

Scientific paper

Anion Change as a Tool for Structure Design: Syntheses and Crystal Structures of Copper(I) Trifluoroacetate and Tetrafluoroborate with 3-[(2-morpholino-4-oxo-4,5-dihydro-1,3-thiazol-5-ylidene)methyl-phenoxy]propene

Evgeny A. Goreshnik,^{1*} Zoran Mazej,¹ Volodymyr V. Karpyak² and Marian G. Mys'kiv²

¹ Department of Inorganic Chemistry and Technology, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia

² Department of Chemistry, Ivan Franko National University, Kyryla & Mefodia, 6, 79005 L'viv, Ukraine

* Corresponding author: E-mail: evgeny.goreshnik@ijs.si

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Dedicated to the memory of Professor Ljubo Golič

Abstract

By alternating-current electrochemical synthesis crystals of two new copper(I) coordination compounds of $\text{Cu}(\text{CF}_3\text{COO})\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$ (**I**) and $[\text{Cu}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_3\text{S})_2]\text{BF}_4$ (**II**) composition have been obtained and structurally investigated. In the crystal structure of **I** the ligand moiety acts as a bridge, being coordinated to one metal center through the C=C-bond of allyl group, and to another Cu atom by nitrogen atom of thiazole ring. Due to such a bridging function dimers of $[\text{Cu}(\text{CF}_3\text{COO})\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_3\text{S}]_2$ composition appear. The trigonal-planar copper atom coordination sphere includes, besides the nitrogen atom and C=C bond, also one oxygen atom from trifluoroacetate anion. In the structure **II** two nitrogen atoms from thiazole rings of two ligand moieties form linear surrounding of copper atom resulting in a formation of $[\text{Cu}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_3\text{S})_2]^+$ complex cations. The $[\text{BF}_4]^-$ anion is completely disordered. Mentioned dimers in **I** and complex cations and $[\text{BF}_4]^-$ anions in **II** are associated by weak interactions only.

Keywords: Copper(I), complex, structure design

1. Introduction

Catalytic properties of the copper(I) halides and a possibility of their olefin π -adducts separation were a basis of the structural chemistry of the copper(I) π -complexes.¹ One may note, that in such adducts halogen atoms occupy usually two or even three places in metal surrounding resulting in polymeric cupro-halide fragments.^{2,3,4} To introduce more active centers of ligand into copper coordination sphere one may use weakly bonded anions such as $[\text{ClO}_4]^-$, $[\text{BF}_4]^-$, $[\text{PF}_6]^-$, $[\text{CF}_3\text{COO}]^-$. In copper(I) coordination compounds with such anions, ligand moieties realize fully their coordination abilities and play dominant role in a 3-D network formation.

Recently copper(I) chloride coordination compound with 3-[(2-morpholino-4-oxo-4,5-dihydro-1,3-thiazol-5-

ylidene)methyl-phenoxy]propene has been prepared and structurally investigated.⁵ In this compound unusual Cu_4Cl_4 inorganic fragment, included in a formation of complicated organic-inorganic 3-D network, has been found. In order to explore 3-D network formation in copper(I) complexes with the same ligand in the presence of weakly bonded anions, compounds $\text{Cu}(\text{CF}_3\text{COO})\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$ (**I**) and $[\text{Cu}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_3\text{S})_2]\text{BF}_4$ (**II**) have been prepared and X-ray structurally investigated.

2. Results and Discussion

In structure **I** with $(\text{CF}_3\text{COO})^-$ anion the ligand moiety acts as a bridge between two metal centers, being coordinated to one copper atom via π -interaction with

the C16=C17 bond, and to another metal atom via N1 atom of thiazole ring. The major part of the ligand molecule is strictly flat: both benzene and thiazole aromatic rings, as same as non-hydrogen atoms of allyl group and N2 atom of morpholine ring lie in common plane. The CF_3COO^- anion in I is bound to the only one metal center through the one oxygen atom. Contrary, in earlier studied $\text{Cu}(\text{CF}_3\text{COO})(\text{olefin})$ compounds trifluoroacetate-anion acts as a bridge, being connected via both oxygen atoms to two copper(I) cations.⁶ Due to the above mentioned bridging function of the ligand molecule, dimers of $[\text{Cu}(\text{CF}_3\text{COO})\text{-L}]_2$ ($\text{L} = \text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_3\text{S}$) composition appear. In such dimers two ligand molecules are oriented in “head to tail” mode (Fig. 1). Further association of such dimers is realized by weak interactions (Fig. 2). The copper atom possesses trigonal-planar environment composed of O5 atom of trifluoroacetate-anion, N1 atom of thiazole ring of one ligand molecule and the C16=C17-bond of allyl group from another ligand moiety with the Cu–O, Cu–N and Cu– m (m is a mid-point of

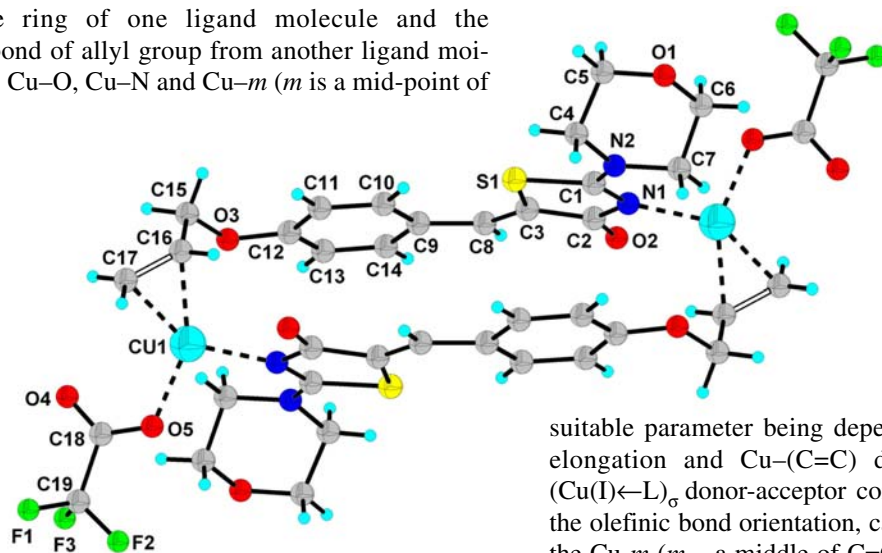


Figure 1. $[\text{Cu}(\text{CF}_3\text{COO})(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_3\text{S})]_2$ dimers in structure of I.

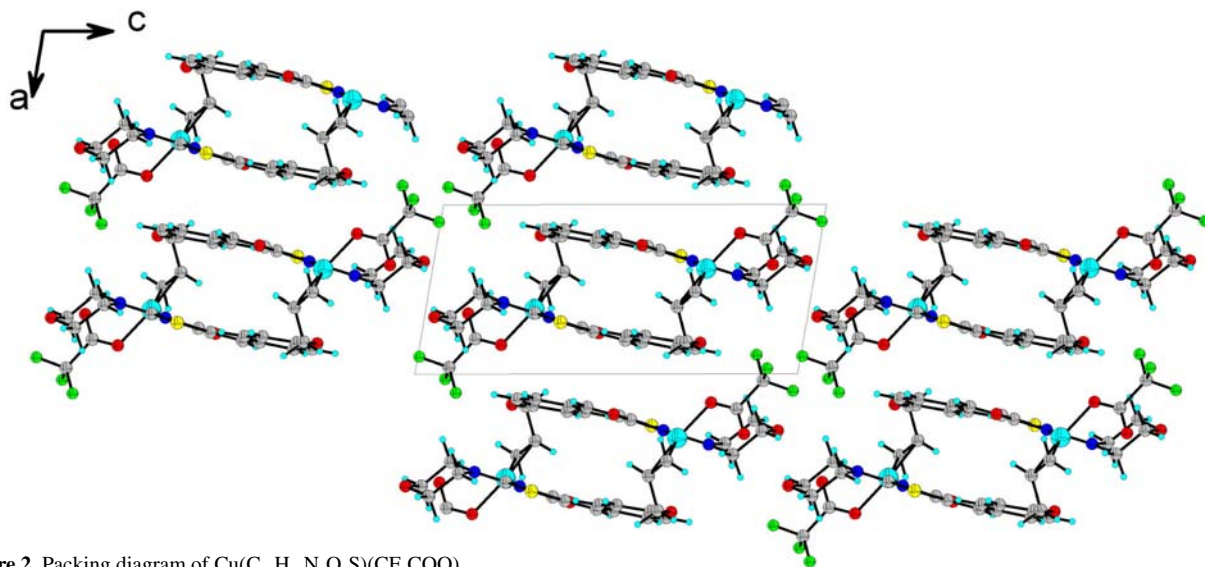


Figure 2. Packing diagram of $\text{Cu}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_3\text{S})(\text{CF}_3\text{COO})$.

C=C-bond) distances of 1.966(4), 1.998(5) and 1.905(7) Å, respectively. The deviation of the metal atom and olefin group from the (N1, O5, m) plane does not exceed 0.1 Å. Such an orientation of olefin bond in Cu^{I} coordination sphere is favoured for effective copper-olefin interaction.

As it follows from the Dewar-Chatt-Dunkanson concept in olefin copper(I) complexes, the π -bond consists of two components: the $(\text{Cu}(\text{I})\leftarrow\text{L})_{\sigma}$ donor-acceptor component, arising from overlapping of the occupied olefinic π_p orbital and the unoccupied $4s^0$ orbital of $\text{Cu}(\text{I})$ atom, and the $(\text{Cu}(\text{I})\rightarrow\text{L})_{\pi}$ -dative component, formed upon electron-density drawing-off from the $3d^{10}$ copper(I) orbitals to the unoccupied antibonding orbital of the C=C-group.⁷ For a numerical characterization of copper-olefin interaction effectiveness C–Cu–C angle provides the most

suitable parameter being dependent on both C=C-bond elongation and Cu–(C=C) distance shortening. The $(\text{Cu}(\text{I})\leftarrow\text{L})_{\sigma}$ donor-acceptor component, less sensitive to the olefinic bond orientation, causes at first shortening of the Cu– m (m – a middle of C=C bond) distance, whereas the $(\text{Cu}(\text{I})\rightarrow\text{L})_{\pi}$ -dative component, being strongly dependent on a proper olefinic group orientation in the met-

al coordination sphere, causes a lengthening of the C=C-bond. Therefore, both components cause an increasing of C–Cu–C angle. In the structure of compound **I**, in addition to rather short Cu–*m* distance one may note that C=C double bond, coordinated to the Cu metal atom, is noticeably elongated to 1.385(9) Å in comparison to the value of 1.33 Å in free olefins.⁸ The C–Cu–C angle appears to be equal to 39.9(3)°, which is one of the highest values observed in copper(I) π -complexes. One may conclude that copper–C=C π -interaction in **I** appears to be rather effective.

In structure **II** with BF₄[−] copper atom is bound to two nitrogen atoms of thiazole rings of two ligand molecules resulting in a formation of centrosymmetric [CuL₂]⁺ complex cation (Fig. 3). Because of the lower coordination number of the metal atom than that in **I** the Cu–N distances are shortened to 1.88(3) Å. Similar copper(I) coordination was found recently in the crystal structure of bis(2-methylbenzimidazole-copper(I) dichlorocupra-

action in **I** allows the metal center coordination with two ligand molecules. The presence of weakly bonded BF₄[−] anion in **II** makes the copper cation practically “naked” and, in turn, resulting in a low copper coordination number 2. Contrary to earlier studied Cu₄Cl₄(C₁₇H₁₈N₂O₃S)₂ compound anions in **I** and **II** do not participate in association of building blocks.

4. Experimental Section

4.1. Synthesis of Ligand

3-[(2-morpholino-4-oxo-4,5-dihydro-1,3-thiazol-5-ylidene)methyl-phenoxy] propene was obtained by refluxing of a mixture of 4-allyloxybenzalrhodanine and morpholine in ethanol (2 h), followed by cooling to a room temperature and recrystallization from ethanol. Measured melting point of synthesized ligand equals to 213–214 °C.

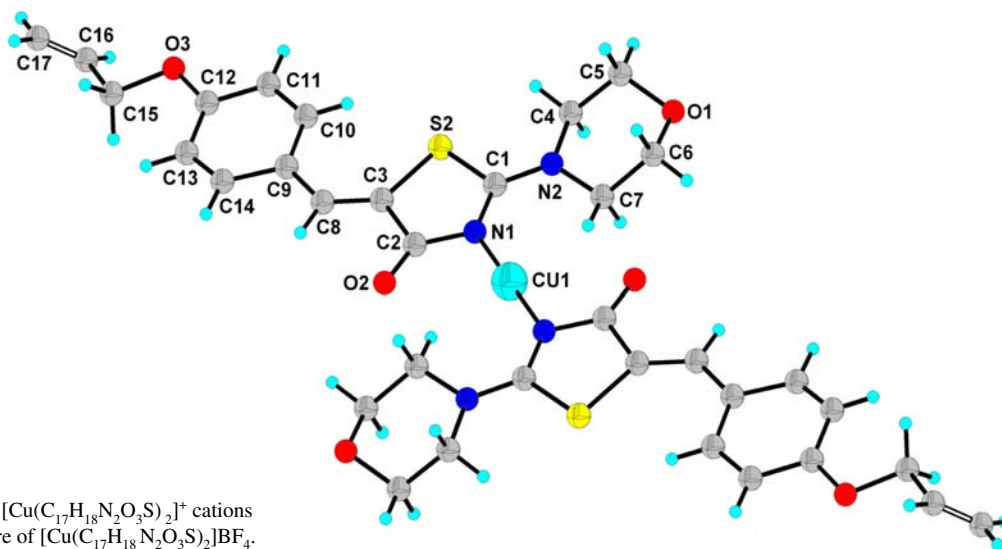


Figure 3. [Cu(C₁₇H₁₈N₂O₃S)₂]⁺ cations in structure of [Cu(C₁₇H₁₈N₂O₃S)₂]BF₄.

te(I).¹⁰ BF₄ unit is found on site symmetry inconsistent with its own, e.g. tetrahedral molecule on an inversion center, so that alternate orientation is generated by a symmetry operation. This positional disorder could be roughly described by pseudo-octahedral model with the occupancy of 0.67 for each F atom. Since the crystal structure of **II** is of a layer type, epitaxial twinning of crystals could be possible reason for low quality of structural investigation.

3. Conclusions

Two new copper(I) coordination compounds with 3-[(2-morpholino-4-oxo-4,5-dihydro-1,3-thiazol-5-ylidene)methyl-phenoxy]propene were synthesized and X-ray structurally investigated. Weak Cu⁺ – CF₃COO[−] inter-

4.2. Synthesis of I and II Compounds

Good quality crystals of **I** were obtained using the alternating-current electrochemical technique starting from ethanol solution containing copper(II) trifluoroacetate and a ligand.¹¹ Because of low ligand solubility the reaction was performed at 50 °C. The starting mixture was placed into a small test-tube and heated to dissolve a ligand. After that copper-wire electrodes in cork were inserted, and alternating current of 0.30 V tension (frequency 50 Hz) was applied. After heating at 50 °C during 9 h with a reflux condenser, the reactor was allowed to stand at 20 °C (under the tension) for a few days. Orange crystals of the title compound appeared on copper electrodes. The density of **I**, measured by flotation method in chloroform-bromoform mixture, was found to be 1.7 g cm^{−3}.

Table 1 Details of experimental and crystallographic data for **I** and **II** compounds

Compound	I	II
Empirical formula	C ₁₉ H ₁₈ CuF ₆ N ₂ O ₅ S	C ₃₄ H ₃₆ BCuF ₄ N ₄ O ₆ S ₂
Formula weight	506.95	811.14
Crystal size, mm	0.2 × 0.15 × 0.1	0.08 × 0.03 × 0.02
Temperature, K	293	293
Radiation	MoK α	MoK α
Color, shape	Orange prism	Colourless needle
sp. gr.	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Unit cell dimensions		
<i>a</i> , Å	7.2458(18)	8.227 (15)
<i>b</i> , Å	9.549 (2)	10.055 (17)
<i>c</i> , Å	15.255 (4)	10.894 (19)
α , °	90.140 (3)	91.991 (17)
β , °	99.173 (2)	97.77 (2)
γ , °	109.24 (3)	97.13 (2)
<i>V</i> , Å ³	982.1 (4)	885 (3)
<i>Z</i>	2	1
<i>D</i> _c g/cm ³	1.714	1.521
<i>D</i> _m g/cm ³	1.7	1.5
μ , mm ⁻¹	1.28	0.81
<i>F</i> (000)	516	418
Scan range θ , °	2.57–29.21	1.89–27.5
Measured reflections	5353	1275
Used (<i>I</i> > 2 σ (<i>I</i>))	2730	901
Parameters refined	280	158
<i>R</i> (F)	0.071	0.145
<i>R</i> (F) ² ; <i>F</i> > 4 σ (<i>F</i>)	0.188	0.327
Goodness-of-fit	1.05	1.29

Similar synthetic route, using Cu(BF₄)₂·6H₂O as a starting copper(II) salt, produces crystals **II**. Their density equals to 1.5 g cm⁻³.

4. 3. Crystallography

Single-crystal data were collected on a Rigaku AFC7 diffractometer equipped by Mercury CCD area detector using graphite monochromatized MoK α radiation. Data treatments were performed using Rigaku CrystalClear software suite program package.¹² All structures were solved by direct methods using SIR-92 program,¹³ implemented in teXan crystallographic software package of Molecular Structure Corporation,¹⁴ and refined with

SHELXL-97 software,¹⁵ implemented in program package WinGX.¹⁶ The figures were prepared using DIAMOND 3.1 software.¹⁷

5. Acknowledgement

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Povzetek

Dve novi bakrovi(I) koordinacijski spojini sta bili sintetizirani z elektrokemijskim postopkom: Cu(CF₃COO) · C₁₇H₁₈N₂O₃S (**I**) in [Cu(C₁₇H₁₈N₂O₃S)₂]BF₄ (**II**). V spojini (**I**) mostovni ligand povezuje preko C=C-vezi alilne skupine in dušikovega atoma tiazolnega obroča dva kovinska centra. Tvorijo se dimeri (CF₃COO) · C₁₇H₁₈N₂O₃S]₂. V spojini (**II**) dva dušikova atoma dveh tiazolnih obročev tvorijo linearno okolico bakrovemu ionu in nastane [Cu(C₁₇H₁₈N₂O₃S)₂]⁺ kompleksni kation. Anion [BF₄]⁻ je v neurejenem stanju.