

Structure of Bis(Lidocaine) Tetrachloridocuprate(II)

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The present paper reports on the synthesis and structure of bis(2-(diethylamino)-N-(2,6-dimethylphenyl)acetamide) or bis(lidocaine) tetrachloridocuprate(II). The complex with the formula $(C_{14}H_{23}ON_2)_2CuCl_4$ (or $(LidH)_2[CuCl_4]$) crystallizes in the monoclinic space group $P2_1/c$ with $a = 15.7831(2)$, $b = 24.2992(2)$, $c = 17.8748(2)$ Å, $\beta = 104.874(1)^\circ$, $V = 6625.58(13)$ Å³, $Z = 8$, and $D_c = 1.355$ Mg/m³. The coordination of the Cu^{2+} ions with chlorine atoms generates two differently distorted tetrahedral anions $[CuCl_4]^{2-}$, while four protonated cations $LidH^+$ remain in an outer coordination sphere. Anions and cations are associated by hydrogen bonds of the N–H \cdots Cl type to form the $2((LidH)_2[CuCl_4])$ molecular dimer, in which the distance between two copper atoms is 8.95 Å. With the help of hydrogen bonds of the type N–H \cdots O and N–H \cdots Cl, each dimer is connected with four neighboring dimers, resulting in a three-dimensional hydrogen-bonded network in which dimers lie at an angle of 28.39° to the a crystallographic axis in the ab planes located at a distance of 10.67 Å from each other. © 2021 Bull. Georg. Natl. Acad. Sci.

Lidocaine complex, X-ray analysis, crystal structure, hydrogen bond

The study of charge transfer complexes of the local anaesthetic and antiarrhythmic drug lidocaine (2-(diethylamino)-N-(2,6-dimethylphenyl)acetamide, Lid) began in the early 1980s and continues to this day due to their role in medical and other applications [1]. A review of studies on lidocaine complexes is given in [2] and in our recent publications [3, 4], and it was shown that the crystal structure, hydrogen-bonding arrangement and conformation of the lidocaine molecule are significantly different for the easily soluble in diethyl ether free base ($C_{14}H_{22}ON_2$), water soluble

lidocaine hydrochloride monohydrate ($C_{14}H_{22}ON_2 \cdot HCl \cdot H_2O$), other salts and complexes.

The purpose of our work was to obtain new complexes of lidocaine and define their physical-chemical properties and structure; this contribution concerns a new copper complex of lidocaine. It is believed that the ability of hydrogen bond donation is essential to the action of lidocaine and other local anaesthetics [5], and special attention is paid to the formation of hydrogen bonds in this complex.

Table 1. Bond lengths and angles between the Cl–Cu–Cl bonds in [CuCl₄]²⁻ ions

Bond	Length (Å)	Bond	Length (Å)
Cu1—Cl11	2.3419	Cu2—Cl21	2.2269
Cu1—Cl12	2.2407	Cu2—Cl22	2.4314
Cu1—Cl13	2.2285	Cu2—Cl23	2.1966
Cu1—Cl14	2.2147	Cu2—Cl24	2.2115
Bonds	Angle (°)	Bonds	Angle (°)
Cl14—Cu1—Cl13	141.611(13)	Cl23—Cu2—Cl24	140.261(13)
Cl14—Cu1—Cl12	100.488(13)	Cl23—Cu2—Cl21	101.921(13)
Cl13—Cu1—Cl12	98.544(12)	Cl24—Cu2—Cl21	103.049(12)
Cl14—Cu1—Cl11	98.577(11)	Cl23—Cu2—Cl22	97.493(11)
Cl13—Cu1—Cl11	96.345(11)	Cl24—Cu2—Cl22	96.822(10)
Cl12—Cu1—Cl11	126.507(12)	Cl21—Cu2—Cl22	118.998(12)

Materials and Methods

Copper(II) complex of lidocaine was prepared in a weakly acidic (pH=5-6) water-methanol solution with 1:2 molar ratio of copper chloride (CuCl₂) and lidocaine hydrochloride monohydrate (C₁₄H₂₂ON₂HCl·H₂O). The prepared mixture was filtered, placed on a magnetic stirrer with heating for a certain time, and then left at room temperature for slow evaporation. Orange prismatic crystals suitable for the X-ray measurements started to form after 7-8 days. The resulting crystals were washed with ether and dried in air; isolated yield 64%, melting point 115°C, the product is easily soluble in water, ethanol, acetone and other organic solvents. Elemental analyses were performed using a Labertherm CHN elemental analyser and a Perkin-Elmer atomic adsorption spectrometer. Elemental analyses data (wt.%): calculated for C₂₈H₄₆Cl₄N₄O₂Cu: C 49.79; H 6.86; N 8.29; Cl 20.98; Cu 9.40; found: C 49.38; H 6.57; N 8.04; Cl 20.81; Cu 9.26.

The crystal structure of the complex was determined by single crystal X-ray diffraction (XRD) method using crystal with sizes 0.44 × 0.28 × 0.21 mm³. XRD measurements were carried out with an Oxford Diffraction XCALIBUR E CCD diffractometer equipped with graphite-monochromated MoK α radiation ($\mu = 1.100 \text{ mm}^{-1}$, $F_{000} = 1422$, $\lambda = 0.71073 \text{ \AA}$, $T = 100(2)\text{K}$). The data collection, cell refinement and data reduction were carried out with the CrysAlis^{PRO} package of Rigaku Oxford Diffraction (version 1.171.38.46, 2015); 2θ

range for data collection was from 5 to 65.4°, 145922 reflections collected, 23126 independent ($R_{\text{int}} = 0.032$). The structure was solved by direct methods and refined against F^2 with full-matrix least-squares using the software complex SHELXL-2014 [6]; final $GOF = 1.001$, $R[F^2 > 2\sigma(F^2)] = 0.031$, $wR_2 = 0.078$, R indices based on 18584 reflections with $I > 2\sigma(I)$ (refinement on F^2), $|\Delta\rho|_{\text{max}} = 0.55 \text{ e\AA}^{-3}$, 751 parameters, 0 restraints. CCDC 2103365 contains the supplementary crystallographic data for this paper; these data can be obtained free of charge via <https://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, Cambridge, UK, deposit@ccdc.cam.ac.uk).

Results and Discussion

According to the XRD crystallography, the prepared compound crystallizes in the monoclinic space group $P2_1/c$ (No. 14) with $a = 15.7831(2) \text{ \AA}$, $b = 24.2992(2) \text{ \AA}$, $c = 17.8748(2) \text{ \AA}$, $\beta = 104.874(1)^\circ$, $V = 6625.58(13) \text{ \AA}^3$, $Z = 8$ and $D_c = 1.355 \text{ Mg/m}^3$.

Molecular structure. The resulting compound has the structure of molecular dimer 2[bis(lidocaine) tetrachloridocuprate(II)], the charge transfer complex in which, upon coordination of each Cu²⁺ ion with four chlorine anions Cl⁻, two [CuCl₄]²⁻ anions are formed, surrounded by four protonated cations LidH⁺ in an outer coordination sphere (Fig.1). A similar picture was described [7] for nicotinium

tetrachlorocuprate (II), $(C_{10}H_{16}N_2)[CuCl_4]$, the structure of which comprises two crystallographically non-equivalent tetrahedral $[CuCl_4]^{2-}$ anions, each of which is linked to two doubly protonated nicotinium cations via hydrogen bonds.

The Cu(II) atoms in the $[CuCl_4]^{2-}$ anions are in distorted tetrahedral coordination geometry, the Cu–Cl interatomic distances deviate from 2.20(2) Å adopted for free $[CuCl_4]^{2-}$ [8], the angles between Cl–Cu–Cl bonds are very different from tetrahedral (96–141°, see Table 1); a similar picture (90–180°) is described for bis-(diethylammonium) tetrachloridocuprate(II) [9].

Distortions of the tetrahedral coordination are caused by the Coulomb interaction between the anions $[CuCl_4]^{2-}$ and asymmetrically arranged cations $LidH^+$, as well as by the hydrogen bonds in which the chlorine atoms participate (see Table 2).

Thus, the chlorine atom Cl11 enters into trifurcated hydrogen bond with the amido nitrogen atoms N111 and N211 of cations 1 and 2, respectively, and with the amino nitrogen atom N414 of the cation 4, while the farthest from copper atom Cu2 chlorine atom Cl22 also enters into

trifurcated hydrogen bond with the amido nitrogen atoms N311 and N411 belonging to cations 3 and 4, respectively, and with the amino nitrogen atom N214^{iv} of the neighboring cation; symmetrically, the intermolecular hydrogen bond N214–H214^{iv}···Cl22ⁱⁱⁱ is formed.

The distance between the donor and acceptor in hydrogen bonds connecting cations with anions exceeds 3.2 Å; therefore, such bonds are very weak, stronger are the bonds formed in the flexible chain of the cation between the aromatic ring and the diethylamino group. The probability of the formation of such intramolecular hydrogen bonds is determined by the conformation. According to the values of the corresponding torsion angles (see CCDC 2103365), the amide group is twisted out from the plane of the aromatic ring by 116.50(12), 83.43(15), ~112.71(12) and 98.12(13)° in cations 1, 2, 3 and 4, respectively. For all four cations the aromatic ring and the oxygen atom adopt a *synperiplanar* (C) conformation with respect to the carboxamide N–C bond, the amido and amino nitrogen atoms adopt staggered *antiperiplanar* (T) conformation excluding the formation of an

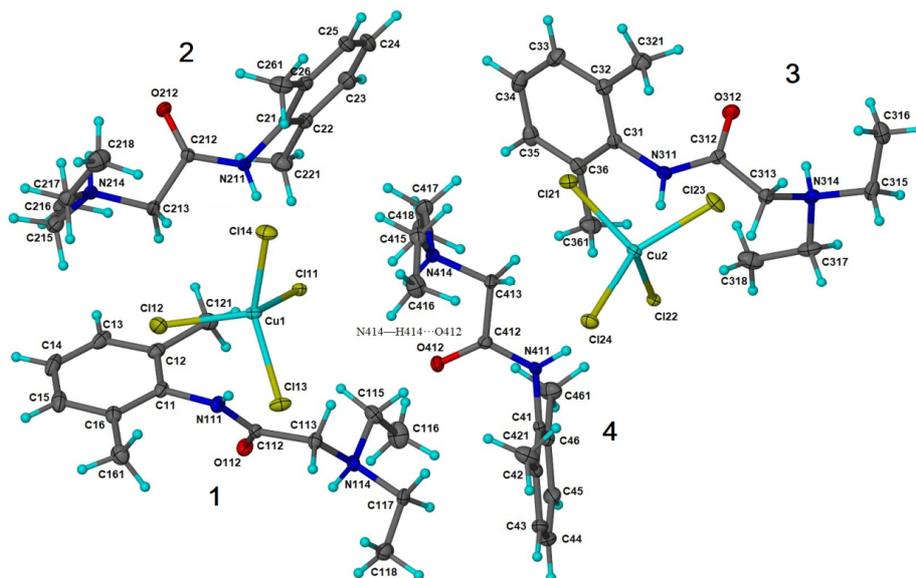


Fig. 1. Molecular structure of the $2((LidH)_2[CuCl_4])$ showing the atom and cation numbering scheme in accordance with CCDC 2103365. Displacement ellipsoids are drawn at 50% of the probability level.

intramolecular hydrogen bond N–H \cdots N noted in the lidocaine free base and its molecular complex, when the nitrogen atoms adopt a C conformation [9].

Earlier it was shown that if the carbonyl oxygen atom and the nitrogen atom of the amino group adopt the C conformation (torsion angle $\theta(\text{O}_{12}, \text{C}_{12}, \text{C}_{13}, \text{N}_{14})$ is in a range of $\pm 30^\circ$), then a relatively strong intramolecular hydrogen bond N–H \cdots O in the LidH $^+$ cations is formed [3, 4]. Corresponding torsion angles in cations **1**, **2** and **4** are 7.95(14), $-2.16(16)$ and $-4.83(15)^\circ$, respectively, while in cation **3**, the torsion angle $\theta(\text{O}_{312}, \text{C}_{312}, \text{C}_{313}, \text{N}_{314}) = -39.04(13)^\circ$ and exceeds the limit determining the conformation C, but the SHELXL software indicates the existence of a hydrogen bond with the distance between the donor and the acceptor of ~ 2.73 Å, slightly longer than the distance in other intramolecular hydrogen bonds (2.64–2.67 Å). At the same time, the SHELXL software does not indicate the N114–H114 \cdots O112 hydrogen bond, although the calculation of the coordinates of the corresponding atoms indicates its reality (the distance between the donor and acceptor is 2.64 Å, the angle is 109° , see Table 2). The amino nitrogen atoms N114 and N314 are also involved in intermolecular hydrogen bonds with oxygen atoms O112 i and O312 v belonging to the neighboring cations **1** i and **3** v and participating in

intramolecular hydrogen bonds N114 i –H114 i \cdots O112 i and N314 v –H314 v \cdots O312 v . Cartesian coordinates of the centers of inversion Cu1 \rightarrow Cu1 i and Cu1 \rightarrow Cu1 v , (7.89(1), 0, 0) and (15.78(2), 12.12(2), 0), respectively, coincide with the coordinates of the points located in the middle between the indicated atoms.

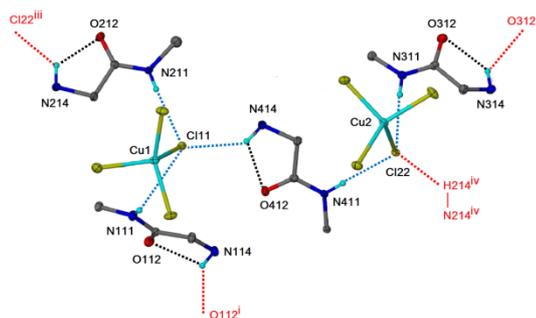


Fig. 2. Intramolecular (black dotted lines), cation-anionic (blue dotted lines) and intermolecular (red dotted lines) hydrogen bonds in $2((\text{LidH})_2[\text{CuCl}_4])$.

Supramolecular structure. The complete diagram of intramolecular, cation-anionic, and intermolecular hydrogen bonds in $2((\text{LidH})_2[\text{CuCl}_4])$ is shown in Fig. 2; the molecule of the complex is connected to four neighboring molecules by two N–H \cdots O and two N–H \cdots Cl hydrogen bonds. These structural features distinguish bis(lidocaine) tetrachloridocuprate(II) from bis(lidocaine) tetrachloridozincate(II), in

Table 2. Hydrogen-bond geometry according to SHELXL data and calculation results (in bold)

D–H \cdots A	D–H (Å)	H \cdots A (Å)	D \cdots A (Å)	D–H \cdots A ($^\circ$)
N111–H111 \cdots Cl11	0.845(16)	2.998(16)	3.4458(10)	115.4(12)
N211–H211 \cdots Cl11	0.798(18)	2.420(18)	3.2111(10)	171.2(16)
N414–H414 \cdots Cl11	0.881(17)	2.526(17)	3.2124(10)	135.3(14)
N311–H311 \cdots Cl22	0.856(16)	2.378(16)	3.2273(10)	171.8(14)
N411–H411 \cdots Cl22	0.840(17)	2.369(17)	3.2071(10)	175.2(15)
N214$^{\text{iv}}$–H214$^{\text{iv}}$$\cdots$Cl22	0.872(17)	2.5363(18)	3.2161(12)	135.4(15)
N114–H114\cdotsO112	0.872(16)	2.261(18)	2.6397(15)	106.09(15)
N214–H214 \cdots O212	0.872(17)	2.104(17)	2.6703(13)	122.1(14)
N314–H314 \cdots O312	0.882(16)	2.225(16)	2.7321(13)	116.2(12)
N414–H414 \cdots O412	0.881(17)	2.117(16)	2.6727(12)	120.3(14)
N114–H114 \cdots O112 i	0.872(16)	2.019(16)	2.8776(12)	167.8(15)
N214–H214 \cdots Cl22 $^{\text{iii}}$	0.872(17)	2.538(18)	3.2167(10)	135.4(14)
N314–H314 \cdots O312 v	0.882(16)	2.051(16)	2.8533(12)	150.8(14)

Symmetry codes: (i) $-x+1, -y, -z; z+1/2$; (iii) $x-1, y, z$; (iv) $x+1, y, z$; (v) $-x+2, -y+1, -z$.

which the molecules are combined into pairs $2((\text{LidH})_2[\text{ZnCl}_4])$, and the pairs form intermolecular $\text{N-H}\cdots\text{Cl}$ hydrogen bonds with four adjacent pairs, arranging them into endless sheets lying in the *bc* plane [4]. First, in zincate, the combination of molecules into pairs occurs due to symmetric bifurcated $\text{N-H}\cdots\text{O}$ hydrogen bonds, while in cuprate, copper atoms are linked by an asymmetric $\text{Cu1-Cl11}\cdots\text{H414-N414-C413-C412-N411-H411}\cdots\text{Cl22-Cu2}$ chain. Second, in zincate, neighboring pairs are linked by the same type of hydrogen bonds, while in cuprate, the interaction occurs by two different types of hydrogen bonds, and the “central” molecular dimer Cu1-Cu2 does not lie in the same plane with all four neighboring $2((\text{LidH})_2[\text{CuCl}_4])$ molecules (Fig. 3).

In $2((\text{LidH})_2[\text{CuCl}_4])$, the distance between the copper atoms Cu1 and Cu2 is $8.9519(19)$ Å, the angle between the line connecting them and the *ab* crystallographic plane is less than 0.13° . The molecular dimer Cu1-Cu2 and two molecular dimers, $\text{Cu1}^{\text{iii}}-\text{Cu2}^{\text{iii}}$ and $\text{Cu1}^{\text{iv}}-\text{Cu2}^{\text{iv}}$, connected by hydrogen bonds of the $\text{N-H}\cdots\text{Cl}$ type, lie in the same *ab* crystallographic plane, while molecular dimers $\text{Cu1}^{\text{i}}-\text{Cu2}^{\text{i}}$ and $\text{Cu1}^{\text{iv}}-\text{Cu2}^{\text{iv}}$ lie in the plane below (Fig. 3).

According to the coordinates of the atoms calculated for 17 molecules (including the “central” Cu1-Cu2 , its four nearest neighbors *i*, *iii*, *iv* and *v*, as well as the “second order” nearest neighbors: conversion $i\rightarrow\text{iii}$, $i\rightarrow\text{iv}$, $i\rightarrow\text{v}$, etc.), all molecules lie

at an angle of 28.39° to the *a* axis in four *ab* planes, but the distance between the two “upper” and two “lower” planes is small (0.02 Å), and this difference can be neglected. It can be assumed that the distance between the planes on which the molecules are located is $10.667(5)$ Å, on the “upper” plane together with the “central” dimer are dimers iii , $\text{v}\rightarrow\text{i}$, $\text{iii}\rightarrow\text{iv}$, $\text{iv}\rightarrow\text{iii}$, iv , etc., and on the “lower” plane there are dimers $\text{i}\rightarrow\text{iii}$, $\text{iv}\rightarrow\text{v}$, i , $\text{iv}\rightarrow\text{v}$, $\text{v}\rightarrow\text{iii}$, v , etc.

The “central” molecule and its nearest neighbors have the same arrangement of cations 1, 2, 3 and 4, or their orientation with respect to the direction from Cu1 to Cu2 (Fig. 3), but some neighbors of the “second order” ($\text{iv}\rightarrow\text{i}$, $\text{v}\rightarrow\text{iv}$, etc.) change this orientation, so that the planes *ab* “propagate” not only along the axes *a* and *b*, but also in both directions of the *c* axis, forming a three-dimensional hydrogen-bonded network.

Conclusion

The single-crystal XRD characterization shows that the bis(lidocaine) tetrachloridocuprate(II) consists of two $[\text{CuCl}_4]^{2-}$ distorted tetrahedral anions and four protonated cations of lidocaine LidH^+ in an outer coordination sphere. In addition to the Coulomb attraction forces, the anions and cations are associated by hydrogen bonds of the $\text{N-H}\cdots\text{Cl}$ type with the formation of a molecular dimer, in which the distance between two copper atoms is 8.95 Å. Four amido and one amino nitrogen atoms

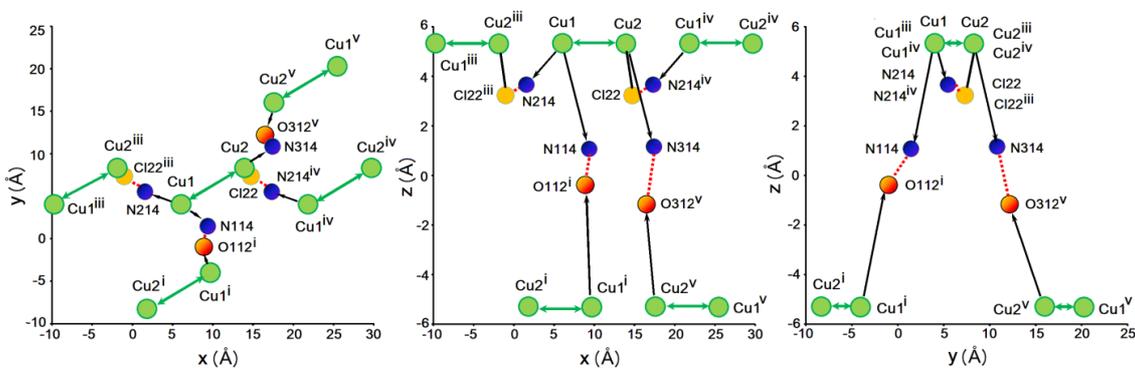


Fig. 3. Intermolecular hydrogen bonds between “central” molecule and its nearest neighbours viewed along $[001]$ (left), $[010]$ (middle) and $[100]$ (right).

participate in the cation-anionic hydrogen bonding, while two amino nitrogen atoms are involved in bifurcated hydrogen bonds providing N-H...O stacks with two neighbouring molecules of $2((\text{LidH})_2[\text{CuCl}_4])$; the other two adjacent molecules are hydrogen bonded through a fourth amino nitrogen atom and a chlorine atom. The three-dimensional hydrogen-bonded structure is constructed as follows: each molecule of the complex $2((\text{LidH})_2[\text{CuCl}_4])$ is associated with four neighboring molecules, lying in pairs in two crystallographic planes *ab*, the distance between

which is 10.67 Å; the vectors connecting the copper atoms $\text{Cu1} \rightarrow \text{Cu2}$ lie at an angle of 28.39° to the *a* axis.

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ქიმიკი

ბის(ლიდოკაინ) ტეტრაქლორიდოკუპრატ(II)-ის სტრუქტურა

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ნაშრომში განხილულია ბის(2-(დიეთილამინო)-N-(2,6-დიმეთილფენილ)აცეტამიდ) ტეტრაქლორიდოკუპრატ(II)-ის სინთეზი და სტრუქტურა. დადგენილია, რომ კომპლექსი ფორმულით $(\text{C}_{14}\text{H}_{23}\text{ON}_2)_2[\text{CuCl}_4]$ (ან $(\text{LidH})_2[\text{CuCl}_4]$), კრისტალიზდება მონოკლინურ სინგონიაში, $P2_1/c$ სივრცით ჯგუფში შემდეგი პარამეტრებით: $a = 15,7831(2)$, $b = 24,2992(2)$, $c = 17,8748(2)$ Å, $\beta = 104,874(1)^\circ$, $V = 6625,58(13)$ Å³, $Z = 8$, და $D_c = 1,355$ მეგაგრამი კუბურ მეტრზე. მოლეკულურ სტრუქტურაში ორი Cu^{2+} იონი კოორდინირდება ლიგანდებთან ორი განსხვავებულად დამახინჯებული ტეტრაედრული ანიონის $[\text{CuCl}_4]^{2-}$ სახით, ხოლო ოთხი პროტონირებული კატიონი LidH^+ რჩება გარე საკოორდინაციო სფეროში. ანიონები და კატიონები დაკავშირებულია ერთმანეთთან N-H...Cl ტიპის წყალბადური ბმებით და წარმოიქმნება $2((\text{LidH})_2[\text{CuCl}_4])$ მოლეკულური დიმერი, რომელშიც სპილენძის ორ ატომს შორის მანძილი 8,95 Å-ია. N-H...O და N-H...Cl ტიპის წყალბადური ბმების საშუალებით თითოეული მოლე-

კულური დიმერი უკავშირდება ოთხ მეზობელ დიმერს, რის შედეგადაც ყალიბდება სამგანზომილებიანი სტრუქტურა, სადაც დიმერები განლაგებულია ერთმანეთისაგან 10,67 Å-ით დაშორებულ ab სიბრტყეებზე, a კრისტალოგრაფიული ღერძის მიმართ 28,4°-ის კუთხით.

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