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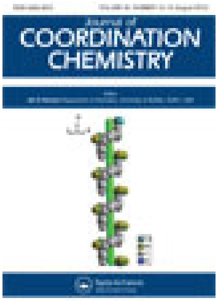

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# Anion-dependent complexation of 2-amino-benzothiazole and 2-imino-3-allyl-benzothiazole with $Cu^+$: synthesis and characterization of $[Cu(\eta_2\text{-}C_{10}H_{10}SN_2)(C_7H_6SN_2)NO_3]$ and $[Cu(C_7H_6SN_2)_2]ClO_4$

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# Anion-dependent complexation of 2-amino-benzothiazole and 2-imino-3-allyl-benzothiazole with $Cu^+$: synthesis and characterization of $[Cu(\eta_2\text{-}C_{10}H_{10}SN_2)(C_7H_6SN_2)NO_3]$ and $[Cu(C_7H_6SN_2)_2]ClO_4$

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Interaction of 2-amino-benzothiazole with allyl chloride in ethanol resulted in a mixture of 2-imino-3-allyl-benzothiazole and unreacted 2-amino-benzothiazole. Using such a mixture and copper(II) nitrate trihydrate in ethanol – acetonitrile and alternating-current electrochemical technique, crystals of $[Cu(\eta_2\text{-}C_{10}H_{10}SN_2)(C_7H_6SN_2)NO_3]$ (**1**) $\pi$-complex, containing 2-imino-3-allyl-benzothiazole and 2-amino-benzothiazole coordinated to copper, have been obtained. The same procedure, starting from copper(II) perchlorate hexahydrate, performed in ethanol, led to formation of $[Cu(C_7H_6SN_2)_2]ClO_4$ (**2**) $\sigma$-compound. Both compounds were structurally characterized. In the structure **1**, 2-imino-3-allyl-benzothiazole is a chelate, bound to metal by C=C-bond of the allyl and nitrogen of the imino group. Another nitrogen from the thiazole core of 2-amino-benzothiazole and oxygen from $NO_3^-$ complete a distorted trigonal-pyramidal environment of copper. $[Cu(\eta_2\text{-}C_{10}H_{10}SN_2)(C_7H_6SN_2)NO_3]$ building blocks are interconnected into infinite chains via N–H$\cdots$O ($NO_3^-$) hydrogen bonds and further linked into 3-D structure via $\pi$–$\pi$ stacking between benzothiazole cores. In **2**, $Cu^+$ coordinates two nitrogens from two 2-amino-benzothiazoles, whereas $ClO_4^-$ locates outside the coordination sphere, fixed in space by N–H$\cdots$O hydrogen bonds, which form puckered ribbons.

*Keywords*: Copper(I); Coordination chemistry; Heterocycles; $\pi$-Interaction

## 1. Introduction

Catalytic properties of copper(I) halides and a possibility of olefin $\pi$-adducts separation were a basis of the structural chemistry of the copper(I) $\pi$-complexes [1, 2]. Such an approach led to investigation of the metal adducts with aliphatic olefin derivatives, whereas copper(I) $\pi$-complexes with heterocyclic ligands were seldom investigated. Metal complexes with heterocyclic ligands with potential biological activity [3, 4] have focused interests on structural investigations of copper(I) $\pi$-complexes with allyl derivatives of heterocyclic compounds. Earlier investigation of the copper(I) chloride

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and bromide complexation with N-allyl derivatives of 2-aminobenzothiazole showed formation of different kinds of $\pi$-complexes (molecular or zwitter-ionic) depending on solvent [5]. We decided to expand this work to other copper(I) salts. In earlier copper(I) $\pi$-complexes [6–12] nitrate demonstrated diverse structural behavior, from bridging covalently bonded to typical weakly bound anion. One of the most-common weakly bonded anions is perchlorate. Thus, using the same ligands mixture [5], we have obtained coordination compounds of copper(I) nitrate and perchlorate.

## 2. Experimental

### 2.1. *Obtaining of 2-imino-3-allylbenzothiazole*

Mixture of 0.05 moles (7.30 g) of 2-aminobenzothiazole, 0.05 moles (4.20 g) of $NaHCO_3$ and 0.054 moles (4.4 mL) of freshly distilled allyl chloride in 75 mL of 95% ethanol was refluxed 14 days (with breaks for nights), as described in [13]. After that precipitate was filtered off, excess alcohol removed by distillation and the concentrated ethanolic solution (L) was used for further syntheses. Treatment of the solid precipitate by dilute HCl and appearance of $CO_2$ bubbles indicates that some $NaHCO_3$ was unreacted, showing that alkylation was not complete. Quantitatively repeating this test, i.e. titration of the dissolved solid phase by HCl, has shown that the ratio between the product and unreacted 2-aminobenzothiazole is 0.77 : 0.23. The allylation is accompanied by tautomeric transformation of 2-aminobenzothiazole into 2-iminobenzothiazole; hereafter L means a concentrated ethanol solution of 77% 2-imino-3-allylbenzothiazole and 23% of 2-aminobenzothiazole.

### 2.2. *Synthesis of 1 and 2*

Electrochemical synthesis is a powerful method for growing high-quality single crystals of copper(I) coordination compounds. Original direct-current technique [14] was modified, improved and converted to an alternating-current method. Usually electrical current is passed through the solution, containing copper(II) salt(s) and ligand(s), and a reaction $Cu^0 + Cu^{2+} \rightarrow 2Cu^+$ occurs. Variation of voltage and current density, starting mixture composition and solvent allows growing high-quality single crystals. The important advantages are absence of additional reducing agents, used frequently for copper(I) synthesis. Respectively, any unneeded by-products (like oxidized reductants) appear and such a method makes unnecessary re-crystallization, which is sometimes complicated for rather unstable copper(I) $\pi$-complexes. Both compounds were prepared using alternating – current electrochemical syntheses [15]. To an acetonitrile solution (2 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ (1 mmol) was added 2 mL of L (~1.2 mmol). The solution was placed into a small test-tube and copper-wire electrodes in cork were inserted. Under applied alternating current (frequency 50 Hz, $U = 0.30$ V, and $I = 0.25$ mA) crystals of **1** appeared on the copper electrodes after 2 days. The density, measured by flotation method in chloroform-bromoform mixture, was 1.63 g cm$^{-3}$. The same synthesis, starting from $Cu(ClO_4)_2 \cdot 6H_2O$ and ethanolic solution of the ligand, previously titrated with 60% $HClO_4$ to pH = 6, resulted in formation of good quality crystals of **2** in 24 h. The density was 1.82 g cm$^{-3}$.

Table 1. Details of experimental and crystallographic data for **1** and **2**.

| Compound | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{17}H_{16}CuN_5O_3S_2$ | $C_{14}H_{12}ClCuN_4O_4S_2$ |
| Formula weight | 466.01 | 463.39 |
| Crystal size ($mm^3$) | $0.1 \times 0.08 \times 0.06$ | $0.12 \times 0.1 \times 0.09$ |
| Temperature (K) | 200 | 200 |
| Radiation | Mo-K$\alpha$ | Mo-K$\alpha$ |
| Space group | $P2_1/n$ | $Pna\ 2_1$ |
| Unit cell dimensions (Å, °) | | |
| $a$ | 12.2071(7) | 14.8327(5) |
| $b$ | 10.1257(6) | 20.2379(6) |
| $c$ | 15.1784(10) | 5.53440(10) |
| $\beta$ | 94.537(3) | |
| Volume (Å$^3$), $Z$ | 1870.3(2), 4 | 1661.33(8), 4 |
| $D_c$ ($g\,cm^{-3}$) | 1.655 | 1.853 |
| $D_m$ ($g\,cm^{-3}$) | 1.63 | 1.82 |
| Absorption coefficient ($mm^{-1}$) | 1.421 | 1.757 |
| $F(000)$ | 952 | 936 |
| $\theta$ range for data collection (°) | 2.42–29.29 | 2.44–29.25 |
| Reflections collected | 14,355 | 6920 |
| Independent reflection | 4144 | 3454 |
| Goodness-of-fit | 1.121 | 1.098 |
| Parameters refined | 263 | 248 |
| $R$ ($F$) | 0.0656 | 0.0493 |
| $R$ $(F)^2$ | 0.1746 | 0.135 |

### 2.3. *Crystallography*

Single-crystal data were collected on a Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector using graphite monochromated Mo-K$\alpha$ radiation. Data were treated using the Rigaku CrystalClear software suite package [16]. Both structures were solved by direct methods using the SIR-92 [17] program (teXan crystallographic software package of Molecular Structure Corporation [18]) and refined on $F^2$ with SHELXL-97 [19] software implemented in the program package WinGX [20]. Hydrogen atoms were partially found on a difference Fourier map, partially included in idealized positions. Thermal parameters of all hydrogens were fixed as 1.2 times $U_{eq}$ of the non-hydrogen atom. Positions of hydrogen atoms attached to carbon atoms were refined with geometrical restrictions; positions of hydrogen atoms connected to nitrogen were refined. The figures were prepared using DIAMOND 3.1 software [21]. Experimental details and crystallographic data are listed in table 1.

## 3. Results and discussion

The initial 2-amino-benzothiazole undergoes a tautomeric transformation during the alkylation. In **1** it occurs, as in $CuCl \cdot C_{10}H_{10}SN_2$ [5] as 2-imino (with C=NH group in a position 3), and initial C–$NH_2$ in five-membered ring is replaced by C=NH. In **1** the ligand chelates, being linked to the metal by C=C of allyl- and nitrogen of imino-groups. The third place in the basal plane of copper is occupied by nitrogen from 2-amino-benzothiazole. At an apical position of the metal, coordination sphere is oxygen from $NO_3^-$ (figure 1). Despite existence of the Coulomb $Cu^+$–$NO_3^-$ interaction, the Cu–O bond is noticeably elongated to 2.486(3) Å (table 2). Similar values of 2.352(3) and 2.271(4) Å were observed in two modifications of $CuNO_3$ complex with diallylamine [6, 7]. Both hydrogen atoms of amino from 2-amino-benzothiazole participate in formation of rather strong N–H···O hydrogen bonds (table 3), involving two non-coordinated oxygen atoms from nitrate. O2 participates in formation of an

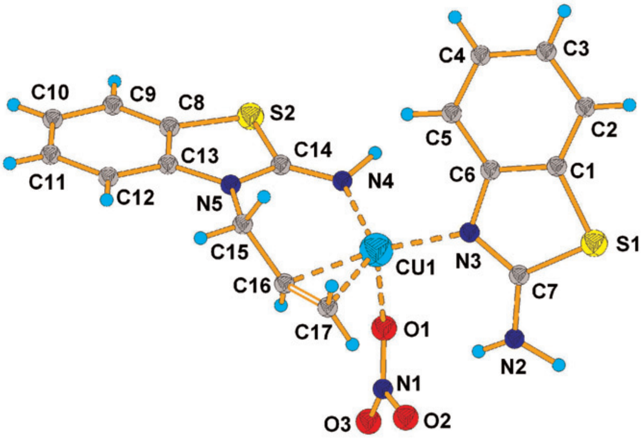

Figure 1. Copper(I) coordination in **1**.

Table 2. Selected bond distances (Å) and angles (°) in **1**.

| | | | | | |
|---|---|---|---|---|---|
| Cu1–N4 | 1.969(3) | O1–N1 | 1.241(3) | N4–Cu1–N3 | 110.85(11) |
| Cu1–N3 | 1.983(2) | O2–N1 | 1.263(4) | N3–Cu1–m | 132.87(4) |
| Cu1–C16 | 2.034(3) | O3–N1 | 1.249(3) | N4–Cu1–m | 111.57(3) |
| Cu1–C17 | 2.061(3) | | | O1–Cu1–N3 | 103.86(4) |
| Cu1–O1 | 2.486(3) | | | O1–Cu1–N4 | 90.42(4) |
| Cu1–m | 1.932(3) | | | O1–Cu1–m | 95.96(3) |
| C16–C17 | 1.365(5) | | | C16–Cu1–C17 | 38.9(1) |

Table 3. Geometry of essential hydrogen bonds in **1** and **2**.

| Bond | D–H | H···A | D···A | ∠(DHA) |
|---|---|---|---|---|
| **1**$^{a}$ | | | | |
| H2–N2···O2 | 0.85(4) | 2.09(4) | 2.911(4) | 165(4) |
| H1–N2···O3$^{i}$ | 0.86(4) | 2.07(4) | 2.932(4) | 174(4) |
| **2**$^{b}$ | | | | |
| N2–H1N2···O1 | 0.96(7) | 2.28(6) | 2.882(7) | 120(5) |
| N2–H2N2···O4$^{i}$ | 0.95(7) | 2.08(7) | 2.976(7) | 158(6) |
| N4–H1N4···O2$^{ii}$ | 0.83(7) | 2.43(7) | 2.908(7) | 117(5) |
| N4–H2N4···O3$^{iii}$ | 0.72(7) | 2.28(7) | 2.970(7) | 160(7) |

Symmetry transformation: $^{a}$(i) $1.5-x$, $0.5+y$, $0.5-z$ $^{b}$(i) $x$, $y$, $z-1$; (ii) $1.5-x$, $-0.5+y$, $-0.5-z$; (iii) $1.5-x$, $-0.5+y$, $0.5-z$

intermolecular hydrogen bond, whereas N2–H1N2···O3 results in formation of infinite chains oriented along the *b*-axis (figure 2). These chains are interconnected into a 3-D structure by weak interactions, mainly $\pi$–$\pi$ stacking between benzothiazole. The $\pi$–$\pi$-interaction between two 2-amino-benzothiazoles, belonging to neighboring chains, creates a link in the [001] direction, and similar interaction between the two closest 2-imino-3-allylbenzothiazoles form bonding in roughly the [110] direction.

The Cu–(C=C) $\pi$-interaction in **1** appears to be strong with carbon–carbon double bond elongated to 1.365(5) Å against 1.33 Å in a free olefin, Cu-m (m is a mid-point of the C=C bond) distance is equal to 1.932(3) Å, and the C–Cu–C angle is 38.9(1)° (table 2). Copper is somewhat (0.25 Å) removed from the (N3, N4, m) plane, and coordinated C16=C17 bond is tilted 6° referring to this plane. Such geometry agrees well with the Dewar–Chatt–Duncanson theory, predicting elongation of the coordinated double bond, proper orientation of this bond in the basal plane of the metal coordination polyhedron and formation of a trigonal pyramidal copper instead of tetrahedral [22]. Distance from copper to the more hydrogenated C17 is, as usually observed, slightly longer than that to the C16 one.

Compound **2** is the ionic copper(I) $\sigma$-complex and consists of [Cu(2-amino-benzothiazole)$_2$]$^+$ (figure 3) and $ClO_4^-$. Because of copper coordination number of two, the Cu–N distances are rather short (1.881(5) Å). Similar short Cu–N bond lengths were earlier observed in, for example, [Cu(2-methylbenzimidazole)$_2$] [CuCl$_2$] [23]. Each oxygen from $ClO_4^-$ forms N–H···O hydrogen bonds (N···O 2.88–2.99 Å) resulting in connection of the anion to four $[Cu(C_7H_6SN_2)_2]^+$. In turn, each complex cation is bound to four perchlorates. The hydrogen bonding results in formation of puckered ribbons (figure 4). Contrary to structure **1** no $\pi$–$\pi$ stacking interaction was observed. Possibly, "3-D" $ClO_4^-$ (contrary to flat $NO_3^-$) "dictates" too long distances between the nearest benzothiazole cores and prevents $\pi$–$\pi$ interaction. Additionally, roughly planar mutual orientation of the hydrogen bonds around nitrate is more favorable for closer packing of the aromatic rings than those around tetrahedral $ClO_4^-$.

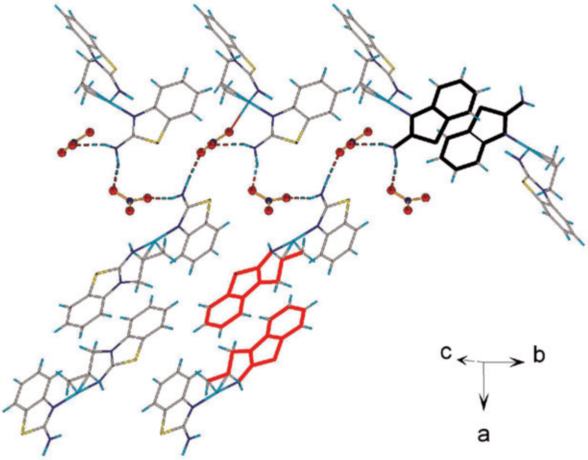

Figure 2. Infinite chains, hydrogen bonding and $\pi$–$\pi$ stacking in **1**. Dotted lines represent N–H···O ($NO_3^-$) hydrogen bonds, thick gray heterocyclic cores are bound in roughly [110] direction and thick black ones are linked in the [001] direction.

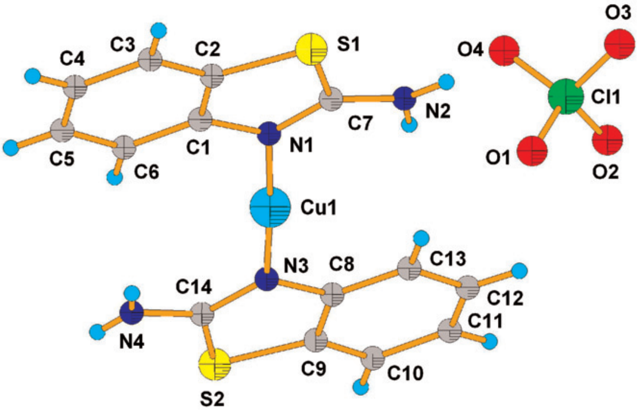

Figure 3. Complex cation and perchlorate in **2**.

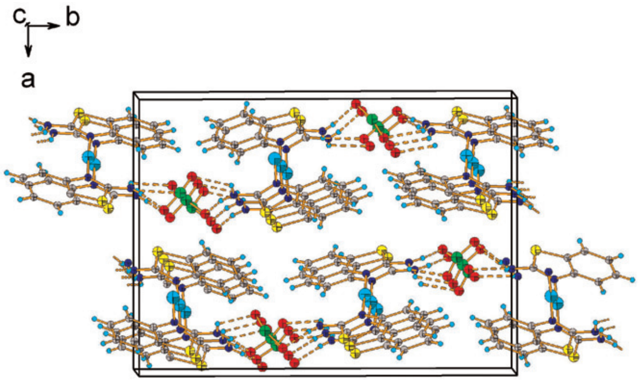

Figure 4. Puckered ribbons in **2**.

Contrary to the presence of sulfur in ligand we did not observe Cu–S interaction, similar to that in complexes of copper(I) chloride with 2-imino-3-allyl-benzothiazole [5] or with (2-allylthio)benzimidazole [24].

## 4. Conclusions

Using the mixture of 2-imino-3-allyl-benzothiazole and 2-amino-benzothiazole one obtains under the same conditions crystals of 2-imino-3-allyl-benzothiazole adduct with CuCl, $[CuCl(C_{10}H_{10}SN_2)]$ [5], mixed-ligand **1** for $CuNO_3$ and coordination compound with 2-amino-benzothiazole **2** in the case of $CuClO_4$. Possible explanation of such selectivity is a difference in the strength of copper–anion interaction. In $(CuCl)C_{10}H_{10}SN_2$, energetically favorable chelate N, C=C ligand requires two places in the copper coordination. Rather closely located (2.195(2) Å) chloride completes metal trigonal coordination sphere. Similar short Cu–Cl distances were observed frequently, for example in complexes with N-allylbenzotriazole [25] (Cu–Cl 2.283(2) Å, metal coordination sphere involves C=C + N + 2 Cl) and with (2-allylthio)benzimidazole [24] (Cu–Cl 2.227(4) Å, copper is surrounded by C=C + N + Cl). One may conclude that the (C=C, N, Cl) trigonal planar coordination of $Cu^+$ appears to be stable, especially in the case of chelate (N,C=C) ligand coordination. Such stability promotes formation of earlier-mentioned CuCl complex with 2-imino-3-allyl-benzothiazole, while 2-amino-benzothiazole cannot compete successfully for a place in copper coordination sphere.

The nitrate in structurally investigated copper(I) $\pi$-complexes demonstrates diverse coordination modes, bound *via* one oxygen with two metal centers resulting in $Cu_2(NO_3)_2$ dimers (as in the complex with N-allylbenzotriazole [26]) or as terminal anion (both complexes with diallylamine [6, 7]); Cu–O distances are noticeably elongated compared with Cu–Cl ones. In **1**, longer (2.486(3) Å) metal–anion distance promotes increasing copper coordination number to four. Because of higher spatial accessibility of nitrogen from 2-amino-benzothiazole this ligand fills the fourth place in the metal coordination sphere.

Typical behavior of $ClO_4^-$ as weakly bonded anion, outside copper coordination sphere, stimulates formation of **2** with the smallest possible copper coordination number 2, characteristic for copper(I) $\sigma$-complexes with large ligands.

## Supplementary material

CCDC 856590 (**1**) and 856589 (**2**) 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).

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