

Scientific paper

# Synthesis and Structure of $[\text{Cu}(\text{Hapn})]\text{NO}_3]\text{NO}_3$ , $[\text{Cu}(\text{Hapn})(\text{H}_2\text{O})_2]\text{SiF}_6$ , $[\text{Cu}(\text{Hapn})(\text{H}_2\text{O})\text{BF}_4]\text{BF}_4 \cdot \text{H}_2\text{O}$ and $[\text{Cu}(\text{Hapn})(\text{NH}_2\text{SO}_3)_2]$ $\pi$ -complexes (apn = 3-(prop-2-en-1-ylamino)propanenitrile)

Mykhailo Luk'yanov,<sup>1,\*</sup> Evgeny Goresnik,<sup>2</sup> Vasyl Kinzhybalo,<sup>3</sup>  
 and Marian Mys'kiv<sup>1</sup>

<sup>1</sup> Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya Str., 6, 79005, Lviv, Ukraine

<sup>2</sup> Department of Inorganic Chemistry and Technology, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

<sup>3</sup> Institute of Low Temperature and Structure Research, Okólna 2, Wrocław, 50-422, Poland

\* Corresponding author: E-mail: mishalukianov@gmail.com;

Tel.: +380 32 23 94 506

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## Abstract

Four copper(I)  $\pi$ -complexes:  $[\text{Cu}(\text{Hapn})\text{NO}_3]\text{NO}_3$  (**1**),  $[\text{Cu}(\text{Hapn})(\text{H}_2\text{O})_2]\text{SiF}_6$  (**2**),  $[\text{Cu}(\text{Hapn})(\text{H}_2\text{O})\text{BF}_4]\text{BF}_4 \cdot \text{H}_2\text{O}$  (**3**) and  $[\text{Cu}(\text{Hapn})(\text{NH}_2\text{SO}_3)_2]$  (**4**) were prepared using alternating-current electrochemical technique, starting from alcohol solutions of 3-(prop-2-en-1-ylamino)propanenitrile (apn) titrated with appropriate acid and copper(II) salts ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{CuSiF}_6 \cdot 4\text{H}_2\text{O}$ ,  $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  or  $\text{Cu}(\text{NH}_2\text{SO}_3)_2 \cdot x\text{H}_2\text{O}$ , respectively). Obtained compounds were characterized by single-crystal X-ray diffraction and partially by IR spectroscopy. In the structures of complexes **1**, **2** and **4** Cu(I) cation possesses a tetrahedral environment formed by the C=C bond of one organic cation Hapn, the N atom of cyano group from another Hapn moiety, and two O atoms (from  $\text{NO}_3^-$  anions in **1**, from  $\text{H}_2\text{O}$  molecules in **2**) or N atoms ( $\text{NH}_2\text{SO}_3^-$  anions in **4**). In compound **3** strongly pronounced trigonal-pyramidal coordination environment of Cu(I) is formed by a mid-point of C=C-bond of one Hapn cation, nitrogen atom (of cyano group) of another Hapn unit, O atom of  $\text{H}_2\text{O}$  molecule in the basal plane, and F atom of  $\text{BF}_4^-$  anion at the apical position.

**Keywords:** Copper(I);  $\pi$ -complex; aminonitrile derivative; crystal structure; coordination polymer

## 1. Introduction

For almost two centuries the attention of scientists within different branches has been paid to aminonitriles, ranging from  $\alpha$ -aminonitriles discovered by A. Strecker as far as in 1850,<sup>1</sup> to various  $\beta$ -,  $\gamma$ -,  $\omega$ - aminonitriles obtained in our days.<sup>2</sup> Representatives of this class are well-known not only as versatile intermediates in organic synthesis and in many other reactions,<sup>3,4</sup> but also as reagents for synthesis of heterocyclic compounds,<sup>5</sup> inhibitors of enzymes,<sup>6</sup> precursors of peptides,<sup>7</sup> amino-acids,<sup>8</sup> which, in turn, exhibit antibiotic,<sup>9</sup> antifungal,<sup>10</sup> and other important biological and pharmacological properties.<sup>11,12</sup>

The coordination behaviour of aminonitriles in the complexation reactions with Cu(I) salts can be characteri-

zed on the basis of only several related,<sup>13,14</sup> or closely related,<sup>15</sup> compounds, though the matter under discussion is still relevant. It has been noticed that atoms of Cl or Br compete for space in coordination polyhedron with allyl groups and cyano group in the halide complexes of Cu(I) with diallylaminopropanenitrile (the tertiary amine N-atom is protonated).<sup>16,17</sup> Still one of the two olefin bonds and halide atoms have a priority, and CN-group (as well as the second C=C-bond) does not coordinate to the metal ion.

Generally speaking, there are few ways for apn-moiety to coordinate with Cu ions. Depending on the status (cation or molecular) of 3-(prop-2-en-1-ylamino)propanenitrile the number of active groups for coordination changes, which, in turn, influences the composition of coordination polyhedron of the Cu ion (other ligand moieties, such as sol-

vent molecules or anions, occupy usually the apical position of the coordination polyhedron) and complexity of the arisen inorganic component in a compound: from  $(\text{CuCl})_2$  to  $(\text{Cu}_2\text{Cl}_3)_n^{n-}$ .<sup>16</sup> Thus, being in molecular state, apn is coordinated to Cu with allyl- and amino- group and  $\text{Cl}^-$  in the following sequence ( $\text{C}=\text{C} \geq \text{NH} > \dots$ ), whereas  $\text{C}\equiv\text{N}$ -group is not coordinated. Cationic form of apn provides these groups the same chance to be coordinated with the metal atom:  $\text{C}=\text{C} \geq \text{C}\equiv\text{N} > \text{Hal}$ . In order to study a coordination ability of  $\text{C}=\text{C}$ -bond or  $\text{C}\equiv\text{N}$ -group to the copper atom, the compounds with ionic copper salts have been studied.

Therefore, we have undertaken the synthesis and crystal structure determination of copper(I)- $\pi$ -complexes with 3-(prop-2-en-1-ylamino)propanenitrile.

## 2. Experimental

### 2.1. Synthesis of 3-(prop-2-en-1-ylamino)propanenitrile (apn)

A mixture of 0.15 mol allylamine (11.2 mL) and 0.10 mol acrylonitrile (6.8 mL) was continuously stirred and cooled (5 h, 20 °C) preventing the temperature rising higher than 30 °C,<sup>18</sup> then it was heated for 1 h in a water bath with a reflux condenser at 60 °C. The product (orange liquid) was purified by distillation in a vacuum of a water-jet pump (85 °C /40 mm Hg). The yield of apn was 88% (15 mL). IR (KBr)  $\nu$  3315(w), 3077(m), 2977(m) 2912(s), 2837(s), 2247(s), 1642 (m), 1528(wv), 1465(s), 1419(s), 1118(s), 996(s), 922(vs)  $\text{cm}^{-1}$ .

### 2.2. Preparation of Complexes

Four crystalline copper(I) compounds with 3-(prop-2-en-1-ylamino)propanenitrile were prepared using alternating-current electrochemical syntheses.<sup>19</sup> The density of crystals of **1–4** was determined by the flotation method in a chloroform-bromoform mixture (Table 1).

#### 2.2.1. Preparation of $[\text{Cu}(\text{Hapn})\text{NO}_3]\text{NO}_3$ (**1**)

The apn (4.8 mmol) in 2 mL of ethanol titrated by  $\text{HNO}_3$  to pH 5.5 was mixed with  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (4.3 mmol) in 2 mL of ethanol. The solution was placed into a small test-tube and copper-wire electrodes in cork were inserted. After applying  $U = 0.50$  V of alternating-current tension (frequency 50 Hz,  $I_{\text{init}} = 0.5$  mA) for 16 h a starting coloured solution was discoloured and good quality colourless crystals of **1** appeared on the copper electrodes. Yield of complex **1** was 70%.

#### 2.2.2. Preparation of $[\text{Cu}(\text{Hapn})(\text{H}_2\text{O})_2]\text{SiF}_6$ (**2**)

The same synthesis (frequency 50 Hz,  $U = 0.55$  V,  $I_{\text{init}} = 0.54$  mA), starting from  $\text{CuSiF}_6 \cdot 4\text{H}_2\text{O}$  (3.8 mmol)

and 4 mL of methanolic solution of the apn (4.2 mmol), previously titrated with an aqueous solution of 19%  $\text{H}_2\text{SiF}_6$  to pH 3, resulted in a formation of good quality crystals of **2** in 12 h. Yield of the complex was 95%. IR (Nujol)  $\nu$  3434(vs), 2953(vs), 2846(vs), 2260(w), 1642 (s), 1458(s), 1376(m), 1019(s), 953(w), 728(s)  $\text{cm}^{-1}$ .

#### 2.2.3. Preparation of $[\text{Cu}(\text{Hapn})(\text{H}_2\text{O})\text{BF}_4]\text{BF}_4 \cdot \text{H}_2\text{O}$ (**3**)

Good quality crystals of complex **3** were obtained in a similar way (alternating-current,  $U = 0.65$  V,  $I_{\text{init}} = 0.5$  mA) starting from 4 mL of propanol solution of the 4 mmol of apn (titrated with  $\text{HBF}_4$  to pH = 4) and  $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  (4 mmol). Colourless prismatic crystals of compound **3** appeared on copper wire electrodes after 120 h. The yield was 60%.

#### 2.2.4. Preparation of $[\text{Cu}(\text{Hapn})(\text{NH}_2\text{SO}_3)_2]$ (**4**)

Colourless needle-like crystals of complex **4** appeared from a methanol solution (4 mL) of  $\text{Cu}(\text{NH}_2\text{SO}_3)_2 \cdot x\text{H}_2\text{O}$  (4.1 mmol) and the apn (4.1 mmol) previously titrated with water solution of 50%  $\text{NH}_2\text{SO}_3\text{H}$  to pH 6.5 under conditions of the alternating-current electrochemical technique ( $U = 0.6$  V,  $I_{\text{init}} = 0.4$  mA) during 7 days. A yield of **4** was 65%. IR (KBr)  $\nu$  3787(vw), 3264(w), 2923(m), 2361(s), 1662(w), 1249(vs), 1203(vs), 1055(m), 787(w), 643(vw), 593(vw), 560(vw)  $\text{cm}^{-1}$ .

### 2.3. Crystallography

The experimental details, crystallographic parameters and summaries of the data collection for **1–4** are presented in Table 1. Single crystals of **1–4** were preliminarily studied by the photo-method and then diffraction data were collected on a Rigaku AFC7R (for **1–2**) or KUMA-KM4/CCD (for **3–4**) diffractometers with graphite monochromated  $\text{MoK}_\alpha$  radiation ( $\lambda = 0.71073$  Å). Corrections to the Lorentz and polarization factors were applied to reflection intensities. The X-ray experimental data were processed using the Rigaku Crystal Clear program,<sup>20</sup> for compounds **1** and **2**. The CrysAlisRED program was used for processing the X-ray data for complexes **3** and **4**.<sup>21</sup> An absorption correction was applied by the analytical method.<sup>22</sup> Structures **1–4** were solved using direct methods and light atoms were revealed from the difference Fourier syntheses using the SHELX program package.<sup>23</sup> Full-matrix least-squares refinements based on  $F^2$  were carried out for the positional and thermal parameters of all non-hydrogen atoms. Four fluorine atoms of  $\text{SiF}_6^{2-}$  anion in **2** are split with roughly 50% s.o.f. The hydrogen atoms in structures **1–4** were revealed from the difference Fourier syntheses and refined in the riding model along with the non-hydrogen atoms (fixed C–H distances and with  $U_{\text{iso}}(\text{H})$  equal to  $1.2U_{\text{eq}}(\text{C})$ ). Hydrogen

**Table 1.** Crystallographic data and experimental details for structures 1–4

| Compound                                    | 1  | 2  | 3  | 4   |
|---|--|--|--|---|
| Empirical formula                           | C <sub>6</sub> H <sub>11</sub> CuN <sub>4</sub> O <sub>6</sub> | C <sub>6</sub> H <sub>15</sub> CuN <sub>2</sub> O <sub>2</sub> F <sub>6</sub> Si | C <sub>6</sub> H <sub>15</sub> CuN <sub>2</sub> O <sub>2</sub> B <sub>2</sub> F <sub>8</sub> | C <sub>12</sub> H <sub>30</sub> Cu <sub>2</sub> N <sub>8</sub> O <sub>12</sub> S <sub>4</sub> |
| Formula weight                              | 298.73   | 352.83   | 384.36   | 733.76  |
| Temperature (K)                             | 200(2)   | 200(2)   | 100(2)   | 100(2)  |
| Space group                                 | <i>P</i> 2 <sub>1</sub> / <i>n</i>                             | <i>P</i> 2 <sub>1</sub> / <i>c</i>   | <i>P</i> 2 <sub>1</sub> / <i>n</i>   | <i>P</i> $\bar{1}$  |
| Unit cell dimensions (Å, °)                 |  |  |  |   |
| <i>a</i>                                    | 8.2341(4)  | 8.5929(9)  | 12.351(4)  | 8.217(2)  |
| <i>b</i>                                    | 7.9905(3)  | 9.7426(8)  | 12.351(4)  | 9.018(3)  |
| <i>c</i>                                    | 17.4008(8)   | 15.2109(16)  | 13.497(4)  | 17.439(5)   |
| $\alpha$                                    | 90   | 90   | 90   | 91.93(3)  |
| $\beta$                                     | 98.959(2)  | 103.448(4)   | 97.98(3)   | 92.52(3)  |
| $\gamma$                                    | 90   | 90   | 90   | 90.21(3)  |
| Volume (Å <sup>3</sup> ), <i>Z</i>          | 1130.91(9), 4  | 1238.5(2), 4   | 1420.9(7), 4   | 1290.3(6), 2  |
| <i>D</i> <sub>c</sub> (g cm <sup>-3</sup> ) | 1.755  | 1.892  | 1.797  | 1.889   |
| <i>D</i> <sub>m</sub> (g cm <sup>-3</sup> ) | 1.73   | 1.88   | 1.80   | 1.88  |
| Absorption coefficient (mm <sup>-1</sup> )  | 1.96   | 1.93   | 1.63   | 2.05  |
| <i>F</i> (000)                              | 608  | 712  | 768  | 752   |
| Measured reflections                        | 4673   | 5091   | 14002  | 11271   |
| Independent reflections                     | 2552   | 2795   | 4825   | 8361  |
| Observed reflections                        |  |  |  |   |
| [ <i>I</i> > 2σ( <i>I</i> )]                | 2163   | 2542   | 3266   | 6055  |
| Goodness-of-fit on <i>F</i> <sup>2</sup>    | 1.09   | 1.12   | 0.99   | 1.00  |
| Parameters refined                          | 155  | 204  | 226  | 343   |
| Final <i>R</i> indices                      | <i>R</i> 1 = 0.049,  | <i>R</i> 1 = 0.052,  | <i>R</i> 1 = 0.036,  | <i>R</i> 1 = 0.032,   |
| [ <i>I</i> > 2σ( <i>I</i> )]                | <i>wR</i> 2 = 0.134  | <i>wR</i> 2 = 0.145  | <i>wR</i> 2 = 0.087  | <i>wR</i> 2 = 0.073   |

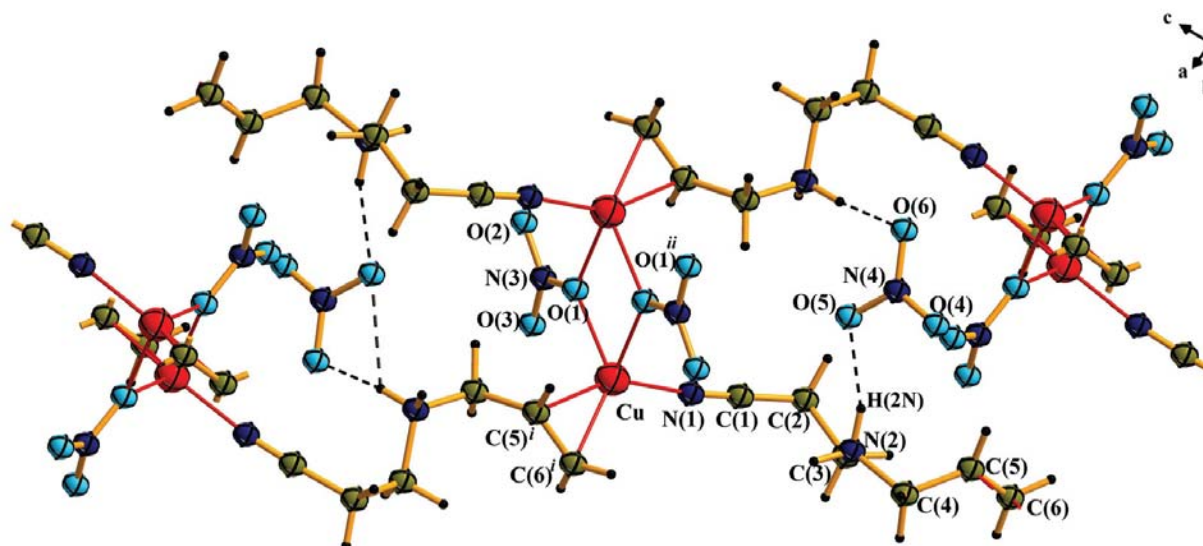
atoms of amino group and water were refined freely. The figures were prepared using DIAMOND 3.1 software.<sup>24</sup>

### 3. Results and Discussion

Analysis of the obtained new Cu(I)  $\pi$ -complexes proves that the type of anion influences strongly on a structure formation in these complexes.<sup>25,26</sup>

#### 3. 1. Crystal Structure of [Cu(Hapn)NO<sub>3</sub>]<sub>3</sub>NO<sub>3</sub> Complex (1)

Complex [Cu(Hapn)NO<sub>3</sub>]<sub>3</sub>NO<sub>3</sub> (1) is formed with anion NO<sub>3</sub><sup>-</sup> which is structurally related to halogenide ones. In this compound due to bridged functions of both Hapn and NO<sub>3</sub><sup>-</sup> units the known [Cu(NO<sub>3</sub>)<sub>2</sub>]<sub>2</sub> inorganic fragments<sup>27–30</sup> are interconnected with organic cations Hapn forming goffer chains in the direction [111] (Fig. 1). The



**Figure 1.** Infinite chains and hydrogen bonding in complex 1. Symmetry operations: (i)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ ; (ii)  $-x + 2, -y, -z + 2$ .

angle between planes passing through two neighbouring inorganic linkers  $[\text{Cu}(\text{NO}_3)_2]$  of the polymer is  $67^\circ$ . For comparison, the analogous angle between planes passing through two neighbouring inorganic units  $[\text{CuCl}]_2$  in the halide complex is  $65^\circ$ .<sup>16</sup>

The metal atom possesses a tetrahedral surrounding consisting of the middle (further *m*) of double  $\text{C}(5)=\text{C}(6)$ -bond, N ( $\text{C}\equiv\text{N}$ -group) and 2 oxygen atoms from two  $\text{NO}_3^-$  anions. Lengths of the bonds are Cu–*m* 1.933(3), Cu–N 1.939(3), Cu–O(1) 2.102(2) and Cu–O(1)<sup>ii</sup> 2.202(2) Å (Table 2). The angle formed by three Cu atoms in the chain  $[\text{Cu}(\text{Hapn})^{2+}]_n$  equals to  $152^\circ$ . The chain is not straight because of an influence of the non-coordinated  $\text{NO}_3^-$  anion, which forms N–H...O hydrogen bonds (Table 3).<sup>31</sup>

Table 2. Selected bond distances and angles for 1–4.

| Distance                  | (Å)      | Angle                             | (°)      |
|---------------------------|----------|-----------------------------------|----------|
| <b>1<sup>a</sup></b>      |          |                                   |          |
| Cu–N1                     | 1.939(3) | $\text{C}6^i\text{–Cu–C}5^i$      | 38.8(2)  |
| Cu– <i>m</i> <sup>i</sup> | 1.933(3) | N1–Cu–O1                          | 104.8(2) |
| Cu–O1                     | 2.102(2) | N1–C1–C2                          | 177.1(4) |
| Cu–O1 <sup>ii</sup>       | 2.202(2) | N1–Cu–O1 <sup>ii</sup>            | 101.0(2) |
| N1–C1                     | 1.129(4) | O1–Cu–O1 <sup>ii</sup>            | 71.9(1)  |
| C5–C6                     | 1.361(4) | <i>m</i> <sup>i</sup> –Cu–N1      | 132.6(1) |
| <b>2<sup>b</sup></b>      |          |                                   |          |
| Cu–N1 <sup>i</sup>        | 1.987(3) | N1 <sup>i</sup> –Cu–O1w           | 107.1(2) |
| Cu–O1w                    | 2.003(3) | N1 <sup>i</sup> –Cu– <i>m</i>     | 118.5(9) |
| Cu– <i>m</i>              | 1.936(3) | N1 <sup>i</sup> –Cu–O2w           | 95.9(2)  |
| Cu–O2w                    | 2.239(3) | O1w–Cu–O2w                        | 93.7(1)  |
| C5–C6                     | 1.363(5) | C1–N1–Cu <sup>ii</sup>            | 162.9(3) |
| N1–C1                     | 1.132(5) | N1–C1–C2                          | 178.4(4) |
| <b>3<sup>c</sup></b>      |          |                                   |          |
| Cu–N1                     | 1.946(2) | N1–Cu–O1w                         | 99.7(7)  |
| Cu–O1w                    | 1.992(2) | O1w–Cu– <i>m</i> <sup>i</sup>     | 129.1(5) |
| Cu– <i>m</i> <sup>i</sup> | 1.893(5) | C1–N1–Cu                          | 169.7(8) |
| N1–C1                     | 1.132(2) | N1–C1–C2                          | 177.7(2) |
| C5–C6                     | 1.364(3) | O1w–Cu–F8 <sup>iii</sup>          | 89.1(6)  |
| <b>4<sup>d</sup></b>      |          |                                   |          |
| Cu1–N11 <sup>i</sup>      | 1.990(2) | N11 <sup>i</sup> –Cu1–N1          | 106.2(7) |
| Cu1–N1                    | 2.061(2) | N11 <sup>i</sup> –Cu1–N2          | 92.2(7)  |
| Cu1– <i>m</i> 1           | 1.977(7) | N1–Cu1–N2                         | 99.2(7)  |
| Cu1–N2                    | 2.275(9) | N11 <sup>i</sup> –Cu1– <i>m</i> 1 | 117.4(6) |
| C16–C15                   | 1.352(3) | N2–Cu1– <i>m</i> 1                | 110.3(5) |
| C11–N11                   | 1.134(3) | C11–N11–Cu1 <sup>i</sup>          | 176.1(8) |
| Cu2–N3                    | 2.039(8) | N3–Cu2–N4                         | 104.6(7) |
| Cu2–N4                    | 2.143(9) | N3–Cu2–N21 <sup>ii</sup>          | 96.6(7)  |
| Cu2– <i>m</i> 2           | 1.971(7) | N21 <sup>ii</sup> –Cu2–N4         | 93.9(8)  |
| Cu2–N21 <sup>ii</sup>     | 2.130(2) | N4–Cu2– <i>m</i> 2                | 111.1(5) |
| C26–C25                   | 1.352(3) | N3–Cu2– <i>m</i> 2                | 130.5(6) |
| C21–N21                   | 1.138(3) | C21–N21–Cu2 <sup>ii</sup>         | 165.8(8) |

*m* – middle point of C5=C6 (in 4: C15=C16 and C25=C26) double bond. Symmetry codes: <sup>a</sup> (i)  $x + 1/2, -y + 1/2, z + 1/2$ ; (ii)  $-x + 2, -y, -z + 2$ ; <sup>b</sup> (i)  $-x + 1, y - 1/2, -z - 1/2$ ; (ii)  $-x + 1, y + 1/2, -z - 1/2$ ; <sup>c</sup> (i)  $-x + 1/2, y - 1/2, -z + 1/2$ ; (iii)  $-x + 1.5, y - 1/2, -z + 1/2$ ; <sup>d</sup> (i)  $-x + 1, -y + 1, -z$ ; (ii)  $-x + 2, -y, -z + 1$ .

Table 3. Geometry of selected hydrogen bonds in 1–4.

| Atoms involved<br>D–H...A    | Distances, Å |       | Angle, deg |         |
|------------------------------|--------------|-------|------------|---------|
|                              | D–H          | H...A | D...A      | D–H...A |
| <b>1<sup>a</sup></b>         |              |       |            |         |
| N2–H1N...O5 <sup>i</sup>     | 0.90         | 2.48  | 3.116(4)   | 128     |
| N2–H1N...O6 <sup>i</sup>     | 0.90         | 1.94  | 2.798(2)   | 159     |
| N2–H2N...O5                  | 0.90         | 1.94  | 2.807(4)   | 161     |
| <b>2<sup>b</sup></b>         |              |       |            |         |
| N2–H1N...F1                  | 0.90         | 1.89  | 2.784(8)   | 174     |
| O1w–H2w1...F2 <sup>i</sup>   | 0.97         | 1.70  | 2.661(1)   | 170     |
| N2–H2N...F2 <sup>ii</sup>    | 0.90         | 1.95  | 2.812(5)   | 160     |
| O2w–H2w2...F1                | 0.96         | 2.39  | 3.259(6)   | 151     |
| <b>3<sup>c</sup></b>         |              |       |            |         |
| O1w–H1w1...F4 <sup>i</sup>   | 0.73         | 1.99  | 2.710(6)   | 169     |
| N2–H1N...O2w <sup>ii</sup>   | 0.86         | 1.88  | 2.725(2)   | 168     |
| O1w–H2w1...F5 <sup>iii</sup> | 0.72         | 2.01  | 2.716(1)   | 169     |
| N2–H2N...F1                  | 0.96         | 1.96  | 2.755(1)   | 139     |
| O2w–H1w2...F7 <sup>iv</sup>  | 0.92         | 1.95  | 2.834(9)   | 160     |
| O2w–H2w2...F8                | 0.84         | 2.09  | 2.827(3)   | 146     |
| <b>4<sup>d</sup></b>         |              |       |            |         |
| N1–H1B...O21 <sup>i</sup>    | 0.92         | 2.02  | 2.919(1)   | 165     |
| N2–H2A...O31                 | 0.92         | 1.93  | 2.820(8)   | 162     |
| N2–H2B...O12 <sup>ii</sup>   | 0.92         | 2.07  | 2.992(1)   | 176     |
| N3–H3B...O43 <sup>iii</sup>  | 0.92         | 2.01  | 2.925(2)   | 173     |
| N22–H2N2...O42 <sup>iv</sup> | 0.92         | 1.81  | 2.730(3)   | 178     |
| N4–H4B...O32 <sup>ii</sup>   | 0.92         | 2.07  | 2.992(6)   | 177     |

Symmetry codes: <sup>a</sup> (i)  $1/2 - x, y - 1/2, 1/2 - z$ ; <sup>b</sup> (i)  $-x, 1 - y, -z$ ; (ii)  $1 - x, y - 1/2, -z$ ; <sup>c</sup> (i)  $-x, -y, 1 - z$ ; (ii)  $x - 1/2, 1/2 - y, z - 1/2$ ; (iii)  $x - 1, y, z$ ; (iv)  $1.5 - x, 1/2 + y, 1/2 - z$ ; <sup>d</sup> (i)  $2 - x, -y, -z$ ; (ii)  $x - 1, y, z$ ; (iii)  $1 - x, 1 - y, 1 - z$ ; (iv)  $-x, 1 - y, 1 - z$ .

### 3. 2. Crystal Structure of $[\text{Cu}(\text{Hapn})(\text{H}_2\text{O})_2]\text{SiF}_6$ Complex (2)

In following two complexes **2** and **3** water molecules act as co-ligands. The structure of the compound **2** consists of infinite metal-organic spiral-like ribbons of  $[\text{Cu}(\text{Hapn})(\text{H}_2\text{O})_2]^{2+}$  composition. The angle between three neighbouring copper atoms is  $63^\circ$ . Located between mentioned ribbons  $\text{SiF}_6^{2-}$  anions are bound to metal-organic fragment *via* O–H...F and N–H...F hydrogen bonds (Fig. 2). Despite the existence of  $\text{Cu}^I$  complexes with hexafluorosilicate-anion with the direct  $\text{Cu}^I\text{–F–Si–F}_5$  bond,<sup>32</sup>  $\text{SiF}_6^{2-}$ -anion does not enter the internal coordination sphere of the metal. Tetrahedral coordination polyhedron of copper(I) ion is formed by a mid-point of C(5) = C(6) bond, one nitrogen ( $\text{C}\equiv\text{N}$ ) and two O ( $\text{H}_2\text{O}$  molecules) atoms. Respective bond lengths are Cu–*m* 1.936(3), Cu–N(1)<sup>i</sup> 1.987(3), Cu–O(1w) 2.003(3) and Cu–O(2w) 2.239(3) Å (Table 2). A system of hydrogen bonds is much more developed in the given complex (table 2) in comparison with **1**. This promotes relatively dense packing of metal-organic chains and the inorganic anions.

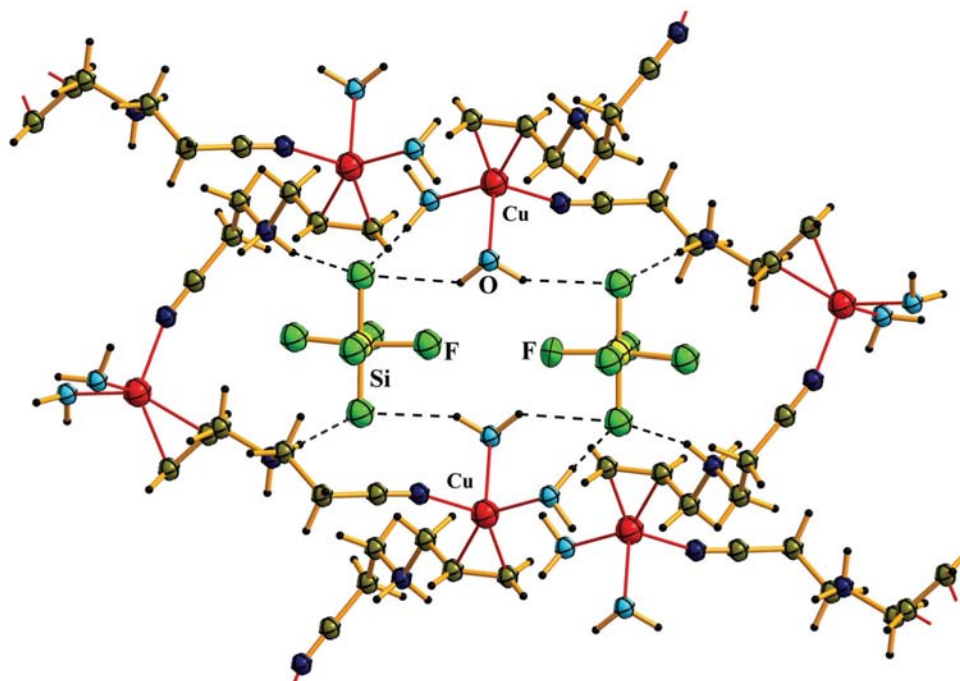


Figure 2. Fragment of molecular structure 2. Disordered fluorine atoms are omitted for clarity.

### 3.3. Crystal Structure of [Cu(Hapn)(H<sub>2</sub>O) BF<sub>4</sub>][BF<sub>4</sub> · H<sub>2</sub>O] Complex (3)

In the complex 3 water molecules and BF<sub>4</sub><sup>-</sup> anions (apart from the active centers of Hapn) are included in

the internal coordination sphere of Cu. The presence of BF<sub>4</sub><sup>-</sup> anions promotes transformation of coordination polyhedron of the metal from tetrahedron to trigonal pyramid formed by *m* of (C=C)-bond, N (C≡N-group) and O (H<sub>2</sub>O) atoms in the basal plane. Fluorine atom

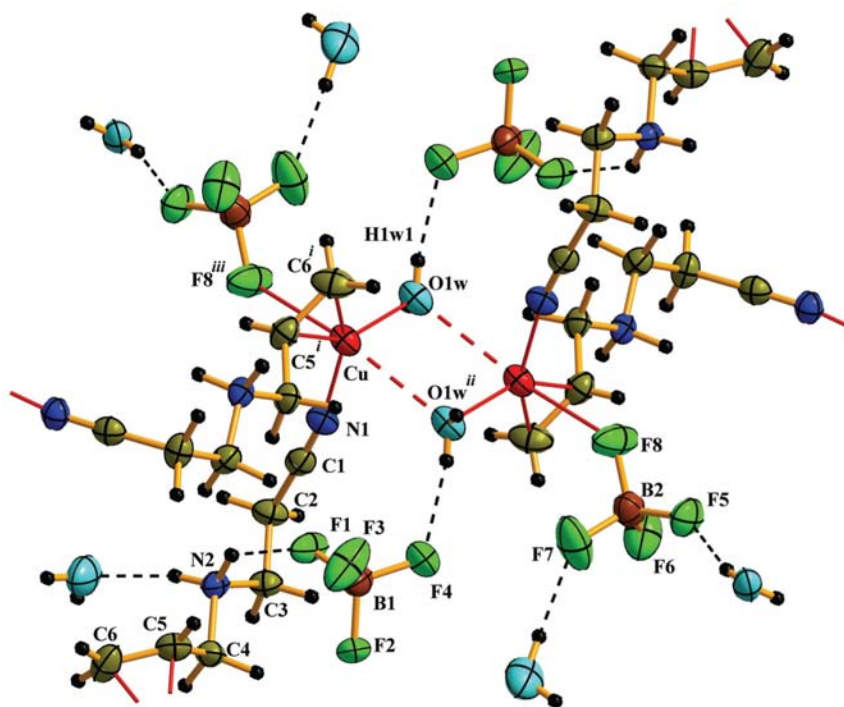


Figure 3. Cu(I) coordination in 3. Structure fragment of complex 3. Symmetry operations: (i)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $-x + 1, -y + 1, -z$ ; (iii)  $-x + 1.5, y - \frac{1}{2}, -z + \frac{1}{2}$ . (80% probability displacement ellipsoids).

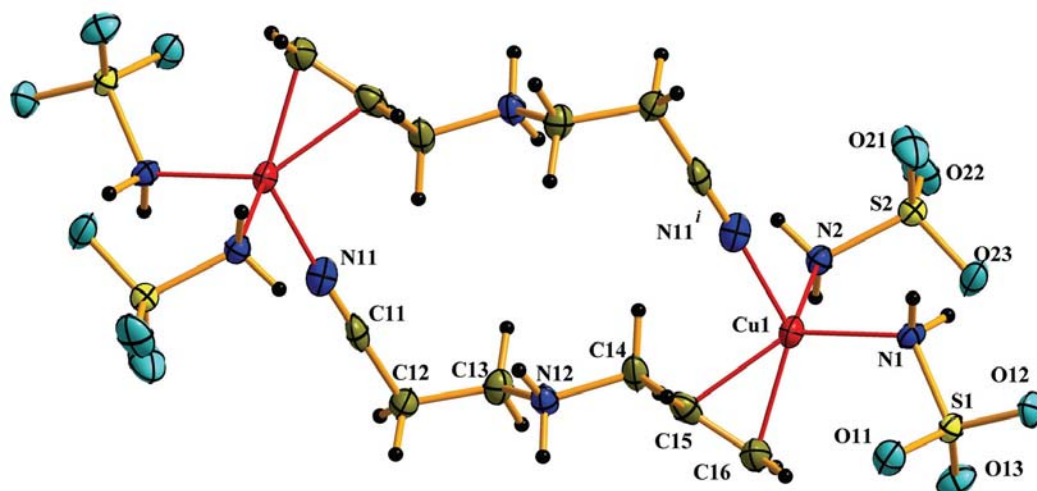
from  $\text{BF}_4^-$  anion occupies the apical position ( $\text{Cu}-\text{F}(8)^{iii}$  2.640(2) Å) of coordination polyhedron. Atom of Cu is somewhat ( $\Delta = 0.03$  Å) removed from the ( $m$ , N, O) plane.

Another crystallographically independent  $\text{H}_2\text{O}$  molecule and  $\text{BF}_4^-$  anion are not coordinated to copper(I) and fixed in a crystal space by relatively strong hydrogen bonds. As one can see from Figure 3, the structure **3** is similar to **2**, but separate fragments of coordination polymer due to the Hapn flexibility demonstrate bulbous chain structure (the angle between three atoms of Cu  $[\text{Cu}(\text{Hapn})^{2+}]_n$  equals to  $59^\circ$ ). Since one distance of  $\text{Cu}-\text{O}(1w)$  equals to 1.992(2) Å, and the other opposite  $\text{Cu}-\text{O}(1w)^{ii}$  is equal to 2.900(2) Å, one may regard from a certain distance ( $\text{Cu}(\text{H}_2\text{O})_2$ ) moiety as dimeric fragment and Cu(I) polyhedron as a trigonal bipyramid.

### 3. 4. Crystal Structure of $[\text{Cu}(\text{Hapn})(\text{NH}_2\text{SO}_3)_2]$ Complex (**4**)

As in complexes **1** and **2**, in the compound **4** coordination polyhedra for both independent Cu(I) ions possess tetrahedral shape. The Cu(1) environment comprises of the mid-point of  $\text{C}(15)=\text{C}(16)$  bond ( $m1$ ), N(11) atom from CN-group and two nitrogen atoms from two  $\text{NH}_2\text{SO}_3^-$  anions. The Cu(2) polyhedron involves  $m2$  ( $\text{C}(25) = \text{C}(26)$ ), N(21) ( $\text{C}\equiv\text{N}$ ) and N(3) and N(4) ( $\text{NH}_2\text{SO}_3^-$ ) centers. Bond lengths:  $\text{Cu}(1)-m1$  1.977(7),  $\text{Cu}(1)-\text{N}(11)^i$  1.990(2),  $\text{Cu}(1)-\text{N}(1)$  2.061(8) and  $\text{Cu}(1)-\text{N}(2)$  2.275(9) Å;  $\text{Cu}(2)-m2$  1.971(7),  $\text{Cu}(2)-\text{N}(21)^{ii}$  2.130(2),  $\text{Cu}(2)-\text{N}(3)$  2.039(8) and  $\text{Cu}(2)-\text{N}(4)$  2.143(9) Å.

The main structural feature of the complex **4** is the appearance of  $[\text{Cu}(\text{Hapn})]_2$  rings (Fig. 4). Two closest rings are tilted by  $72^\circ$  and linked with H-bonds among inorganic anions and organic cations ( $\text{N}(2)-\text{H}(2A)\cdots\text{O}(31)$  1.93 Å etc. Table. 3).



**Figure 4.** Copper(I) coordination in **4** and  $[\text{Cu}(\text{Hapn})]_2$ . Symmetry operation: ( $i$ )  $-x + 1, -y + 1, -z$ ; (80% probability displacement ellipsoids).

## 4. Conclusions

Flexibility of Hapn allows using it as a convenient tool in a construction of coordination compounds. In all the above-mentioned compounds Hapn totally realizes its coordination abilities attaching to the metal atom with ( $\text{C}=\text{C}$ )-bond of allyl- and N atom of cyano-group. The protonated N-amine atom being deprived of its donor ability participates actively in a formation of strong  $\text{N}-\text{H}\cdots\text{X}$  hydrogen bonds (Table 2). On the other hand, the combination of Hapn with ionic copper(I) salts ( $\text{CuNO}_3$ ,  $\text{Cu}_2\text{SiF}_6$ ,  $\text{CuBF}_4$ ,  $\text{CuSO}_3\text{NH}_2$ ) promotes an effective interaction of both  $\pi$ - and  $\sigma$ -ligands with the central atom, which serve to a formation of stable frameworks.

## 5. Supplementary Material

CCDC 913397 (**1**), 913398 (**2**), 913399 (**3**) and 913400 (**4**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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## Povzetek

Pripravili smo štiri bakrove(I)  $\pi$ -komplekse:  $[\text{Cu}(\text{Hapn})\text{NO}_3]\text{NO}_3$  (**1**),  $[\text{Cu}(\text{Hapn})(\text{H}_2\text{O})_2]\text{SiF}_6$  (**2**),  $[\text{Cu}(\text{Hapn})(\text{H}_2\text{O})\text{BF}_4]\text{BF}_4 \cdot \text{H}_2\text{O}$  (**3**) in  $[\text{Cu}(\text{Hapn})(\text{NH}_2\text{SO}_3)_2]$  (**4**) z uporabo elektrokemijske tehnike z izmenično napetostjo iz alkoholnih raztopin 3-(prop-2-en-1-ilamino)propannitrila (apn) titriranega z ustrežno kislino ter z bakrovo(II) soljo ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{CuSiF}_6 \cdot 4\text{H}_2\text{O}$ ,  $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  ali  $\text{Cu}(\text{NH}_2\text{SO}_3)_2 \cdot x\text{H}_2\text{O}$ ). Pripravljene spojine smo okarakterizirali z monokristalno rentgensko difrakcijo in delno z IR spektroskopijo. Pri strukturah **1**, **2** in **4** ima Cu(I) kation tetraedrično razporeditev ligandov, ki nastane z C=C vezjo enega organskega kationa Hapn, N atoma ciano skupine iz drugega Hapn liganda ter dveh O atomov (iz  $\text{NO}_3^-$  aniona pri **1**, iz  $\text{H}_2\text{O}$  molekule pri **2**) oziroma N atoma (anion  $\text{NH}_2\text{SO}_3^-$  pri **4**). Pri spojini **3** je prisotna trigonala-piramidalna koordinacija Cu(I) s sredinsko točko C=C-vezi enega Hapn kationa, N atoma (iz ciano skupine) drugega Hapn liganda in O atoma molekule  $\text{H}_2\text{O}$  v osnovni ravnini ter s F atomom iz  $\text{BF}_4^-$  aniona v navpični legi.