n = 3, m=1) **2** (n = 2, m=2) and **3** (n = 3, m = 2) with different arm lengths.

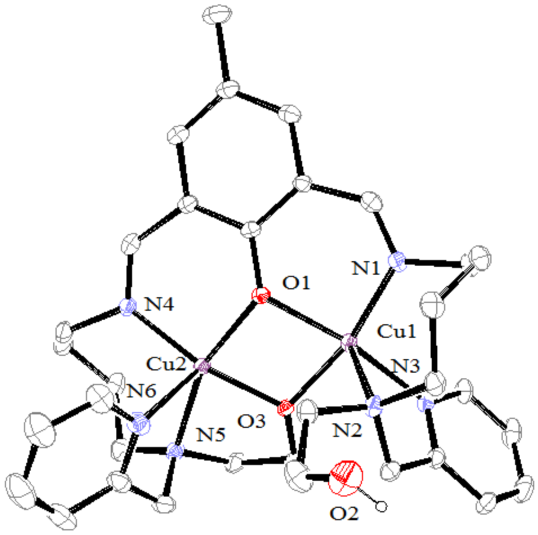


Figure 2. Perspective view of $[Cu_2\mathbf{L^1}](ClO_4)_2$. Hydrogen atoms and anions are omitted for clarity. Cu, C, N and O are represented in brown, gray, blue and red, respectively.

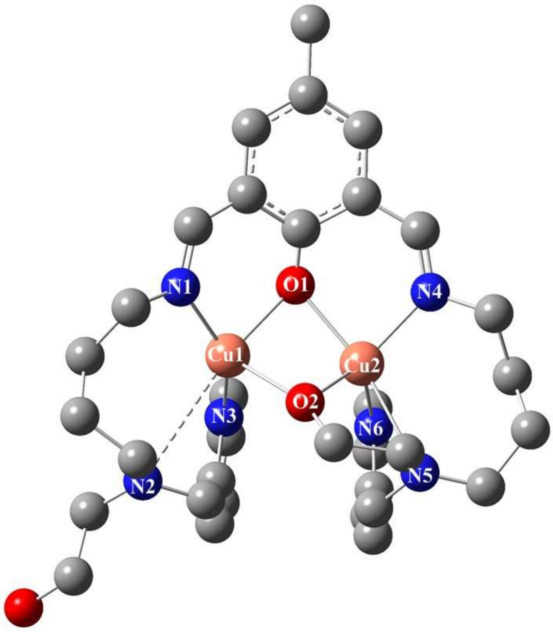


Fig. 3. Optimized structure of $[Cu_2L^1]^{2+}$ at M062X/LANL2DZ level in vacuo with atomic labelling.

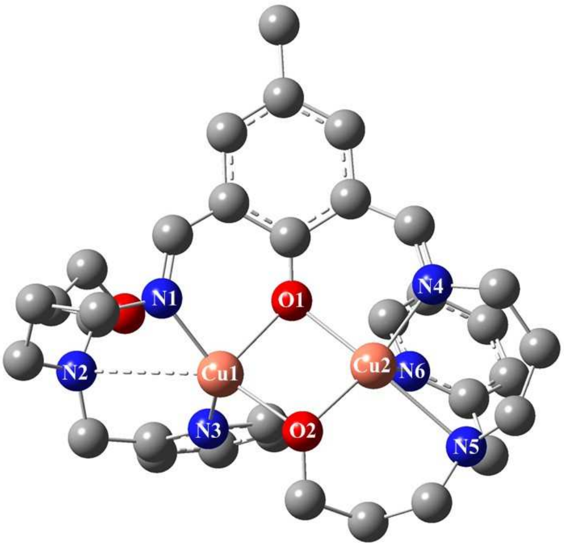


Fig. 4. Optimized structure of $[Cu_2L^2]^{2+}$ at M062X/LANL2DZ level in vacuo with atomic labelling.

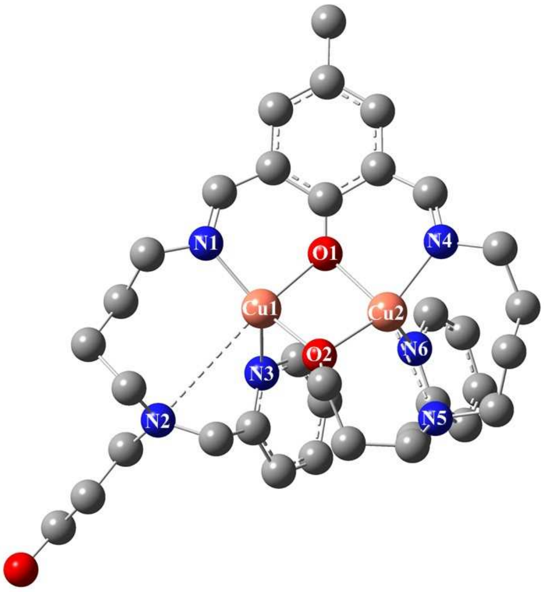


Fig. 5. Optimized structure of $[Cu_2L^3]^{2+}$ at M062X/LANL2DZ level in vacuo with atomic labelling.

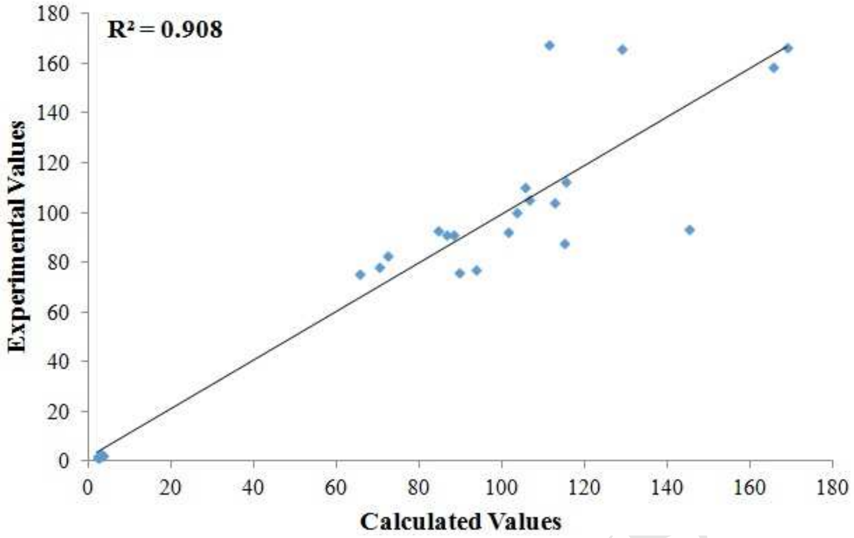


Fig. 6. Distribution graph and its regression coefficients for $[Cu_2L^1]^{2+}$ complex ion.

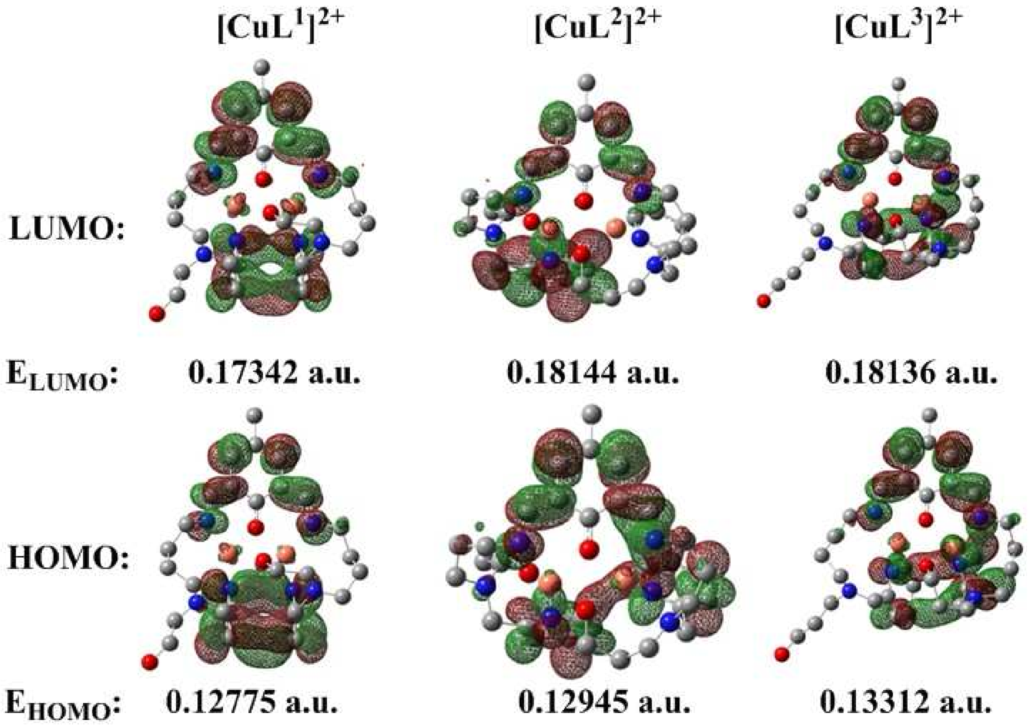


Fig. 7. Frontier molecular orbitals of mentioned Cu(II) complexes at M062X/LANL2DZ level in vacuo.

Table 1. Crystal data and structure refinement parameters for [Cu_2**L**^{1}](ClO_4)$_2$.

Empirical formula	$C_{34}H_{48}Cl_2Cu_2N_6O_{12}$
Formula weight	930.76
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P21/n
Unit cell dimensions	
a (Å)	9.5930 (13)
b (Å)	31.382 (4)
c (Å)	13.1055 (18)
β (°)	96.295 (3)
Volume (Å^3)	3921.5 (9)
Z	4
Calculated density(Mg/m3)	1.576
Absorption coefficient (mm-1)	0.740
Crystal size (mm3)	0.34 × 0.29 × 0.20
Theta range for data collection (°)	1.3 to 25.1
Limiting indices	-11≤h≤11, -37≤k≤37, -15≤l≤15
Reflections collected / unique	5194 / 2822 [R(int) = 0.041]
Completeness to theta=25.00	99.4 %
Absorption correction	Empirical
Max. and min. transmission	0.773 and 0.651
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6956 / 0 / 508
Goodness-of-fit on F^2	1.046
Final R indices [I>2σ(I)]	R1 = 0.041, wR2 = 0.1162
R indices (all data)	R1 = 0.0666, wR2 = 0.996
Largest diff. peak and hole(e.A^{-3})	0.71 and -0.75

Table 2. Comparison of selected bond lengths [Å] and angles [°] for [Cu$_2$**L**^{1}](ClO$_4$)$_2$complex.

	[Cu$_2$**L**^{1}](ClO$_4$)$_2$	Sq pyr Cu(II) in the literature	References
Bond length [Å]			
Cu(1)-N(1)$_{\text{imine}}$	1.957 (3)	1.923-1.969	[56], [70-72]
Cu(2)-N(4)$_{\text{imine}}$	1.954 (3)		
Cu(1)-N(3)$_{\text{py}}$	2.028 (3)	1.925-2.006	[70], [72-74]
Cu(2)-N(6)$_{\text{py}}$	2.366 (4)		
Cu(1)-N(2)$_{\text{amine}}$	2.467 (3)	1.979-2.062	[61], [73- 76]
Cu(2)-N(5)$_{\text{amine}}$	2.092 (3)		
Cu(1)-O(1)$_{\text{phenolic}}$	2.003 (3)	1.917-2.096	[61], [70-72], [77-81]
Cu(2)-O(1)$_{\text{phenolic}}$	1.988 (3)		
Cu(1)-O(3)$_{\text{hydroxyalkyl}}$	1.925 (3)	1.916-2.339	[61], [71]
Cu(2)-O(3)$_{\text{hydroxyalkyl}}$	1.902 (3)		
Cu(1)···Cu(2)	3.062	2.2729-3.001	[61], [70, 71]
Bond angle [°]			
O(1)$_{\text{phenolic}}$-Cu(1)-N(1)$_{\text{imine}}$	91.55 (12)		
O(1)$_{\text{phenolic}}$-Cu(1)-N(3)$_{\text{py}}$	166.51 (12)		
O(1)$_{\text{phenolic}}$-Cu(1)-N(2)$_{\text{amine}}$	110.45 (11)		
N(1)$_{\text{imine}}$-Cu(1)-N(3)$_{\text{py}}$	100.15 (14)		
N(3)$_{\text{py}}$-Cu(1)-N(2)$_{\text{amine}}$	75.68 (12)		
N(1)$_{\text{imine}}$-Cu(1)-N(2)$_{\text{amine}}$	93.86 (13)		
O(3)$_{\text{hydroxyalkyl}}$-Cu(1)-N(2)$_{\text{amine}}$	92.69 (12)		
O(3)$_{\text{hydroxyalkyl}}$-Cu(1)-N(1)$_{\text{imine}}$	167.61 (12)		
O(3)$_{\text{hydroxyalkyl}}$-Cu(1)-O(1)$_{\text{phenolic}}$	76.30 (10)		
O(3)$_{\text{hydroxyalkyl}}$-Cu(1)-N(3)$_{\text{py}}$	91.65 (12)		
O(1)$_{\text{phenolic}}$-Cu(2)-N(4)$_{\text{imine}}$	93.15 (12)		
O(1)$_{\text{phenolic}}$-Cu(2)-N(6)$_{\text{py}}$	112.83 (12)		
O(1)$_{\text{phenolic}}$-Cu(2)-N(5)$_{\text{amine}}$	158.98 (12)		
N(4)$_{\text{imine}}$-Cu(2)-N(6)$_{\text{py}}$	88.13 (14)		
N(6)$_{\text{py}}$-Cu(2)-N(5)$_{\text{amine}}$	78.34 (14)		
O(3)$_{\text{hydroxyalkyl}}$-Cu(2)-N(5)$_{\text{amine}}$	82.82 (12)		
O(3)$_{\text{hydroxyalkyl}}$-Cu(2)-N(4)$_{\text{imine}}$	166.27 (13)		
O(3)$_{\text{hydroxyalkyl}}$-Cu(2)-N(6)$_{\text{py}}$	104.53 (13)		
O(3)$_{\text{hydroxyalkyl}}$-Cu(2)-O(1)$_{\text{phenolic}}$	77.19 (11)		
N(4)$_{\text{imine}}$-Cu(2)-N(5)$_{\text{amine}}$	105.32 (13)		

Table 3. Optimized structural parameters of mentioned complex ions at M062X/LANL2DZ level in vacuo

Assignments[1]	$[Cu_2L^1]^{2+}$	$[Cu_2L^2]^{2+}$	$[Cu_2L^3]^{2+}$
Bond Lengths (Å)			
Cu1-N1	2.029	2.047	2.051
Cu1-N2	3.269	3.256	3.637
Cu1-N3	2.029	2.186	2.204
Cu1-O1	2.160	2.161	2.137
Cu1-O2	2.357	2.139	2.057
Cu2-N4	2.102	2.053	2.116
Cu2-N5	2.768	2.513	2.856
Cu2-N6	2.110	2.345	2.134
Cu2-O1	2.220	2.210	2.198
Cu2-O2	2.152	2.061	2.126
Cu1 ··· Cu2	2.859	3.119	2.999
Bond Angles (°)			
N1-Cu1-N2	103.13	66.39	96.71
N1-Cu1-N3	145.09	125.5	117.82
N1-Cu1-O1	88.07	86.94	87.5
N1-Cu1-O2	111.19	140.73	153.84
N2-Cu1-N3	65.4	62.15	55.49
N2-Cu1-O1	168.79	118.26	154.63
N2-Cu1-O2	86.33	147.62	95.18
N3-Cu1-O1	105.35	101.9	100.49
N3-Cu1-O2	101.18	93.74	88.06
O1-Cu1-O2	89.53	86.14	91.64
N4-Cu2-N5	106.45	95.64	116.74
N4-Cu2-N6	114.67	85.93	101.8
N4-Cu2-O1	84.35	88.59	86.08
N4-Cu2-O2	128.84	155.64	144.97
N5-Cu2-N6	69.98	70.16	71.91
N5-Cu2-O1	165.32	159.72	156.17
N5-Cu2-O2	72.07	96.96	76.92
N6-Cu2-O1	115.09	90.44	97.9
N6-Cu2-O2	112.34	117.99	113.22
O1-Cu2-O2	93.45	86.78	88.14
Cu1-O1-Cu2	81.49	86.14	91.64
Cu1-O2-Cu2	78.56	86.78	88.14

[1] Atomic labelings are represented in Figs. 3, 4 and 5.

Table 4. Calculated vibrational frequencies (cm^{-1}) of mentioned copper complexes at M062X/LANL2DZ level in vacuo

Assignments	$[Cu_2L^1]^{2+}$	$[Cu_2L^2]^{2+}$	$[Cu_2L^3]^{2+}$
$\nu_{O\text{-}H}$	3757	3662	3761
$\nu_{C\text{-}H_{aromatic}}$	3172	3200	3183
$\nu_{C\text{-}H_{aliphatic}}$	3051	2919	2944
$\nu_{C=N}$	1672, 1608	1647, 1590	1611, 1584
$\nu_{C=N_{pyridine}}$	1630	1570	1604
$\nu_{C\text{-}O}$	1587	1570	1575
$\nu_{C\text{-}N}$	1257	1340	1298
$\nu_{Cu\text{-}N}$	618	615	627
$\nu_{Cu\text{-}O}$	485	441	478

Table 5. The calculated total static dipole moment (μ), the average linear polarizability (α), the anisotropy of polarizability (Δα) and first hyperpolarizability (β) for mentioned complexes

Parameters	$[Cu_2L^1]^{2+}$	$[Cu_2L^2]^{2+}$	$[Cu_2L^3]^{2+}$
μ_x[1]	1.4618	0.1665	4.1831
μ_y[1]	-0.4543	-2.1168	-2.1908
μ_z[1]	-1.3674	-0.3040	-0.1222
α_{xx}[2]	1070.0351	904.7777	862.3206
α_{yy}[2]	-315.9058	-63.5447	-138.0120
α_{zz}[2]	917.6358	912.1914	1123.2710
α_{xy}[2]	146.9606	-117.0510	29.8817
α_{xz}[2]	-100.2095	-174.5640	-200.1180
α_{yz}[2]	432.5574	559.9266	476.4716
β_{xxx}[2]	-2326.0259	-7936.5319	17165.4460
β_{yyy}[2]	-119.7353	-2016.2421	-2139.5031
β_{zzz}[2]	-2308.8697	7190.3899	3920.5001
β_{xyy}[2]	694.9712	-8165.6782	8763.3580
β_{xxy}[2]	-596.7072	-5021.3023	-1164.0767
β_{xxz}[2]	-1,418.3991	756.6837	-3275.8795
β_{xzz}[2]	-3134.8157	-3134.5991	-2210.4600
β_{yzz}[2]	-904.6014	-6079.5677	1164.2191
β_{yyz}[2]	-395.9493	3307.3093	44.06349
μ[1]	2.0526	2.1450	4.723671
α[3]	82.5766	86.61013	91.26093
Δα[3]	229.0435	210.5032	216.4556
β[4]	5.62×10^{-26}	2.23×10^{-25}	2.06×10^{-25}
$E_{LUMO-HOMO}$[5]	120.43	137.29	126.65

[1] in Debye, [2] in atomic unit (a.u.), [3] in $Å^3$, [4] in cm^5/esu, [5] in kJ mol^{-1}

Dinuclear Cu(II) complexes of compartmental Schiff base ligands formed from unsymmetrical tripodal amines of varying arm lengths: Crystal structure of $[Cu_2L^1](ClO_4)_2$ and theoretical studies

Hassan Keypour[a,]*, Maryam Shayesteh[a], Majid Rezaeivala[b], Koray Sayin [C]

Highlights

- Synthesis of new compartmental Schiff base ligands formed from unsymmetrical tripodal amines of varying arm lengths
- Synthesis of dinuclear Cu(II) complexes of new compartmental Schiff base ligands
- X-ray crystal structure determination of one new Cu complex
- Computational investigation of mentioned binuclear Cu(II) complexes