

Scientific paper

Cu(I) Arylsulfonate π -Complexes with 3-Allyl-2-thiohydantoin: The Role of the Weak Interactions in Structural Organization

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Abstract

The present work is directed toward preparation and structural characterization of two novel Cu(I) arylsulfonate π -complexes with 3-allyl-2-thiohydantoin, namely $[\text{Cu}_2(\text{Hath})_4](\text{C}_6\text{H}_5\text{SO}_3)_2$ (**1**) and $[\text{Cu}_2(\text{Hath})_4](p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$ (**2**) (*Hath* = 3-allyl-2-thiohydantoin), obtained by the means of alternating current electrochemical synthesis and studied with X-ray diffraction method. In both structures, the inner coordination sphere is represented by the cationic dimer $[\text{Cu}_2(\text{Hath})_4]^{2+}$ with one crystallographically independent copper(I) atom which has a trigonal pyramidal coordination environment formed by three *Hath* thiogroup S atoms and double C=C bond of its allyl group. $[\text{Cu}_2(\text{Hath})_4]^{2+}$ fragments in both coordination compounds are very similar, despite some divergences such as a big difference in Cu–S distance to the apical S atom (3.0374(8) Å in **1** and 2.7205(9) Å in **2**). This difference was explained by the impact of the system of weak interactions, which are quite different.

Keywords: Copper(I) arylsulfonate; π -complex; thiohydantoin; weak interaction; crystal structure.

1. Introduction

In the last years both 2-thiohydantoin (2-thioximidazolidin-4-ones) and hydantoin core fragments were studied as useful scaffolds in medicinal chemistry due to their synthetic feasibility and versatility of substituents.^{1–5} Moreover, their derivatives are already used in commercially available drugs such as Phenytoin, Dantrolene and Allantoin. The presence of several active chemical groups, as well as simple synthetic route advantages, could make them interesting not only as biologically active compounds but also as compounds of great interest in the chemistry of coordination compounds too. Although, due to the presence of capable for complex compound formation functional groups, 2-thiohydantoin based compounds were

found to have an application in the analytical chemistry as reagents for the determination of several *d*-metals (including Cu and Ag).^{6,7} Despite the small number of such representatives (according to the Cambridge Crystallographic Database only 12 copper coordination compounds with 2-thiohydantoin still known),⁸ it was already investigated that they could have a potential interest as optical materials due to their fluorescence sensing properties and luminescence towards Cu^+ and Cu^{2+} as well as the possibility of successful usage in crystal engineering of organometallics.^{9,10} Moreover, previously, we have shown, that Cu(I) π -complexes with allyl derivatives of heterocycles can possess noticeable non-linear optical properties.^{11–15}

This work is the continuation of our previous studies, in which we have studied the coordination behavior of

3-allyl-2-thiohydantoin (*Hath*) regarding Ag(I), where obtained coordination compounds have already shown interesting structural peculiarities, confirming the status of 2-thiohydantoin-based molecules as the potential ligands in the structural engineering.^{16,17}

2. Experimental

2. 1. General Consideration

Unless otherwise mentioned, all chemicals were obtained from a commercial source (Sigma Aldrich) and used without further purification. The NMR experiments: ¹H NMR (500 MHz), ¹³C{¹H} NMR (125 MHz) spectra for *Hath* were recorded on a Bruker Avance 500 MHz NMR spectrometer. The chemical shifts are reported in ppm relative to the residual peak of the deuterated CD₃OD for the ¹H and ¹³C{¹H} NMR spectra. Carbon, hydrogen, nitrogen and sulfur contents for *Hath*, **1** and **2** compounds were determined using a CHNS elemental analyzer vario EL cube (Elementar) operating in the CHNS mode. The infrared (IR) spectrum for *Hath* was recorded on the Bruker IFS-88 spectrometer as nujol mulls. Diffraction data for **1** and **2** were collected on a Gemini+ diffractometer with Mo K_α radiation (λ = 0.71073 Å) and Atlas CCD detector.

2. 2. Preparation of 3-allyl-2-thioxoimidazolidin-4-one (*Hath*)

Ligand *Hath* was synthesized from allylthiocyanate and glycine at the presence of triethylamine and pyridine, in accordance with the reported method.¹⁶ Yield 57%. M.p. 91–92 °C. Anal. calcd. for C₆H₈N₂OS: C, 46.13; H, 5.16; N, 17.93; S, 20.53; found: C, 45.93; H, 5.44; N, 17.92; S, 20.65.

¹H NMR (500 MHz, CD₃OD) δ, 5.84 p.p.m. (ddt, *J* = 17.1, 10.4, 5.6 Hz, =CH), 5.18 p.p.m. (ddd, *J* = 17.1, 2.9, 1.5 Hz, 1H, CH₂=), 5.14 p.p.m. (ddd, *J* = 10.5, 2.5, 1.0 Hz, 1H, -CH₂=), 4.38 p.p.m. (dt, *J* = 5.6 Hz, 1.5 2H, CH₂), 4.14 (s, 2H, CH₂).

¹³C{¹H} NMR (125 MHz, CD₃OD) δ, p.p.m. 185.74 p.p.m. (-C=S), 174.17 p.p.m. (-C=O), 132.62 p.p.m. (=CH), 117.94 p.p.m. (CH₂=), 49.48 p.p.m. (CH₂), 43.80 p.p.m. (CH₂).

IR (nujol, cm⁻¹): 3488 (w), 3225 (s), 3091 (w), 3011 (vw), 1864 (vw), 1751 (vs), 1650 (m), 1524 (vs), 1431 (vs), 1367 (w), 1344 (vs), 1306 (s), 1289 (w), 1260 (s), 1176 (vs), 1106 (m), 1048 (m), 1029 (m), 994 (m), 977 (w), 930 (s), 893 (m), 755 (vw), 719 (w), 700 (vs), 610 (m), 581 (m), 563 (m), 541 (m), 515 (m), 474 (m), 440 (vw).

2. 3. Preparation of Complexes

2. 3. 1. Preparation of [Cu₂(*Hath*)₄](C₆H₅SO₃)₂ (**1**)

To the solution of Cu(C₆H₅SO₃)₂·6H₂O (0.157 g, 0.4 mmol) in 4.5 ml of *n*-propanol 0.156 g (1 mmol) of 3-allyl-

2-thiohydantoin (*Hath*) was added and obtained mixture was stirred. The resulting orange-brown solution was placed into a 5 mL test tube and then copper-wire electrodes in cork were inserted. The inner mixture in the obtained cell was subjected to alternating-current electrochemical recovery (0.6 V, 50 Hz) for 5 days.¹⁸ Crystals **1**, suitable for X-ray diffraction studies, were formed on copper wires while maintaining this reactor for 2 weeks at -3 °C. Yield 35%. M.p. 128 °C. Anal. calcd. for C₁₈H₂₁CuN₄O₅S₃: C, 40.55; H, 3.97; N, 10.51; S, 18.04; found: C, 40.08; H, 3.72; N, 10.67; S, 17.86.

2. 3. 2. Preparation of [Cu₂(*Hath*)₄](*p*-CH₃C₆H₄SO₃)₂ · 2H₂O (**2**)

To 5 ml of a solution of 0.198 g (0.4 mmol) of Cu(*p*-CH₃C₆H₄SO₃)₂ · 6H₂O in *n*-propanol was added 0.156 g (1 mmol) of 3-allyl-2-thiohydantoin (*Hath*) and stirred. The resulting orange-brown solution was placed into a 5 mL test tube and then copper-wire electrodes in cork were inserted. The inner mixture in the obtained cell was subjected to alternating-current electrochemical recovery (0.6 V, 50 Hz) during 2 days. Crystals **2**, suitable for X-ray diffraction studies, were formed on copper wires. Yield 43%. M.p. 113 °C. Anal. calcd. for C₁₉H₂₅CuN₄O₆S₃: C, 40.38; H, 4.46; N, 9.91; S, 17.02; found: C, 40.17; H, 4.34; N, 9.86; S, 17.21.

2. 4. X-Ray Crystal Structure Determination

The collected data for **1** & **2** were processed with CrysAlis Pro program.¹⁹ The structures were solved by dual-space algorithm using SHELXT and refined by least squares method on *F*² by SHELXL-2014 with the following graphical user interfaces of OLEX^{2.20–22}. Atomic displacements for non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The figures were prepared using DIAMOND 3.1 software. Crystal parameters, data collection and the refinement parameters are summarized in Table 1.

3. Results and Discussion

π-Complex [Cu₂(*Hath*)₄](C₆H₅SO₃)₂ (**1**) forms triclinic crystals in the centrosymmetric space group *P* $\bar{1}$. This compound is composed of the centrosymmetric cationic [Cu₂(*Hath*)₄]²⁺ dimers (Fig. 1) with one crystallographically independent Cu atom and outer coordination sphere represented by benzenesulfonate anions. Cu(I) atom in **1** has a trigonal pyramidal coordination environment (geometric index τ₄ = 0.80).²³ Sulfur atom and C5A=C6A olefine group from one *Hath* moiety and S centre from another ligand unit form basal plane of the metal ion coordination

Table 1. Selected crystal data and structure refinement parameters of **1** and **2**.

| | [Cu ₂ (Hath) ₄] (C ₆ H ₅ SO ₃) ₂ (1) | [Cu ₂ (Hath) ₄] (CH ₃ C ₆ H ₄ SO ₃) ₂ × 2H ₂ O (2) |
|--|--|--|
| Formula weight (g·mol ⁻¹) | 533.11 | 565.15 |
| Crystal system and space group | Triclinic, <i>P</i> $\bar{1}$. | Triclinic, <i>P</i> $\bar{1}$. |
| <i>a</i> (Å) | 9.1664(6) | 9.4494(3) |
| <i>b</i> (Å) | 10.7387(6) | 10.3035(4) |
| <i>c</i> (Å) | 12.4008(6) | 14.4419(6) |
| α (°) | 93.096(4) | 94.228(3) |
| β (°) | 95.581(5) | 94.821(3) |
| γ (°) | 114.254(6) | 116.983(4) |
| <i>V</i> (Å ³) | 1101.71(12) | 1238.64(9) |
| <i>Z</i> | 2 | 2 |
| <i>D</i> (g/cm ³) | 1.607 | 1.515 |
| μ (mm ⁻¹) | 1.31 | 1.18 |
| <i>F</i> (000) | 548 | 584 |
| Crystal size (mm) | 0.53 × 0.42 × 0.34 | 0.60 × 0.36 × 0.25 |
| Crystal colour | colourless | colourless |
| Temperature of the data collections (K) | 150(2) | 150(2) |
| θ range for data collection (°) | 3.7 – 28.9 | 3.5–28.8 |
| | –12 ≤ <i>h</i> ≤ 9 | –11 ≤ <i>h</i> ≤ 11 |
| Index ranges | –14 ≤ <i>k</i> ≤ 13 | –13 ≤ <i>k</i> ≤ 13 |
| | –16 ≤ <i>l</i> ≤ 16 | –19 ≤ <i>l</i> ≤ 18 |
| Measured reflections | 7786 | 8562 |
| Independent reflections | 4534 | 5143 |
| Reflections with <i>I</i> > 2 σ (<i>I</i>) | 3954 | 4274 |
| Refined parameters | 288 | 302 |
| <i>R</i> _{int} | 0.022 | 0.024 |
| <i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)] | 0.038 | 0.047 |
| <i>wR</i> (<i>F</i> ²) | 0.091 | 0.132 |
| $\Delta\rho_{\max}/\Delta\rho_{\min}$ (e/Å ³) | 1.11, –0.65 | 1.04, –0.78 |

Table 2. Selected bond lengths (Å) and angle values (°) in **1** and **2**.

| | 1 | 2 |
|--------------------------|--------------|-----------|
| Bond | <i>d</i> , Å | |
| Cu1–S1 | 2.2573(8) | 2.2785(8) |
| Cu1–S2 | 2.2556(7) | 2.2644(9) |
| Cu1–S1 ^X | 3.0374(8) | 2.7205(9) |
| Cu1– <i>m</i> * | 1.978(3) | 1.994(3) |
| C5A–C6A | 1.361(4) | 1.363(5) |
| Angles | ω , ° | |
| S2–Cu1–S1 | 112.97(3) | 112.06(3) |
| S1–Cu1–S1 ^{X**} | 97.04(3) | 97.21(3) |
| <i>m</i> –Cu1–S1 | 117.03(8) | 116.37(3) |
| <i>m</i> –Cu1–S2 | 129.53(8) | 128.32(3) |

m* – middle point of C5A–C6A bond; **S1^X – S1ⁱ atom for **1 and S1ⁱⁱ atom for **2** Symmetry codes: (i) 1–*x*, 2–*y*, 1–*z*; (ii) 2–*x*, 1–*y*, 1–*z*.

sphere, and sulfur atom from one more *Hath* molecule is located at the apical position. The distance to the apical sulfur atom Cu1–S1ⁱ is equal to 3.0374(8) Å and is significantly greater than Cu–S distances to the equatorial S1 and S2 atoms (Table 2).

In the mentioned cationic fragment [Cu₂(Hath)₄]²⁺ there are two crystallographically independent molecules of organic ligand *Hath*. One of them is coordinated to the Cu atom by the thiogroup S1 atom and double C=C bond of the allyl group. Thus, the first ligand molecule possesses a bidentate chelate function, forming a seven-membered {C₄NSCu} cycle. The aforementioned S1 atom of the first ligand is also coordinated to the Cu1ⁱ atom, and, due to the centrosymmetry of the structure, a flat four-membered {Cu₂S₂} cycle with a S1–Cu1–S1ⁱ angle of 97.04(3)° is formed. Second ligand molecule is coordinated to the Cu1 atom only through its S2 atom, complementing copper's coordination number to four. Accordingly – allyl group of the second ligand molecule doesn't participate in the metal bonding and is freely located in the crystal structure with anticlinal conformation (119.8(3)°) relative to the C4B–C5B bond.

The structure of the complex [Cu₂(Hath)₄](*p*-CH₃C₆H₄SO₃)₂ · 2H₂O (**2**) is quite similar to the structure **1**. It has similar cationic [Cu₂(Hath)₄]²⁺ fragments, but the outer coordination sphere is filled with *p*-toluenesulfonate anions and water molecules (Fig. 3). Regarding the cationic fragment, the main differences are in the noticeable shortening of the Cu–S distance to the apical atom

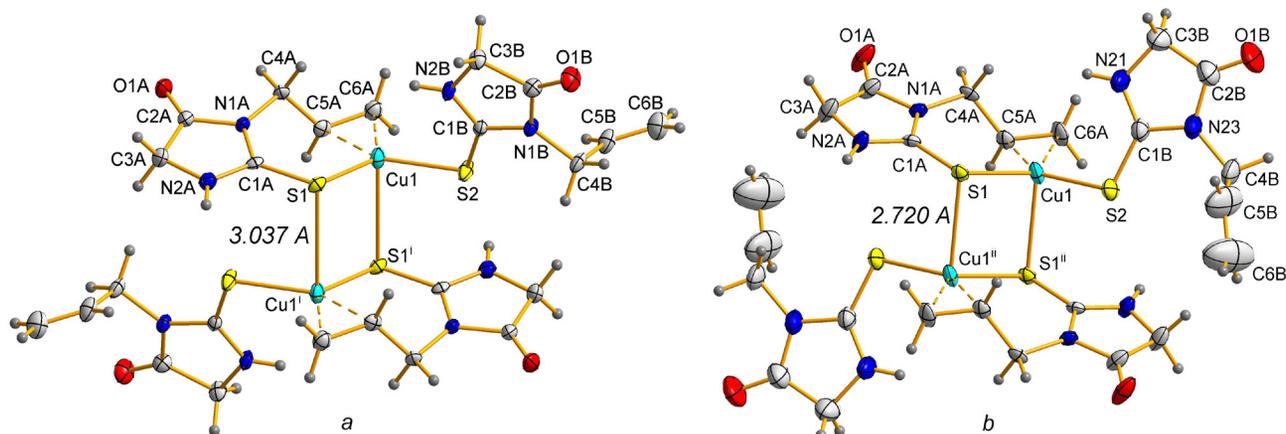


Figure 1. Cationic fragment $[\text{Cu}_2(\text{hath})_4]^{2+}$ in the structures **1** (a) and **2** (b). Symmetry codes: (i) $1-x, 2-y, 1-z$; (ii) $2-x, 1-y, 1-z$.

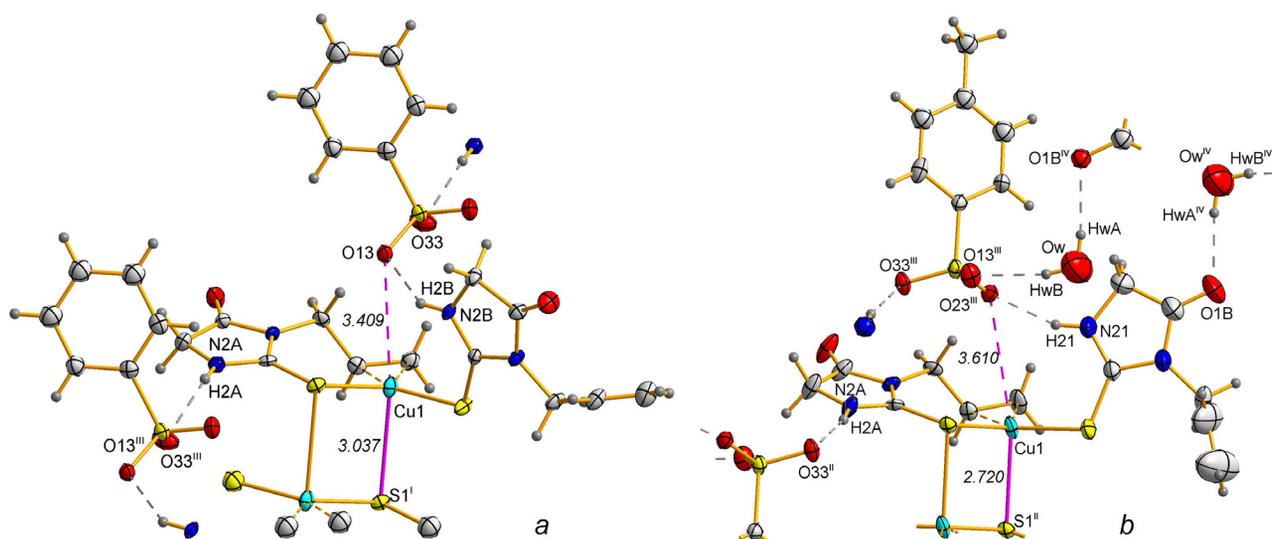


Figure 2. Systems of weak bonding in the structure **1** (a) and **2** (b). Symmetry codes: (i) $1-x, 2-y, 1-z$; (ii) $2-x, 1-y, 1-z$; (iii) $x-1, y, z$; (iv) $1-x, -y, -z$.

(2.7205(9) Å in **2** compared to 3.0374(8) Å in **1**) (Table 2) and a slightly different conformation of the uncoordinated ligand molecule, in particular, the torsion angle N23–C4B–C5B–C6B is equal to 142.6(7)° (in contrast to 119.8(3)° in **1**). These differences can be explained, taking into account some features of the differences in the outer coordination sphere (Fig 2).

Benzenesulfonate anions are located in the outer coordination sphere and take part in the formation of weak bonding in the structure **1**. Two out of three oxygen atoms of the same anion (O13 and O33) participate in N–H...O

bonding (Table 3, Fig. 2) with N–H groups of different cationic fragments, connecting them into infinite H-bonded chain (Fig 3). Also, one of the oxygen atoms of $\text{C}_6\text{H}_5\text{SO}_3^-$ anion (O13) forms a weak Cu–O contact with a bond length of 3.409(5) Å. Nevertheless, this distance is noticeably longer than the sum of van der Waals radii of Cu and O by Bondi (2.92 Å),^{24,25} it is still less than the corresponding value according to both Batsanov and Alvarez studies – namely 3.55 Å and 3.88 Å respectively.^{26,27}

The system of hydrogen bonding in **2** is much more complicated than in **1** due to the presence of the water

Table 3. Geometry of selected hydrogen bonds in **1**.

| Atoms involved D–H...A | Distances, Å | | | Angle, deg D–H...A |
|------------------------------|--------------|-------|----------|-----------------------|
| | D...H | D...A | H...A | |
| N2A–H2A...O33 ⁱⁱⁱ | 0.86 | 1.99 | 2.743(3) | 146 |
| N2B–H2B...O13 | 0.86 | 2.01 | 2.774(3) | 148 |

Symmetry code: (iii) $x-1, y, z$.

Table 4. Geometry of selected hydrogen bonds in **2**.

| Atoms involved D–H...A | Distances, Å | | | Angle, deg D–H...A |
|---|--------------|-------|----------|-----------------------|
| | D...H | H...A | D...A | |
| N21–H21...O23 ⁱⁱⁱ | 0.88 | 1.93 | 2.761(4) | 156 |
| N2A–H2A...O33 ⁱⁱ | 0.88 | 1.91 | 2.764(3) | 164 |
| O _w –H _w A...O1B ^{iv} | 0.85 | 2.00 | 2.841(6) | 173 |
| O _w –H _w B...O13 ⁱⁱⁱ | 0.85 | 2.08 | 2.914(5) | 168 |

Symmetry codes: (ii) 2–x, 1–y, 1–z; (iii) x–1, y, z; (iv) 1–x, –y, –z.

molecule (Table 4, Fig 3). As one of the results of its presence in **2** all three anion's O atoms participate in a formation of hydrogen bonding – two of them (O23 and O33) form N–H...O bonding, like in **1**, and the third one (O13) is connected with water molecule H_wB atom. Second water hydrogen H_wA atom is involved in O_w–H_wA...O1B^{iv} H-bonding with carbonyl C=O *Hath* group. As a result of all bonding, 2D H-bonded net is formed (Fig 3). Also, like in **1**, there is a weak Cu–O bonding but in structure **2**, the corresponding distance is noticeably greater and is equal to 3.610(3) Å, which is still less than the sum of van der Waals radii by Alvarez (3.88 Å).

As it was shown before, Cu1–S1^X distance to the apical S1^X atom (X = *i* in **1** and *ii* in **2**) is noticeably different in these two structures. Moreover, since all other distances and angles within the coordination environment of Cu atom are almost the same (Table 2) as well as a composition of the cationic fragment, it can be concluded that the cause of these differences should be found in the outer coordination sphere. As a possible reason, we would like to introduce the confrontation of Cu–S bonding and Cu–O weak interaction. One can notice that in **1** structure Cu–S interaction is weaker (3.0374(8) Å) in comparison with **2** (2.7205(9) Å) and vice versa – Cu–O interaction in **1** is

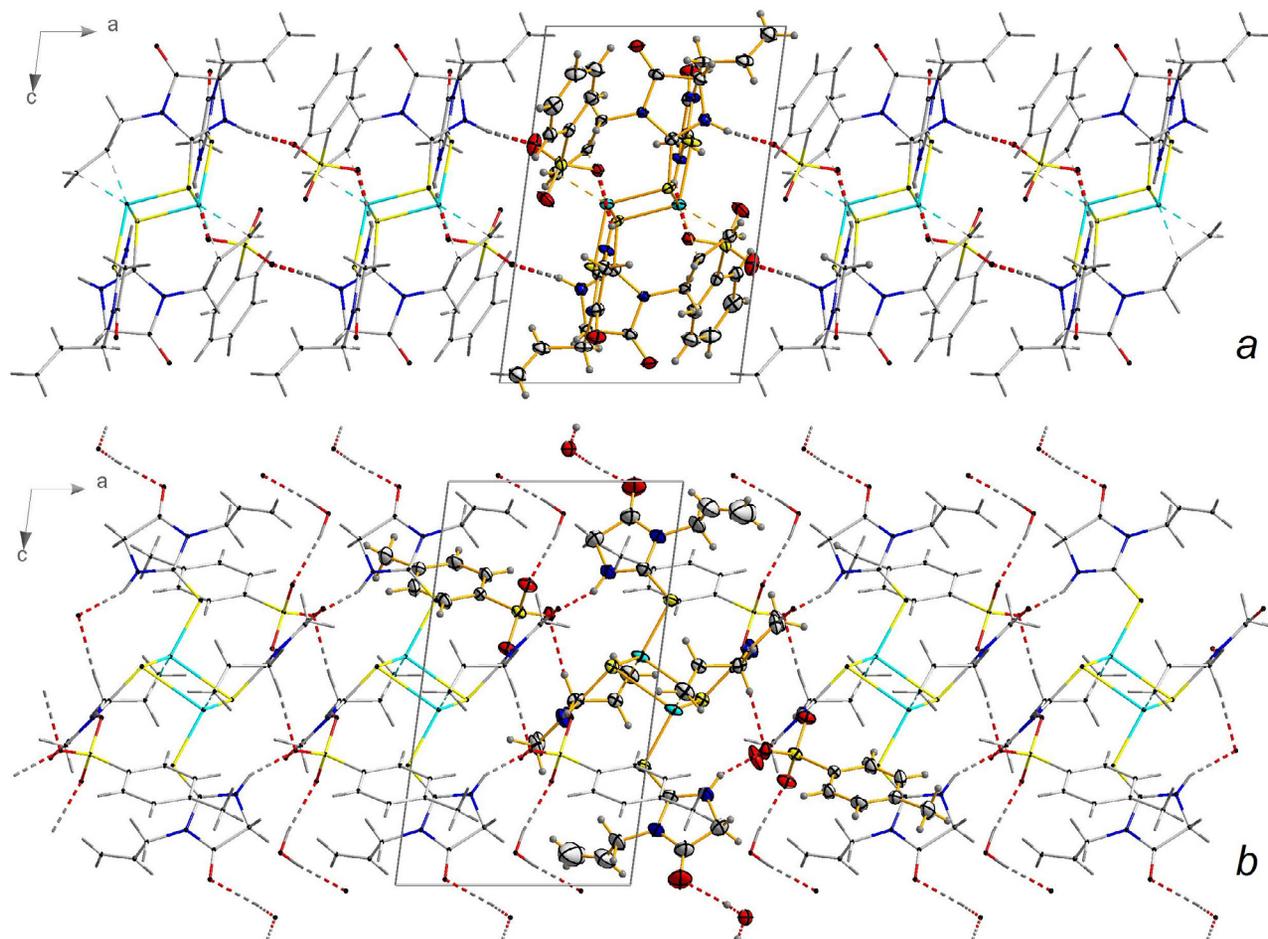


Figure 3. 1D H-bonded chain in **1** (a) and 2D H-bonded net in **2** (b).

stronger (3.409(3) Å) than in **2** (3.610(3) Å) (Fig 2). In our previous works we have shown an impact of a weak interactions, including hydrogen bonding, on the structural organization in π -complex compounds.^{28–30} The weakening of the Cu–O interaction in **2** (and the strengthening of Cu–S as a result) can be explained by the fact, that the anion in **2** is involved in a larger number of the H-bonding, due to the presence of the water molecule, all of which competes with the Cu–O interaction. Finally, since the water was presented in both reaction mixtures, but co-crystallized only in **2**, its presence in its crystal structure should be explained by the different character of benzene- and *p*-toluenesulfonate anions.

In our previous works we have synthesized a series of Ag(I) arylsulfonates coordination compounds with *Hath* possessing a completely different geometry and more complicated geometry, namely $[\text{Ag}_2(\text{Hath})_4(\text{C}_6\text{H}_5\text{SO}_3)_2] \cdot 0.5\text{C}_3\text{H}_7\text{OH}$, $[\text{Ag}_2(\text{Hath})_4(\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2]$ and $[\text{Ag}_2(\text{Hath})(\text{ath})(\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)]$.^{16,17} In the first two coordination compounds, a complex coordination chain is formed, within which there are three crystallographically independent Ag(I) atoms with different coordination environments (tetragonal pyramidal, seesaw and distorted octahedral), four crystallographically independent molecules of *Hath* ligand and two anions of benzene- or toluenesulfonate. The *Hath* molecule is coordinated exclusively through the S atom of the thiogroup, which is bonded to several metal centers simultaneously. In complex $[\text{Ag}_2(\text{Hath})(\text{ath})(\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)]$, part of the molecules of 3-allyl-2-thiohydantoin is in the deprotonated form (*ath*). In all these three compounds double bonds of allyl groups have stayed unbounded. The lack of coordination of the 2-thiohydantoin ligand C=C by the double bond of the allyl group in the case of Ag(I) complexes in contrast to Cu(I) ones, can be explained by the greater philicity of the Ag(I) atom to the exocyclic Sulfur atom, which in case of Ag(I) complexes tend to be bonded with a maximal amount of Ag(I) atoms.

4. Conclusions

Two novel copper(I) π -complexes $[\text{Cu}_2(\text{Hath})_4](\text{C}_6\text{H}_5\text{SO}_3)_2$ (**1**) and $[\text{Cu}_2(\text{Hath})_4] \cdot 2\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3 \cdot 2\text{H}_2\text{O}$ (**2**) (*Hath* = 3-allyl-2-thiohydantoin) were synthesized and characterized by the X-ray diffraction method. Both structures contain centrosymmetric cationic dimer $[\text{Cu}_2(\text{Hath})_4]^{2+}$ in which Cu(I) atom has a trigonal pyramidal coordination environment. In contrast to $\text{Ag}(\text{C}_6\text{H}_5\text{SO}_3)$ & $\text{Ag}(\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)$ complexes, in which Ag(I) prefers to be bound with ligand by S-atom only, copper(I) coordination environment in **1** & **2** includes both ligand's exocyclic sulfur atom and allylic C=C bond. Nevertheless, both $[\text{Cu}_2(\text{Hath})_4]^{2+}$ are very similar, there are some differences, including the difference in the Cu1–S1^X distance (3.0374(8) Å in **1** and 2.7205(9) Å in **2**). As a possi-

ble explanation, the confrontation of Cu–S and Cu–O weak interaction was proposed. Due to this model this difference is explained by the fact, that the anion in **2** is involved in a larger number of the H-bonding, due to the presence of the water molecule in it, and acts on Cu(I) atom weaker than in **1**.

Supplementary material

CCDC numbers 1997084 (**1**) and 1997085 (**2**) contains the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on applications to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +(1223)336–033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

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Povzetek

V tem delu je predstavljena sinteza in strukturna karakterizacija dveh novih Cu(I) arilsulfonatnih π -kompleksov z 3-alil-2-tiohidantoinom, in sicer $[\text{Cu}_2(\text{Hath})_4](\text{C}_6\text{H}_5\text{SO}_3)_2$ (**1**) in $[\text{Cu}_2(\text{Hath})_4](p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3)_2 \cdot 2\text{H}_2\text{O}$ (**2**) (*Hath* = 3-alil-2-tiohidantoin). Spojini smo pridobili z elektrokemijsko sintezo s spremenljivim tokom in preučevali z rentgensko difrakcijo. V obeh spojinah je notranja koordinacijska sfera sestavljena iz kationskega dimera $[\text{Cu}_2(\text{Hath})_4]^{2+}$ z enim kristalografsko neodvisnim Cu(I) atomom ki ima trigonalno piramidalno okolje ki ga tvorijo trije S atomi iz *Hath* tiokupin in dvojna C=C vez iz alilne skupine. Fragmenti $[\text{Cu}_2(\text{Hath})_4]^{2+}$ so zelo podobni v obeh koordinacijskih spojinah kljub nekaterim odstopanjem, npr. Veliki razliko v razdalji Cu-S do apikalnega S atoma (3.0374(8) Å v **1** in 2.7205(9) Å v **2**). To razliko lahko razložimo z vplivom sistema šibkih interakcij, ki so bistveno različne.



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