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Scientific paper

Anion Modulated Structural Variations in Copper(II) Complexes with a Flexidentate Ligand Derived from 2-((2-Aminoethyl)Amino)Ethan-1-ol: Synthesis and Spectroscopic and X-ray Structural Characterization

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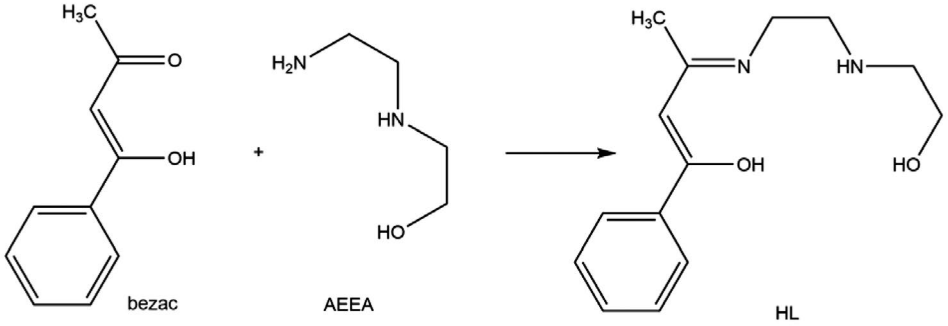
Abstract

Flexidentate ligand, HL has been prepared by the condensation of aminoethylethanolamine (AEEA) with benzoylacetone (bezac). On reaction with copper(II) salts it gives complexes $CuLClO_4.H_2O$ (**1**), $CuLN_3$ (**2**) and $[Cu_3L_3Br]Br_2 \cdot H_2O$ (**3**). All complexes have been characterized by X-ray crystallography. The results show that the hydroxyl group of the flexidentate ligand can coordinate to the Cu(II) center or remain as an uncoordinated group. In (**1**), the coordination number around the copper(II) ion is five coordinated and the ligand is tetradentate with the OH group coordinated to the copper(II) ion. Complex (**2**) has a square planar geometry and the L^- ligand is tridentate with the hydroxyl group left uncoordinated. The X-ray diffraction analysis of the trinuclear complex (**3**) shows that the copper(II) centers are five-coordinate and L^- is a tetradentate ligand with the hydroxyl group being both terminal and bridging. The Hirshfeld surface analysis and the 2D fingerprint plot were used to analyze all of the intermolecular contacts in the crystal structures.

Keyword: Flexidentate ligand; hydroxyl group; hirshfeld surface; fingerprint plot; tridentate; tetradentate

1. Introduction

The design and synthesis of new transition metal complexes with polynuclating ligands, which represent themselves as potential chelating ligands with more than set of donor atoms, have been of interest for many years.[1–7] The ability of transition metal ions to bond to possible coordination sites of these ligands depends on the type of the metal ion, the donor atoms of the ligand, the flexibility of the ligand and the counter-anions used. The term “flexidentate” is used to describe the coordination behavior of this type of ligand.[7–12] Complexes of the transition metal with Schiff base ligands derived from amine-alcohols are



Scheme 1. Synthesis of the flexidentate ligand

probably the best know examples of this. In these compounds, the hydroxyl group coordinates to the metal ions when the other coordination sites of the metal are weakly coordinated (e,g. ClO_4^- and halogens), but the hydroxyl group remains as an uncoordinated OH group when the other coordination sites of the metal ions are occupied by strongly coordinating groups (for example N_3^-).[13–17]

Herein we report the synthesis, spectral characterization and crystal structure of several new copper(II) complexes formed by the reaction of the flexidentate Schiff base ligand aminoethyl ethanolamine benzoylacetone, HL (scheme 1), with Cu(II) in the presence of several counter anions. The Schiff base ligand was obtained by condensation of 2-((2-aminoethyl)amino)ethan-1-ol (aminoethylethanolamine, AEEA) and benzoylacetone (bezac). This flexidentate ligand can be tridentate or tetradentate with copper(II), depending on the coordinating abilities of the other ligands which are present; the hydroxyl group of this ligand may coordinate to Cu(II) or may remain uncoordinated.

2. Experimental Section

2. 1. Starting Materials

All chemicals were of analytical reagent grade and were used without further purification.

Caution! Azide salt is potentially explosive. Only small amounts should be used and it should be handled with great care.

2. 2. Physical Measurements

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 using methanol and dimethylformamide (DMF) solutions in a GBC UV-Visible Cintra 101 spectrophotometer with a 1 cm quartz cell, in the range 200–800 nm. Elemental analyses (C, H, N) were performed by using a CHNS-O 2400II PERKIN-ELMER elemental analyzer.

2. 3. X-ray Crystallography

Diffraction images were measured at 150 K on an Agilent SuperNova diffractometer using Cu Kα (λ = 1.54180 Å) radiation. Data were extracted using the CrysAlis PRO package.[18] The structures were solved by direct methods with the use of SIR92.[19] The structures were refined on F^2 by full matrix last-squares techniques using the CRYSTALS program package.[20] Atomic coordinates, bond lengths and angles and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre. The H atoms were initially refined with soft re-

Table 1. Crystallographic data of the complexes **1**–**3**

Compound	**1**	**2**	**3**
Chemical formula	$C_{14}H_{21}ClCu_4N_2O_7$	$C_{14}H_{19}CuN_5O_2$	$C_{42}H_{59}Br_3Cu_3N_6O_7$
Formula weight	428.33	352.88	1190.31
Temperature (K)	150	150	150
Space group	Monoclinic, $P2_1/n$, Z = 4	orthorhombic, *Pbca*, Z = 8	Monoclinic, $P2_1/n$, Z = 4
Unit cell dimensions			
a (Å)	10.2326 (2)	7.2877 (1)	12.2525 (1)
b (Å)	13.2639 (2)	18.1046 (1)	25.5177 (2)
c (Å)	13.1667 (2)	22.1217 (2)	16.5499 (1)
α (°)	90	90	90
β (°)	103.6655 (14)	90	90.0015 (6)
γ (°)	120	90	90
V (Å^3)	1736.45 (5)	1178.85 (3)	4566.09 (6)
F(000)	844	1464	2404
D_{Calc} (g cm^{-3})	1.638	1.606	1.731
Crystal size (mm)	0.26 × 0.08 × 0.06 mm	0.28 × 0.06 × 0.06 mm	0.30 × 0.16 × 0.03 mm
μ (mm^{-1})	3.56	2.25	5.15
θ range (°)	5–73	3–74	3–74
Limiting indices	$-12 \leq h \leq 11$	$-7 \leq h \leq 8$	$-15 \leq h \leq 15$
	$-16 \leq k \leq 16$	$-22 \leq k \leq 22$	$-24 \leq k \leq 27$
	$-16 \leq l \leq 16$	$-27 \leq l \leq 27$	$-20 \leq l \leq 20$
R[F2 > 2σ(F2)]	0.034	0.032	0.0399
wR(F2) (all data)	0.087*	0.087**	0.111***

*w = $1/[\sigma^2(F^2) + (0.05P)^2 + 1.84P]$, where P = $(\max(F_o^2,0) + 2F_c^2)/3$ **w = $1/[\sigma^2(F^2) + (0.06P)^2 + 1.89P]$, where P = $(\max(F_o^2,0) + 2F_c^2)/3$ *** method Chebychev polynomial, [weight] = $1.0/[A_0*T_0(x) + A_1*T_1(x) \ldots+(A_{n-1})*T_{n-1}(x)]$, method Robust weighting, W = [weight]*[1-(deltaF/6*sigmaF)^2]^2 where A_i = 0.165E + 04 0.171E + 04 708.155 and x = F/F_{max}

straints on the bond lengths and angles to regularize their geometry (C—H in the range 0.93–0.98 Å, N—H = 0.87 Å, O—H = 0.82 Å) and with U_{iso}(H) in the range 1.2–1.5 times U_{eq} of the parent atom. After this, the positions of the H atoms bonded to O and N were refined without constraints whereas those bonded to C ride on the atoms to which they are bonded. Crystallographic data and refinement details for the complexes are given in Table 1.

2. 4. Synthesis of the Schiff-base Ligand Aminoethylethanolaminebenzoylacetone (HL).

The flexidentate Schiff base HL was synthesized by a general method using the condensation reaction of aminoethylethanolamine (1 mmol, 0.10 ml) and benzoylacetone (1 mmol, 0.162 g) in methanol medium (30 mL) under reflux for 2 hours.[21,22] The bright yellow solution containing the Schiff base ligand (HL) was used for synthesis of the complexes without further purification. The IR spectrum of the HL ligand shows a characteristic strong band at 1580 cm^{-1}, which is assigned as νC=N.

2. 5. Synthesis of Copper(II) Complexes

$CuX_2.nH_2O$, (X = ClO_4, n = 6, 0.370 g, **1**; X = NO_3, n = 3, 0.242 g, **2** and; X = Br, n = 0, 0.223 g, **3**), (1 mmol) was added to a solution of the ligand HL, aminoethylethanolaminebenzoylacetone (1 mmol) in methanol (30 mL) and the resulting solution was stirred at room temperature for 2 h. The solution's color turned green. For complex **2**, after 2 h of continuous stirring of the copper(II) nitrate trihydrate and ligand solution, finely powdered sodium azide (0.065 g, 1.0 mmol) was added to the solution and stirring was continued for a further 2 h.

$CuLClO_4.H_2O$, 1. The solution was filtered and the clear green filtrate was kept in a beaker to allow slow evaporation of the solvent. A solid green powder was obtained. Dark-green prismatic crystals suitable for X-ray crystallography were obtained from methanol / cyclohexane (3:1 v/v) and were filtered, washed with cold ethanol and dried in the air. Yield: 72%. Anal. Calc. for $C_{14}H_{21}ClCuN_2O_7$: C, 39.26; H, 4.94; N, 6.54%. Found: C, 39.48; H, 4.99; N, 6.60%. IR (KBr, ν_{max}/cm^{-1}) bands: 1555, and 1061. UV-Vis, λ_{max}(methanol)/nm: 577 (log ε, 1.88), 281 (4.20) and 211 (4.57).

$CuLN_3$, 2. Stirring was continued for 2 h after addition of sodium azide, The solution was filtered and the filtrate was left aside for crystallization. Dark-green prism crystals suitable for X-ray diffraction appeared at the bottom of the vessel upon slow evaporation of the solvent at room temperature, and were collected by filtration, washed with cold ethanol and dried in the air. Yield: 82%. Anal. Calc. for $C_{14}H_{19}CuN_5O_2$: C, 47.65; H, 5.43; N, 19.85%. Found: C, 47.73; H, 5.60; N, 19.42%. IR (KBr, ν_{max}/cm^{-1}) bands: 2043 and 1556. UV-Vis, λ_{max}(dimethylformamide, DMF)/nm: 567 (log ε, 2.19) and 326 (3.18).

$[Cu_3L_3Br]Br_2.H_2O$, 3. The solution was filtered and the clear green filtrate was kept in a beaker to allow slow evaporation of the solvent. A solid green powder was obtained. Green crystals suitable for X-ray crystallography were obtained from dichloromethane /2-propanol (3:1 v/v) in an open beaker and were filtered, washed with cold ethanol and dried in the air. Yield: 48%. Anal. Calc. for $C_{42}H_{59}Br_3Cu_3N_6O_7$: C, 42.38; H, 5.00; N, 7.06%. Found: C, 42.13; H, 5.01; N, 7.01%. IR (KBr, ν_{max}/cm^{-1}) band: 1552. UV-Vis, λ_{max}(methanol)/nm: 567 (log ε, 2.58) and 346 (3.70).

Many attempts made to synthesize the CuLX (X= NO_3, Cl, 0.5 SO_4) complexes failed and the sole product isolated from the preparative mixtures was the $Cu(bezac)_2$ complex which was identified by the X-Ray structure (see Fig. S1).

3. Results and Discussion

3. 1. Synthesis and Characterization of the Complexes

The flexidentate Schiff base HL was obtained by the in-situ condensation of aminoethylethanolamine and benzoylacetone under reflux in methanol solvent. Reactions of appropriate copper(II) salts with an equimolar amount of the ligand HL in methanol solution led to the formation of complexes **1**–**3**. The Schiff base HL can adopt both chelating and bridging modes. The ligand undergoes deprotonation during the reaction and the anionic form of the ligand L^-, coordinates to the metal center.

In the mononuclear $CuLClO_4$ complex **1**, which was formed from copper(II) perchlorate, L^- acts as a tetradentate ligand. In mononuclear $CuLN_3$ complex **2** which was obtained with copper(II) nitrate in the presence of N_3^-. L^- act as a tridentate ligand. On the other hand, reaction of HL with $CuBr_2$ leads to the formation of a trinuclear copper(II) complex where L^- acts as a tetradentate ligand with the ligand adopting both chelating and bridging modes (vide infra). However, the green solutions which were obtained by the reaction of HL with $Cu(NO_3)_2$, $CuCl_2$ or $CuSO_4$ contain the $Cu(bezac)_2$ complex, showing that HL underwent hydrolysis under the same conditions. This complex was characterized by elemental analyses and X-Ray crystallography (SI). $Cu(bezac)_2$ has been reported previously and can be obtained by directed reaction of $Cu(CH_3COO)_2$ and benzoylacetone in methanol medium.[23]

The IR spectrum of the free HL ligand shows a band at 1580 cm^{-1}, which is assigned as νC=N. In free Schiff base ligands the frequency of the hydroxyl group (phenol and alcohol) is observed in the 3200–3400 cm^{-1} region, due to intramolecular hydrogen bonding between OH and the nitrogen atoms of the ligand. The IR spectra of complexes **1**–**3** show a decrease in νC=N of about 25 cm^{-1} in comparison with the free ligand, which indicates coordination of the imine nitrogen atom to the copper ion.[24–26] Complex **1**, [CuLClO$_4$], shows strong bands at 1061 cm^{-1} corresponding to stretching frequencies of the perchlorate group.[27] The IR spectra of the complex **2** exhibit a band about 2043 cm^{-1}, which is characteristic of a coordinated azide group ligand.[27]

3. 2. Crystal Structures

3. 2. 1. Description of the Complex 1

Single crystals of complex **1** suitable for X-ray were obtained from a solution of **1** in methanol/cyclohexane. The complex crystallizes in the monoclinic space group *P2$_1$/n*. The molecular structure of the complex with labeling of selected atoms is shown in Fig. 1. Selected bond lengths and angles are listed in Table 2. The molecular structure shows that the copper(II) ion is five coordinated. L$^-$ acts as a N$_2$O$_2$ tetradentate ligand which forms two five-membered and one six-membered chelate rings with the Cu(II) metal center with the hydroxyl group coordinated to the metal ion. The fifth position at the Cu ion is occupied by an O atom of the ClO$_4$ anion. There is disorder in the packing of the ligand over two positions, which have relative occupancies of 85%:15%. In Fig.1, the molecular structure of the complex shows only the major position for each disordered atom, while Fig. S2 shows both positions of the disordered atoms.

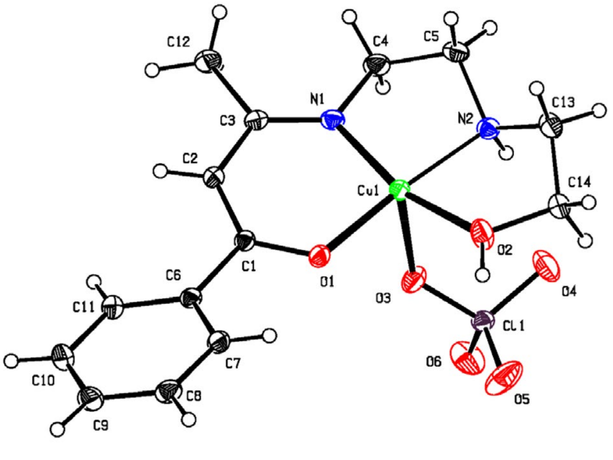


Fig. 1. The molecular structure of [CuL(ClO$_4$)], **1** with labeling of selected atoms.

The coordination geometry about the copper ion is close to square pyramidal with the Addison parameters τ = 0.19. τ is defined as τ = (a–b)/60, (a > b), where a and b are the two largest angles around the Cu center; τ = 1 for a regular trigonal bipyramid and τ = 0 for a regular square pyramid.[28] According to the bond lengths between the copper and the coordinating atoms (i.e., four bonds with short distances of 1.8935(14)–2.004(2) Å and one bond with a long distance of 2.5173(16) Å) the square base consists of the N2 O2 donors from the flexidentate Schiff base ligand and the apical position is occupied by the oxygen atom from the perchlorate anion and has the longer Cu–O distance. The Cu–O and Co–N bond lengths are in good agreement with analogous Cu(II) complexes previously reported.[21, 29, 30] The copper atom is displaced from the basal plane of N2O2 by 0.063 Å towards the apical oxygen atom.

The NH amine of Schiff base ligand plays a role in the H bonding network with there being an intramolecular hydrogen bond between the hydrogen atom H1 of the amine with the oxygen atom O4 of the perchlorate anion. Also, there are intramolecular hydrogen bonds between

Table 2. Selected bond lengths (Å) and angles (°) in complexes **1**–**3**

Complex 1			
Cu1–O1	1.894 (1)	O1–Cu1–O2	94.36 (6)
Cu1–O2	1.967 (2)	O1–Cu1–O3	89.76 (6)
Cu1–O3	2.517 (2)	O2–Cu1–O3	99.33 (7)
Cu1–N1	1.911 (2)	O1–Cu1–N1	97.09 (7)
Cu1–N2	2.004 (2)	O2–Cu2–N1	163.74 (7)
Cu1–N92	2.013 (8)	O1–Cu2–N2	175.08 (8)
Cl1–O3	1.439 (2)	O3–Cl1–O6	109.9 (1)
Cl1–O6	1.417 (2)	O4–Cl1–O6	109.5 (1)
Complex 2			
Cu1–O1	1.918 (1)	O1–Cu1–N1	93.10 (5)
Cu1–N1	1.940 (1)	N1–Cu1–N2	85.25 (6)
Cu1–N2	2.036 (1)	N2–Cu1–N3	92.45 (6)
Cu1–N3	1.988 (2)	O1–Cu1–N2	177.68 (6)
O1–C1	1.303 (2)	N1–Cu1–N3	167.70 (7)
O2–C14	1.413 (2)	Cu1–N3–N4	118.3 (1)
N3–N4	1.195 (2)	N3–N4–N5	176.9 (2)
N4–N5	1.160 (2)		
Complex 3			
Cu1–O1	1.887 (2)	O1–Cu1–O2	91.28 (8)
Cu1–O2	2.029 (2)	N1–Cu1–N2	86.90 (9)
Cu1–O22	2.508 (2)	O2–Cu1–N2	84.55 (9)
Cu1–N2	1.988 (2)	O1–Cu1–N2	175.75 (9)
Cu1–N1	1.905 (2)	O2–Cu1–O22	90.07 (7)
Cu2–O21	1.906 (2)	N21–Cu2–O22	107.61 (8)
Cu2–O22	2.380 (2)	O21–Cu2–O22	98.10 (8)
Cu2–N21	1.948 (2)	O21–Cu2–Br1	159.86 (7)
Cu2–N22	2.017 (2)	O21–Cu2–N22	173.2 (1)
Cu2–Br1	2.463 (5)	O22–Cu2–Br1	91.85 (5)
Cu3–O31	1.842 (2)	O32–Cu3–N32	84.2 (1)
Cu3–O32	2.008 (2)	O31–Cu3–N32	172.7 (1)
Cu3–N31	1.910 (2)	O31–Cu3–O32	92.04 (8)
Cu3–N32	1.985 (2)	N31–Cu3–N32	86.8 (1)
Cu3–Br1	3.015 (5)	N31–Cu3– Br1	88.32 (7)
Cu1…Cu2	4.356	Cu1–O22–Cu2	128.02
Cu2…Cu3	3.910	Cu2–Br1–Cu3	90.50

the hydrogen atoms of the uncoordinated water molecule with the oxygen atoms O5 and O1 of the perchlorate anion and with the hydroxyl group. The hydrogen atom of the coordinated hydroxyl group is involved in intermolecular hydrogen bonding interaction with the oxygen atom O7 (–x, –y+1, –z+1) of the uncoordinated water molecule. Full details of the hydrogen bonding are given in Table 3.

3. 2. 2. Description of the Complex 2

The molecular structure of **2** is shown in Fig. 2. Complex **2** is monomeric and crystallizes in orthorhombic space group *Pbca*. The single crystal X-ray diffraction data for compound **2** is listed in Table 1. Selected bond lengths and angles are summarized in Table 2.

The Schiff base ligand acts as a tridentate monoanionic ligand, L^-. The ligand forms one five-membered and one six-membered chelate ring with the Cu(II) metal center via the two nitrogen atoms of the amine and imine groups and one oxygen atom of one phenoxy group, and the hydroxyl group is left uncoordinated. The coordination geometry around the Cu(II) ions is four coordinated with a N3O donor set, N2O from the Schiff base ligand and one nitrogen from the azide ligand. The copper center

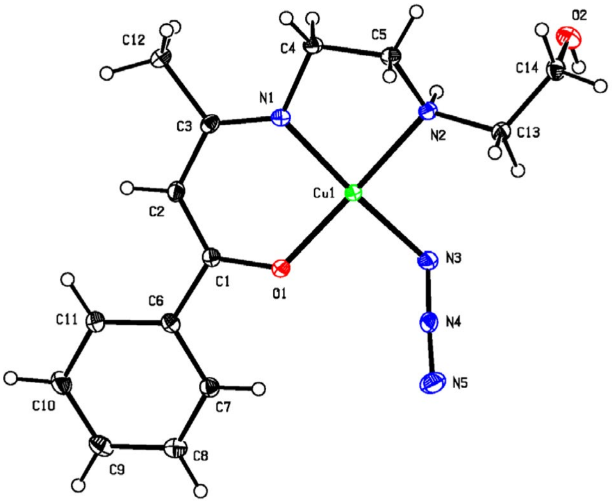


Fig. 2. The molecular structure of $[CuL(N_3)]$, **2** with labeling of selected atoms.

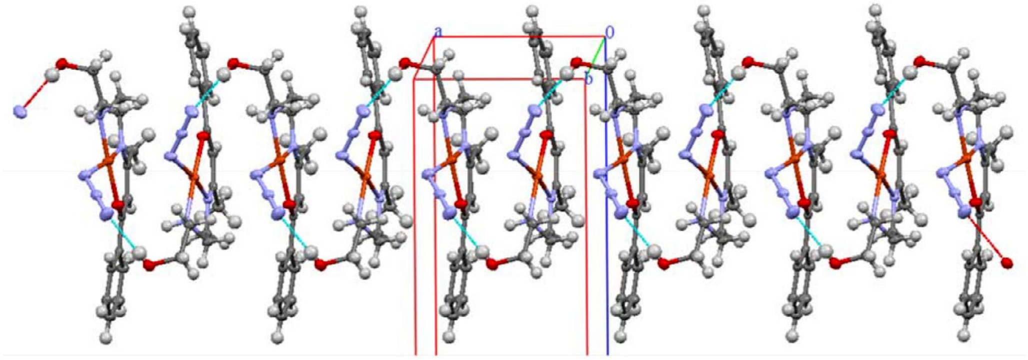


Fig. 3. The intermolecular hydrogen bonding between uncoordinated hydroxyl group of ligand and terminal nitrogen atom of neighboring coordinated azide ligand in complex **1** along a axis.

Table 3. Hydrogen bonding (Å) and angles (°) in copper complexes

	D–H···*A*	**D–H**	**H···*A***	**D...*A***	**D–H···*A***	**Symmetry code**
1	N2–H1···O4	0.87 (4)	2.32 (4)	3.113 (5)	152 (3)	
	O2–H2···O7*	0.83 (4)	1.78 (4)	2.597 (2)	168 (3)	−x, −y+1, −z+1
	O7–H3···O5	0.74 (4)	2.10 (4)	2.883 (2)	178 (4)	
	O7–H4···O1	0.82 (4)	2.05 (4)	2.848 (2)	166 (4)	
2	N2–H1···O1*	0.87 (2)	2.43 (2)	3.160 (2)	142 (2)	x−1/2, y, −z+1/2
	O2–H2···N5*	0.71 (3)	2.22 (3)	2.922 (2)	172 (3)	x−1/2, y, −z+1/2
3	N2–H1···O21	0.87 (3)	2.22 (3)	3.057 (3)	160 (4)	
	N22–H2···N31	0.88 (3)	2.29 (2)	3.091 (3)	150 (3)	
	N32–H3···O1*	0.88 (2)	2.46 (3)	3.212 (3)	143 (3)	−x+1/2, y−1/2, −z+3/2
	O2–H4···Br2	0.81 (2)	2.34 (3)	3.141 (2)	169 (4)	
	O22–H5···Br2	0.85 (3)	2.32 (3)	3.145 (2)	165 (4)	
	O32–H6···Br3*	0.84 (3)	2.28 (2)	3.119 (2)	177 (4)	−x+1/2, y−1/2, −z+3/2
	O41–H7···Br3*	0.86 (3)	2.56 (4)	3.393 (3)	166 (3)	−x+1, −y+1, −z+1
	O41–H8···Br1	0.88 (4)	2.47 (3)	3.345 (3)	172 (4)	

has a τ_4 index of 0.104. The τ_4 parameter is [360° – (α + β)]/141°, where α and β are the largest angles around the central metal in the complex; $\tau_4 = 1$ for a regular tetrahedron and $\tau_4 = 0$ for a regular square planar geometry.[31] In **2**, the Cu–O bond length is 1.9184(11) Å and the Cu–N bonds range from 1.9402(13)–2.0363(14) Å. The Cu–N(azide) bond length (1.9879(16) Å), is longer than Cu–N(imine) (1.9402(13) Å) and shorter than Cu–N(amine) (2.0363(14) Å). The Cu–N bond length suggesting that azide ligand interacts with copper(II) center more strongly in comparison to the nitrogen atom of the amine and weaker than the nitrogen atom of the imine. The azide ligand is almost linear with N3-N4-N5 bond angle 176.85(19)°.

The uncoordinated hydroxyl group of the Schiff base ligand plays a significant role in the intermolecular hydrogen bonding. There is an intermolecular hydrogen bonding between the hydrogen atom of the hydroxyl group with the terminal nitrogen atom of a neighboring coordinated azide ligand, with a donor–acceptor distance of 2.922(2) Å and D–H···A angle 172(3)°, which build a 1D chain structure running through the a axis (Fig. 3). Full details of the hydrogen bonding are given in Table 3.

3. 2. 3. Description of the Complex 3

Complex **3** crystallizes in the monoclinic space group $P2_1/c$. The molecular structure of the complex with labeling of selected atoms is shown in Fig. 3. Selected bond lengths and angles are listed in Table 2. From the crystal structure, it has been found that complex **3** is trinuclear, $[Cu_3L_3Br]Br_2$, with a hydroxyl group bridge and one asymmetric Br anion bridge. The copper(II) centers are five-coordinated and L^- acts as a tetradentate ligand with the oxygen atom of the hydroxyl group coordinating in both terminal and bridging ligands. On the basis of atoms donor set around each copper, there are three types of Cu(II) ions, i.e., $[CuN_2O_2(\mu\text{-}OH)]$ for Cu1, $[CuN_2O(\mu\text{-}OH)(\mu\text{-}Br)]$ for Cu2 and $[CuN_2O_2(\mu\text{-}Br)]$ for Cu3.

The bond angles at Cu(II) between two donor atoms in the *cis* position are in the range 84.17(10)–107.61(8)° and between two donor atoms in the *trans* position they are in the range 159.86(7)° and 175.75(9)° (Table 2). The coordination geometry around each of the central copper is distorted square pyramidal, according to Addison τ parameter values of 0.17, 0.22 and 0.06 for Cu1, Cu2, and Cu3, respectively.[28] The deviation of copper(II) atoms from the basal plane towards the axially coordinated site are 0.104, 0.135, 0.005 Å for Cu1, Cu2 and Cu3, respectively.

In the case of Cu1 center, the four equatorial positions are occupied by two oxygen (O1 and O2) and two nitrogen atoms (N1 and N2) of the Schiff base and the apical position is occupied by one oxygen atom (O22)

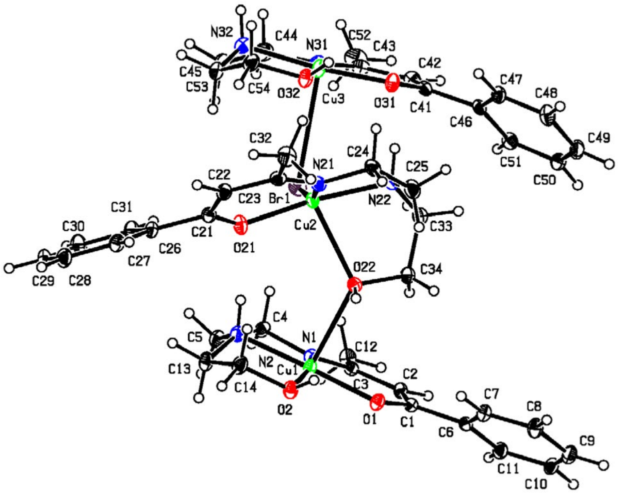


Fig. 4. The molecular structure of $[Cu_3L_3Br]^{2+}$ cations **3** with labeling of selected atoms.

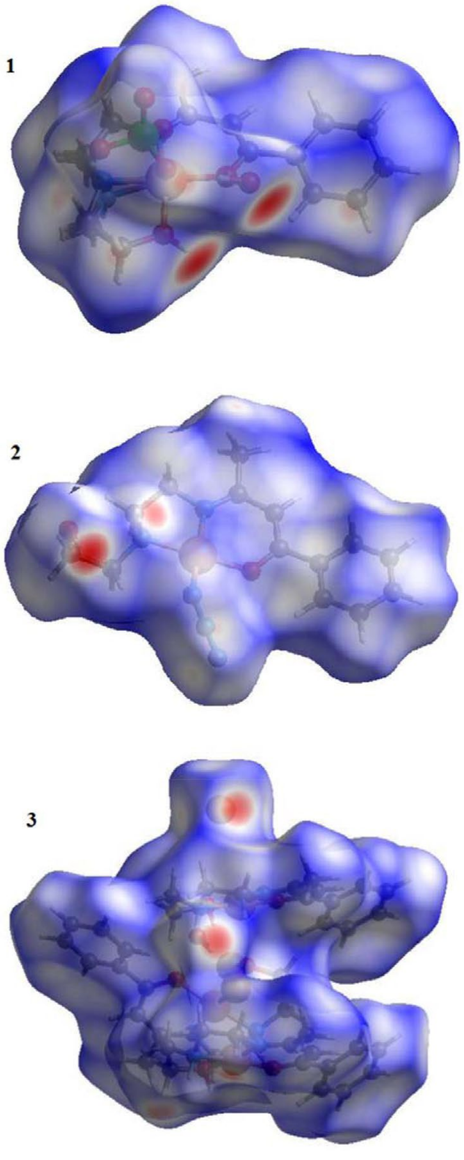


Fig. 5. Hirshfeld surface mapped with d_{norm} for complexes **1**–**3**.

from an adjacent Schiff base ligand of the next unit of the trinuclear complex. In the Cu2, the four equatorial positions are occupied by one oxygen (O21) and two nitrogen atoms (N21 and N22) of the Schiff base and a μ-Br1 anion, while the apical position is occupied by the oxygen atom (O22) of the hydroxyl group of the Schiff base. The hydroxyl oxygen atom acts as a bridge connecting two Cu1 and Cu2 centers. The remaining copper center, Cu3 is

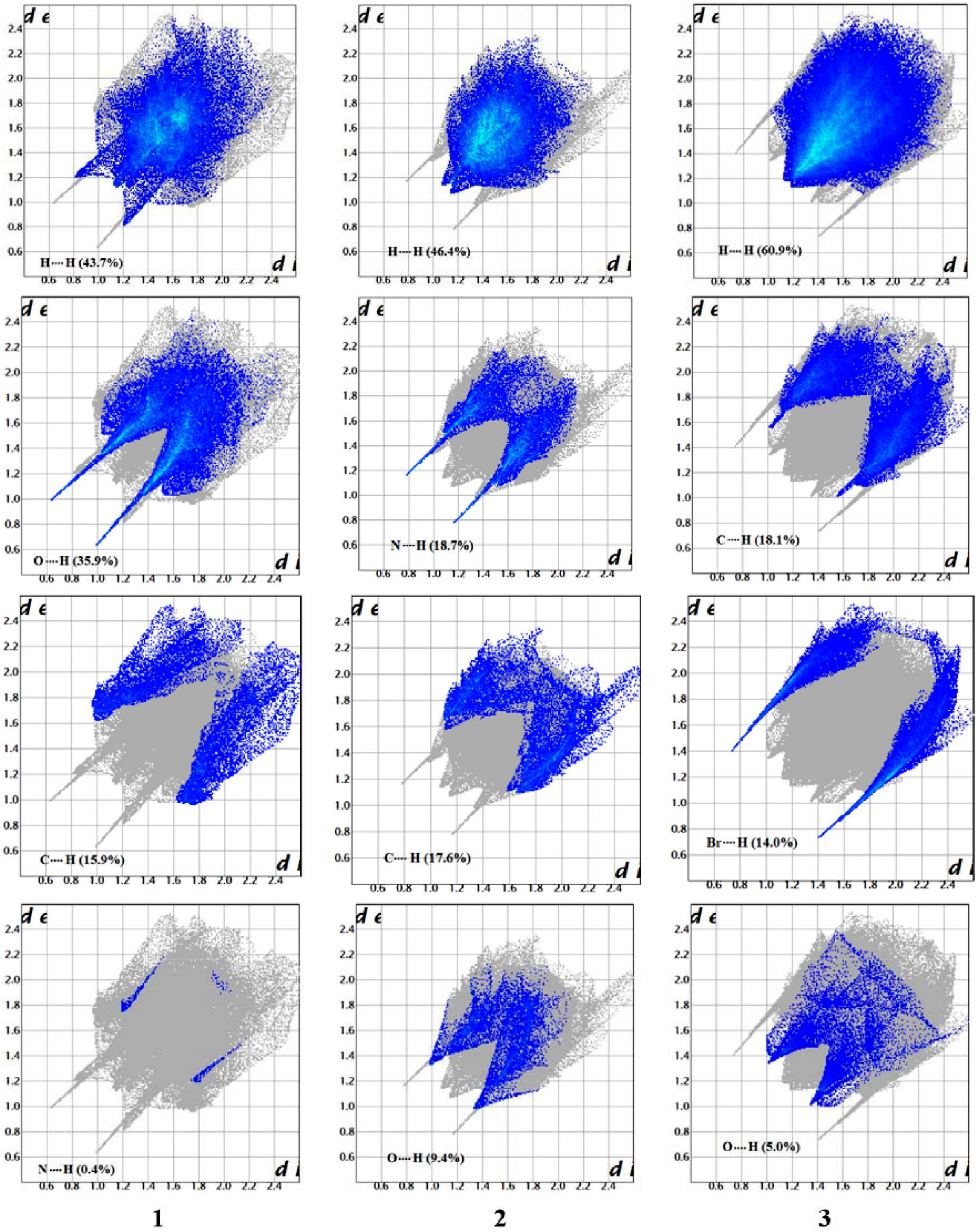


Fig. 6. The 2D fingerprint plots and relative contributions to the percentage of Hirshfeld surface for various interactions in **1**–**3**.

similar to Cu1 in that the four equatorial positions are occupied by the Schiff base with N_2O_2 donor atoms, while the apical position is occupied by a μ-Br1 anion. The bridging Br1 anion connects two Cu2 and Cu3 ions with each other.

The Cu–O and Cu–N bond lengths in the equatorial plane are in the range of 1.872(2)–2.029(2) and 1.905 (2) to 2.017(2) Å, respectively (Table 2). As shown in Table 2, the Cu–O(hydroxy) bond lengths in the apical position (Cu1–O22 = 2.508(2) and Cu2–O22 = 2.380(2) Å) are longer than the Cu–O(hydroxy) bond lengths in the equatorial positions (Cu1–O1 = 2.029(2) and Cu3–O32 = 2.008(2)), which is consistent with analogous systems observed in the literature.[17, 22, 26, 32]

The NH amine of the Schiff base ligand plays a significant role in the hydrogen bonding. There are intramolecular and intermolecular hydrogen bonds between the hydrogen atoms of the NH groups of the amines with the oxygen atoms of hydroxyl groups. Also, there are intramolecular and intermolecular hydrogen bonding between the hydrogen atoms of the uncoordinated water molecule and hydroxyl groups with the uncoordinated Br anions. Full details of the hydrogen bonding are given in Table 3.

3. 3. Hirshfeld Surface Analysis

In order to profoundly examine the strength and role of the intermolecular contacts, and to estimate their importance for the crystal lattice stability, Hirshfeld surface analysis has been conducted. The Hirshfeld surface of the complexes **1–3** is illustrated in Fig. 5. The normalized contact distance, d_{norm} defined in terms of d_e (distance from a point on the surface to the nearest nucleus outside the surface), d_i (distance from a point on the surface to the nearest nucleus inside the surface) and the van der Waals radii of the atoms, r^{vdW} given by equation 1:

$$d_{norm} = \frac{d_i - r_i^{vdw}}{r_i^{vdw}} + \frac{d_e - r_e^{vdw}}{r_e^{vdw}} \qquad (1)$$

The value of the d_{norm} can be positive or negative when intermolecular contacts are longer or shorter than the sum of the atoms vdw radii, respectively. The d_{norm} values are mapped onto the Hirshfeld surface using a red–blue–white color scheme. Red regions correspond to closer contacts and negative d_{norm} value, the blue regions correspond to longer contacts and positive d_{norm} value. The white-colored regions correspond to weak contacts and the distance of contacts is around the vdW separation ($d_{norm} \approx 0$).[33,34]

The 2D fingerprint plots are used to analyses all of the intermolecular interactions. The full fingerprint plot for 1–3 and the contribution of each type of interaction are shown in Fig. 6. The highest contribution occurs due to H···H contacts. Fig. 6 shows the percentage of contribution of various intermolecular close contacts which play an important role in the stabilization of molecular structures.

4. Conclusion

Three complexes have been synthesized by reaction of Cu(II) ion with the flexidentate Schiff base ligand derived from the condensation of aminoethylethanolamine and benzoylacetone. All complexes have been characterized by X-ray crystallography. In complexes **1** and **3**, the ClO_4^- and Br^- anions are coordinated to the copper ion, and the hydroxyl group of the flexidentate ligand coordinates to the Cu(II) center such that the ligand is tetradentate. However, in complex **2,** the presence of the N_3 anion with its strong coordinating ability, leads to the ligand being tridentate, with the hydroxyl group left uncoordinated.

5. Supplementary Material

The deposition numbers of the studied complexes, **1–3** are CCDC 1912996-1912998, 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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6. References

1. C. Papatriantafyllopoulou, T. C. Stamatatos, W. Wernsdorfer, S. J. Teat, A. J. Tasiopoulos, A.t Escuer, S. P. Perlepes, *Inorg. Chem.* **2010,** *49,* 10486–10496. **DOI:**10.1021/ic1014829
2. M. Das, B. N. Ghosh, K. Rissanen, S. Chattopadhyay, *Polyhedron,* **2014,** *77,* 103–114. **DOI:**10.1016/j.poly.2014.03.027
3. P. Bhowmik, S. Chatterjee, S. Chattopadhyay, *Polyhedron,* **2013,** *63,* 214–221. **DOI:**10.1016/j.poly.2013.07.023
4. A. Beheshti, A. Lalegani, G. Bruno, H. A. Rudbari, *J. Mol. Struct.* **2014,** *1071,* 18–22. **DOI:**10.1016/j.molstruc.2014.04.048
5. K. Bhar, S. Choubey, P. Mitra, G. Rosair, J. Ribas, B. K. Ghosh, *J. Mol. Struct.* **2011,** *988,* 128–135. **DOI:**10.1016/j.molstruc.2010.12.042
6. S. Mondal, S. Hazra, S. Sarkar, S. Sasmal, S. Mohanta, *J. Mol. Struct.* **2011,** *1004,* 204–214. **DOI:**10.1016/j.molstruc.2011.08.005
7. I. Beloso, J. Borras, J. Castro, J. A. Garcıa-Vazquez, P.

Perez-Lourido, J. Romero, A. Sousa, *Eur. J. Inorg. Chem.* **2004,** 635–645. **DOI:**10.1002/ejic.200300338

8. N. A. I. Hisham, H. Khaledi, H. M. Ali, H. A. Hadi, *J. Coord. Chem.* **2012,** *65,* 2992–3006. **DOI:**10.1080/00958972.2012.708412
9. S. Mukhopadhyay, D. Mandal, D. Ghosh, I. Goldberg, M. Chaudhury, *Inorg. Chem.,* **2003,** *42,* 8439–8445. **DOI:**10.1021/ic0346174
10. H. Y. Wang, H. Y. Liu, *Transit. Met. Chem.* **2017,** *42,* 165–173. **DOI:**10.1007/s11243-017-0121-4
11. Y. Sunatsukia, R. Kawamotoa, K. Fujita, H. Maruyamaa, T. Suzukia, H. Ishidaa, M. Kojimaa, S. Iijima, N. Matsumoto, *Coord. Chem. Rev.,* **2010,** *254,* 1871–1881. **DOI:**10.1016/j.ccr.2009.11.016
12. S. Mukhopadhyay, D. Mandal, D. Ghosh, I. Goldberg, M. Chaudhury, *Inorg. Chem.,* **2003,** *42,* 8439–8445. **DOI:**10.1021/ic0346174
13. R. Dıaz-Torres and S. Alvarez, *Dalton Trans.,* **2011,** *40,* 10742–10750. **DOI:**10.1039/c1dt11000d
14. H. Keypour, M. Shayesteh, M. Rezaeivala, K. Sayin, *J. Mol. Struct.,* **2016,** *1112,* 110–118. **DOI:**10.1016/j.molstruc.2016.02.004
15. A. S. de Sousa, M. A. Fernandes, K. Padayachy, H. M. Marques, *Inorg. Chem.,* **2010,** *49,* 8003–8011. **DOI:**10.1021/ic101018b
16. S. H. Hsieh, Y. P. Kuo, H. M. Gau, *Dalton Trans.,* **2007,** 97–106. **DOI:**10.1039/B613212J
17. Y. C. Shi, H. J. Cheng, S. H. Zhang, *Polyhedron,* **2008,** *27,* 3331–3136. **DOI:**10.1016/j.poly.2008.04.057
18. Z. Otwinowski, W. Minor. Methods in Enzymology, edited by C. W. Carter Jr & R. M.W. Sweet, New York: Academic Pressn, **1997,** 276, pp. 307–326. **DOI:**10.1016/S0076-6879(97)76066-X
19. A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.,* **1994,** *27,* 435–436. **DOI:**10.1107/S0021889894000221
20. P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, D. J. Watkin, *J. Appl. Cryst.,* **2003,** *36,* 1487–1487. **DOI:**10.1107/S0021889803021800
21. R. Vafazadeh, Z. Moghadas, A.C. Willis, *J. Coord. Chem.,* **2015,** *68,* 4255–5271. **DOI:**10.1080/00958972.2015.1096349
22. R. Vafazadeh, F. Jafari, M. M. Heidari, A. C. Willis, *J. Coord. Chem.,* **2016,** *69,* 1313–1325. **DOI:**10.1080/00958972.2016.1163547
23. S. K. Dey, B. Bag, Z. Zhou, A. S. C. Chan, S. Mitra, *Inorg. Chim. Acta,* **2004,** *357,* 1991–1996. **DOI:**10.1016/j.ica.2003.12.014
24. R. Vafazadeh, M. Alinaghi, A. C. Willis, A. Benvidi, *Acta Chim. Slov.,* **2014,** *61,* 121–125.
25. M.T.H. Tarafder, A. Kasbollah, K.A. Crouse, A.M. Ali, B.M. Yamin, H.K. Fun, *Polyhedron,* **2001,** *20,* 2363–2370. **DOI:**10.1016/S0277-5387(01)00817-8
26. R. Vafazadeh, A. C. Willis, *J. Coord. Chem.* **2015,** *68,* 2240–2252. **DOI:**10.1080/00958972.2015.1048688
27. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, fourth ed., Wiley, New York, **1986.**
28. A.W. Addison, T.N. Rao, J. Reedijk, J. Vanrijn, G.C. Verschoor. *J. Chem. Soc., Dalton Trans.,* **1984,** 1349–1356. **DOI:**10.1039/DT9840001349
29. R. Vafazadeh, M. Namazian, M. Chavoshiyan, A. C. Willis, P. D. Carr, *Acta Chim. Slov.,* **2017,** *64,* 613–620. **DOI:**10.17344/acsi.2017.3401
30. R. Vafazadeh, N. Abdollahi, A. C. Willis, *Acta Chim. Slov.,* **2017,** *64,* 409–414. **DOI:**10.17344/acsi.2017.3263
31. P. Seth, S. Ghosh, A. Figuerola, A. Ghosh, *Dalton Trans.,* **2014,** *43,* 990–998. **DOI:**10.1039/C3DT52012A
32. Z. Lu, T. Fan, W. Guo, J. Lu, C. Fan, *Inorg. Chim. Acta,* **2013,** *400,* 191–196. **DOI:**10.1016/j.ica.2013.02.030
33. N. Khelloul, K. Toubal, N. Benhalima, R. Rahmani, A. Chouaih, A. Djafri, F. Hamzaoui, *Acta Chim. Slov.,* **2016,** *63,* 619–626. **DOI:**10.17344/acsi.2016.2362
34. M. A. Spackman, D. Jayatilaka, *CrystEngComm,* **2009,** *11,* 19–32. **DOI:**10.1039/B818330A

Povzetek

Večevezni ligand (HL), smo pripravili s kondenzacijo aminoetiletanolamina (AEEA) z benzoilacetonom (bezac). Pri reakciji z bakrovimi (II) solmi nastanejo kompleksi $CuLClO_4.H_2O$ (**1**), $CuLN_3$ (**2**) in $[Cu_3L_3Br]Br_2 \cdot H_2O$ (**3**). Vse kompleksne smo karakterizirali z rentgensko strukturno analizo monokristalov. Rezultati kažejo, da se hidroksilna skupina liganda lahko koordinira na Cu(II) center ali ostane kot nekoordinirana skupina. V kompleksu (**1**) je koordinacijsko število bakrovega(II) iona pet, od tega štiri vezavna mesta pripadajo ligandu (HL). V kompleksu (**2**) najdemo kvadratno ploskovno geometrijo, ligand (HL) je tridentatni, pri čemer hidroksilna skupina ni vezana na Cu(II) center. V kompleksu (**3**) je Cu(II) koordiniran s petimi atomi, od tega štirje pripadajo ligandu (HL). Za analizo vseh interakcij med molekulami v kristalnih strukturah smo uporabili Hirshfeldovo površinsko analizo in 2D prstni odtis.