Synthesis and structural characterization of copper(II) complexes with a tetradentate semicarbazone ligand derived from 2,5-hexadione

Rasoul Vafazadeh¹ · Mahboobeh Ehsani¹ · Anthony C. Willis²

Received: 23 October 2018 / Accepted: 17 June 2019 / Published online: 21 June 2019
© Iranian Chemical Society 2019

Abstract

Four Cu(II) complexes $[\text{CuLH}_2\text{O}](\text{ClO}_4)_2$, **1**; $[\text{CuLCl}]\text{Cl}\cdot\text{H}_2\text{O}$, **2**; $[\text{CuLBr}]_2(\text{Cu}_3\text{Br}_5)$, **3**; and $[\text{CuLH}_2\text{O}](\text{NO}_3)_2$, **4**; where L = tetradentate semicarbazone ligand, have been synthesized and characterized by elemental analysis, FT-IR and UV-Vis. The structures of compounds **1** and **3** have been determined by single-crystal X-ray diffraction analyses. In mononuclear **1**, the semicarbazone, L acts as a tetradentate neutral ligand and a water molecule also coordinates to the Cu atom. There are two independent $[\text{CuL}(\text{H}_2\text{O})]^{2+}$ cations and four perchlorate anions in the crystallographic asymmetric unit. One of the cations has a weak interaction between its Cu atom and a O atom of an adjacent perchlorate anion. The structure of **3** contains two independent $[\text{CuLBr}]^+$ cations and a $(\text{Cu}_3\text{Br}_5)^{2-}$ anion. The coordination geometry around the cation's Cu(II) ion is five-coordinated square pyramidal, with L acting as a tetradentate neutral ligand and with a Br at the apical position. The $\text{Cu}_3\text{Br}_5^{2-}$ anions link to one another to form an infinite one-dimensional $(\text{Cu}_3\text{Br}_5^{2-})_n$ chain. Furthermore, the Hirshfeld surface analyses and the 2D fingerprint plot have been discussed.

Keywords Copper complex · Semicarbazone · 2,5-Hexadione · Disorder · Tetradentate

Introduction

Studies of semicarbazone and thiosemicarbazone ligands and their complexes with transition and non-transition metals have received considerable attention, as they possess important biological properties and structural diversities [1–7]. The biological activity of the ligands is often increased upon coordination to transition metals [7–10].

Semicarbazone and thiosemicarbazone ligands are formed by condensation reactions between semicarbazide/thiosemicarbazide and relevant aldehydes or ketones [10–12]. Semicarbazone derivatives may have an advantage over their thiosemicarbazone analogues due to lower toxicity. However, the complexes of transition metals with bis(semicarbazone) have

been reported to have lower stability than the complexes of the analogous bis(thiosemicarbazone), which may be due to the fact that the bis(semicarbazone) can often undergo cyclization reactions, especially in the presence of metal ions [13–15]. Tetradentate bis(semicarbazone) ligands are prepared by condensation reaction of semicarbazide with 1, 2-diketones, such as benzil in a 2:1 ratio (L^1). They can lose one of their hydrazinic units to form a L^2 ligand (Scheme 1) [14–16]. On the other, 1, 3-diketones usually exist predominantly as enol forms due to conjugation of the enol or enolate with the other carbonyl group. The semicarbazone ligands prepared by the condensation of 1, 3-diketones with semicarbazide mostly act as monoanionic tridentate ligands and coordinate to metal ions via a phenoxo or hydroxo oxygen, an imine nitrogen and an amide oxygen atoms (Scheme 1) [17–19].

In order to investigate the effect of the chain length of the diketone on the molecular structure of the semicarbazone complexes, we report the syntheses of several new copper(II) complexes, formed by the reaction of a neutral tetradentate semicarbazone derived from 2 equiv. of semicarbazide and 1 equiv. of 2,5-hexadione with copper(II) and various counter anions (Scheme 2).

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s13738-019-01721-3>) contains supplementary material, which is available to authorized users.

✉ Rasoul Vafazadeh
rvafazadeh@yazd.ac.ir; rvafazadeh@gmail.com

¹ Department of Chemistry, Yazd University, Yazd, Iran

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

Scheme 1 Reaction of the 1,2-diketone and 1,3-diketone with semicarbazide

Scheme 2 Reaction of the 1,4 diketone with semicarbazide

Experimental section

Starting materials

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

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 in the solvent dimethylformamide (DMF) using GBC UV–Visible Cintra 101 spectrophotometer with 1 cm quartz, in the range 200–1000 nm. Elemental analyses (C,

H, N) were performed by using a CHNS-O 2400II PERKIN-ELMER elemental analyzer.

X-ray crystallography

Diffraction images were measured at 150 K on an Agilent SuperNova diffractometer using CuKα ($\lambda = 1.54180 \text{ \AA}$) radiation. Data were extracted using the CrysAlis PRO package [20]. The structures were solved by direct methods with the use of SIR92 [21]. The structures were refined on F^2 by full matrix least-squares techniques using the CRYSTALS program package [22]. 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 restraints 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 = 0.83

Å) and with $U_{\text{iso}}(\text{H})$ 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. Details of the refinement procedures for the structures are given in the Supplementary Information.

Hirshfeld surfaces and the associated two-dimensional fingerprint plots for the complexes were calculated with CrystalExplorer 3.1 program [23]. The d_{norm} surface and 2D fingerprint were used to analyses intermolecular interaction in the crystal packing.

Syntheses

Synthesis of semicarbazone ligand, L

The new tetradentate semicarbazone ligand L was synthesized by a general method as previously reported elsewhere

by us and others [24, 25], by condensation of semicarbazide hydrochloride (0.558 g, 5 mmol), sodium acetate (0.410 g, 5 mmol) and 2,5-hexadione (0.3 ml, 2.5 mmol) in an aqueous solution (30 ml). The mixture was stirred at room temperature for 1 h during which a white precipitate was formed. The precipitate was filtered, washed with distilled water and dried at room temperature. The precipitate is insoluble in most common organic solvents such as methanol, ethanol, acetone, acetonitrile and dichloromethane and also is only very slightly soluble in DMF. Yield 47%. Anal. Calcd. for $\text{C}_8\text{H}_{16}\text{N}_6\text{O}_2$: C, 42.10; H, 7.07; N, 36.82. Found: C, 42.28; H, 7.15; N, 37.05. IR (KBr, cm^{-1}): $\nu_{\text{C}=\text{N}}$ = 1581, $\nu_{\text{C}=\text{O}}$ = 1683.

Synthesis of copper(II) complexes, 1–4

$\text{CuX}_2 \cdot n\text{H}_2\text{O}$ (1 mmol, $X = \text{ClO}_4$, $n = 6$, 0.370 g, **1**; $X = \text{Cl}$, $n = 2$, 0.170 g, **2**; $X = \text{Br}$, $n = 0$, 0.224 g, **3**; $X = \text{NO}_3$, $n = 3$, 0.242 g, **4**) was added to a stirred suspension of

Table 1 Crystallographic data of the complexes **1** and **3**

Compound	1	3
Chemical formula	$\text{C}_8\text{H}_{18}\text{Cl}_2\text{CuN}_6\text{O}_{11}$	$(\text{C}_8\text{H}_{16}\text{BrCuN}_6\text{O}_2^+)_2 \cdot (\text{Cu}_3\text{Br}_5^{2-})$
Formula weight	508.72	1333.57
Temperature (K)	150	150
Space group	Monoclinic, $P2_1/n$, $Z = 8$	Monoclinic, $P2_1/n$, $Z = 4$
<i>Unit cell dimensions</i>		
a (Å)	15.6432 (1)	11.9172 (1)
b (Å)	13.3892 (1)	11.1891 (1)
c (Å)	18.7237 (1)	26.7601 (2)
α (°)	90	90
β (°)	110.7881 (7)	99.3920 (6)
γ (°)	90	90
V (Å ³)	3666.37 (4)	3520.43 (5)
$F(000)$	2072	2536
D_{Calc} (g cm ⁻³)	1.843	2.516
Crystal size (mm)	0.24 × 0.08 × 0.06	0.32 × 0.09 × 0.01 mm
μ (mm ⁻¹)	5.03	13.03
θ range (°)	3–74	4–74
Limiting indices	$-15 \leq h \leq 19$ $-16 \leq k \leq 16$ $-23 \leq l \leq 23$	$-14 \leq h \leq 14$ $-12 \leq k \leq 13$ $-33 \leq l \leq 33$
No. of unique reflns	7436	7102
No. of parameters	609	397
$R[F^2 > 2\sigma(F^2)]$	0.034	0.041
$wR(F^2)$ (all data)	0.089*	0.106**
S	1.00	0.99

* $w = 1/[\sigma^2(F^2) + (0.05P)^2 + 4.48P]$, where $P = (\max(F_o^2, 0) + 2F_c^2)/3$

** Method Chebyshev polynomial, $[\text{weight}] = 1.0/[A_0 * T_0(x) + A_1 * T_1(x) \dots + (A_{n-1}) * T_{n-1}(x)]$

Method robust weighting, $W = [\text{weight}] * [1 - (\Delta F / 6 * \sigma(F)^2)^2]$

where $A_1 = 0.226E + 04$ 0.370E + 04 0.233E + 04974.219 and $x = F/F_{\text{max}}$

the semicarbazone ligand (1 mmol, 0.228 g) in methanol (30 mL), and the reaction mixture was stirred at room temperature for 3 h.

[CuL(H₂O)](ClO₄)₂, **1.** The solution turned a blue-green color. The solution was filtered, and the clear blue-green filtrate was left in a beaker to allow slow evaporation of the solvent. Analytically pure complex **1** precipitated out as a green powder. Blue-green prism crystals suitable for X-ray crystallography were obtained from acetone/2-propanol (2:1 v/v). Yield: 83%. Anal. Calc. for C₈H₁₈Cl₂CuN₆O₁₁: C, 18.89; H, 3.57; N, 16.52%. Found: C, 19.06; H, 3.55; N, 16.55%. IR (KBr, cm⁻¹): νC=N = 1556, νC=O = 1649. UV-Vis, λ_{max}(DMF)/nm, (log ε): 725 (1.88) and 360 (2.10).

[CuLCl]Cl·H₂O, **2.** The solution turned a green color. The resultant suspension was filtered, washed with methanol and dried in air. Several attempts were made to obtain crystals, using various techniques, but the resultant crystals were always small and of poor quality. Yield: 37%. Anal. Calc. for C₈H₁₈Cl₂CuN₆O₃: C, 25.24; H, 4.77; N, 22.07%. Found: C, 25.27; H, 4.79; N, 22.26%. IR (KBr, cm⁻¹): νC=N = 1544, νC=O = 1645. UV-Vis, λ_{max}(DMF)/nm, (log ε): 986 (2.19), 428(sh) (3.16) and 373(sh) (3.49).

[CuLBr]₂Cu₃Br₅, **3.** The solution was filtered, and the clear green filtrate was kept in a beaker to allow slow evaporation of the solvent. The analytically pure complex CuLBr₂·H₂O precipitated out. The green powder which was obtained was filtered, washed with methanol and dried in air. Yield: 73%. Anal. Calc. for C₈H₁₈Br₂CuN₆O₃: C, 20.46; H, 3.86; N, 17.90%. Found: C, 20.68; H, 3.79; N, 17.73%.

Upon recrystallized from methanol/2-propanol (2:1 v/v), blue-green crystal was obtained which was filtered, washed with 2-propanol and dried in air. From this sample, several long, thin needles were studied by single-crystal X-ray crystallography and proved to be [CuLBr]₂Cu₃Br₅, **3**. IR (KBr, cm⁻¹): νC=N = 1543, νC=O = 1674. UV-Vis, λ_{max}(DMF)/nm, (log ε): 983 (2.77) and 353 (3.22).

Other crystals from this sample gave a different diffraction pattern, which was unfortunately always of very poor quality. The structure appears to be [CuLBr]Br·H₂O, but there is massive disorder of the water molecule, the anion, and even the cation, and the refinement was not of publishable standard.

[CuLH₂O](NO₃)₂, **4.** The solution was filtered, and the clear green filtrate was kept in a beaker to allow the solvent to slowly evaporate. Analytically pure complex **4** precipitated out. The green powder which was obtained was filtered, washed with methanol and dried in air. Several attempts to prepare single crystals of X-ray quality were unsuccessful. Yield: 84%. Anal. Calc. for C₈H₁₈CuN₈O₉: C, 22.15; H, 4.18; N, 25.83%. Found: C, 21.67; H, 4.17; N, 26.15%. IR (KBr, cm⁻¹): νC=N = 1563, νC=O = 1648. UV-Vis, λ_{max}(DMF)/nm, (log ε): 738 (1.83) and 374 (2.84).

Results and discussion

Syntheses and characterization of the complexes

The tetradentate semicarbazone ligand was obtained by condensation of semicarbazide hydrochloride and 2,5-hexadione at room temperature in an aqueous solution. Copper(II) complexes **1–4** were obtained by reacting the ligand with the corresponding Cu(II)X₂ salt in equimolar ratio at room temperature in methanol solvent.

The complexes have low stability as a seven-member chelate ring is formed (vide infra). The size effect of the chelate ring on complexes stability has been reported previously [26–29], where it has been shown that the complex stability decreases as the chelate ring size increase so that seven-member chelated rings lead to less stable complexes than five- and six-member chelate rings.

The reaction of the semicarbazone ligand with CuBr₂ results in the formation of the complex [CuLBr]Br·H₂O. Upon recrystallization, blue-green crystals of this compound were obtained, but they were not of sufficient quality to give X-ray diffraction data leading to a publishable structure. The attempted refinement did, however, firmly suggest that the structure was, indeed, [CuLBr]Br·H₂O.

Other blue-green crystals from this sample were shown by single-crystal X-ray crystallography to be [CuLBr]₂Cu₃Br₅, and refinement of the structure was satisfactory (vide infra). The Cu₃Br₅²⁻ anion appears to have increased the stability of the [CuLBr]⁺ complex and helped the growth of suitable crystals. The above observations suggest that the solvent methanol and 2-propanol play a role in for the reduction of copper(II) to copper(I) in the presence of the Br⁻ anion. It is interesting that the reduction process was observed in an aerobic situation.

Complex **2** only yielded poor-quality crystals, and a structure determination attempt gave unsatisfactory results. The existence of [CuLCl]Cl did appear to be observed in the partial refinement, however.

Preparation of single crystals of complex **4** suitable for X-ray analysis was unsuccessful. However, on the basis of the similarity of the spectroscopic properties of **4** with complex **1**, [CuL(H₂O)](ClO₄)₂, for which the crystal structure has been determined (vide infra), it can be inferred that **4** has similar structure to that of **1** complex, i.e., [CuL(H₂O)](NO₃)₂.

Besides elemental analysis, all the complexes were initially characterized by infrared spectral. A comparison of the spectra of the free ligand and complexes indicates that the ligand is coordinated to the copper center. The IR spectrum of the free semicarbazone ligand shows bands at 1581 and 1683 cm⁻¹, which are assigned as νC=N and νC=O, respectively. In the copper complexes, the strong

$\nu\text{C}=\text{N}$ and $\nu\text{C}=\text{O}$ bands are shifted toward lower energy in comparison with the free ligand, which indicates coordination of the imine nitrogen atom and carbonyl group to the copper ion [24, 30].

The semicarbazone ligand **L** is insoluble in most common organic solvents and also is only very slightly soluble in DMF, since the almost complete insolubility of the ligand made it impossible to obtain a UV–Vis spectrum.

The electronic spectra of the copper complexes **1–4** in DMF show a broad band at 725, 986, 983 and 738 nm which arise from a spin-allowed $d-d$ transition of copper(II) (d^9 electronic configuration), respectively. The copper(II) complexes exhibit a strong bond in the UV region (353–428 nm) which could be attributed to charge transfer transition [18, 19].

X-ray crystal structures

Description of the complex 1

Single crystals of complex **1** suitable for X-ray were obtained from acetone/2-propanol. The complex crystallized in the monoclinic space group $P2_1/n$. The crystallographic asymmetric unit consists of two independent $[\text{CuL}(\text{H}_2\text{O})]^{2+}$ cations and four perchlorate anions. Both cations show coordination of the copper(II) to the semicarbazone ligand and to a water molecule. There is disorder in the locations of some oxygen atoms of two of the perchlorate anions. The $[\text{CuL}(\text{H}_2\text{O})]^{2+}$ cation is monomeric with a tetradentate neutral ligand and a water molecule coordinated to the Cu atom. There is a small difference between the two independent cations: for one, there is weak interaction between Cu1 and a disordered oxygen atom of a neighboring perchlorate anion, while for Cu2, there is no such interaction. The structure of the cation with the labeling of selected atoms is shown in Fig. 1. Selected bond lengths and angles are

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

<i>Complex 1</i>			
Cu1–O1	1.9371(15)	Cu2–O4	1.9362(15)
Cu1–O2	1.9669(15)	Cu2–O5	1.9677(15)
Cu1–O3	2.2048(17)	Cu2–O6	2.2181(18)
Cu1–N3	2.0385(18)	Cu2–N9	2.0286(18)
Cu1–N4	1.9692(18)	Cu2–N10	1.9827(18)
Cu1...O12	2.813(6)	Cu2...O15	3.070(2)
O1–Cu1–O2	89.36(6)	O4–Cu2–O5	88.99(6)
O1–Cu1–O3	93.50(7)	O4–Cu2–O6	92.62(7)
O1–Cu1–N4	166.26(7)	O4–Cu2–N10	139.59(7)
N3–Cu1–N4	103.51(7)	N9–Cu2–N10	105.68(7)
O1–Cu1–N3	82.11(7)	O4–Cu2–N9	82.14(7)
<i>Complex 3</i>			
Cu1–O1	1.931(3)	Cu2–O3	1.917(4)
Cu1–O2	1.970(4)	Cu2–O4	1.977(3)
Cu1–N3	2.031(4)	Cu2–N9	2.056(4)
Cu1–N4	1.968(4)	Cu2–N10	1.965(4)
Cu1–Br1	2.7271(9)	Cu2–Br2	2.6791(9)
Cu3–Br3	2.4359(10)	Cu3–Br5	2.5471(11)
Cu4–Br7	2.4659(10)	Cu4–Br5	2.5756(13)
Cu5–Br7	2.3518(10)	Cu5–Br6	2.9939(9)
Cu3...Cu4	2.7126(12)	Cu4...Cu5	2.8351(13)
O1–Cu1–O2	88.94(15)	O3–Cu2–O4	89.80(14)
O1–Cu1–N3	82.87(15)	O3–Cu2–N9	82.38(15)
O1–Cu1–N4	169.04(16)	O3–Cu2–N10	169.22(16)
N3–Cu1–N4	102.92(16)	N9–Cu2–N10	102.37(16)
Br1–Cu1–O1	96.43(11)	Br2–Cu2–O3	96.14(11)
Br1–Cu1–N3	102.34(12)	Br2–Cu2–N9	106.52(12)
Br3–Cu3–Br5	112.96(4)	Br3–Cu3–Br4 ^a	105.33(4)
Br5–Cu4–Br6	102.13(3)	Br3–Cu3–Br5	110.06(4)
Br6–Cu4–Br7	95.99(4)	Br7–Cu4–Br6 ^b	107.48(4)

Symmetry code: *a*, $-x+2, -y+2, -z+1$; *b*, $-x+1, -y+2, -z+1$

Fig. 1 The molecular structure of $[\text{CuL}(\text{H}_2\text{O})]^{2+}$ cations **1** with labeling of selected atoms

listed in Table 2. The copper(II) centers are five-coordinated with a N_2O_3 donor set from the semicarbazone ligand and a water molecule. The coordination spheres of the copper atoms in the complex are best described as distorted square pyramids with the water molecule apical. The Addison parameter τ values are 0.08 (for Cu1) and 0.18 (for Cu2), where the parameter τ is defined as $\tau = (\alpha - \beta)/60$, $\alpha > \beta$, where α and β are the largest angles, with $\tau = 1$ for a regular trigonal bipyramid and $\tau = 0$ for a regular square pyramid [31]. The Cu–O and Cu–N bond lengths in the equatorial plane are in the range of 1.9362(15)–1.9677(15) Å and 1.9692(18)–2.0385(18) Å, respectively (Table 2), which are agreement with similar compound [32–34].

The apical oxygen atoms show longer Cu–O bond lengths (2.2048(17), for Cu1 and 2.2381(18) Å, for Cu2) than the equatorial oxygen atoms [32, 34–36]. The elongation of the Cu–O axial bonds is due to a pseudo-Jahn–Teller distortion of the d^9 copper center. The lengths of the bonds between the copper atoms and the donor atoms are within the range of values normally found for such systems [32, 33, 37–39]. The copper atoms Cu1 and Cu2 are displaced from the basal plane of N_2O_2 by 0.248 and 0.216 Å toward the apical oxygen atom, respectively.

In the first $[\text{CuL}(\text{H}_2\text{O})]^{2+}$ cation, the distance between the copper atom Cu1 and the disordered oxygen atom of the perchlorate anion (O12, with an occupancy of 0.4) is 2.813(6) Å (Fig. 2) which is significantly longer than the typical Cu–O covalent bond (1.98 Å), but it is shorter than the sum of the van der Waals radii (2.92 Å) [39]. This distance is within the range of 2.2–2.9 Å, known for axial Cu–O bonds [40, 41] and hence suggests that the oxygen of the perchlorate anion may weakly coordinate to the copper ion in an axial position.

Fig. 2 The contacts between copper ion and the disordered oxygen atom of the perchlorate anion in complex 1

For the second cation, the shortest $\text{Cu2}\cdots\text{O}(\text{perchlorate anion})$ distance is 3.070(2) Å ($\text{Cu2}\cdots\text{O15}$), which indicates the absence of any interaction between the copper center and perchlorate anion.

The oxygen atoms of the perchlorate anions are involved in intramolecular and intermolecular hydrogen bonding interaction with the hydrogen atoms of the coordinated water molecule, NH and NH_2 groups of semicarbazone ligand. Also, there is an intermolecular hydrogen bonding between the hydrogen atoms of the NH_2 groups of the semicarbazone ligand and the oxygen atom of a neighboring amide. Full details of the hydrogen bonding are given in Table 3.

Description of the complex 3

Suitable crystals of complex 3 for X-ray structure studies were obtained from methanol/2-propanol. The complex crystallized in the monoclinic space group $P2_1/n$. The crystallographic asymmetric unit consists of two independent $[\text{CuLBr}]^+$ cations (copper centers labeled with Cu1 and Cu2) and a $(\text{Cu}_3\text{Br}_5)^{2-}$ anion (copper centers labeled with Cu3, Cu4 and Cu5). The anions link to one another to form an infinite one-dimensional $(\text{Cu}_3\text{Br}_5^{2-})_n$ chain.

The molecular structure of the complex with the labeling of selected atoms is shown in Figs. 3 and 4. Selected bond lengths and angles are listed in Table 2.

The $[\text{CuLBr}]^+$ cations of complex 3 show copper(II) centers which are five-coordinated, with a N_2O_2 donor set from the semicarbazone neutral ligand and a apical Br^- anion. The Addison parameters, τ , are 0.20 and 0.25 for Cu1 and Cu2, respectively, which indicates a distorted square pyramid geometry. Cu1 and Cu2 are displaced from the basal plane of N_2O_2 by 0.257 and 0.282 Å toward the apical Br anion, respectively. The Cu–Br bond lengths are 2.7271(9) and 2.6791(9) Å for Cu1 and Cu2, respectively.

The Cu–O and Cu–N bond lengths in the equatorial plane are in the range of 1.917(4)–1.977(3) Å and 1.965(4)–2.056(4) Å, respectively, which are very similar to the corresponding distances in 1 (Table 2) and are in good agreement with analogous Cu(II) complexes observed in the literature [32–34].

In the $(\text{Cu}_3\text{Br}_5)^{2-}$ anion, each Cu(I) is bridged to two adjacent Cu by four Br^- anions. The Cu(I) center adopts a tetrahedral geometry with four Br^- ligands. The Br–Cu–Br bond angles are in the range 95.99(4)–123.60(4)°. The geometries of the copper atoms are best described as a tetrahedral with τ_4 index 0.93, 0.90 and 0.74 for Cu3, Cu4 and Cu5, respectively. The parameter τ is defined as $\tau_4 = [360^\circ - (\alpha + \beta)]/141^\circ$, where a and b 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 [42]. On the basis of the mode coordination of the Br^- ligands (μ_2 -bridging and μ_3 -bridging), there are three

Table 3 Hydrogen bonding (Å) and angles (°) for complex **1**

D–H···A	D–H	H···A	D···A	D–H···A	Symmetry code
O3–H1···O8*	0.72(4)	2.10(4)	2.798(3)	165(4)	$-x+3/2, y-1/2, -z+3/2$
O3–H2···O10*	0.72(4)	2.15(4)	2.800(3)	152(4)	$-x+3/2, y-1/2, -z+3/2$
O3–H2···O23	0.77(4)	2.02(4)	2.793(3)	175(4)	
N1–H3···O4*	0.78(4)	2.39(4)	3.036(3)	141(3)	$-x+3/2, y+1/2, -z+1/2$
N1–H4···O9*	0.83(3)	2.32(3)	3.004(3)	139(3)	$-x+3/2, y+1/2, -z+1/2$
N1–H4···O11*	0.83(3)	2.41(3)	3.212(3)	161(3)	$-x+3/2, y+1/2, -z+1/2$
N2–H5···O13*	0.83(3)	2.29(3)	3.09(3)	163(3)	$-x+3/2, y+1/2, -z+1/2$
N5–H6···O22*	0.78(3)	2.10(3)	2.832(3)	157(3)	$-x+3/2, y+1/2, -z+3/2$
N6–H7···O22*	0.85(3)	2.41(3)	3.105(3)	140(3)	$-x+3/2, y+1/2, -z+3/2$
N6–H7···N24*	0.85(3)	2.38(3)	2.903(3)	120(2)	$x-1/2, -y+1/2, z+1/2$
N6–H8···N21*	0.73(3)	2.35(3)	3.067(3)	166(3)	$-x+3/2, y+1/2, -z+3/2$
O6–H9···O19	0.81(3)	2.20(3)	2.967(3)	160(3)	
O6–H9···O28	0.81(3)	2.11(3)	2.725(3)	133(3)	
O6–H10···O16	0.77(3)	2.20(3)	2.871(3)	147(3)	
N7–H11···O1*	0.82(3)	2.34(3)	3.028(3)	142(3)	$-x+1, -y+1, -z+1$
N7–H11···O2*	0.82(3)	2.55(3)	3.110(3)	127(3)	$-x+1, -y+1, -z+1$
N7–H12···O21*	0.86(3)	2.19(3)	2.981(3)	154(3)	$x-1/2, -y+1/2, z-1/2$
N8–H13···O18*	0.78(3)	2.25(3)	2.982(3)	159(3)	$x-1/2, -y+1/2, z-1/2$
N8–H13···O26*	0.78(3)	2.39(3)	3.074(3)	148(3)	$x-1/2, -y+1/2, z-1/2$
N8–H13···O27*	0.78(3)	2.55(3)	3.023(3)	120(3)	$-x+3/2, y+1/2, -z+1/2$
N11–H14···O14*	0.84(3)	2.10(3)	2.921(3)	166(3)	$x-1/2, -y+1/2, z+1/2$
N12–H15···O17*	0.81(3)	2.08(3)	2.884(3)	171(3)	$x-1/2, -y+1/2, z+1/2$
N12–H16···O8	0.78(3)	2.31(3)	3.055(3)	160(3)	
N12–H16···O11	0.78(3)	2.26(3)	3.013(3)	161(3)

Fig. 3 The molecular structure of $[\text{CuLBr}]^+$ cations **3** with labeling of selected atoms

types of Cu(I) atoms, i.e., $[\text{Cu}_3(\mu_2\text{-Br})_3(\mu_3\text{-Br})]$, $[\text{Cu}_4(\mu_2\text{-Br})_2(\mu_3\text{-Br})_2]$ and $[\text{Cu}_5(\mu_2\text{-Br})(\mu_3\text{-Br})_3]$. The average Cu- μ_3 -Br distance is 2.643 Å which is slightly longer than the Cu- μ_2 -Br distance (2.450 Å). The distances between adjacent Cu-centers in the $(\text{Cu}_3\text{Br}_5)^{2-}$ anion are 2.7126(12)

Å for Cu3···Cu4 and 2.8351(13) Å for Cu4···Cu5, which show no indication of attractive interactions between Cu-centers [43]. A fragment of the polymeric structure of the $(\text{Cu}_3\text{Br}_5)^{2-}$ anion is shown in Fig. 4, and the bond lengths and valence angles are given in Table 2.

Fig. 4 The molecular structure of the $(\text{Cu}_3\text{Br}_5)^{2-}$ anion in **3** with labeling of selected atoms

Fig. 5 Hirshfeld surface mapped with d_{norm} for complexes **1** (a) and **3** (b)

Hirshfeld surface analysis

The Hirshfeld surface analysis and the fingerprint plots provide some useful quantitative information about the strength and role of the hydrogen bonds and other intermolecular contacts in the crystal packing. In Fig. 5, the 3D Hirshfeld surface mapped is shown over a d_{norm} range of -0.512 – 1.471 and -0.512 – 1.350 Å for **1** and **3**, respectively. The surface is shown as transparent to allow visualization of the molecular moiety. The circular depressions (deep red) visible on the surfaces are indicative of hydrogen bonding contacts, and the other color spots are indicative of the presence of other intermolecular interactions in the crystal packing. The 2D fingerprint plot and the contribution of each type of interaction for **1** and **3** are described in Fig. 6. The main intermolecular interaction in **1** are O/H (64.1%) and H/H (19.3%) and in **2** are Br/H (31.7%) and H/H (25.8%), which correspond to hydrogen bonds and the Van der Waals interactions.

Conclusion

A novel the tetradentate neutral ligand semicarbazone has been synthesized, and its coordination with different copper(II) salt has been studied. The crystal structures of two complexes have been determined by single-crystal X-ray diffraction analyses. The structures of the complexes are influenced by the anions that are present. When Cl and Br anions were used, the anion can act as a ligand, and $[\text{CuLX}]^+$ ($\text{X}=\text{Cl}$ and Br) cationic complexes were isolated. However, when the Br anion was used, copper(II) could be reduced to copper(I), and a $\text{Cu}_3\text{Br}_5^{2-}$ species could also be formed. When nitrate and perchlorate anions were used, a $[\text{CuLH}_2\text{O}]^{2+}$ cation complex was formed, and the nitrate and

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

perchlorate act as a counter ions. The X-ray single crystal shows that the complexes **1** and **3** have square pyramidal geometry.

The Hirshfeld surface analysis was employed for **1** and **3**, allowing quantification of the various interactions within the structures.

Acknowledgements The authors are grateful to the Yazd University and the Australian National University for partial support of this work.

References

- D.G. Calatayud, E. López-Torres, M.A. Mendiola, *Polyhedron* **101**, 133 (2015)
- S. Janardan, P. Suman, G. Swapna, A. Amrita, R. Priya, R. Siva, K. Vijayakrishna, A. Sivaramakrishna, *Appl. Biochem. Biotechnol.* **173**, 596 (2014)
- S. Prasad, R.K. Agarwal, A. Kumar, *J. Iran. Chem. Soc.* **8**, 825 (2011)
- R. Vafazadeh, N. Abdollahi, A.C. Willis, *Acta Chim. Slov.* **64**, 409 (2017)
- T.A. Reena, E.B. Seená, M.R.P. Kurup, *Polyhedron* **27**, 3461 (2008)
- E. López-Torres, D.G. Calatayud, C.J. Pastor, M.A. Mendiola, *Polyhedron* **27**, 2507 (2008)
- A.A. Abou-Hussen, W. Linert, *Synth. React. Inorg.* **39**, 570 (2009)
- H. Chen, X.Q. Ma, Y. Lv, L. Jia, J. Xu, Y. Wang, Z. Ge, *J. Mol. Struct.* **1109**, 146 (2016)
- V. Jevtovic, D. Cvetkovic, D. Vidovic, *J. Iran. Chem. Soc.* **8**, 727 (2011)
- R. Vafazadeh, N. Hasanzade, M.M. Heidari, A.C. Willis, *Acta Chim. Slov.* **62**, 122 (2015)
- S. Hasnain, M. Zulfequar, N. Nishat, *J. Coord. Chem.* **64**, 952 (2011)
- V.L. Siji, M.R. Sudarsanakumar, S. Suma, *Polyhedron* **29**, 2035 (2010)
- R. Vafazadeh, A.C. Willis, *Acta Chim. Slov.* **63**, 186 (2016)
- S. Chandra, Sangeetika, S. Thakur, *Transit. Met. Chem.* **29**, 925 (2004)
- E. López-Torres, U. Abram, *Inorg. Chem.* **47**, 2890 (2008)
- R.N. Butler, A.B. Hanahoe, A.M. O'Donohue, *J. Chem. Soc. Perkin Trans.* **1**, 1246 (1979)
- W. Caminati, J.U. Grabow, *J. Am. Chem. Soc.* **128**, 854 (2006)
- R. Vafazadeh, M. Alinaghi, A.C. Willis, A. Benvidi, *Acta Chim. Slov.* **61**, 121 (2014)
- R. Vafazadeh, F. Jafari, M.M. Heidari, A.C. Willis, *J. Coord. Chem.* **69**, 1313 (2016)
- Z. Otwinowski, W. Minor, in *Methods in Enzymology*, ed. by C.W. Carter Jr., R.M.W. Sweet (Academic Press, New York, 1997), pp. 307–326
- A. Altomare, G. Cascarano, G. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.* **27**, 435 (1994)
- P.W. Betteridge, J.R. Carruthers, R.I. Cooper, K. Prout, D.J. Watkin, *J. Appl. Cryst.* **36**, 1487 (2003)
- K. Wolff, D.J. Grimwood, J.J. McKinnon, M.J. Turner, D. Jayatilaka, M.A. Spackman, *CrystalExplorer*, Version 3.0. University of Western Australia (2012)
- R. Vafazadeh, R. Esteghamat-Panah, A.C. Willis, A.F. Hill, *Polyhedron* **48**, 51 (2012)
- J. Patole, S. Dutta, S. Padhye, E. Sinn, *Inorg. Chim. Acta* **318**, 207 (2001)
- L.C. Nathan, J.E. Koehne, J.M. Gilmore, K.A. Hannibal, W.E. Dewhurst, T.D. Mai, *Polyhedron* **22**, 887 (2003)
- R. Vafazadeh, S. Bidaki, *Acta Chim. Slov.* **61**, 153 (2014)
- R. Vafazadeh, S. Bidaki, *Acta Chim. Slov.* **57**, 310 (2010)
- R.D. Hancock, *Acc. Chem. Res.* **23**, 253 (1990)
- M.T.H. Tarafder, A. Kasbollah, K.A. Crouse, A.M. Ali, B.M. Yamin, H.K. Fun, *Polyhedron* **20**, 2363 (2001)
- A.W. Addison, N. Rao, J. Reedijk, J.V. Rijn, G.C. Verschoor, *J. Chem. Soc. Dalton Trans.* **1349**, 1356 (1984)
- R. Vafazadeh, A.C. Willis, *J. Coord. Chem.* **68**, 2240 (2015)
- P. Bhowmik, N. Aliaga-Alcalde, V. Gómez, M. Corbella, S. Chattopadhyay, *Polyhedron* **49**, 269 (2013)
- R. Vafazadeh, Z. Moghadas, A.C. Willis, *J. Coord. Chem.* **68**, 4255 (2015)
- M.-L. Liu, M. Jiang, K. Zheng, Y.-T. Li, Z.-Y. Wu, C.-W. Yan, *J. Coord. Chem.* **67**, 630 (2014)
- J. Lakshmipraba, S. Arunachalam, R. Vijay Solomon, P. Venuvanalingam, *J. Coord. Chem.* **68**, 1374 (2015)
- J. Chakraborty, S. Thakurta, G. Pilet, D. Luneau, S. Mitra, *Polyhedron* **28**, 819 (2009)
- P. Mukherjee, M.G.B. Drew, M. Estrader, C. Diaz, A. Ghosh, *Inorg. Chim. Acta* **361**, 161 (2008)
- B. Cordero, V. Gómez, A.E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Arragán, S. Alvares, *Dalton Trans.* 2832 (2008)
- I.M. Procter, B.J. Hathaway, P. Nicholls, *J. Chem. Soc. A*, 1678 (1968)
- R. Vafazadeh, A. Dehgany-Firouabadi, A.C. Willis, *Acta Chim. Slov.* **64**, 686 (2017)
- P. Seth, S. Ghosh, A. Figuerola, A. Ghosh, *Dalton Trans.* **43**, 990 (2014)
- M. Maekawa, K. Sugimoto, T. Okubo, T. Kuroda-Sowa, M. Munakata, *Polyhedron* **29**, 2807 (2010)