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# Synthesis, Experimental and Theoretical Characterization of ($\mu_4$-oxo)hexakis($\mu_2$-chloro)-tetrakis[1-(allyl)-1*H*-imidazole]tetracopper(II)

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**Abstract:** A new [$Cu_4OCl_6L_4$] cluster [L = 1-(allyl)-1*H*-imidazole] has been isolated and its crystal structure and spectroscopic properties determined. The compound crystallizes as a yellow solid in the monoclinic system, space group *P*2$_1$, with cell constants *a* = 10.6937(7) Å, *b* = 13.1004(7) Å, *c* = 13.2452(9) Å, *β* = 93.537(6)°, and two formula units per cell. The title tetranuclear complex has a central $\mu_4$-oxide ion surrounded tetrahedrally by four Cu$^{II}$ atoms. Each Cu atom is connected to three others *via* bridging Cl atoms. The fifth coordination position, located on the central Cu–O axis on the outside of the cluster, is occupied by an N atom of the monodentate imidazole ligand. The resulting coordination geometry of the metal ion is a slightly distorted trigonal bipyramid with the O and N atoms in the axial positions. The molecular structure and spectroscopic data were obtained using density functional theory (DFT/HSEH1PBE) method with the cc-pVDZ basis set for C, H, N, O and Cl atoms, and the LANL2DZ basis set for the Cu atoms, and compared with the experimental data. Consequently, the experimental data well coherences with the theoretical ones.

**Keywords**: $Cu_4OCl_6$ cluster, X-ray crystallography, spectroscopy, DFT.

## INTRODUCTION

**P**OLYNUCLEAR copper complexes have received increasing attention in recent years, owing to their applications in metallobiochemistry,[1–3] material science,[4–6] theoretical chemistry,[7,8] and magnetism.[9,10] Since the first example of clusters of the type [$Cu_4OX_{10-n}L_n$]$^{n-4}$ (X = Br or Cl; L = Lewis-base ligand) was described by Bertrand and Kelly in 1966,[11] a number of these compounds of formulas [$Cu_4OX_6L_4$] and [$Cu_4OX_{10}$]$^{4-}$ have been reported.[12–15] The clusters have the same structural framework, with four copper atoms at the corners of a tetrahedron around the central $\mu_4$-bridging oxygen and six $\mu$-bridging halide atoms over each edge of the tetrahedron.

These clusters have been studied largely because of their unique magnetic properties.[9,16] Most of these compounds show a magnetic susceptibility which has a maximum in the plot of the magnetic moment versus temperature.[17] In some, a strong anti-ferromagnetic coupling has been associated with the presence of more than one oxo-Cu bridge.[14,18] Oxo-Cu(II) species are important in many copper-catalyzed reactions that take place in biological systems which involve a reduction of oxygen molecules by Cu(I).[19,20] Model studies in this field have encouraged cluster syntheses. Potential applications in pharmacology and industrial catalytic processes have also been resulted.[21,22]

Although tetranuclear copper(II) complexes with imidazole are known in the literature,[9,16,23–32] to the best of our knowledge, no theoretical studies on the structure and spectroscopic properties of these complexes have been reported so far. Therefore, we have synthesized a new tetranuclear $\mu_4$-oxo-bridged copper(II) complex with the monodentate 1-(allyl)-1*H*-imidazole ligand, and characterized it by FT-IR and UV-vis. spectroscopy. The molecular structure of the complex has been determined by single crystal X-ray diffraction. In addition, the theoretical calculations have been performed by using DFT method.

## MATERIALS AND METHODS

### General Remarks

All chemicals were obtained from commercial suppliers and used without further purification. Infrared spectra were recorded on an ATR Spectrum-II, PerkinElmer spectrometer. The UV-spectra were measured on a Shimadzu UV-1900i UV-VIS spectrometer in $10^{-5}$ M $CHCl_3$. Quartz cuvettes of 1 cm path length were used for the measurements. Melting points were measured with a Stuart SMP30 melting point apparatus. Elemental analyses were performed by ODTU Microlab (Ankara, Turkey).

### Synthesis

1-(Allyl)-1*H*-imidazole (1.0 mL, 9.2 mmol) was added to a solution of $CuCl_2 \cdot 2H_2O$ (3.15 g, 18.5 mmol) in ethanol (5.0 mL). The reaction mixture was stirred at room temperature for 24 h, during which time a yellow precipitate formed (Figure 1). The mixture was then filtered. The crude product was recrystallized from $CH_2Cl_2/Et_2O$. Yield: 4.40 g, 52 %. M.p.: 240–242 °C. *Anal*. Calc. for $[Cu_4Cl_6O(C_6H_8N_2)_4]$ (915.43 g/mol): C: 31.49; H: 3.52; N: 12.24. Found: C: 31.21; H: 3.50; N: 12.05 %. IR (KBr, $cm^{-1}$): 3130, 1522, 1438, 1419, 1233, 1105, 1091, 957, 831, 750, 653, 564.

### X-Ray Crystallography

Data collection was performed on a STOE IPDS II diffractometer at room temperature (296 K) using graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) by applying the $\omega$-scan method. The structure was solved by direct methods using SHELXS-2013[33] and refined with full-matrix least-squares calculations on $F^2$ using SHELXL-2014[33] implemented in WinGX[34] program suit. Hydrogen atoms were placed in idealized positions with isotropic thermal parameters fixed at 1.2 times the value of the attached atom. In the compound, the carbon atoms of the allylimidazole moieties (as a whole or only allyl part) were disordered over two positions, and the refined site-occupancy factors of the disordered parts are 0.72(5)/0.28(5) for C5-C6, 0.78(2)/0.22(2) for C7-C12, 0.74(6)/0.26(6) for C17-C18 and 0.61(4)/0.39(4) for C19-C24. The disordered atoms were refined using the SIMU, DELU, SADI and FLAT restraints of SHELXL-2014, which resulted in 608 restraints. Data collection: X-AREA,[35] cell refinement: X-AREA, data reduction: X-RED32.[35] Crystal data, data collection and structure refinement details are summarized in Table 1. The general-purpose crystallographic tool PLATON[36] was used for the structure analysis and presentation of the results. Molecular graphic was generated by using ORTEP-3.[34]

CCDC 1063735 contains the supplementary crystallographic data for the compound reported in this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/structures/.

### Computational Procedure

The Cartesian coordinates of the X-ray structure were used as the starting geometry for the calculations. Quantum-chemical computations were carried out with the GaussView 5[37] molecular visualization program and the Gaussian 09 program package.[38] The optimized geometry
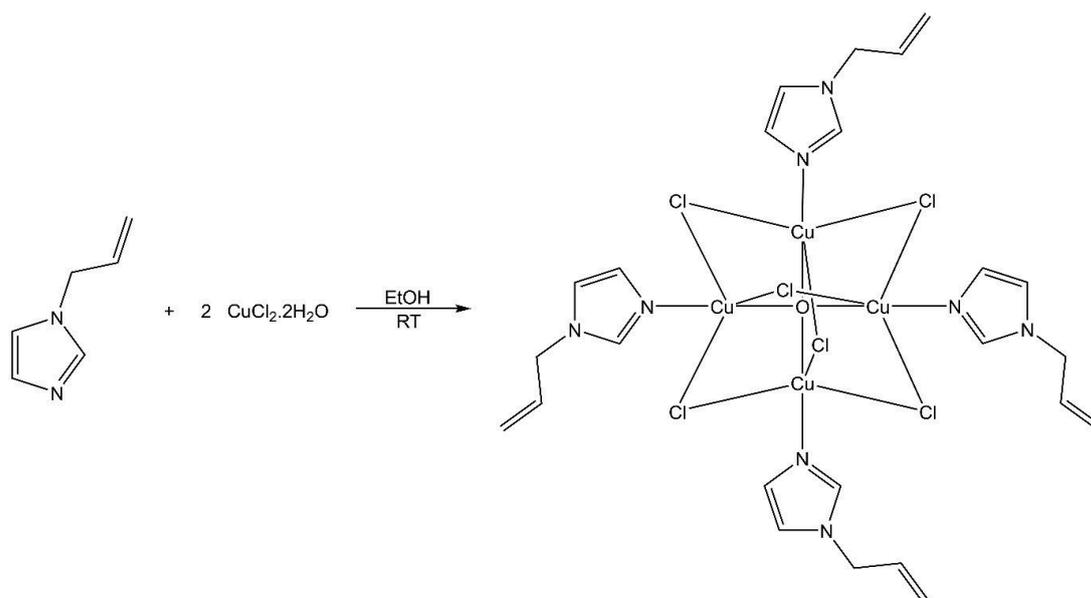


**Figure 1.** Synthesis pathway of the title complex.

**Table 1.** Crystal data and structure refinement parameters for the title complex

| | |
|---|---|
| CCDC deposition no. | 1063735 |
| Color/shape | Yellow/plate |
| Chemical formula | $[Cu_4Cl_6O(C_6H_8N_2)_4]$ |
| Formula weight | 915.43 |
| Temperature (K) | 296 |
| Wavelength (Å) | 0.71073 |
| Crystal system | Monoclinic |
| Space group | $P2_1$ (No. 4) |
| Unit cell parameters | |
| $a, b, c$ (Å) | 10.6937(7), 13.1004(7), 13.2452(9) |
| $\alpha, \beta, \gamma$ (°) | 90, 93.537(6), 90 |
| Volume (Å³) | 1852.0(2) |
| $Z$ | 2 |
| $D_{calc}$ (g/cm³) | 1.642 |
| $\mu$ (mm⁻¹) | 2.729 |
| Absorption correction | Integration |
| $T_{min}$, $T_{max}$ | 0.3755, 0.9520 |
| $F_{000}$ | 916 |
| Crystal size (mm³) | 0.55 × 0.24 × 0.02 |
| Diffractometer/measurement method | STOE IPDS II/rotation ($\omega$ scan) |
| Index ranges | $-12 \leq h \leq 12, -15 \leq k \leq 15, -15 \leq l \leq 15$ |
| $\theta$ range for data collection (°) | $1.91 \leq \theta \leq 25.00$ |
| Reflections collected | 13259 |
| Independent/observed reflections | 6232/3051 |
| $R_{int}$ | 0.111 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data/restraints/parameters | 6232/608/536 |
| Goodness-of-fit on $F^2$ | 0.931 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0688, wR_2 = 0.1325$ |
| $R$ indices (all data) | $R_1 = 0.1461, wR_2 = 0.1620$ |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/Å³) | 0.53, −0.31 |

and other electronic properties were obtained using the HSEH1PBE density functional method[39–42] with the cc-pVDZ basis set[43] for C, H, N, O and Cl atoms, and the LANL2DZ basis set[44–46] for the metal atoms. The calculated vibrational wavenumbers without imaginary frequencies were scaled by 0.962. The electronic absorption spectra were obtained using the time-dependent density functional theory (TD-DFT)[47] at the same level, in which solvent effect was inserted by using the default method.[48]

# RESULTS AND DISCUSSION

## Experimental and theoretical structures

A perspective view showing the complex and the labeling scheme appears in Figure 2(a), while the DFT-optimized structure is drawn in Figure 2(b). Also, some of the experimental and theoretical findings are given in Table 2. The basic moiety of the molecular structure contains a core comprising a cluster and four 1-allyl-1H-imidazole ligands.

The cluster core consists of four Cu, one $\mu_4$-O and six $\mu_2$-Cl atoms, in which the cupric ions bonded to a single central oxo ion tetrahedrally. The Cu₄($\mu_4$-O) tetrahedron is almost regular with the Cu–O–Cu angles changing from 108.3(6) to 110.9(6)°. In the optimized structure, the Cu–O–Cu angles are found between 95.52 and 115.61°. In addition, the intermetallic distances span the ranges 3.095(3)-3.127(4) Å in the X-ray structure and 2.921–3.232 Å in the theoretical structure, while the Cu···Cu···Cu angles range from 59.43(7) to 60.62(8)° in the X-ray structure and from 54.44 to 64.15° in the theoretical structure. Each of the Cu$^{II}$ ions are five-coordinated by three bridging chloride anions [Cu–Cl distances vary from 2.378(6) to 2.469(6) Å] in the equatorial plane, and the oxygen atom [Cu–O distances

**(a)**



**(b)**
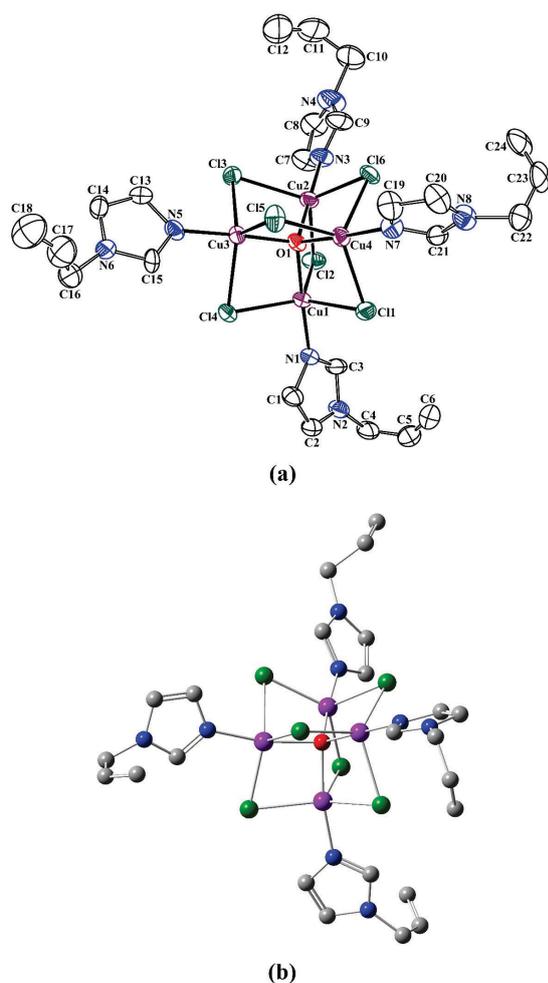
**Figure 2.** Molecular structure diagram of the title cluster, showing atom-numbering scheme and 20% displacement ellipsoids. Hydrogen atoms are omitted for clarity and only the major parts of the disordered fragments are shown (a). Calculated structure of the title complex (b).

vary from 1.890(14) to 1.915(12) Å] and the imidazole nitrogen [Cu–N distances vary from 1.917(19) to 1.970(19) Å] in the axial positions. These bonds have been calculated at 2.357–2.574 Å, 1.900–1.974 Å and 1.968–2.005 Å, respectively. The distortion of a five coordination can be best described by the structural parameter $\tau_5$.[49] The $\tau_5$ value can be conveniently utilized to estimate the degree of distortion from square-pyramidal to trigonal-bipyramidal structures. In the case of an ideal square-pyramidal geometry, the $\tau_5$ value is equal to zero, while it becomes unity for a perfect trigonal-bipyramidal geometry. The copper atoms exist in a slightly distorted trigonal-bipyramidal environment, with $\tau_5$ values of 0.92 (Cu1 and Cu3), 0.91 (Cu2) and 0.82 (Cu4). The $\tau_5$ values in the calculated structure are 0.73 (Cu1 and Cu3), 0.57 (Cu2) and 0.78 (Cu4). The value for the Cl–Cu–Cl angles varies

markedly around the value for the non-distorted equatorial angle in a trigonal bypiramid of 120°, ranging from 113.4(2) to 126.2(3)° in the X-ray structure, and 108.34 to 133.25° in the theoretical structure. The axial-axial O–Cu–N angles of the bipyramid deviates slightly from 180°, with the values being between 175.5(6) and 178.1(7)°. The N–Cu–Cl angles range from 91.7(5) to 97.3(6)°, whereas the O–Cu–Cl angles are significantly smaller [83.8(4)–86.5(4)°], which reflects the fact that the Cu atom is displaced out of the plane of the three equatorial Cl atoms by 0.2 Å towards the nitrogen atom of 1-allyl-1H-imidazole acting as a monodentate ligand. The O–Cu–N, N–Cu–Cl and O–Cu–Cl angles are theoretically predicted in the range of 167.32–178.29°, 90.94–97.37° and 78.45–94.20°, respectively.

Each of the six edges of the copper tetrahedron is occupied by a bridging $\mu_2$-chloride ion so that each copper ion is linked to each of the other three metal ions through the central oxygen and through three separate chloride bridges. The values for the Cu–Cl–Cu angle do not show a great variation around the average value of 80.10°, which has a theoretical average value of 79.46°. The six chloride ions comprise a fairly regular concentric $Cl_6$-pseudo-octahedron around the central oxygen atom; the Cl···Cl, O···Cl distances and cis and trans Cl···O···Cl angles vary as follows: Cl···Cl = 4.084(9)–4.256(9) Å, O···Cl = 2.935(13)–2.963(14) Å, Cl···O···Cl = 87.3(3)–92.6(4)°, Cl···O···Cl = 176.6(5)–177.4(5)°. The corresponding values of these parameters in the theoretical structure are found to be 3.946–6.066 Å, 2.859–3.214 Å, 82.73–96.67° and 171.17–174.35°, respectively. The bond lengths and angles in the cluster are in fair agreement with those observed previously for molecules possessing a $\mu_4$-oxo, $\mu_2$-chloro $Cu_4Cl_6O$ core structure.[9,16,23–32]
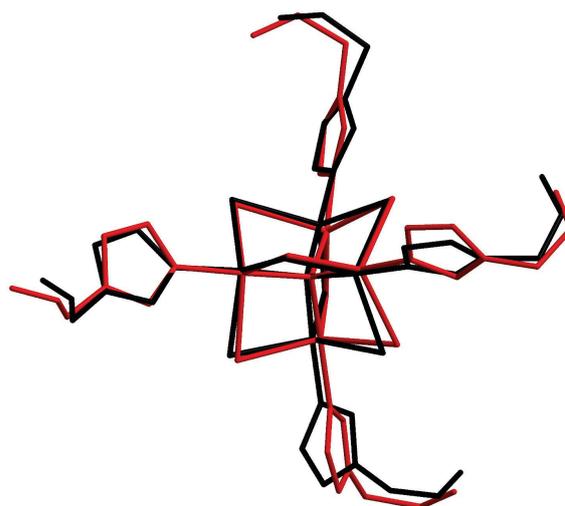


**Figure 3.** Atom-by-atom superimposition of the calculated structure (grey) over the X-ray structure (black) for the title complex (c).

**Table 2.** Selected geometric parameters for the title complex

| Parameters | X-Ray | DFT | Parameters | X-Ray | DFT |
|---|---|---|---|---|---|
| Bond lengths (Å) | | | | | |
| Cu1–Cl1 | 2.451(6) | 2.574 | Cu4–Cl5 | 2.389(6) | 2.381 |
| Cu1–Cl2 | 2.403(6) | 2.396 | Cu4–Cl6 | 2.466(6) | 2.473 |
| Cu1–Cl4 | 2.390(6) | 2.574 | Cu1–O1 | 1.912(13) | 1.974 |
| Cu2–Cl2 | 2.417(6) | 2.408 | Cu2–O1 | 1.906(12) | 1.972 |
| Cu2–Cl3 | 2.469(6) | 2.627 | Cu3–O1 | 1.890(14) | 1.901 |
| Cu2–Cl6 | 2.378(6) | 2.467 | Cu4–O1 | 1.915(12) | 1.900 |
| Cu3–Cl3 | 2.417(6) | 2.357 | Cu1–N1 | 1.93(2) | 2.005 |
| Cu3–Cl4 | 2.422(6) | 2.383 | Cu2–N3 | 1.929(18) | 2.005 |
| Cu3–Cl5 | 2.432(6) | 2.518 | Cu3–N5 | 1.917(19) | 1.970 |
| Cu4–Cl1 | 2.383(6) | 2.394 | Cu4–N7 | 1.970(19) | 1.968 |
| Bond angles (°) | | | | | |
| Cu1–O1–Cu2 | 108.3(6) | 95.52 | O1–Cu1–Cl4 | 85.3(4) | 80.55 |
| Cu1–O1–Cu3 | 109.3(6) | 108.95 | O1–Cu2–Cl2 | 85.7(4) | 93.92 |
| Cu1–O1–Cu4 | 109.4(6) | 112.53 | O1–Cu2–Cl3 | 83.8(4) | 78.45 |
| Cu2–O1–Cu3 | 110.9(6) | 113.16 | O1–Cu2–Cl6 | 86.5(4) | 84.58 |
| Cu2–O1–Cu4 | 109.5(6) | 109.35 | O1–Cu3–Cl3 | 85.6(4) | 87.08 |
| Cu3–O1–Cu4 | 109.5(6) | 115.61 | O1–Cu3–Cl4 | 84.8(4) | 87.24 |
| Cl1–Cu1–Cl2 | 119.4(2) | 120.88 | O1–Cu3–Cl5 | 84.7(4) | 79.28 |
| Cl1–Cu1–Cl4 | 116.8(3) | 112.45 | O1–Cu4–Cl1 | 85.9(4) | 86.46 |
| Cl2–Cu1–Cl4 | 121.6(3) | 124.60 | O1–Cu4–Cl5 | 85.4(5) | 82.99 |
| Cl2–Cu2–Cl3 | 113.4(2) | 110.68 | O1–Cu4–Cl6 | 83.8(4) | 85.92 |
| Cl2–Cu2–Cl6 | 123.7(3) | 133.25 | N1–Cu1–Cl1 | 92.9(6) | 92.93 |
| Cl3–Cu2–Cl6 | 121.0(2) | 114.67 | N1–Cu1–Cl2 | 95.5(7) | 97.37 |
| Cl3–Cu3–Cl4 | 122.2(3) | 130.90 | N1–Cu1–Cl4 | 96.2(6) | 93.71 |
| Cl3–Cu3–Cl5 | 118.2(2) | 115.49 | N3–Cu2–Cl2 | 96.1(6) | 96.35 |
| Cl4–Cu3–Cl5 | 117.5(3) | 111.17 | N3–Cu2–Cl3 | 96.1(5) | 90.94 |
| Cl1–Cu4–Cl5 | 126.2(3) | 131.31 | N3–Cu2–Cl6 | 91.9(4) | 93.73 |
| Cl1–Cu4–Cl6 | 115.5(3) | 108.34 | N5–Cu3–Cl3 | 96.3(6) | 94.92 |
| Cl5–Cu4–Cl6 | 116.1(3) | 118.06 | N5–Cu3–Cl4 | 92.8(6) | 95.23 |
| Cu1–Cl2–Cu2 | 79.9(2) | 74.90 | N5–Cu3–Cl5 | 95.7(6) | 95.29 |
| Cu1–Cl4–Cu3 | 80.23(17) | 78.92 | N7–Cu4–Cl1 | 95.3(5) | 95.25 |
| Cu1–Cl1–Cu4 | 80.46(19) | 80.78 | N7–Cu4–Cl5 | 97.3(6) | 95.96 |
| Cu2–Cl3–Cu3 | 79.56(19) | 80.67 | N7–Cu4–Cl6 | 91.7(5) | 93.41 |
| Cu2–Cl6–Cu4 | 80.19(16) | 79.51 | O1–Cu1–N1 | 177.0(7) | 168.38 |
| Cu3–Cl5–Cu4 | 80.24(19) | 82.00 | O1–Cu2–N3 | 178.1(7) | 167.32 |
| O1–Cu1–Cl1 | 84.1(4) | 80.11 | O1–Cu3–N5 | 177.5(7) | 174.55 |
| O1–Cu1–Cl2 | 85.9(4) | 94.20 | O1–Cu4–N7 | 175.5(6) | 178.29 |

As can be seen from the Table 2, coherence between the optimized and X-ray structures are not good in general, especially in some parameters. Bond distances agree within ca. 0.18 Å, while the largest deviation in the bond angles reaches up to 12.78°. When the X-ray structure is compared with its optimized counterpart (Figure 3), as expected, some conformational discrepancies are also observed between them, and the root mean square deviation (RMSD) obtained by superimposing two structures (except for H atoms) is 0.471 Å. Anyway, the differences are related to the fact that the theoretical calculations are based on the isolated molecule in the gas phase, while the experimental results are based on the molecule in the solid state.

In the crystal structure, there are no classical hydrogen bonds. The crystal packing is stabilized by Van der Waals interactions.

## Spectroscopy

The FT-IR spectral data of the allyl-imidazole ligand and its corresponding tetranuclear complex exposed different bands in the 400–4000 cm$^{-1}$ region (Figure 4). The characteristic bands of allyl-imidazole ligand are $v$(C=C) at 1645 and 1421 cm$^{-1}$ and $v$(C=N) at 1505 cm$^{-1}$, which are calculated at 1674, 1404 and 1509 cm$^{-1}$, respectively. The band indexed by the allyl-imidazole ligand spectrum relating to the C=N bond is shifted on the IR spectrum of the studied complex [$v$(C=N) = 1523 cm$^{-1}$], which confirms the participation of the N atom in the coordination sphere of the complex studied. This band are appeared at 1521 cm$^{-1}$ in the theoretical spectrum of the complex. The aromatic C–H stretching, in-plane bending and out-of-plane bending vibrations usually appear in the region 3150–2900, 1500–1100, and 1000–750 cm$^{-1}$, respectively. These vibrations are monitored at 3130, 1438, and 831 cm$^{-1}$ in the FT-IR spectrum and calculated at 3168, 1252 and 703 cm$^{-1}$, respectively. In addition, the complex exhibits strong IR absorptions at 564 cm$^{-1}$, which can be associated with
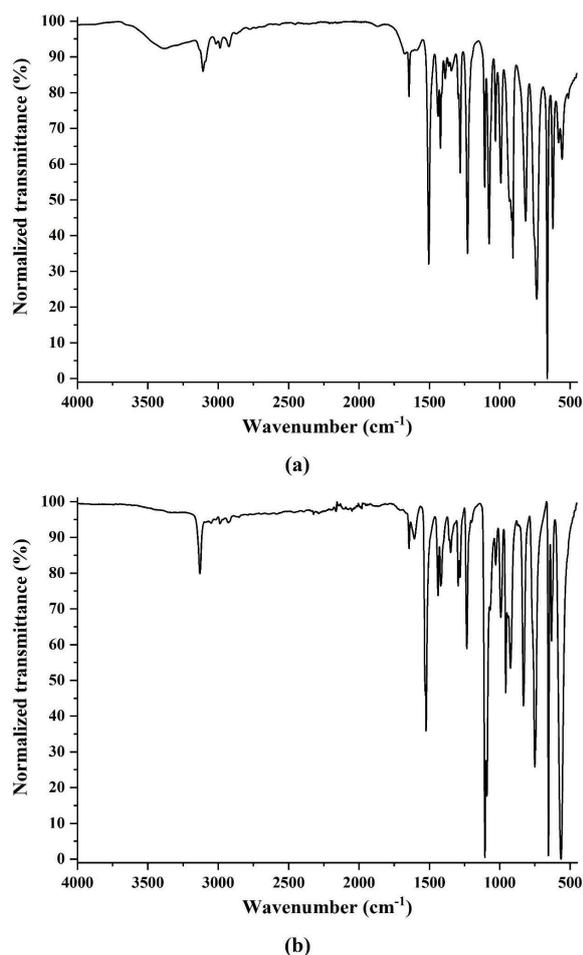


**Figure 4.** IR spectrum of allyl-imidazole ligand (a) and Cu complex (b).
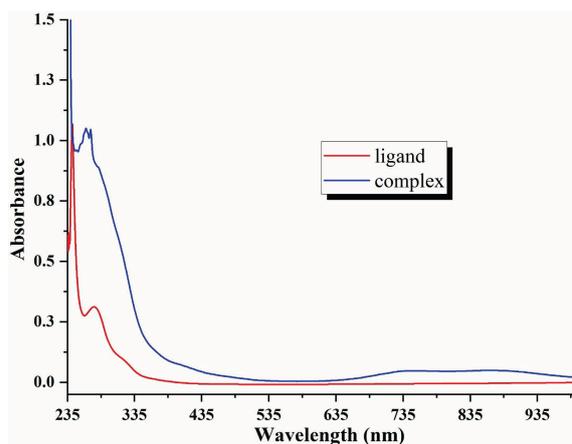


**Figure 5.** The UV-Vis spectra of the ligand (1-(allyl)-1*H*-imidazole) and [Cu$_4$($\mu_4$-O)($\mu_2$-Cl)$_6$L$_4$] complex in CHCl$_3$ (10$^{-5}$ M).

$v$(Cu–O) frequencies originating from vibrations in the Cu$_4$O core.[10] The band observed at 403 cm$^{-1}$ in the theoretical spectrum is attributed to $v$(Cu–O) vibration.

The electronic spectra of [1-(allyl)-1*H*-imidazole] and [Cu$_4$($\mu_4$-O)($\mu_2$-Cl)$_6$L$_4$] complex were recorded in CHCl$_3$ solution at room temperature. The ligand shows shoulders at 280 nm with absorption due to ligand-centered n - π* / π - π* (LL) transitions. The UV-vis spectrum of the complex shows three absorption peaks at 272, 754 and 874 nm (Figure 5). The absorption band at 272 nm is attributed to a ligand-to-metal charge transfer (LMCT) transition. This demonstrates metal coordination with the ligand. The spectrum further features very weak broad band in the visible region at 754 and 874 nm due to the typical forbidden *d-d* transition (MM) between copper(II) ions.[50–53] The TD-DFT calculations predict an absorption peak at 287 nm for the ligand and two absorption peaks at 264 and 803 nm for the complex.

## CONCLUSIONS

In this study, a new $\mu_4$-oxo-bridged cluster of formula [Cu$_4$($\mu_4$-O)($\mu_2$-Cl)$_6$L$_4$] (in which L = 1-(allyl)-1*H*-imidazole) has been synthesized and characterized by elemental analysis, FT-IR and UV-vis spectroscopies. The structure of the complex has been determined by single-crystal X-ray diffraction (XRD) method. The result of the elemental analysis was consistent with the expected structure. The complex has a tetrameric structure of four copper(II) ions connected to a central oxo group in an approximately tetrahedral arrangement. Copper coordination is completed by three $\mu_2$-chloride ions and an imidazole nitrogen atom, defining a trigonal-bipyramidal environ-ment around each copper ion. The Cu–O frequency of the complex, caused by vibration in the Cu$_4$O core, exhibited strong IR absorption at 564 cm$^{-1}$. The UV-Vis spectrum of

the complex showed three absorption bands at 272, 754 and 874 nm, respectively, which are attributed to a ligand-to-metal charge transfer (LMCT) transition and the *d-d* transition between copper(II) ions. Computational studies of the complex were also done at the HSEH1PBE/cc-pVDZ/LANL2DZ level. The theoretical structure is in agreement with the experimental one by a root mean square deviation of 0.471 Å. The theoretical spectroscopic values support the experimental findings as well.

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