COMPARATIVE PECULIARITIES OF POLYTYPY OF CRYSTALS Cu(D-Ala)(L-Ser) AND Cu_2(D-Ala)(L-Ala)(D-Ser)(L-Ser)

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Abstract

Atomic structures of two polytypic modifycations of crystals of mixed cooper (II) compound Cu(D-Ala)(L-Ser) with optically active α-alanine (Ala) and serine (Ser) were studied by the electron diffraction analysis method: modification I - a=9.26(2) Å, b=9.60(1) Å, c=4.98(1) Å, γ=91.2(3)°, Z=2, space group of symmetry $P2_1$; modification II - a=*18.52*(2) Å, b=9.60(1) Å, c=4.98(1) Å, γ=91.2(3)°, Z=4, space group of symmetry $C2_1$.

It was demonstrated that the modifications of the crystals of two compounds Cu(D-Ala)(L-Ser) and Cu_2(D-Ala)(L-Ala)(D-Ser)(L-Ser) with racemic amino acids, correspondingly, belong to the same family of polytypic modifications.

Introduction

Earlier, there has been demonstrated the ability of the mixed cooper (II) compound containing racemic α-alanine (Ala) and serine (Ser) to crystallize in polytypic modifications [1]. In this connection, it is interesting to elucidate the possibilities of analogous modification formation by the crystals of cooper (II) compound with active α-alanine and serine. For this purpose, the study of earlier obtained crystals of mixed compound Cu(D-Ala)(L-Ser) was continued. Paper [2] describes the method of crystal Cu(D-Ala)(L-Ser) synthesis in solid state (modification I), the data about crystal structure of this compound are given in [3-5]. The electron diffraction structural data analysis showed that compounds Cu(D-Ala)(L-Ser) and Cu_2(D-Ala)(L-Ala)(D-Ser)(L-Ser) have layered structure [4, 5]. Both structures are made up by one and the same initial structural fragment in the form of a band, along which separate mixed complexes Cu(D-Ala)(L-Ser) are periodically arranged. Their difference consists in the method of mutual arrangement of these bands in the layers. In the layers of structure of cooper (II) compound with D-α-alanine and L-serine the neighbouring bands are crystallographically connected by second order screw axes, whereas in the layers of structure with racemic α-alanine and serine the neighbouring bands are crystallographically connected by the planes of sliding reflection. The interatomic distances and bond angles are practically identical in both structures. The unit-cell parameters are almost identical too. For the crystals Cu(D-Ala)(L-Ser) (modification I) a=9.26(2) Å, b=9.60(1) Å, c=4.98(1) Å, γ=91.2(3)°, Z=2, space group of symmetry $P2_1$; for the crystals Cu_2(D-Ala)(L-Ala)(D-Ser)(L-Ser) (modification I) a=*9.51*(2) Å, b=9.57(1) Å, c=5.04(1) Å, γ=92.3(3)°, Z=1, space group of symmetry *Pb*.

As it can be seen, there is a small difference in the values of *a*-metrical parameters that characterizes the interlayer distances in both structures. These differences are attributed to unequal symmetry of interlayer space of structures [5]. Thus, these structures can be referred to polytypic diversity. It should be mentioned that these polytypic structures are formed not due to different combinations of variants of the physical layers in three-dimensional structures, as it can be observed in the stratified structures of semiconductor compounds and minerals [6], but due to different ways of structural fragments arrangement in the physical layer limits.

Polytypy of crystals Cu(D-Ala)(L-Ser)

During preparation and study by electron diffraction method of crystals Cu(D-Ala)(L-Ser) samples, in addition to the earlier described crystals (modification I), another modification of these crystals (modification II) was detected. Elementary unit cell of crystals of this modification in comparison with the unit cell of modification I is twice as much: *a=18.52*(2) Å, *b*=9.60(1) Å, *c*=4.98(1) Å, γ=91.2(3)°, Z=4. In the diffraction images of modification II reflections *00l* with *l=2n+1* and *hkl* with *h+k=2n+1* are absent. This character of reflection intensity distribution corresponds to basic centered space groups of symmetry $C2_1$ and $C2_1/m$. However, its realization is impossible in the crystals Cu(D-Ala)(L-Ser) because in this case the compound will contain the optical isomers of α-alanine and serine of different sign, correspondingly. The mentioned reflection extinguishment indicates also that the structural units in the structure Cu(D-Ala)(L-Ser) of modification II are crystallographically connected in pairs by [½½0] translation. The electron diffraction data indicated that the structure Cu(D-Ala)(L-Ser) of modification II is constructed from the same complexes as the structure of modification I. The coordinates of basic atoms of structure modification II are listed in Table 1, and interatomic distances and bond angles that practically do not differ from structure modification I of corresponding values, are listed in Table 2. For clearness, the fragments of structures modifications I and II are shown in Fig. 1 and Fig. 2. The complexes Cu(D-Ala)(L-Ser) in modification II are arranged in the analogous layers that are parallel to the *bc* plane as well as in modification I. However, the combination rule of adjacent layers in modification II differs from modification I. In structure modification II the adjacent layers are displaced one to another by *±1/2b,* whereas in structure modification I these displacements are absent (Fig. 1 and 2). In addition, there are distinctions in the peculiarity of interlayer spaces. In structure modification I the adjacent layers contact with one another by hydroxyl groups O8H and O5H and by oxygen O4 and O9 of the carboxyl groups of serine residue (O8H…O4 3.15 Å; O5H…O93.15 Å), whereas in modification II – by hydroxyl groups O5H and O8H of serine residues and by oxygen O6 and O9 of the carboxyl groups of α-alanine residue (O5H…O9 3.21 Å; O8H…O6 3.21 Å). The values of the mentioned contacts, including interlayer distance are identical in both modifications. Thus, there is a possibility of principle for the crystals Cu(D-Ala)(L-Ser) of the polytypic variety. The structures of both modifications are made up from the common two-dimensional structural unit (layer). This structural unit, remaining invariable, forms different structures due to variations of its mutual arrangement.

Conclusions

Polytypy, as a crystallochemical phenomenon in structures modifications I and II of the crystals Cu(D-Ala)(L-Ser) and also in modifications I and II of the crystals Cu_2(D-Ala)(L-Ala)(D-Ser)(L-Ser), is realized to all its volume of the structure, and, perhaps, it should be

called three-dimensional polytypy, whereas in structures modification I of crystals Cu(D-Ala)(L-Ser) and Cu_2(D-Ala)(L-Ala)(D-Ser)(L-Ser) and also in modifications II of the same crystals, polytypy is realized in the layer limit and it should be call the two-dimensional polytypy. The discovered modifications of crystals Cu(D-Ala)(L-Ser) and Cu_2(D-Ala)(L-Ala)(D-Ser)(L-Ser) should be attributed to one family of polytypic modifications, the structure of which is characterized by common to all one-dimensional structural unit [Cu(D-Ala)(L-Ser) bands] and are realized only by their mutual arrangement in space.

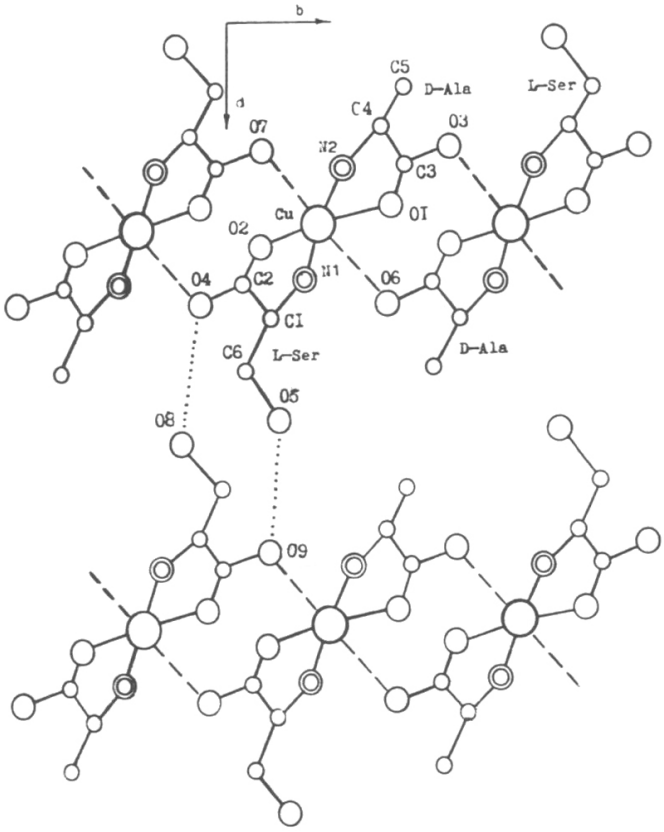

Fig. 1. Model of the Cu(D-Ala)(L-Ser) structure, modification I.

Table 1. Coordinates of non-hydrogen atoms in the structure Cu(D-Ala)(L-Ser), modification II.

Atom	x/a	y/b	z/c
Cu	0.000	0.250	0.250
O1	-0.020(7)	0.415(6)	0.442(7)
O2	0.018(7)	0.085(6)	0.052(7)
O3	-0.098(7)	0.584 (6)	0.446(7)
O4	0.102(7)	-0.084(6)	0.043(7)
O5	0.231(7)	0.113(6)	0.569(7)
N1	0.071(7)	0.188(6)	0.515(7)
N2	-0.071(7)	0.312(6)	-0.015(7)
C1	0.117(8)	0.089(7)	0.364(8)
C2	0.073(8)	0.028(7)	0.135(8)
C3	-0.073(8)	0.476(7)	0.363(8)
C4	-0.113(8)	0.413(7)	0.126(8)
C5	-0.175(8)	0.466(7)	-0.012(8)
C6	0.175(8)	0.035(7)	0.519 (8)

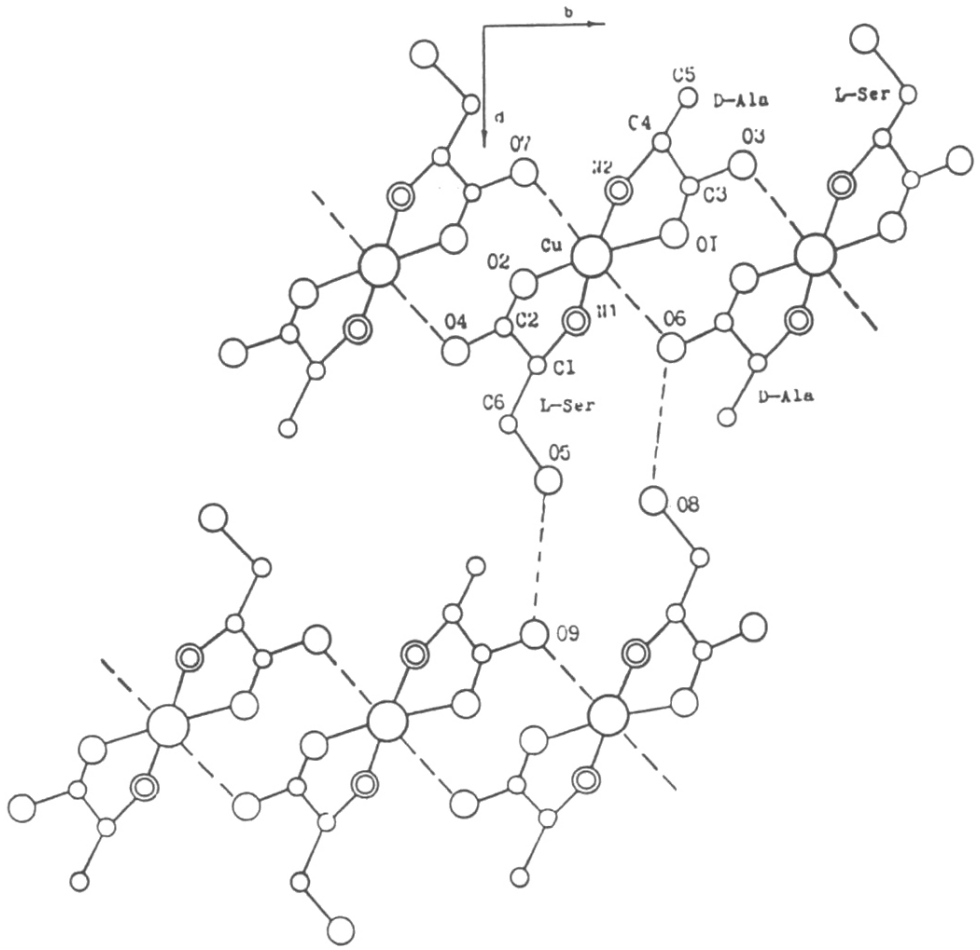

Fig. 2. Model of the Cu(D-Ala)(L-Ser) structure, modification II.

Table 2. Interatomic distance (Å) and bond angles (degree) in the structure Cu(D-Ala)(L-Ser), modification II.

Atoms	Distance	Atoms	Angle
Cu-O1	1.89(2)	N1-Cu-O1	93.9
Cu-O2	1.91(2)	N1-Cu-O2	87.7
Cu-N1	1.96(2)	N2-Cu-O1	86.1
Cu-N2	1.96(2)	N2-Cu-O2	92.3
C2-O4	1.30(3)	O4-C2-O2	127.6
C2-O2	1.24(3)	O4-C2-C1	111.3
C2-C1	1.51(3)	O2-C2-C1	121.1
C1-C6	1.49(3)	C2-C1-N1	108.6
C1-N1	1.50(3)	C2-C1-C6	131.7
O5-C6	1.27(3)	C6-C1-N1	114.3
C3-C4	1.51(3)	C1-C6-O5	119.5
C4-N2	1.45(3)	C3-C4-C5	127.8
C4-C5	1.46(3)	N2-C4-C5	117.5
C3-O1	1.23(3)	C3-C4-N2	112.4
C3-O3	1.26(3)	C4-C3-O1	116.2
		C4-C3-O3	117.9
		O1-C3-O3	125.8

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