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SYNTHESIS, CRYSTAL STRUCTURE, HIRSHFELD SURFACE ANALYSIS AND QUANTUM CHEMICAL CALCULATIONS OF $[Cu_2(C_6H_9N_3S)_2(ClO_4)_2]$ Π-COMPLEX WITH 2-ALLYLAMINO-5-METHYL-1,3,4-THIADIAZOLE

This work is focused on the synthesis and structure characterization of the novel Cu(I) π-complex $[Cu_2(Thiaz1)_2(ClO_4)_2]$ (**1**) with 2-allylamino-5-methyl-1,3,4-thiadiazole (Thiaz1) ligand. The crystals of the compound were obtained by means of the alternating-current electrochemical technique and studied using single crystal X-ray diffraction. The crystal structure of the complex **1** is constructed from the centrosymmetric dimers, in which two copper(I) ions are coordinated by two Thiaz1 molecules through thiadiazole N atoms and allylic C=C bond. Energy framework computational analysis for structure **1** has been performed.

Keywords: copper(I) π-complex, thiadiazole derivatives, crystal structure, DFT calculation, Hirshfeld surface analysis.

1,3,4-Thiadiazoles have a wide range of applications in pharmaceutical chemistry [1] and due to their electron-deficient nature, good electron-accepting ability and chemical stability were found to be excellent precursors for the crystal engineering of organometallic materials with potential catalytic, magnetic, luminescent, nonlinear optic activity [2]. An appearance of the olefin C=C bond in a skeleton of the substituents, attached to the 1,3,4-thiadiazole ring, may serve as actual key for the selected coordination of transition metal ions due to metal-olefin π-bonding [3, 4]. As it was shown recently, allyl derivatives of 1,3,4-thiadiazoles, which unite rigid heterocyclic cores and conformation-flexible allyl group, were found suitable for the preparation of π-coordination compounds with unknown (or less stable) in a free state Cu(I) salts. For instance, the first examples of $Cu(C_6H_5SO_3)$ π-complexes as well as the direct Cu(I)···F(SiF_6^{2-}) interaction have been observed in copper(I) π-compounds with 2-allylamino-5-methyl-1,3,4-thiadiazole (Thiaz1) and 2-amino-5-allylthio-1,3,4-thiadiazole (Thiaz2) ligands [5]. According to the Cambridge Structural Database, more than fifteen π-complexes of Cu(I) salts (CuCl, $CuNO_3$, $CuBF_4$, Cu_2SiF_6, $Cu(C_6H_5SO_3)$) with mono- and diallyl derivatives of 1,3,4-thiadiazoles have been obtained and studied by X-ray crystallography [6]. As part of our ongoing studies in this area, the synthesis and structure of a novel $[Cu_2(Thiaz1)_2(ClO_4)_2]$ (**1**) π-complex are reported here.

Experimental section

Unless otherwise mentioned, all chemicals were obtained from a commercial source (Sigma Aldrich) and used without further purification. ^1H NMR spectrum for Thiaz1 was measured on a Bruker Avance 400 MHz NMR spectrometer. The chemical shifts are reported in ppm relative to the residual peak of the deuterated solvent – $CDCl_3$. The

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infrared spectrum for Thiaz1 was recorded on a Bruker Vertex 70 FTIR spectrometer in KBr pellets. Diffraction data for **1** were collected on a Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector, graphite monochromatized MoK_α radiation. Energy framework calculations were performed on the DFT/B3LYP/6–31G(d, p) level using the CrystalExplorer 17.5 software [7, 8].

Thiaz1 was prepared according to the reported previously procedure [9] starting from the 4-allylthiosemicarbazide. Thiaz1: NMR1H (400 MHz, $CDCl_3$), δ, ppm 6.36 (s, 1H), 5.97–5.87 (m, 1H), 5.32 (d, *J* = 17.2, 1H), 5.22 (d, *J* = 10.4, 1H), 3.94 (d, *J* = 5.6 Hz, 2H), 2.57 (s, 3H). IR (KBr, cm^{-1}): 3179(vs), 3076(m), 2978(vs), 2915(s), 2855(m), 2768(m), 2357(m), 2334(w), 1643(m), 1566(vs), 1491(vs), 1456(s), 1435(m), 1417(s), 1336(m), 1267(m), 1214(s), 1187(m), 1145(w), 1084(m), 1008(w), 992(m), 960(m), 925(s), 814(w), 756(m), 650(m), 617(w), 522(w).

Crystals of the coordination compound $[Cu_2(Thiaz1)_2(ClO_4)_2]$ (**1**) were obtained via alternating current electrochemical synthesis [10]. Equimolar quantities (1 mmol) of $Cu(ClO_4)_2{\cdot}6H_2O$ and Thiaz1 were dissolved in 5 mL of 95% ethanol. The solution was placed into a glass tube where it was sealed with a minimal volume of residual air using a rubber stopper equipped with two copper wire electrodes. Alternating voltage of 0.5 V with frequency of 50 Hz was applied to the electrodes for three weeks. Single crystals appropriate for X-ray diffraction measurements were collected from the electrodes. The yield was about 30%.

The collected diffraction data were processed with the Rigaku CrystalClear software suite program package [11]. The structure was solved using SIR-92 program and refined by least squares method on F^2 by ShelXL program with the graphical user interface of WinGX [12–14]. Atomic displacements for non-hydrogen atoms were refined using an anisotropic model. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Crystal parameters, data collection and the refinement parameters are summarized in Table 1.

Table 1

Selected crystal data and structure-refinement parameters of 1

Empirical formula	$C_{12}H_{18}Cl_2Cu_2N_6O_8S_2$
Formula weight	636.46
Temperature, K	200
Wavelength	MoK_α
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions, Å	
a, Å; α, °	7.8911(7); 112.483(3)
b, Å; β, °	8.0996(9); 90.2844(19)
c, Å; γ, °	10.4198(10); 118.682(2)
V, $Å^3$	525.05(9)

Continued table 1

Z	1
Calculated density, g/cm^3	2.013
Absorption coeff., mm^{-1}	2.534
F(000)	320
Crystal size, mm^3	0.07 × 0.08 × 0.10
Theta range for data collection, °	2.1–28.9
Measured reflections	5123
Used in refinement	2210
Refined parameters	145
$R[F^2 > 2\sigma(F^2)]$	0.0438
$wR(F^2)$	0.1144
$\Delta\rho_{\mathrm{max}}/\Delta\rho_{\mathrm{min}}$(e/Å^3)	0.597–0.797

RESULTS AND DISCUSSION

Compound $[Cu_2(Thiaz1)_2(ClO_4)_2]$ (**1**) crystallizes in the centrosymmetric space group $P\bar{1}$, with one organic molecule and one Cu(I) ion in the asymmetric unit. Thiaz1 molecule acts as bridging chelate π, σ-ligand being attached to Cu(I) by means of the C=C bond of allyl group and two N atoms of 1,3,4-thiadiazole ring (Fig. 1). The copper(I) ion adopts trigonal-pyramidal (τ_4=0.79, τ_4 – four-coordinate geometry index) surrounding, including in the basal plane of the polyhedron the N2 atom and the allylic C=C bond of one Thiaz1 molecule, the N1 atom of neighboring heterocyclic ring. The apical position of the pyramid is occupied by O1 atom of the anion. Thus, metal ions connect two Thiaz1 ligands into centrosymmetric $[Cu_2(Thiaz1)_2(ClO_4)_2]$ fragment with one six-member $\{Cu_2N_4\}$ cycle and two six-member $\{CuN_2C_3\}$ rings. Similar centrosymmetric dimers were found previously in the structure of $CuNO_3$ and $Cu(CF_3SO_3)$ π-complexes with Thiaz1 [9] as well as $CuNO_3$ and $CuClO_4$ π-complexes based on 2-allylthio-5-phenyl-1,3,4-oxadiazole ligand [15]. The strength of Cu(I)–(C=C) interaction in **1** is confirmed by the fact that allylic C=C bond is elongated to 1.355(5) Å (compared with a nominal value of 1.33 Å and a value of 1.340(7) Å in Thiaz1 structure itself [5]) due to back-donation from an occupied 3*d* metal orbital to a low-lying empty π* orbital of the olefin. Short Cu–*m* of 1.957(3) Å (*m* – a middle point of C5=C6 bond) distance and moderately large C–Cu-C of 38.2(2)° angle also confirm this conclusion. The Cu(I) ion deviates from the base of the trigonal pyramid only by 0.08(3) Å, while the angle between the C=C bond and the polyhedron basal plane is 12.2(1)°.

Through N – H···O hydrogen bonds between the H atom of the ligand amino group and the O toms of the ClO_4^- anion neighbouring [Cu_2(Thiaz1)$_2$(ClO_4)$_2$] fragments are linked into hydrogen-bonded stair-like chains (Fig. 1).

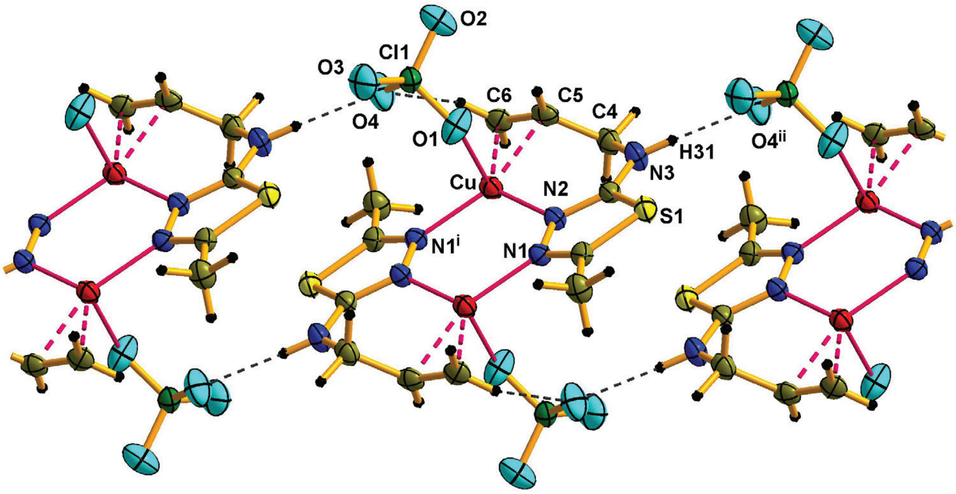


Fig. 1. Fragment of crystal structure **1** with displacement ellipsoids drawn at the 50% probability level. Symmetry codes: (*i*) –*x*,–*y*,–*z*; (*ii*) –1–*x*,–1–*y*,–*z*.

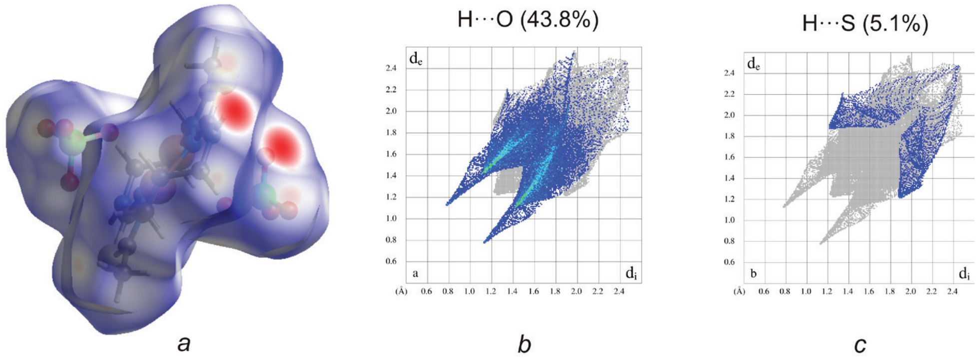
Table 2

Selected bond distances (Å) and angles (°) in the structure 1

Bond		**Angle**	
Cu – O1	2.628(3)	O1—Cu – *m*	97.8(1)
Cu – N1^i	1.972(3)	N1^i – Cu – *m*	133.5(1)
Cu – N2	2.014(3)	N2—Cu – *m*	111.5(1)
Cu – *m*	1.957(3)	N1^i – Cu – N2	114.6(1)
Cu – C5	2.057(3)	O1—Cu – N1^i	95.8(1)
C5—C6	1.355(5)	C5—Cu – C6	38.2(2)

m – is a mid-point of C5—C6 double bond. Symmetry code: (*i*) –*x*,–*y*,–*z*.

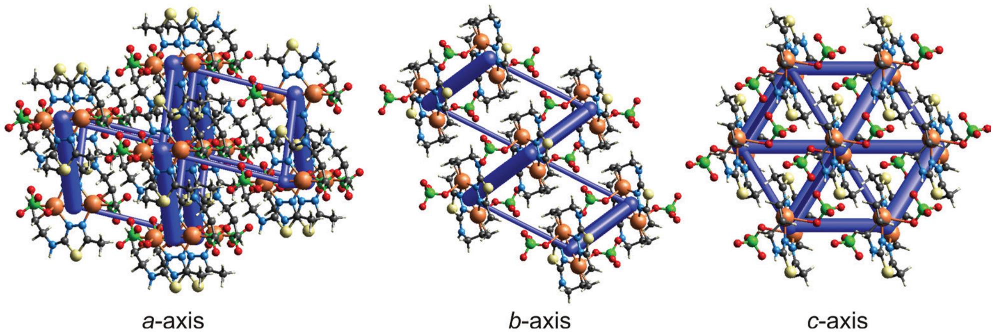
For the deeper analysis of the intermolecular interactions among the fragments of **1**, Hirshfeld surface analysis through the mapping of the normalized contact distance (d_{norm}) as well as calculation of the interaction energies were performed using the *CrystalExplorer* software. The most prominent interactions N – H···O among the amino-group H atoms and anion O atoms of neighboring moieties can be seen in the Hirshfeld surface plot as the strongly red areas (Fig. 2(a)). The other poorly red and white areas on the surface plot correspond mainly to the C – H···O interactions. Fingerprint plots were produced to show the intermolecular surface bond distances with the regions highlighted for H···O and H···S interactions. The contribution to the surface area for H···H contacts is 24.5%.



a *b* *c*

Fig. 2. Hirshfeld surface for dimeric fragment of **1** mapped with d_{norm} over the range –0.55 to 1.16 (*a*). Fingerprint plots for molecule resolved into O···H/H···O (*b*) and S···H/H···S (*c*) contacts.

The energy framework calculations discussed in this paper were performed on the DFT/B3LYP/6–31G(d, p) level. All the calculations were provided for clusters of $[Cu_2(Thiaz1)_2(ClO_4)_2]$ fragments within a radius of 3.8 Å, which were generated around a single fragment. This method provides a qualitative picture of the 3*D*-topology of the main interactions in the crystal packings. The values of interaction energy calculated between the dimeric fragments in **1** are tabulated in Table 3 and visualized in Fig. 3. The cylinders in the energy framework represent the relative strengths of molecular packing in the different directions – interaction energies are proportional to the thickness of cylinders joining the centroids of fragments.



a-axis *b*-axis *c*-axis

Fig. 3. Energy frameworks of **1** representing the total interaction energy (blue) along the different crystallographic directions.

According to the calculations (Fig.4 & Table 3), the main intermolecular interactions, which corresponds to the N – H···O hydrogen bonding with two dimers **I**, cover the total energy of –151.6 kJ/mol, with significant influence of electrostatic interaction. The interaction energy with the next neighboring fragments **II**, which are located above and below the main fragment, is –111.3 kJ/mol. The last value indicates significant influence of the C – H···O hydrogen bonding between mentioned moieties. In contrast to **I**, **II** and **IV**, interactions of the main fragment with **III** are mostly determined by dispersion interactions of ligand Thiaz1 methyl group. The total energy of all interaction between the dimers in **1** appears to be –379.4 kJ/mol.

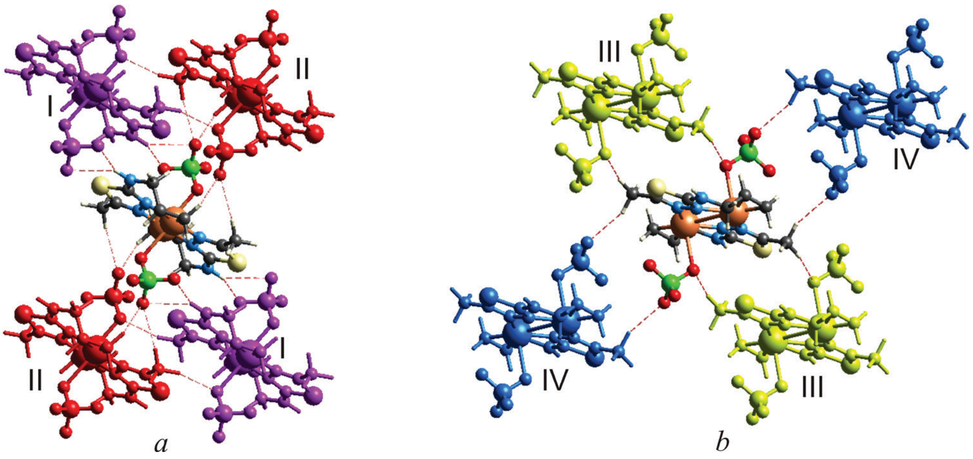


Fig. 4. The principal interactions between fragments [Cu_2(Thiaz1)$_2$(ClO_4)$_2$] in **1** with numbering of molecules involved in the interactions with the selected one.

Table 3

The most prominent molecular interaction energies (kJ/mol) for the [Cu_2(Thiaz1)$_2$(ClO_4)$_2$] dimers in 1

№	*N* [a]	Symop	*R* [b]	*E*_ele	*E*_pol	*E*_dis	*E*_rep	*E*_tot [c]
I	2	1+*x*, 1+*y*, *z* –1-*x*,–1-*y*, -*z*	8.16	-119.5	-54.1	-66.3	117.4	-151.6
II	2	1+*x*, *y*, *z* –1-*x*, 1-*y*, -*z*	7.89	-67.8	-34.9	-42.9	38.2	-111.3
III	2	*x*,–1+*y*, *z* – *x*, 1-*y*, -*z*	8.10	-27.4	-27.2	-56.9	50.3	-67.6
IV	2	1+*x*, 1+*y*, 1+*z* –1-*x*,–1-*y*,–1-*z*	10.48	-23.1	-15.8	-22.0	13.6	-46.8

[a] *N* is the number of molecules involved in the interactions with the selected one.
[b] *R* is the distance between molecular centroids (mean atomic position) in Å.
[c] Each energy should be multiplied by the conversion factors k_{ele} = 1.057, k_{pol} = 0.740, k_{dis} = 0.871, k_{rep} = 0.618 to obtain the total energy (E_{tot}).

CONCLUSIONS

We presented the synthesis and structure characterization of the novel π-complex $[Cu_2(Thiaz1)_2(ClO_4)_2]$ (**1**) with 2-allylamino-5-methyl-1,3,4-thiadiazole (Thiaz1) ligand. Organic molecule reveals quite common coordination behaviour of allyl 1,3,4-thiadiazoles, being attached to the metal ion by means of allylic C=C bond and two heterocyclic N atoms. Energy frameworks computational analysis confirms the major role of N – H···O interactions (with predominance of electrostatic factor) in the crystal structure organization: through N – H···O hydrogen bonds neighboring $[Cu_2(Thiaz1)_2(ClO_4)_2]$ fragments are linked into hydrogen-bonded stair-like chains. The energy of C – H···O interactions were also quite high which confirms their considerable impact in stabilizing the structure of **1**.

SUPPLEMENTARY MATERIAL

CCDC number 2052890 (**1**) contains 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).

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СИНТЕЗ, КРИСТАЛЛИЧЕСКАЯ СТРУКТУРА, АНАЛИЗ ПОВЕРХНОСТИ ХИРШФЕЛДА И КВАНТОВО-ХИМИЧЕСКИЕ РАСЧЕТЫ П-КОМПЛЕКСА $[Cu_2(C_6H_9N_3S)_2(ClO_4)_2]$ С 2-АЛЛИЛАМИНО-5-МЕТИЛ-1,3,4-ТИАДИАЗОЛОМ

Цель этой роботы – синтез и определение кристаллической структуры нового π-комплекса Cu(I) состава $[Cu_2(Thiaz1)_2(ClO_4)_2]$ (**1**) с 2-аллиламино-5-метил-1,3,4-тиадиазолом (Thiaz1). Кристаллы соединения получены методом переменно-токового электрохимического синтеза и исследованы рентгеноструктурно. Кристаллическая структура комплекса **1** построена из центросимметрических димеров, в которых два иона меди(I) координированы двумя молекулами Thiaz1 атомами N тиадиазола и аллильною связью C=C лиганда Thiaz1. Проведены анализ поверхности Хиршфелда для димерной частицы комплекса и квантово-химические расчеты энергий межмолекулярных взаимодействий.

Ключевые слова: медь(I) π-комплекс, производные тиадиазола, кристаллическая структура, расчеты DFT, анализ поверхности Хиршфелда.

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СИНТЕЗ, КРИСТАЛІЧНА СТРУКТУРА, АНАЛІЗ ПОВЕРХНІ ГІРШФЕЛЬДА ТА КВАНТОЛВО-ХІМІЧНІ ОБЧИСЛЕННЯ П-КОМПЛЕКСУ $[Cu_2(C_6H_9N_3S)_2(ClO_4)_2]$ З 2-АЛІЛАМІНО-5-МЕТИЛ-1,3,4-ТІАДІАЗОЛОМ

Стаття присвячена синтезу та дослідженню кристалічної будови нового π-комплексу Cu(I) складу $[Cu_2(Thiaz1)_2(ClO_4)_2]$ (**1**) з 2-аліламіно-5-метил-1,3,4-тіадіазолом (Thiaz1). Thiaz1 синтезовано за відомою методикою, виходячи із 4-алілтіосемікарбазиду. Якісні монокристали **1** одержано методом змінно-струмного електрохімічного синтезу на мідних електродах (при напрузі 0.5 В, частота 50 Гц) із етанольного розчину органічного ліганду та купруму(II) перхлорату гексагідрату. Сполука **1** кристалізується в центросиметричній просторовій групі $P\bar{1}$, з однією органічною молекулою та одним іоном Cu(I) в асиметричній частині комірки. Молекула Thiaz1 виконує в структурі роль містково-хелатного ліганду, координуючись до іонів Cu(I) зв'язком C=C алільної групи та двома атомами N 1,3,4-тіадіазольного ядра. Іон купруму(I) формує тригонально-пірамідальне оточення (геометричний індекс $\tau_4 = 0,79$), яке у базальній площині поліедра включає атом N2 та зв'язок C=C однієї молекули Thiaz1, а також атом N1 сусіднього гетероциклічного ядра. Апікальну позицію піраміди посідає атом O перхлорат-аніону. Внаслідок π-координації до центрального атома подвійний зв'язок C=C дещо видовжився до 1,355(5) Å, у порівнянні із некоординованим у структурі самого Thiaz1. Через водневі зв'язки N – H···O між атомами H аміногрупи ліганду та атомами O перхлорат-аніонів сусідні фрагменти $[Cu_2(Thiaz1)_2(ClO_4)_2]$ об'єднуються у воднево-зв'язаний сходинковий ланцюг. Для детального аналізу міжмолекулярних взаємодій між фрагментами проведено аналіз поверхні Гіршфельда. Внесок контактів O···H, S···H і H···H у площу поверхні становить 43,8%, 5,1% і 24,5%, відповідно. Розрахунки енергій міжмолекулярних взаємодій, проводились на рівні DFT/B3LYP/6–31G(d, p). Всі розрахунки здійснено для кластерів фрагментів $[Cu_2(Thiaz1)_2(ClO_4)_2]$ в радіусі 3,8 Å, які були сформовані навколо одного фрагмента. За результатами розрахунків, енергія основних міжмолекулярних взаємодії, що відповідають водневим зв'язкам N – H···O з двома димерами, складає –151,6 кДж/моль. Сумарна енергія всіх міжмолекулярних взаємодій у структурі **1** становить –379.4 кДж/моль.

Ключові слова: π-комплекс купруму(I), похідні тіадіазолу, кристалічна структура, обчислення DFT, аналіз поверхні Гіршфельда.

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