CRYSTALLOCHEMICAL FEATURES OF MIXED COPPER(II) COMPOUNDS CONTAINING OPTICALLY ACTIVE ISOMERS OF SERINE AND THREONINE IN THE RATIO OF 1 : 1

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This paper is dedicated to the memory of academician Tadeush Malinowski —
the founder of crystallographic research in Moldova

Abstract

The polytypism of the crystals of mixed copper(II) compounds with α-amino acids with the CuSerTre composition was investigated by the electron diffraction method. The crystal characteristics and atomic structure of nine polytypic modifications containing optically active antipodes of serine (Ser) and threonine (Tre) in the ratio of D : L = 1 : 1 were determined and described.

1. Introduction

This paper is the continuation of investigation of the crystallochemical phenomena in crystals of biologically active complexes with α-amino acids [1, 2]. These phenomena (polytypism, polysomatism, etc.) contribute to a better understanding of the structural and crystallographic aspects of these compounds, their symmetrical and diffraction specific features; this provides the possibilities for theoretical conclusion, description, and experimental identification of new unknown compounds with α-amino acids that exhibit useful properties.

2. Results and discussion

The studies were carried out by the electron diffraction method. The ability of mixed complex compounds with the general formula CuSerTre, which contain optically active isomers of serine and threonine in the ratio of D : L = 1 : 1, to crystallize in polytypic modifications was revealed via this method [3, 4]. According to electron diffraction structural data obtained previously [5-7], the observed polytypic modifications are built up from separate mixed complexes of two types: Cu(D-Ser)(L-Tre) and Cu(L-Ser)(D-Tre). In the structures of these modifications, the mixed complexes are packed in two-dimensional structural units (layers) parallel to the *bc*-coordination plane of the crystal lattices in such a way that the complexes of each type form separate one-dimensional structural units (band) within the layer parallel to the *b*-axis of the crystal lattices [8]. It was determined that the layers, as well as the band within the layer, can be located relative to each other in various ways in the mentioned structures without violating the crystallochemical conditions of their vicinity. This crystallochemical phenomenon, which is called polytypism, in some modifications takes place within the layers; in the others, the major role in this phenomenon is played by the forces of interaction of CH_3 methyl and OH hydroxyl groups (corresponding to C(4) and O(3a)) of threonine and serine residues located in the interlayer space (see Figs. 1-4).

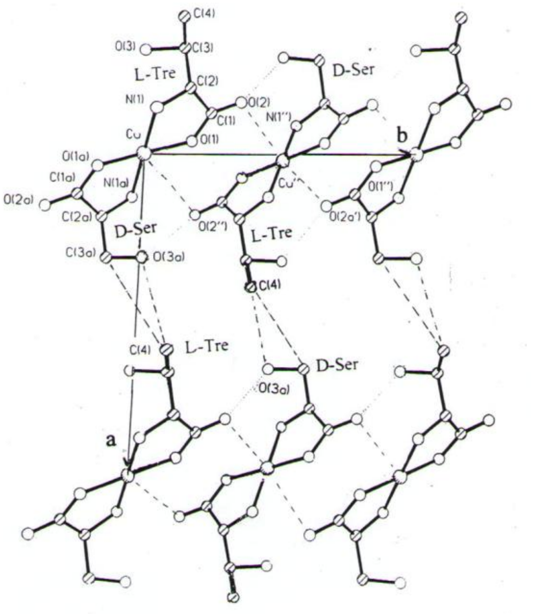

Fig. 1. Fragment of the Cu(D-Ser)(L-Tre) crystal structure, modification I.

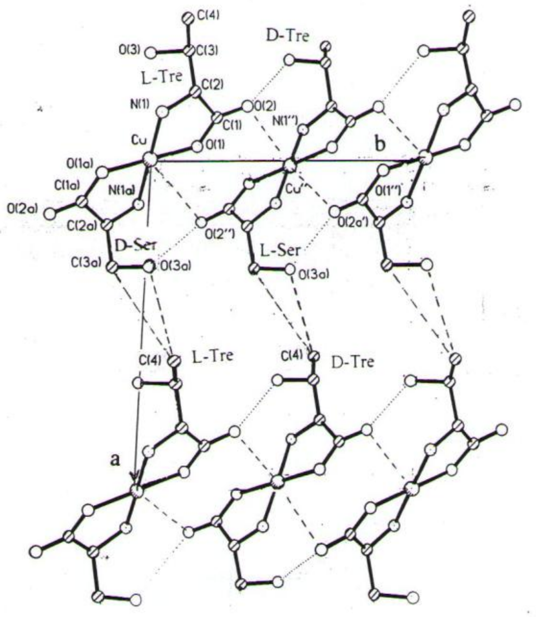

Fig. 2. Fragment of the Cu_2(D-Ser)(L-Ser)(D-Tre)(L-Tre) crystal structure, modification II.

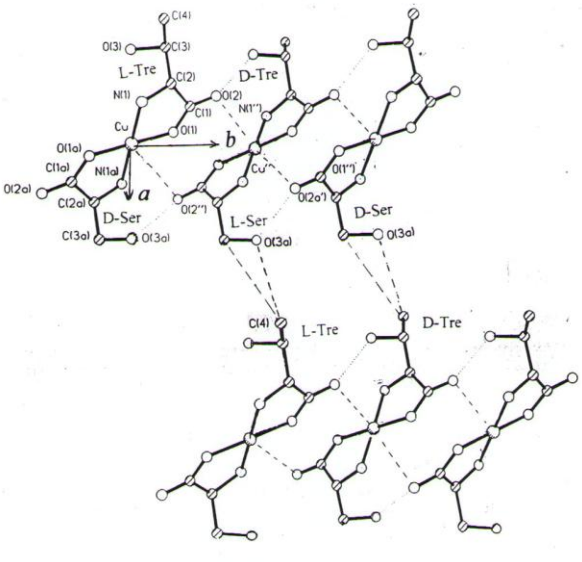

Fig. 3. Fragment of the Cu_2(D-Ser)(L-Ser)(D-Tre)(L-Tre) crystal structure, modification III.

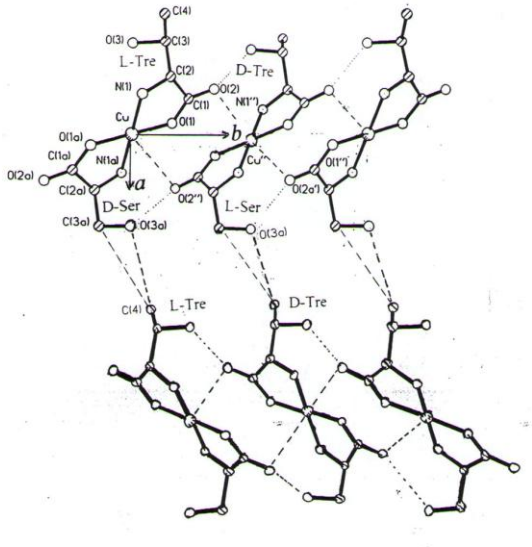

Fig. 4. Fragment of the Cu_2(D-Ser)(L-Ser)(D-Tre)(L-Tre) crystal structure, modification IV.

The diagrams of the structures and layers of four out of the nine discovered polytypic modifications (I, II, III, IV) of CuSerTre crystals are represented in Figs. 1-4. The values of the unit cell parameters and space groups of symmetry of polytypic modifications I, II, III, and IV are

I a=10.74(2) Å, b=9.65(1) Å, c=5.08(1) Å, γ=92.7(2)°, $P2_1$;

II a=10.76(2) Å, b=9.63(1) Å, c=5.08(1) Å, γ=92.8(1)°, Pb;

III a=21.52(2) Å, b=9.64(1) Å, c=5.08(1) Å, γ=92.8(2)°, Cb;

IV a=21.51(2) Å, b=9.64(1) Å, c=5.07(1) Å, $Pnb2_1$;

The layers in the above mentioned structures are formed from the same initial band of complexes Cu(D-Ser)(L-Tre) and differ only in the alternation of these bands within the layer. In the crystals of modification I, the neighboring bands are symmetrically interconnected within the layer by 2_1-two folder screw axis parallel to the c-axis of the crystal lattice, whereas in the layers of crystals of modifications II, III, and IV, these structural units are connected symmetrically by the b-glide plane. The location of the C(4) methyl and O(3a) hydroxyl groups in the interlayer space in modification II is of such nature, that in the result of displacement of adjacent layers relative to each other along the b-axis at ±1/2b the crystallochemical conditions of layer vicinity are almost unchanged, including the configuration of the interlayer space. The same effect is obtained as a result of rotation of adjacent layers relative to each other at 180° around the a-axis, together with the displacement of the layers relative to each other at ±1/4b along the b-axis. The structures of modifications II, III and IV are built up by identical layers and differ in mutual arrangement of the layers. In modification II, the method of layers packing is determined by translation [100]; in modification III, by translation [½ ½ 0]; in modification IV, by layers rotating relative to each other at 180° around the a-axis together with translation [½ ¼ 0].

3. Conclusion

In summary, the crystallographic characteristics and atomic structures of nine polytypic modifications of crystals CuSerTre (D : L = 1 : 1) were found and identified on the basis of the theory of polytypism [4]; five of them were identified by electron diffraction.

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