

Scientific paper

Synthesis, X-ray Structural Characterization, and DFT Calculations of Binuclear Mixed-ligand Copper(II) Complexes Containing Diamine, Acetate and Methacrylate Ligands

Rasoul Vafazadeh,^{1,*} Mansoor Namazian,¹ Mahshad Chavoshiyan,¹
Anthony C. Willis² and Paul D. Carr²

¹ Department of Chemistry, Faculty of Science, Yazd University, Yazd, Iran.

² Research School of Chemistry, Australian National University, Canberra, ACT 2601, Australia.

* Corresponding author: E-mail: rvafazadeh@yazd.ac.ir
Tel: +98 3538214778; Fax: +98 3537250110

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Abstract

The dinuclear Cu(II) complexes [Cu(en)(MAA)(μ -CH₃COO)]₂ (**1**) and [Cu(pn)(MAA)(μ -CH₃COO)]₂ (**2**) where MAA, en and pn are methacrylate, ethylenediamine and 1,3-propylenediamine, respectively, have been synthesized and characterized by elemental analysis, FT-IR and UV-Vis spectroscopy. The structures of the complexes have been determined by single-crystal X-ray diffraction analyses. In the dinuclear complexes **1** and **2** the two copper centers are five-coordinated and exhibit distorted square pyramidal geometries. The theoretical geometries of the studied compounds have been calculated by means of density functional theory (DFT) at the B3LYP/6-311+G(d,p)/LanL2DZ level considering effective core potential (ECP).

Keyword: Copper complex; Dinuclear; Methacrylate; Diamine; DFT

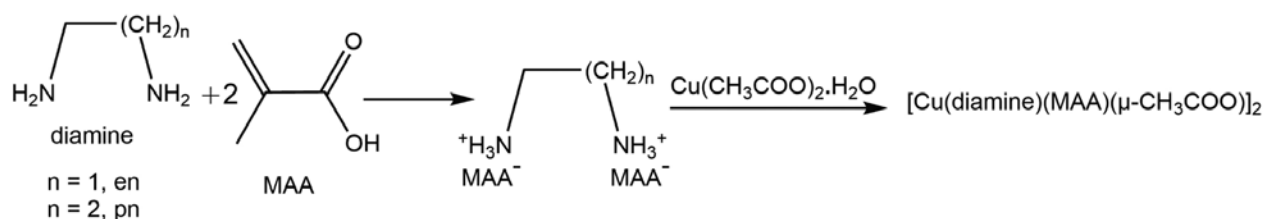
1. Introduction

Recently, specific attention have been paid to the synthesis of multinuclear complexes because of their importance in the fields of bioinorganic chemistry,^{1–4} molecular magnetic materials,^{5,6} catalysts,^{7,8} and their interesting chemical structures.^{2,8–13} One strategy for synthesis of di- and multi-nuclear compounds includes the use of bridging ligands and so metal centers are forced by the molecular topology to stay close to each other.^{10–14} The carboxylates and their derivatives exhibit various possible bonding modes when coordinating to metal ions such as monodentate and bidentate either by forming bridges or chelation. Nevertheless, carboxylate ligands commonly act as bidentate ligand in the transition metal complexes. Generally, each of the two oxygen atoms of the carboxylate group are coordinated to a different metal ion as bridging ligands.^{15–17} However, metal complexes with these ligands could adopt different coordination modes, depending on the nature of metal ion and the presence of other ligands.^{17–19}

Copper is an essential element to biological functions. The exchangeable portion of copper in blood plasma occurs mainly as a result of mixed-ligand formation involving copper–nitrogen interactions. Cu(II) mixed-ligand antineoplastic agents, containing diamine ligands exhibit cytotoxicity, genotoxicity, and antitumor effects.^{20,21}

In the present work, we report the synthesis, spectroscopic characterization, structural aspects and density functional theory (DFT) calculations for two new mixed-ligand Cu(II) complexes containing diamine, acetate and methacrylate ligands. The complexes are synthesized by reaction of diamine-methacrylic acid salt (diamine are ethylenediamine, en, and 1,3-propylenediamine, pn) with Cu(II) acetate (Scheme 1).

Here, the carboxylate ligands (acetate from the initial metal acetate input and methacrylate from diamine-methacrylic acid salt) are of particular interest, since the carboxylate can coordinate to metals in different modes. The carboxylate ligands are coordinated to the copper(II)



Scheme 1. Synthesis of the complexes **1** and **2**

ion in both monodentate and bidentate modes, and binuclear copper complexes can be formed.

2. Experimental

2.1. Materials and Methods

All chemicals were of analytical reagent grade and were used without further purification. Infrared spectra were taken with an Equinox 55 Bruker FT-IR spectrometer using KBr pellets in the 400–4000 cm^{-1} range. Absorption spectra were determined in the solvent of methanol using GBC UV-Visible Cintra 101 spectrophotometer with 1 cm quartz in the range of 200–800 nm. Elemental analyses (C, H, N) were performed by using a CHNS-O 2400 II PERKIN-ELMER elemental analyzer.

2.2. X-ray Crystallography

Diffraction images **1** and **2** were measured at 150 K on Agilent Xcalibur and SuperNova diffractometers using Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) and Cu $K\alpha$ ($\lambda = 1.54180 \text{ \AA}$) radiation, respectively. Data were extracted using the CrysAlis PRO package.²² The structures were solved by direct methods with the use of SIR92.²³ The structures were refined on F^2 by full-matrix least-squares techniques using the CRYSTALS program package.²⁴ The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry (C–H in the range 0.93–0.98, N–H = 0.87, O–H = 0.82 \AA) and with $U_{\text{iso}}(\text{H})$ in the range 1.2–1.5 times U_{eq} of the parent atom, after which the positions were refined with riding constraints for those bonded to C and without constraints for those bonded to N or O. Atomic coordinates, bond lengths and angles and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. Crystallographic data and refinement details for the complexes are given in Table 1. Details of the refinement procedures for the structures are given in the Supplementary Information.

2.3. Theoretical Calculations

All computations were performed by means of standard DFT method using the Gaussian09 (G09) pro-

Table 1. Crystallographic data and structural refinement for complexes **1–2**

Compound	1	2
Empirical formula	$\text{C}_{16}\text{H}_{32}\text{Cu}_2\text{N}_4\text{O}_8$	$\text{C}_{18}\text{H}_{36}\text{Cu}_2\text{N}_4\text{O}_8$
Formula weight	535.54	563.60
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
T (K)	150	150
a / \AA	6.8324 (3)	6.8283 (3)
b / \AA	8.6113 (3)	9.3019 (3)
c / \AA	10.4862 (3)	10.6562 (3)
α / $^\circ$	68.132 (4)	70.211 (6)
β / $^\circ$	88.717 (3)	80.563 (7)
γ / $^\circ$	72.239 (4)	76.054 (6)
V / \AA^3	542.37 (4)	615.58 (8)
Z	1	1
$F(000)$	278	294
D_{calc} (g cm^{-3})	1.640	1.520
μ (mm^{-1})	2.01	2.55
Measured reflections	12128	9439
Independent reflections	2724	2424
R_{int}	0.032	0.023
Observed reflections	2412	2360
$R[F^2 > 2\sigma(F^2)]$	0.028	0.024
$wR(F^2)$ (all data)	0.058*	0.061**

$$*w = 1/[\sigma^2(F^2) + (0.01P)^2 + 0.69P], \text{ where } P = (\max(F_o^2, 0) + 2F_c^2)/3$$

$$**w = 1/[\sigma^2(F^2) + (0.03P)^2 + 0.52P], \text{ where } P = (\max(F_o^2, 0) + 2F_c^2)/3$$

gram package.^{25,26} The geometries of the studied complexes have been optimized at the B3LYP level of theory.²⁷ The basis set of 6-31G(2df,p) was used for the C, H, N, and O atoms as recommended by Curtiss and his co-workers, while the basis set of LanL2DZ was employed for Cu atom considering the size of complexes and hardware limitations.^{28–30} Special care was taken to select the (global) minimum energy conformation via systematic conformational searching at this level. The nature of each stationary point was established by frequency calculations at the same level of B3LYP/6-31G(2df,p)/LanL2DZ. The geometry optimizations have been completed in the absence of solvent molecules and other impurities, and the optimized structures were compared with the crystalline structures. Charges on atoms have been calculated using Natural Bond Orbital (NBO) theory at the higher level of B3LYP/6-311+G(2df,p)/LanL2TZf.^{31,32}

2. 4. Syntheses

Synthesis of **1**, 2-di(λ^4 -azanyl)ethane dimethacrylate, **L**¹ and 1,3-di(λ^4 -azanyl)propane dimethacrylate, **L**².

The diaminium-methacrylic acid salts **L**¹ and **L**², were prepared by reaction between two equivalents of methacrylic acid (20 mmol, 1.70 mL) and one equivalent of related diamine, 1,2-ethylenediamine (10 mmol, 0.67 mL) and 1,3-propanediamine (10 mmol, 0.84 mL) in methanol medium (40 mL), respectively. The resulting bright yellow solution was heated to reflux for two hours. After two days, solid yellow powder obtained was filtered, washed with acetone and acetonitrile, and dried in air.

L¹, Yield: 1.76 g (76%), m.p. 148 °C. Anal. Calc. for C₁₀H₂₀N₂O₄ (232.28): C, 51.71; H, 8.68; N, 12.06%. Found: C, 51.79; H, 8.69; N, 12.36%. IR (KBr, ν_{\max} /cm⁻¹) bands: 3500, 1650, 1530, 1455, 1380 and 1230. UV-Vis, λ_{\max} (CH₃OH)/nm: 226 (log ϵ , 4.50).

L², Yield: 1.50 g (61%), m.p. 123 °C. Anal. Calc. for C₁₁H₂₂N₂O₄ (246.31): C, 53.64; H, 9.00; N, 11.37%. Found: C, 53.36; H, 8.97; N, 11.65%. IR (KBr, ν_{\max} /cm⁻¹) bands: 3393, 1646, 1543, 1455, 1386 and 1234. UV-Vis, λ_{\max} (CH₃OH)/nm: 216 (log ϵ , 3.73).

2. 4. 1. Synthesis of Copper(II) Complexes

Cu(CH₃COO)₂·H₂O (2.00 mmol, 0.399 g) was slowly added to a methanol solution (40 mL) of the related ligand (**L**¹, 2.00 mmol, 0.464 g and **L**², 2.00 mmol, 0.492 g) and the resulting solution was stirred for two hours at room temperature. The color of solution turned to blue and after two days solid blue powder was obtained.

[Cu(en)(MAA)(μ -CH₃COO)]₂, **1**

Yield: 0.99 g (93%). The blue solid product was recrystallized from acetonitrile/toluene (3:1 v/v). Blue crystals appeared at the bottom of the vessel upon slow evaporation of the solvents, which were filtered and dried in air. Anal. Calc. for C₁₆H₃₂Cu₂N₄O₈ (534.54): C, 35.88; H, 6.02; N, 10.46%. Found: C, 35.62; H, 6.18; N, 10.36%. IR (KBr, cm⁻¹): 3254, 3154, 1630, 1592, 1559, 1454 and 1382. Electronic spectra for CH₃OH: d-d, λ_{\max} (log ϵ) 332 nm (4.03), 633 nm (1.83).

[Cu(pn)(MAA)(μ -CH₃COO)]₂, **2**

Yield: 0.48 g (43%). The blue solid product was recrystallized from dichloromethane/n-hexane/toluene (5:1:1 v/v). Blue crystals were obtained upon slow evaporation of the solvents, which were filtered and dried in air. Anal. Calc. for C₁₈H₃₆Cu₂N₄O₈ (563.60): C, 38.36; H, 6.44; N, 9.94%. Found: C, 38.53; H, 6.53; N, 9.63%. IR (KBr, cm⁻¹): 3235, 3138, 1644, 1591, 1558, 1454 and 1384. Electronic spectra for CH₃OH: d-d, λ_{\max} (log ϵ) 255 nm (4.38), 643 nm (2.07).

3. Results and Discussion

3. 1. Syntheses and Characterization of the Complexes

The diaminium-methacrylic acid salt ligands was obtained by reaction of related diamine (ethylenediamine, en, and 1,3-propylenediamine, pn) and methacrylic acid in methanol under reflux. Copper(II) complexes **1** and **2** were obtained from the reaction mixture of the related ligand with the corresponding Cu(CH₃COO)₂·H₂O salt in equimolar ratio in methanol as a solvent at room temperature. The reaction of copper(II) acetate with **L**¹ and **L**² ligands leads to the formation of dinuclear complexes **1** and **2**.

The most significant IR bands for ligands and complexes are given in the experimental section. The IR spectra of the free ligands, **L**¹ and **L**², shows ν (N–H) bands at 3500 and 3393, ν (C=C) bands at 1530 and 1543, respectively. The two strong bands at 1650 and 1455 cm⁻¹ (for **L**¹) and 1646 and 1455 cm⁻¹ (for **L**²) corresponding to stretching frequencies of the carboxylate group: asymmetric ν_{asym} (COO⁻) and symmetric ν_{sym} (COO⁻), respectively.

In IR spectra of complexes **1** and **2**, the N–H stretches (NH₂) were observed at 3254 and 3154 cm⁻¹ (for **1**), 3235 and 3138 cm⁻¹ (for **2**). Complex **1**, [Cu(en)(MAA)(μ -CH₃COO)]₂, shows strong bands at 1630 and 1420 cm⁻¹ (for methacrylate ion, MAA), 1601 and 1454 cm⁻¹ (for acetate ion) corresponding to stretching frequencies of the carboxylate groups: asymmetric ν_{asym} (COO⁻) and symmetric ν_{sym} (COO⁻), respectively. For the acetate ion the difference between asymmetric and symmetric frequencies $\Delta[\nu_{\text{asym}}(\text{COO}^-) - \nu_{\text{sym}}(\text{COO}^-)] < 200$ cm⁻¹ indicates a bridging coordination mode.^{17,33,34} The infrared spectrum of complex **2** is quite similar with the complex **1**. The bands for the asymmetric and symmetric stretching vibrations, due to the carboxylate groups appear at 1644 and 1402 cm⁻¹ (for methacrylate ion, MAA), 1591 and 1454 cm⁻¹ (for acetate ion).

The absorption spectra of the free ligands **L**¹ and **L**² in methanol solution show band n- π^* transition at 226 and 216 nm, respectively. The electronic spectra of the copper complexes **1** and **2** in methanol solution show a broad band at 633 and 643 nm and a sharper signal at 255 and 246 nm, which arise from a spin-allowed d-d transition of the copper(II) ion (d⁹ electronic configuration) and a charge transfer transition, respectively.^{35,36}

3. 2. Description of X-ray Crystal Structures **1** and **2**

The molecular structures of **1** and **2** are shown in Fig. 1. Both complexes **1** and **2** have dimeric structure. Compounds crystallize in triclinic space group P $\bar{1}$ and there is one molecule in the unit cell (Z = 1). The single crystal X-ray diffraction data for compounds **1** and **2** are li-

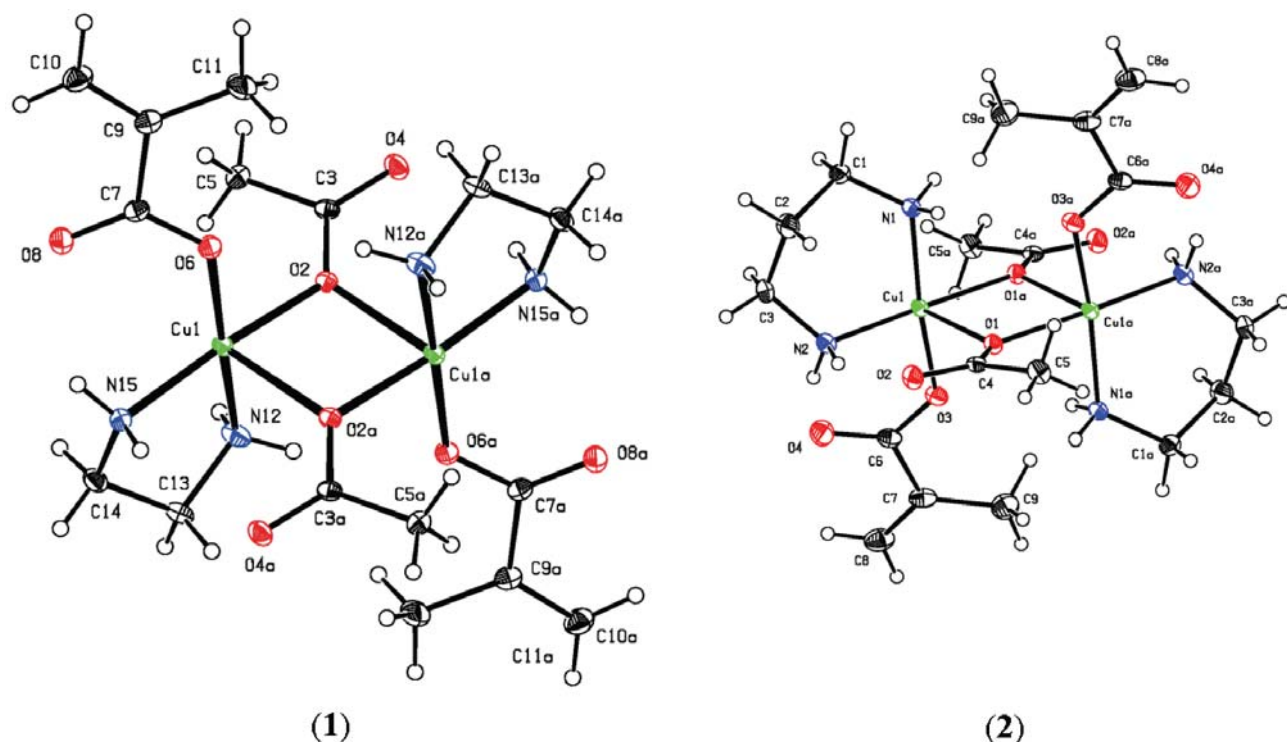


Fig. 1. The ORTEP view of complexes **1** and **2** showing 30% probability thermal ellipsoids. Symmetry codes: $-x, -y + 2, -z + 1$ for **1** and $x + 1, -y + 1, -z + 1$ for **2**.

sted in Table 1. Selected bond lengths and angles as well as interatomic distances are summarized in Table 2.

In the dimeric structures of **1** and **2**, the two copper centers are five-coordinate with distorted square pyramidal geometry. Coordination geometry about each copper ion complexes **1** and **2**, are close to square pyramidal with the Addison parameters $\tau = 0.015$ and 0.121 . The parameter of τ is defined as $\tau = (\alpha - \beta)/60$, ($\alpha > \beta$), where α and β are two largest angles around the Cu center; $\tau = 1$ for a regular trigonal bipyramid and $\tau = 0$ for a regular square pyramid.³⁷ According to the bond lengths between the copper and the coordinating atoms, the square base consists of two nitrogen atoms of the ethylenediamine (for **1**) and 1,3-propanediamine (for **2**) ligand, the oxygen atom of the methacrylate ion and the bridging acetate oxygen atom, and the apical position is occupied by the oxygen atom of the bridging acetate which has the longer Cu–O distance (i.e., the square base position consists of four short bond lengths of 1.9507(14)–2.0015(17) Å (for **1**); 1.9689(12)–2.0104(14) Å (for **2**), along the apical position with longer bond lengths of 2.2837(13) Å and 2.3069(11) Å, for **1** and **2**, respectively). The copper ion in complexes **1** and **2** is displaced from the basal plane of N_2O_2 by 0.046 and 0.024 Å towards the apical oxygen atom, respectively. The deviations from orthogonality of the *cis* bond angles (80.29(4)–98.98(6)°) and from linearity of the *trans* bond angles (168.70(5)–175.96(6)°) shows distortions from ideal square pyramidal geometry around the Cu centers.

Table 2. Selected bond lengths (Å) and angles (°) in Cu(II) complexes

bond lengths (Å)		bond angles (°)	
Complex 1			
Cu1–O2	1.9742(13)	O2–Cu1–O2 ^a	82.87(5)
Cu1–O2 ^a	2.2837(13)	O2–Cu1–O6	87.26(5)
Cu1–O6	1.9507(14)	N15–Cu1–O2	173.75(6)
Cu1–N12	2.0015(17)	N12–Cu1–O6	172.83(7)
Cu1–N15	1.9879(16)	N12–Cu1–O2	88.13(6)
C3–O2	1.282(2)	N15–Cu1–O6	98.98(6)
C3–O4	1.237(2)	O6–C7–O8	125.53(18)
Cu1...Cu1 ^a	3.1987(5)	Cu1–O2–Cu1 ^a	97.13(5)
Complex 2			
Cu1–O1	2.3069(11)	O1–Cu1–O1 ^a	80.29(4)
Cu1–O1 ^a	1.9850(11)	O3–Cu1–O1	95.73(5)
Cu1–O3	1.9689(12)	N1–Cu1–O3	168.70(5)
Cu1–N1	2.0101(14)	N2–Cu1–O1 ^a	175.96(6)
Cu1–N2	1.9825(14)	N1–Cu1–O1	89.72(5)
C4–O1	1.2867(19)	N1–Cu1–N2	94.08(6)
C4–O2	1.235(2)	O3–C6–O4	125.39(16)
Cu1...Cu1 ^a	3.2874(3)	Cu1–O1–Cu1 ^a	99.71(4)

Symmetry codes: $-x, -y + 2, -z + 1$ for **1** and $x + 1, -y + 1, -z + 1$ for **2**.

The Cu...Cu distance within the dinuclear **1** is 3.1987(5) Å which is slightly shorter than in dinuclear **2** (3.2874(3) Å). The bond lengths Cu–O and Cu–N are in the range of 1.9507(14)–2.3837(13) Å and 1.9825(14)–

2.0104(14) Å, see Table 2), respectively, which have good agreement with analogous square pyramidal Cu(II) complexes previously reported.^{9,17,38–40}

In **1**, the Cu1–(μ-O)–Cu1^a (symmetry code a: $-x, -y + 2, -z + 1$) bond angle is 97.13(5)°, which is similar to that in **2** (99.71(4)°, symmetry code a: $x + 1, -y + 1, -z + 1$, Table 2) and are in good agreement with analogous Cu(II) complexes observed in the literature.^{2,9,17,41} In complexes **1** and **2**, the C–O bond lengths of carboxylate groups in methacrylate and acetate ions are very similar (see Table 2).

The oxygen atoms of carboxylate groups (acetate and methacrylate ions) and the NH₂ amine groups of the

diamine ligand (ethylenediamine for **1** and 1,3-propylenediamine for **2**) play a significant role in intramolecular and intermolecular hydrogen-bonding interactions (Figs. 2 and 3). In **1**, the hydrogen atoms of the coordinated ethylenediamine molecule are involved in an intermolecular hydrogen-bonding interaction with the oxygen atoms of a neighboring coordinated methacrylate ion and the oxygen atoms of uncoordinated methacrylate and acetate ions. Also, there is an intramolecular hydrogen bonding between the hydrogen atom H151 of the NH of the ethylenediamine molecule with the oxygen atom O8 of uncoordinated methacrylate ion. In **2**, there are intermolecular hydrogen bonding interaction between the hydrogen

Table 3. Hydrogen bonding (Å) and angles (°) in complexes **1** and **2**

	D–H...A	D–H	H...A	D...A	D–H...A	Symmetry code
1	N15–H152...O4	0.88(3)	2.33(3)	3.084(3)	144(1)	$-x, -y + 2, -z + 1$
	N15–H152...O8	0.88(3)	2.58(3)	3.156(3)	128(1)	$-x + 1, -y + 1, -z + 1$
	N15–H151...O8	0.87(3)	2.24(3)	2.948(3)	138(1)	x, y, z
	N12–H122...O6	0.89(3)	2.40(3)	3.229(3)	155(1)	$-x, -y + 2, -z + 1$
	N12–H121...O4	0.86(3)	2.24(3)	2.997(3)	148(1)	$-x + 1, -y + 2, -z + 1$
2	N1–H1...O3	0.81(2)	2.58(2)	3.257(3)	143(2)	$-x + 1, -y + 1, -z + 1$
	N1–H2...O2	0.84(2)	2.12(2)	2.930(3)	161(2)	$x - 1, y, z$
	N2–H3...O2	0.86(2)	2.25(2)	3.028(3)	152(2)	x, y, z
	N2–H4...O4	0.82(2)	2.13(2)	2.862(3)	149(2)	x, y, z

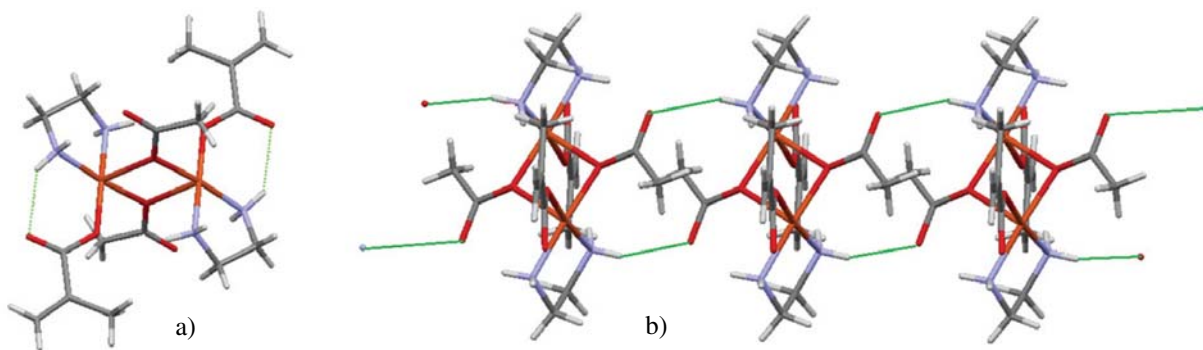


Fig. 2. Various hydrogen bonding interactions in complex **1** (a) intramolecular (b), intermolecular.

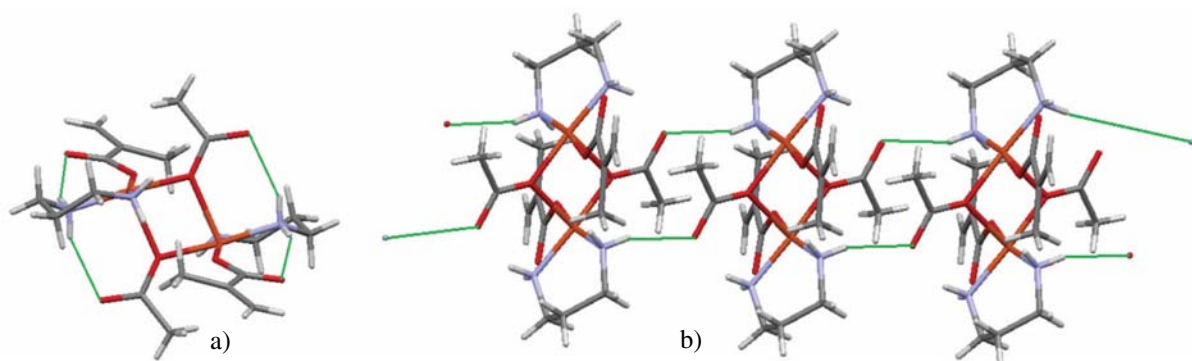


Fig. 3. Various hydrogen bonding interactions in complex **2** (a) intramolecular (b), intermolecular.

atoms of the coordinated 1,3-propylenediamine molecule with the uncoordinated oxygen atom O2 of the bridging acetate ligand and coordinated oxygen atom O3 of the methacrylate ion. Also, there are intramolecular hydrogen bonding between the hydrogen atom of the NH of the 1,3-propylenediamine molecule with the uncoordinated oxygen atoms O2 and O4 of acetate and methacrylate ions, respectively. Full details of the hydrogen bonding are given in Table 3.

3. 3. DFT Optimized Geometries

The geometry optimization of copper complexes were carried out in their singlet and triplet spin states. The optimized geometric parameters at their most stable, triplet states, is shown in Fig. 4.

As shown in Table 4, the calculated bond lengths for the studied complexes agree well with the X-ray experimental data. For example, the calculated Cu1–N12, Cu1–N15, Cu–O6 and Cu–O2 bond lengths for the dinuclear complex **1** are 2.00, 2.05, 1.96 and 2.00 Å, and they correlate nicely with the experimental values of 2.00, 1.99, 1.95 and 1.97 Å, respectively.

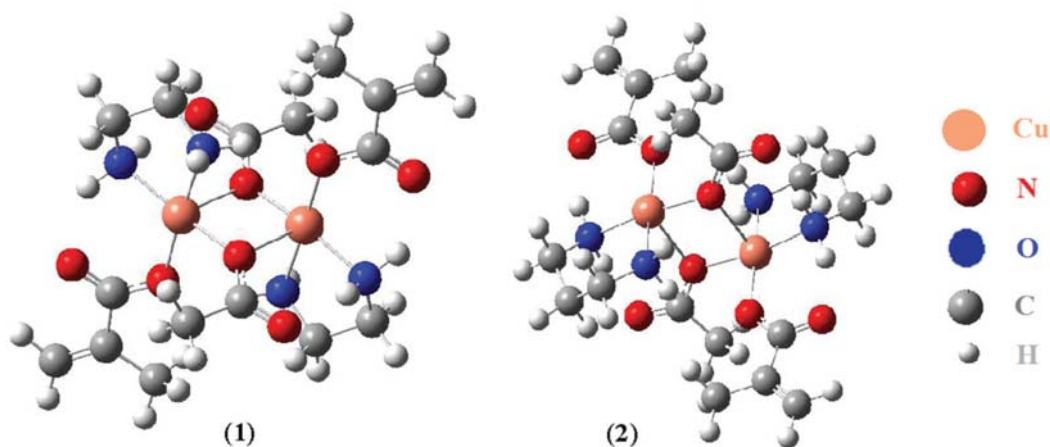


Fig. 4. The optimized structures of the complexes **1** and **2**.

Table 4. Selected geometric parameters from X-ray and DFT-B3LYP calculations

	Bond length (Å)	Expt.	Calc.	\Delta L	Bond angle (°)	Expt.	Calc.	\Delta L\theta
1	Cu1...Cu1 ^a	3.20	3.09	0.11	O2–Cu1–O6	87.3	91.1	3.8
	Cu1–O2	1.97	2.00	0.03	N12–Cu1–O2	88.1	85.3	3.0
	Cu1–O6	1.95	1.96	0.01	N15–Cu1–N12	85.4	82.6	3.0
	Cu1–N12	2.00	2.00	0.08	N15–Cu1–O6	99.0	100.9	1.9
	C3–O2	1.28	1.29	0.02	Cu1–O2–Cu1 ^a	97.1	94.4	2.7
2	Cu1...Cu1 ^a	3.29	3.26	0.03	O3–Cu1–O1	95.7	97.7	2.0
	Cu1–O3	1.97	2.00	0.03	N1–Cu1–O3	168.7	165.19	3.5
	Cu1–N2	1.98	2.01	0.03	N1–Cu1–N2	94.1	95.5	1.4
	C4–O1	1.29	1.30	0.01	N2–Cu1–O3	95.2	97.8	2.6
					Cu1–O1–Cu1 ^a	99.7	97.0	2.7

Symmetry codes: $-x, -y + 2, -z + 1$ for **1** and $x + 1, -y + 1, -z + 1$ for **2**.

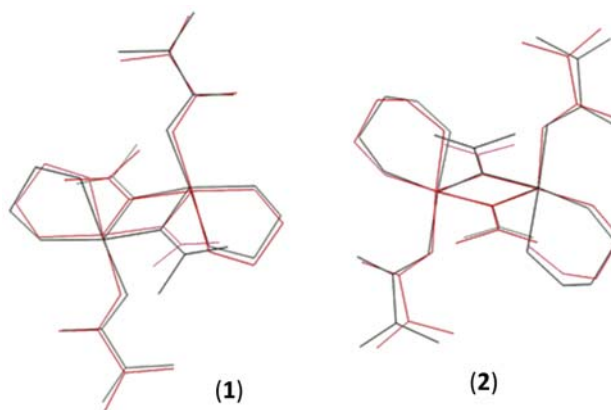


Fig. 5. Atom-by-atom superimposition of the calculated structures (black) over the X-ray structure (red); hydrogen atoms have been removed for clarity.

The differences between optimized geometrical parameters and experiment are less than 0.05 Å (bond distances) and 2° (bond angles) in most cases (see also Fig. 5).

In general, the predicted bond lengths are slightly longer in comparison with the values based upon the X-ray crystal structure data. The geometrical differences might

be a result of crystal packing forces which have an influence on the molecules as expected for the experimental ones (solid state), but the calculated geometries are in the gas phase.^{40,42} The crystal packing forces, which have an influence on the molecules, as expected for the experimental parameters (solid state), are a reason for the difference of calculated bond lengths in the gas phase and solid phase.

The calculated charges on the metal centers in complexes **1** and **2** are +0.875 and +0.873 respectively, and these values are greatly lower than the formal charge of +2. These differences are a result of charge donation from the donor atoms of ligands.

4. Conclusion

The reaction of copper(II) acetate with L¹ and L² ligands led to the formation of dinuclear copper(II) complexes **1** and **2**. The crystal structures were determined for two studied complexes. An acetate oxygen bridge, a relatively rare bridging mode of the carboxylate group, has been found in dinuclear complexes **1** and **2**. Coordination geometry for each copper ion was square pyramid. The optimized structure of complexes have been studied using the B3LYP/6-31G(d)/LanL2DZ level of theory. The calculated molecular geometries are in a very good agreement with the experimental data. It has been revealed that the triplet state for copper complexes **1** and **2** are more stable than their singlet state.

5. Supplementary Material

The deposition numbers of the studied complexes **1** and **2** are CCDC 1481551 and 1481552, respectively. These data can be obtained free-of-charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033.

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Povzetek

Sintetizirali smo dva dvojedrna Cu(II) kompleksa $[\text{Cu}(\text{en})(\text{MAA})(\mu\text{-CH}_3\text{COO})]_2$ (**1**) in $[\text{Cu}(\text{pn})(\text{MAA})(\text{SSTimes-CH}_3\text{COO})]_2$ (**2**), kjer so MAA, en in pn metacrilat, etilendiamin in 1,3-propilendiamin, ter jih okarakterizirali z elementno analizo, FT-IR in UV-Vis spektroskopijo. Strukturi kompleksov sta bili določeni z monokristalno rentgensko difrakcijo. V dvojedrnih kompleksih **1** in **2** imajo bakrovi centri koordinacijsko število pet s popačeno kvadratno piramidarno geometrijo. Izračunane geometrije proučevanih spojin so bile določene s pomočjo teorije gostotnostnega funkcionala (DFT) na B3LYP/6-311+G(d,p)/LanL2DZ nivoju z uporabo ECP.