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A.I. Yanchak^a, *Yu.I. Slyvka*^a, *V.V. Kinzhybalov*^b, *T.J. Bednarchuk*^b, *M.G. Mys'kiv*^a**THE FIRST COPPER(I) HALIDE π -COMPLEXES WITH ALLYL DERIVATIVES OF UREA AND PARABANIC ACID**^a Ivan Franko National University of Lviv, Lviv, Ukraine^b Institute of Low Temperature and Structure Research, Wroclaw, Poland

By means of alternating current electrochemical synthesis with wire copper electrodes in methanolic solutions of corresponding ligands and copper(II) halide salts, two novel copper(I) π -complexes [Cu₂(dau)Cl_{1.58}Br_{0.42}] (I) and [Cu₂(dapa)Cl_{1.74}Br_{0.26}] (II) (where dau and dapa are 1,3-diallylurea and 1,3-diallylparabanate, respectively) were prepared in well-shaped crystalline form and studied with X-ray diffraction method. Compound I crystallizes in orthorhombic crystal system, space group P2₁2₁2₁; a=8.047(3) Å, b=8.154(3) Å, c=16.533(5) Å, V=1085.8(76) Å³, Z=4. Compound II crystallizes in monoclinic crystal system, space group I2/a: a=6.420(3) Å, b=8.088(3) Å, c=49.020(9) Å, β =90.92(3)°, V=2545.03(16) Å³, Z=8. Both structures contain two crystallographically independent copper(I) ions with one half in trigonal planar coordination environment and the other half in trigonal pyramidal one. Both compounds are built of parallel copper halide polymeric chains of one type in I and two types in II, cross-linked by organic ligand molecules to produce 3D-polymer bulk in I and 2D-layered structure in II. In compound I, 1,3-diallylurea is both π - and σ -bonded to copper(I) halide chains (by means of two allylic C=C bonds and carbonyl O atom), whereas 1,3-diallylparabanate is a solely π -donor ligand in compound II. The structure of II is noteworthy due to the combination of two different chain types that have been previously observed only separately in copper(I) halide coordination compounds.

Keywords: copper(I) halides, π -complex, diallylurea, diallylparabanate, crystal structure.**DOI:** 10.32434/0321-4095-2019-124-3-67-73**Introduction**

Copper(I) halides are known to form diverse structures in combination with organic ligands [1], including the ones capable of being π -coordinated, for example described in [2–4].

A large number of olefin-copper(I) π -complexes is known to date. A common approach toward the design of ligands is combining rigid fragments such as heteroatom-containing molecules (σ -donors) with flexible allyl group substituents (π -coordination) [5]. Additional hydrogen atoms connected to heteroatoms are involved in hydrogen bonds formation, that further stabilizes the crystal structures.

A good example of such fragment, which possesses both potential σ -donating oxygen atom as well as groups capable of hydrogen bonds formation is urea. Its 1,3-diallyl derivative (dau) has already been investigated as a ligand for π -complexation of silver [6] due to the structural similarity to 1,3,5-

cyanuric acid (Fig. 1) and has demonstrated its ability to be a linker in coordination polymers. Nevertheless, its behavior in presence of compounds that can catenate on their own has never been tested prior to this moment. An example of such partners for dau are copper(I) halides.

Another ligand, structurally related to 1,3-diallylurea, is 1,3-diallylparabanate (dapa) (Fig. 1). This compound has been studied in context of useful polymer materials preparation [7]. Nevertheless, its use as a ligand for copper(I) π -coordination is novel. This ligand has a similar spatial arrangement of allyl groups, as in 1,3-diallylurea, while not being able to donate hydrogen bonds and being more sterically hindered. 1,3-Diallylparabanate possesses only oxygen atoms as potential σ -donor with their hard basic properties not favorable for bonding with soft acidic Cu⁺. Consequently, the dapa ligand is a good candidate for solely π -complexation while possibly

retaining bridging function.

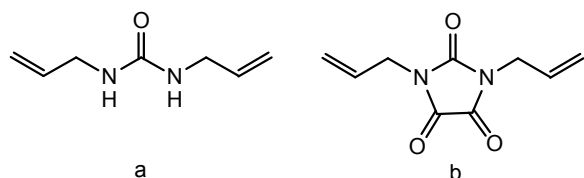


Fig. 1. Chemical structures of 1,3-diallylurea (dau) (a) and 1,3-diallylparabanate (dapa) (b)

Inspired by respective earlier studied silver complexes of dau [6], two compounds, $[\text{Cu}_2(\text{dau})\text{Cl}_{1.58}\text{Br}_{0.42}]$ (I) and $[\text{Cu}_2(\text{dapa})\text{Cl}_{1.74}\text{Br}_{0.26}]$ (II), were prepared and studied by X-ray diffraction in this work.

Experimental

Synthesis of the ligands

1,3-diallylurea (dau) was prepared starting from the unsubstituted urea and allylamine in a similar approach as described elsewhere [8].

For the synthesis of 1,3-diallylparabanate (dapa), sodium parabanate was prepared starting from urea and diethyloxalate according to the known procedure [9]. The salt was then alkylated in methanol with allyl bromide yielding dapa.

Preparation of $[\text{Cu}_2(\text{dau})\text{Cl}_{1.58}\text{Br}_{0.42}]$ (I)

To 4 mL of ethanol solution of $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ (2.4 mmol, 0.409 g), 0.322 g (2.3 mmol) of dau and 0.247 g (2.4 mmol) of NaBr were added. The mixture was carefully stirred and the resulting solution was placed into a 5 mL test tube and then copper-wire electrodes in cork were inserted. With the application of an alternating current (voltage of 0.56 V, frequency of 50 Hz) for 3 days the good quality colorless crystals of I appeared on the copper electrodes in a very small amount.

Preparation of $[\text{Cu}_2(\text{dapa})\text{Cl}_{1.74}\text{Br}_{0.26}]$ (II)

To methanol solution (4 mL) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (2.4 mmol, 0.409 g), 0.447 g (2.3 mmol) of dapa and 0.247 g (2.4 mmol) of NaBr were added. The mixture, after careful stirring, was subjected to an alternating current (voltage of 0.70 V, frequency of 50 Hz) for 4 days. Crystals of II appeared on the copper electrodes. The yield was about 45%. IR (FT-IR Spectrum BX-II (Perkin Elmer), nujol, cm^{-1}): 1770(m), 1727(s), 1656(m), 1636(m), 1627(m), 1548(m), 1523(w), 1414(m), 1405(m), 1351(m), 1336(m), 1318(m), 1296(w), 1258(w), 1174(vw), 1167(vw), 1140(vw), 1132(vw), 1106(vw), 1076(vw), 1033(vw), 981(vw), 956(vw), 942(w), 925(w), 916(vw), 882(vw), 854(vw), 846(vw), 832(vw), 823(vw), 767(vw), 758(w), 742(vw), 722(w), 677(vw),

649(vw), 578(vw), 553 (vw), 522(w), 488(w), 471(vw), 449(vw), 435(vw).

Single crystal X-ray diffraction studies

Diffraction data for I and II crystals were collected on an Oxford Diffraction Xcalibur four-circle diffractometer with MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$) and an Atlas CCD detector. The collected diffraction data were processed with the CrysAlis PRO program. The structures were solved by ShelXT program [13] and refined by least squares method on F^2 by ShelXL program [14] with the following graphical user interface of OLEX² [15]. Atomic displacements for non-hydrogen atoms were refined using an anisotropic model. Chlorine and bromine in both structures statistically occupy the halogen positions (ratios of 0.796(3):0.204(3) & 0.782(3):0.218(3) in complex I and ratios of 0.860(16):0.140(16) & 0.879(15):0.121(15)) in complex II). Hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The crystallographic parameters and summaries of data collection for I and II are presented in Table 1.

Results and discussion

1,3-Diallyl urea (dau) in the structure of π -complex $[\text{Cu}_2(\text{dau})\text{Cl}_{1.58}\text{Br}_{0.42}]$ (I) serves as a ligand possessing both σ - and π -coordination abilities. Atom Cu1 in I adopts trigonal pyramidal coordination surrounding ($\tau_4 = 0.78$, where τ_4 is the geometry index calculated elsewhere [10]) that consists of C7=C8 bond of the allyl group and O1 atom of the same dau molecule and two halogen ions (Hal1 & Hal2) of the endless copper(I) halide polymer chain. Cu1 deviates from the base plane of coordination polyhedron by 0.28(1) Å , whereas the angle between C7=C8 line and the base plane is 9.6(1) $^\circ$. Ion Cu2 in I possesses planar trigonal coordination environment formed by C10=C11 bond of the other allyl group of dau and two halogen ions of the neighboring infinite chain (Fig. 2, Table 2). π, σ -Coordination of the one half of copper ions and π -coordinated to the other half of copper shows similarity to dau's behavior in silver (I) complexes [6].

Copper halide 1D-polymer chains (Fig. 3) stretch along [010] in the crystal of the complex I. The chains are linked by the bridging molecules of dau into 3D-polymer.

1,3-Diallyl parabanate is exclusively π -coordinated in the structure of the compound $[\text{Cu}_2(\text{C}_9\text{H}_{10}\text{N}_2\text{O}_3)\text{Cl}_{1.74}\text{Br}_{0.26}]$ (II). Ion Cu1 forms trigonal pyramidal surrounding ($\tau_4 = 0.76$) that consists of Hal1, Hal1ⁱ and Hal1ⁱⁱ ions of the ladder-like copper halide polymer chain and C7=C8-bond of

Table 1

Selected crystal data and structure refinement parameters of I and II

Characteristics	I	II
CCDC number ^a	1890065	1870895
Empirical formula	C ₇ H ₁₂ Br _{0.42} Cl _{1.58} Cu ₂ N ₂ O	C ₉ H ₁₀ Br _{0.26} Cl _{1.74} Cu ₂ N ₂ O ₃
Formula weight	356.95	403.78
Temperature, K	100	100
Wavelength	MoK _α	MoK _α
Crystal system, space group	Orthorhombic, P2 ₁ 2 ₁ 2 ₁	Monoclinic, I2/a
Unit cell dimensions: a, Å	8.047(3)	6.420(3)
b, Å	8.154(3)	8.088(3)
c, Å	16.533(5)	49.020(9)
β, °	90	90.92(3)
V, Å ³	1084.8(7)	2545.0(16)
Z	4	8
Calculated density, g cm ⁻³	2.186	2.108
Absorption coeff., mm ⁻¹	5.831	4.526
F(000)	702	1590
Crystal size, mm ³	0.32×0.13×0.12	0.15×0.09×0.04
Color	colorless	colorless
Theta range for data collection, °	2.5–29.6	4.1–28.0
Measured reflections	57513	1739
Used in refinement	2945	1248
Refined parameters	130	105
R[F ² >2σ(F ²)], wR(F ²), S	0.0192, 0.0407, 1.097	0.0805, 0.2176, 1.005

Note: ^a CCDC 1890065 and 1870895 contain 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).

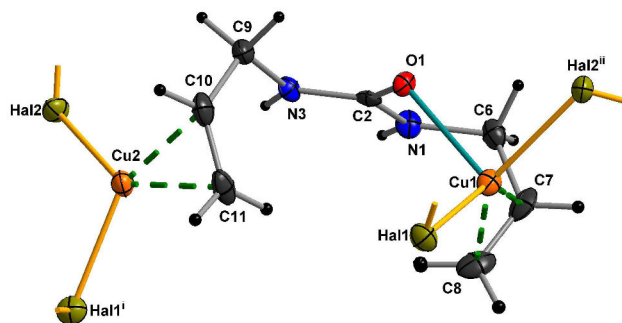


Fig. 2. Numbering scheme in structure of compound I.

Thermal ellipsoids are shown at 70% probability level.

Symmetry codes: (i) $x+1/2, -y+1/2, -z+1$; (ii) $-x+1/2, -y+1, z+1/2$

the allyl group (Fig. 4, Table 3). Cu1 deviates from the base plane of coordination polyhedron by 0.38(1) Å, whereas the angle between C7=C8 line and the base plane is 4.3(1)°. In contrast to Cu1, Cu2 ion is located in the trigonal surrounding that consists of Hal2 and Hal2ⁱⁱⁱ ions and C10=C11 bond of the other allyl group of the same dapa molecule. However,

Table 2

Selected bond distances and angles in the structure of compound I

Bond	d, Å	Angle	ω, °
Cu1–C7	2.098(3)	Hal1–Cu1–m ₁	124.14(9)
Cu1–C8	2.071(3)	O1–Cu1–m ₁	97.17(10)
Cu1–m ₁ ^a	1.970(3)	Hal2 ⁱⁱ –Cu1–m ₁	123.64(9)
C7–C8	1.362(5)	Hal1–Cu1–Hal2 ⁱⁱ	107.42(2)
Cu1–Hal1	2.3017(10)	O1–Cu1–Hal2 ⁱⁱ	92.23(5)
Cu1–Hal2 ⁱⁱ	2.3753(10)	O1–Cu1–Hal1	102.28(5)
Cu1–O1	2.279(2)	Hal2–Cu2–m ₂	126.56(9)
Cu2–C10	2.092(3)	Hal1 ⁱ –Cu2–m ₂	128.76(9)
Cu2–C11	2.060(3)	Hal2–Cu2–Hal1 ⁱ	104.04(2)
Cu2–m ₂ ^b	1.962(3)	Hal1–Cu1–Hal2 ⁱⁱ	107.42(2)
C10–C11	1.359(4)	Cu1–Hal1–Cu2 ^{iv}	90.57(3)
Cu2–Hal1 ⁱ	2.3086(10)	Cu2–Hal2–Cu1 ⁱⁱⁱ	117.06(3)
Cu2–Hal2	2.2950(8)		

Note: ^am₁ is the midpoint of C7=C8 bond; ^bm₂ is the midpoint of C10=C11 bond. Symmetry codes: (i) $x+1/2, -y+1/2, -z+1$; (ii) $-x+1/2, -y+1, z+1/2$; (iii) $-x+1/2, -y+1, z-1/2$; (iv) $x-1/2, -y+1/2, -z+1$. Hal stands for statistically present halogen ions: chloride and bromide.

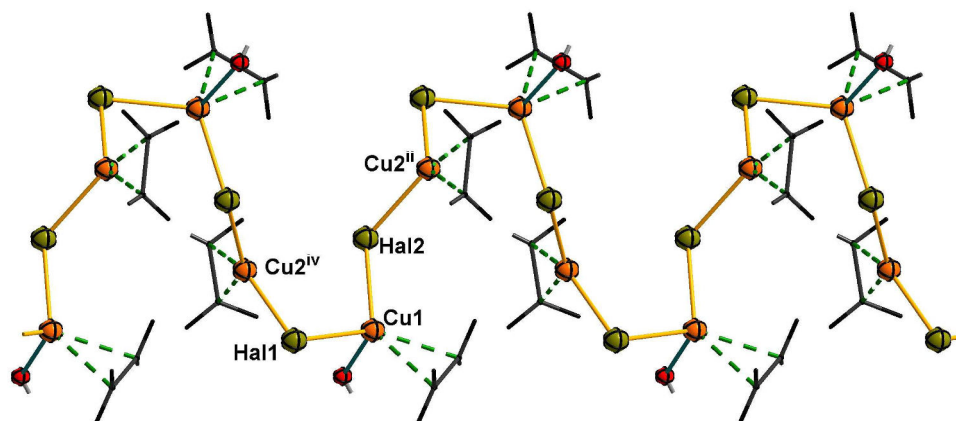


Fig. 3. Fragment of polymer copper(I) halide chain in compound I. Symmetry codes:
(ii) $-x+1/2, -y+1, z+1/2$; (iv) $x-1/2, -y+1/2, -z+1$

Table 3
Selected bond distances and angles in the structure of
compound II

Bond	d, Å	Angle	$\omega, ^\circ$
Cu1–C7	2.08(2)	Hal1 ⁱ –Cu1–m ₁	101.8(6)
Cu1–C8	2.09(2)	Hal1–Cu1–m ₁	128.2(6)
Cu1–m ₁ ^a	1.97(2)	Hal1 ⁱⁱ –Cu1–m ₁	124.2(6)
C7–C8	1.37(3)	Hal1 ⁱⁱ –Cu1–Hal1	98.30(18)
Cu1–Hal1 ⁱ	2.704(5)	Hal1 ⁱⁱ –Cu1–Hal1 ⁱ	105.06(17)
Cu1–Hal1	2.366(5)	Hal1 ⁱ –Cu1–Hal1	92.84(14)
Cu1–Hal1 ⁱⁱ	2.364(6)	Hal2–Cu2–m ₂	132.3(6)
Cu2–C10	2.09(2)	Hal2 ⁱⁱⁱ –Cu2–m ₂	118.4(6)
Cu2–C11	1.99(2)	Hal2 ⁱⁱⁱ –Cu2–Hal2	109.3(2)
Cu2–m ₂ ^b	1.91(2)	Cu1–Hal1–Cu1 ⁱ	86.84(14)
C10–C11	1.44(3)	Cu1 ⁱ –Hal1–Cu1 ⁱⁱ	81.70(18)
Cu2–Hal2	2.254(5)	Cu1 ⁱ –Hal1–Cu1 ⁱⁱ	99.40(18)
Cu2–Hal2 ⁱⁱⁱ	2.291(6)	Cu2–Hal2–Cu2 ^{iv}	111.1(2)

Note: ^am₁ is the midpoint of C7=C8 bond; ^bm₂ is the midpoint of C10=C11 bond. Symmetry codes: (i) $-x+1/2, y, -z+1$; (ii) $-x+1, \llcorner y, -z+1$; (iii) $x+1/2, -y+1, z$; (iv) $x-1/2, -y+1, z$. Hal stands for statistically present halogen ions: chloride and bromide.

σ -coordination is not observed for any oxygen atom in dapa in comparison to oxygen atom in dau, what is in consistence with harder Lewis basicity.

The two types of infinite copper(I) halide polymer chains propagating in parallel direction are cross-linked by the dapa molecules into 2D-sheets and for every a-type double strand chain (Cu1&Hal1) two b-type chains (Cu2&Hal2) are present (Fig. 5). Similar chain geometries were observed in other copper(I) halide complexes in both a-type [11] (copper(I) iodide) and b-type [12] chains (copper(I) chloride and iodide).

The sheets are stacked on each other with

protrusions of the sheet entering the depressions of the adjacent sheets and vice versa. Cu2 and Hal2 ions in the adjacent sheets approach each other close to the sum of van der Waals radii threshold providing electrostatic attraction that holds the sheets together.

The O3 and C5 atoms in the neighboring dapa moieties approach each other to a distance shorter than the sum of respective van der Waals radii, which could be interpreted as a consequence of dipole-dipole interaction or packing effects.

Compounds I and II demonstrate the joint action of copper(I) halide catenation and cross-linkage by organic molecules resulting into formation of polymers of higher dimension than copper(I) halide chains on their own. Their case illustrates how increase in hardness of potential σ -donating atoms causes a transition from one coordination mode to the other in ligands with similar geometry of copper(I) binding site.

Conclusions

Two copper(I) π -complexes, [Cu₂(dau)Cl_{1.58}Br_{0.42}] (I) and [Cu₂(dapa)Cl_{1.74}Br_{0.26}] (II), (where dau and dapa are 1,3-diallylurea and 1,3-diallylparabonate, respectively) were prepared and characterized for the first time in this work. Both structures contain two crystallographically independent copper(I) ions with one half in trigonal planar coordination environment and the other half in trigonal pyramidal one. Both compounds are built of parallel copper halide polymeric chains of one type in I and two types in II, cross-linked by organic ligand molecules to produce 3D-polymer bulk in I and 2D-layered structure in II. The structure of II is noteworthy due to the combination of two different chain types that have been previously observed only separately in copper(I) halide coordination compounds.

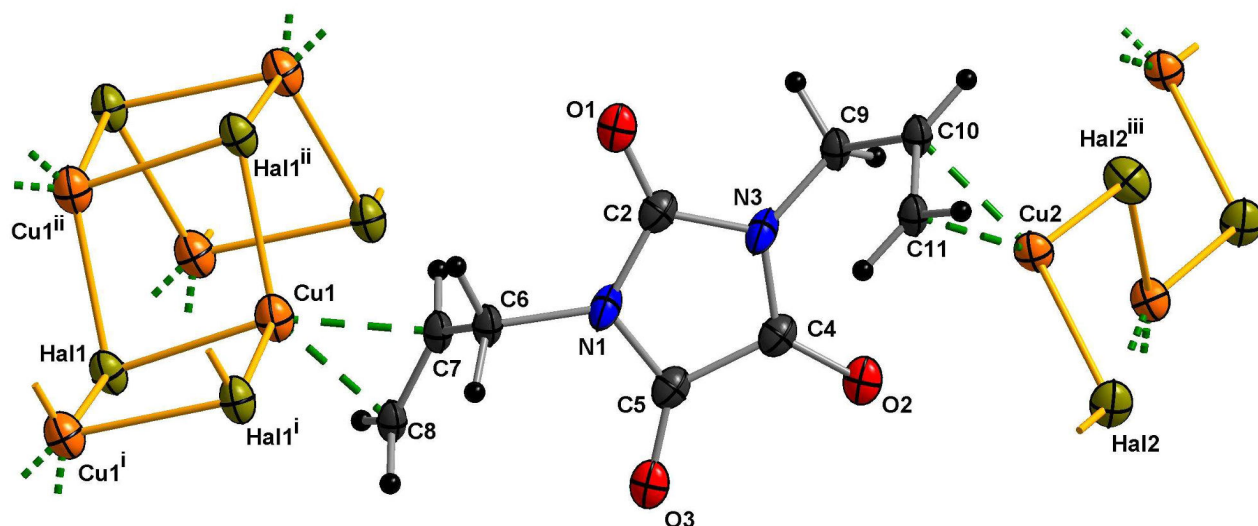


Fig. 4. Numbering scheme in structure of compound II. Thermal ellipsoids are shown at 50% probability level. Symmetry codes: (i) $-x+1/2, y, -z+1$; (ii) $-x+1, -y, -z+1$; (iii) $x+1/2, -y+1, z$

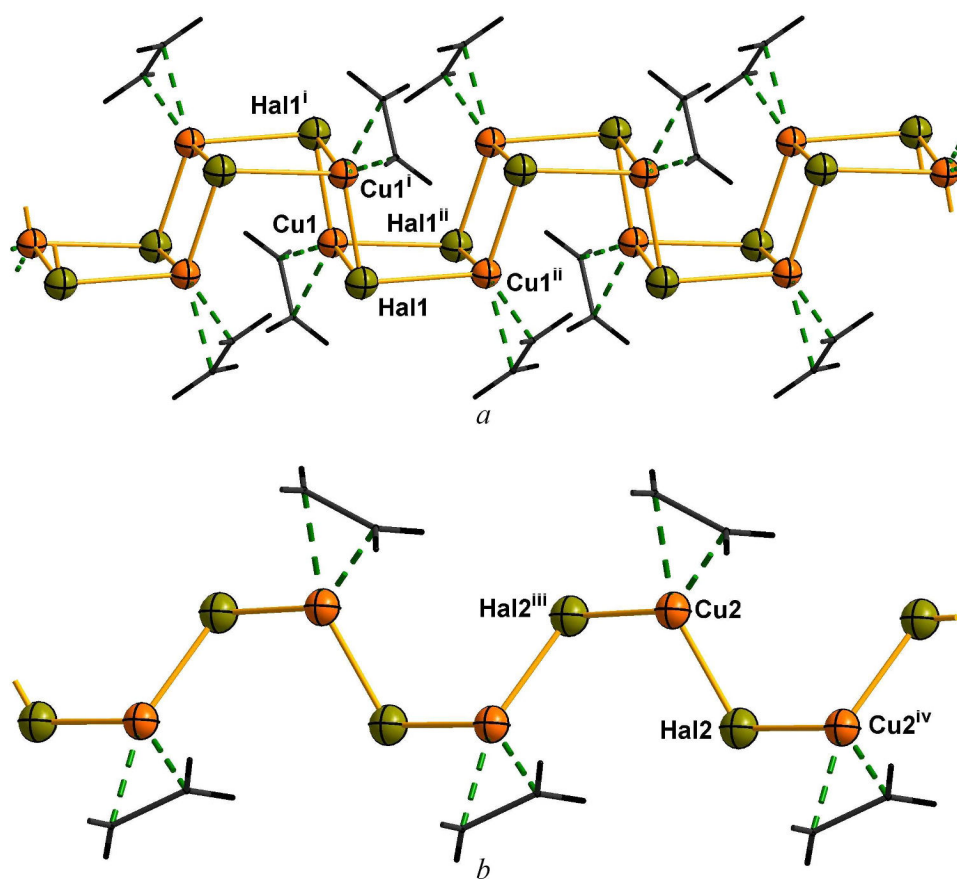


Fig. 5. Two types of copper(I) halide chains in structure of compound II. Symmetry codes: (i) $-x+1/2, y, -z+1$; (ii) $-x+1, -y, -z+1$; (iii) $x+1/2, -y+1, z$; (iv) $x-1/2, -y+1, z$

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ПЕРШІ π -КОМПЛЕКСИ ГАЛОГЕНІДІВ КУПРУМУ(I) З АЛІЛЬНИМИ ПОХІДНИМИ СЕЧОВИНИ І ПАРАБАНОВОЇ КИСЛОТИ

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Шляхом електрохімічного синтезу зі змінним струмом у метанольному розчині реагентів на мідних електродах було одержано два нових π -комплексів міді(I): $[\text{Cu}_2(\text{dau})\text{Cl}_{1.58}\text{Br}_{0.42}]$ (I) і $[\text{Cu}_2(\text{dara})\text{Cl}_{1.74}\text{Br}_{0.26}]$ (II) (dau – 1,3-діалілсечовина, dara – 1,3-діалілпарабанат) – виходячи з відповідних діаліл-похідних і галогенідів купруму(II). Сполука I кристалізується в орторомбічній сингонії, просторова група $P2_12_1$; $a=8.047(3)$ Å, $b=8.154(3)$ Å, $c=16.533(5)$ Å, $V=1085.8(76)$ Å³, $Z=4$. Сполука II кристалізується в моноклінній сингонії, просторова група $I2/a$; $a=6.420(3)$ Å, $b=8.088(3)$ Å, $c=49.020(9)$ Å, $\beta=90.92(3)^\circ$, $V=2545.03(16)$ Å³, $Z=8$. Обидві структури містять по два кристаліграфічно незалежних атоми Купруму, з яких одна половина знаходиться в тригональному координаційному оточенні, тоді як інша знаходиться у тригонально-пірамідальному оточенні. Обидві сполуки побудовані із паралельних ланцюгів галогенідів купруму(I) одного типу в I й двох типів у II, сполучених між собою молекулами органічних лігандів, що призводить до тривимірного каркаса в I і двовимірних шарів у II. В I 1,3-діалілсечовина одночасно π - і σ -зв'язана із ланцюгами галогенідів купруму(I) (за рахунок двох алільних груп і карбонільного атома Оксигену), тоді як в II 1,3-діалілпарабанат – виключно π -донорний ліганд. Структура сполуки II варта уваги через сумісну присутність двох різних типів полімерних ланцюгів галогенідів купруму(I), які до цього спостерігались в кристалічних структурах лише окремо.

Ключові слова: галогеніди купруму(I), π -комплекс, діалілсечовина, діалілпарабанат, кристалічна структура.

THE FIRST COPPER(I) HALIDE π -COMPLEXES WITH ALLYL DERIVATIVES OF UREA AND PARABANIC ACID

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By means of alternating current electrochemical synthesis with wire copper electrodes in methanolic solutions of corresponding ligands and copper(II) halide salts, two novel copper(I) π -complexes [Cu₂(dau)Cl_{1.58}Br_{0.42}] (I) and [Cu₂(dapa)Cl_{1.74}Br_{0.26}] (II) (where dau and dapa are 1,3-diallylurea and 1,3-diallylparabanate, respectively) were prepared in well-shaped crystalline form and studied with X-ray diffraction method. Compound I crystallizes in orthorhombic crystal system, space group P2₁2₁2₁; a=8.047(3) Å, b=8.154(3) Å, c=16.533(5) Å, V=1085.8(76) Å³, Z=4. Compound II crystallizes in monoclinic crystal system, space group I2/a: a=6.420(3) Å, b=8.088(3) Å, c=49.020(9) Å, β =90.92(3)°, V=2545.03(16) Å³, Z=8. Both structures contain two crystallographically independent copper(I) ions with one half in trigonal planar coordination environment and the other half in trigonal pyramidal one. Both compounds are built of parallel copper halide polymeric chains of one type in I and two types in II, cross-linked by organic ligand molecules to produce 3D-polymer bulk in I and 2D-layered structure in II. In compound I, 1,3-diallylurea is both π - and σ -bonded to copper(I) halide chains (by means of two allylic C=C bonds and carbonyl O atom), whereas 1,3-diallylparabanate is a solely π -donor ligand in compound II. The structure of II is noteworthy due to the combination of two different chain types that have been previously observed only separately in copper(I) halide coordination compounds.

Keywords: copper(I) halides; π -complex; diallylurea; diallylparabanate; crystal structure.

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