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ORIGINAL ARTICLE **OPEN ACCESS**

Synthesis and Structural - Chemical Research of Coordination Compounds of Tetraaqua Bisbenzol -1,2,4,5 - Tetracarboksilat Dizinc (II)

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ABSTRACT

For the first time, complex compound of zinc (II) 1,2,4,5-benzenetetracarboxylic acid with a porous structure was synthesized. Individuality and chemical formula of a complex compound was determined according to X-ray diffraction, elemental, IR spectroscopy and derivatographic analysis. The process of thermal decomposition of the resulting compound was also studied. It is also found that, despite the fact that the parameters of the unit cell of the crystal are significantly different from the known complex, it retains its layered polymer and porous structure.

Keywords: *complex compound, a layered porous structure, thermal decomposition, benzenetetracarboxylic acid, a chemical formula.*

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INTRODUCTION

Previously, we synthesized carboxylates of two main acids, in particular, phthalic and terephthalic acids. It has been established that they have a correspondingly zigzag and bandlike structure which give compounds of "host-guest" inclusion type [1 -5] with organic acids (acetic and formic).

It is also found out that formation of these types of connections is directly related to their structures, that is, when they are in contact with these acids due to their polymeric structures, acid molecules are positioned in interchain spaces. The number of included molecules depends on size and geometric forms of these molecules, that is, their clathrate formation is dependent on the size factor.

In addition to the size factor, pH medium is also of great importance. Depending on pH values, their structures change for easy clathrate formation [5]. We have also synthesized and decoded crystal structure of decahydrate complex of copper (II) with 1,2,4,5 – benzenetetracarboxylic (pyromellitic) acid (Fig. 1) [6].

From the crystal structure it is seen that the complex consists of polymeric nets of parallel planes (011). The acid anion for coordination impact uses all four carboxyl groups.

The composition of the crystalline compound coordinately bound with copper atoms of water molecules also includes two molecules of water of crystallization, which by means of hydrogen bonds covering all oxygen atoms bind the layers into a single unit in the form of 3D crystal structure. Wherein one layer of complexes (light) is slightly shifted in the plane (011) with respect to other layer systems (black). Based on the above mentioned, it can be assumed that in the absence of water molecules of crystallization, there would not occur displacement of layers. In this case, large pores in the carcass layers would lie on top of each other and large through columns with ability to include "guest" molecules would be formed. It should be noted that in this structure the interlayer space is also available for the inclusion of appropriate molecules.

Thus, the aim of this work is to study the complexation of pyromellitic acid, with further receipt of its non-bonded joints on its basis.

This work presents the results of the synthesis, physical and chemical and structural and chemical studies of complex compounds of zinc (II of) resulting in a weakly acidic medium (pH = 6.8).

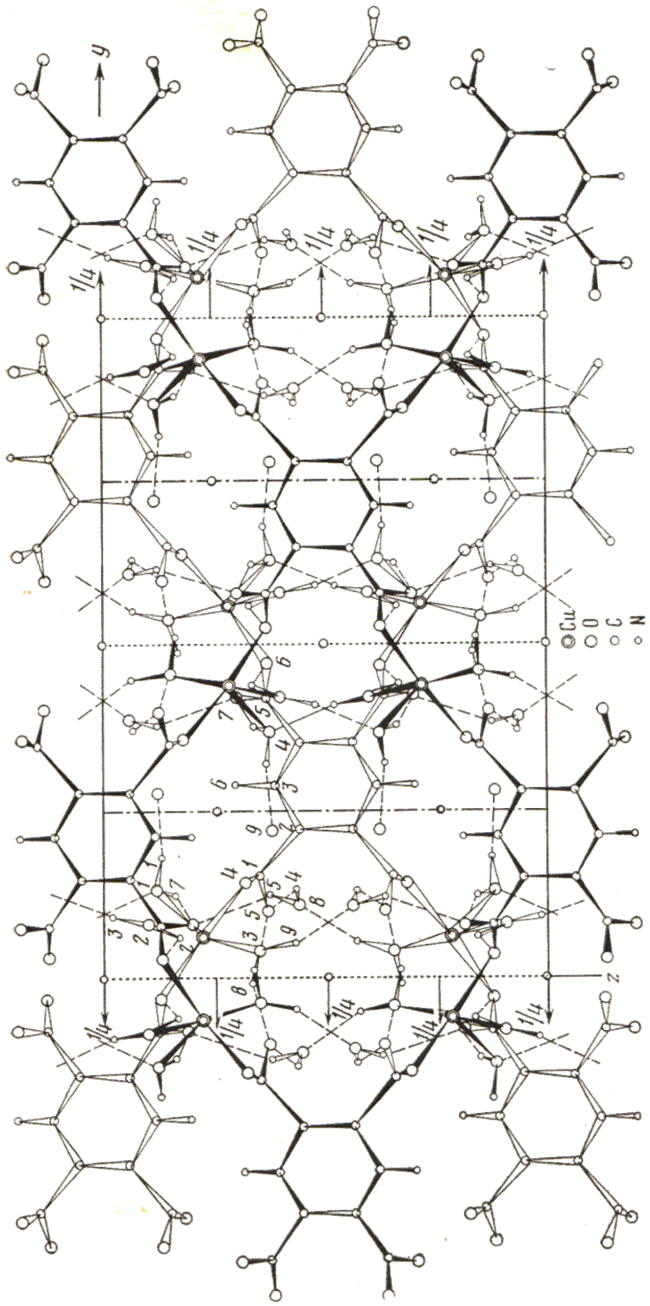

Fig. 1. The crystal structure of the complex

EXPERIMENTAL PART

The elemental composition of the obtained compound was defined by gas chromatography method by means of an analyzer CHN30E Carlo ERBA. The content of the metal was calculated on the basis of the weight loss curve by the quantity of oxide obtained after being heated on derivatograph up to 800°C. X-ray phase analysis was performed on the device Commander Sample ID (Coupled Two Theta/Theta) WL 1.54060.

IR spectra were recorded on a device SPECORD-MBO in 400 - 4000 cm^1 area. Derivatograms recorded derivatograph on NETZSCH STA 449F3 STA449F3A-0836-M (range 21 / 10.0 (K / min) / 800).

Synthesis of the compound. The starting materials were $C_6H_2(COO)_4$, $Zn_2(CH_3COO)_2$ of qualification 4 (GOST 3759 - 75). The complex is prepared by reacting pyromellitic acid with zinc acetate at a

stoichiometric ratio of 1: 2. The solution was refluxed until disappearance of the odor of acetic acid, filtered while hot and cooled to room temperature.

Upon cooling small transparent single crystals dropped from the solution which were filtered and washed for several times with warm distilled water, and were left to dry on filter paper at room temperature. Chemical composition of the complex compound was defined on the basis of the data obtained from phase X-ray, elemental, thermogravimetric and IR spectroscopic analysis.

It should be noted that these focal nanostructured polymers are a new generation of reagents that improve the rheological properties of heavy (nonyuton) crude oils.

RESULT AND DISCUSSION

Radiograph of the complex is shown in Figure 2.

As seen in Figure 2, the complex compound is highly crystalline and has a high symmetry. With X-ray indexing unit cell parameters were computed: a = 9,78, b = 19,7, c = 11,76Å.

Comparison of the parameters of the complex compound with parameters of the known complex compounds of copper (II) the crystal structure of which was decoded (a = 9,679 (5), b = 18,17 (2), c = 12,18 Å) showed that they differ respectively by 0.11; 1 and 0,42 Å. As it is seen, the parameters of a and b increase, whereas parameter of c decreases. These values are low, so at the first approach it would be found out that they are isostructural.

But the results of the elemental, IR spectroscopy and differential thermal analyzes have not confirmed these isostructural compounds, as elemental analysis results showed that the content of the complex is very different from the complex [1]. Elemental analysis results are presented in Table 1.

Table 1:The results of elemental analysis of the complex compounds of copper and zinc (II).

Found out, %			Composition of compounds	Calculated, %		
H	C	Zn, Cu		Zn, Cu	C	H
-	-	-	$Cu_2C_{10}H_{22}O_{18}$	22,812	21,541	3,950
2,315	26,721	29,011	$Zn_2C_{10}H_{10}O_{12}$	28,877	26,505	2,209

As it is seen from the table, the compositions of the compounds are very different from each other. The composition of the newly obtained compound has the preliminary chemical formula $Zn_2(C_6H_2(COO)_4)(H_2O)_4$, whereas the chemical formula of the famous complex is $Cu_2(C_6H_2(COO)_4)(H_2O)_{10}$

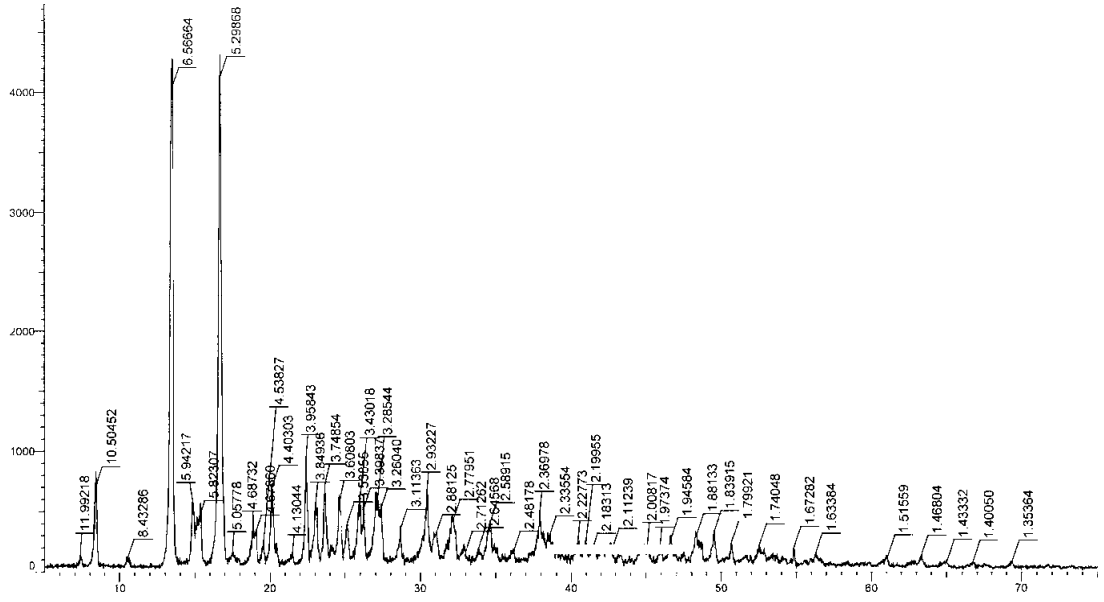

Fig. 2. Diffraction pattern of the complex compound $Zn_2(C_6H_2(COO)_4)(H_2O)_4$.

Termogravigramma of the complex compound of zinc (II) is shown in Fig. 3. Decomposition of the complex compounds of zinc (II) begins at 90°C in the temperature range of 90–138°C and is accompanied by a shallow but clear endothermic effect at 110°C and corresponds to the removal of two molecules of water.

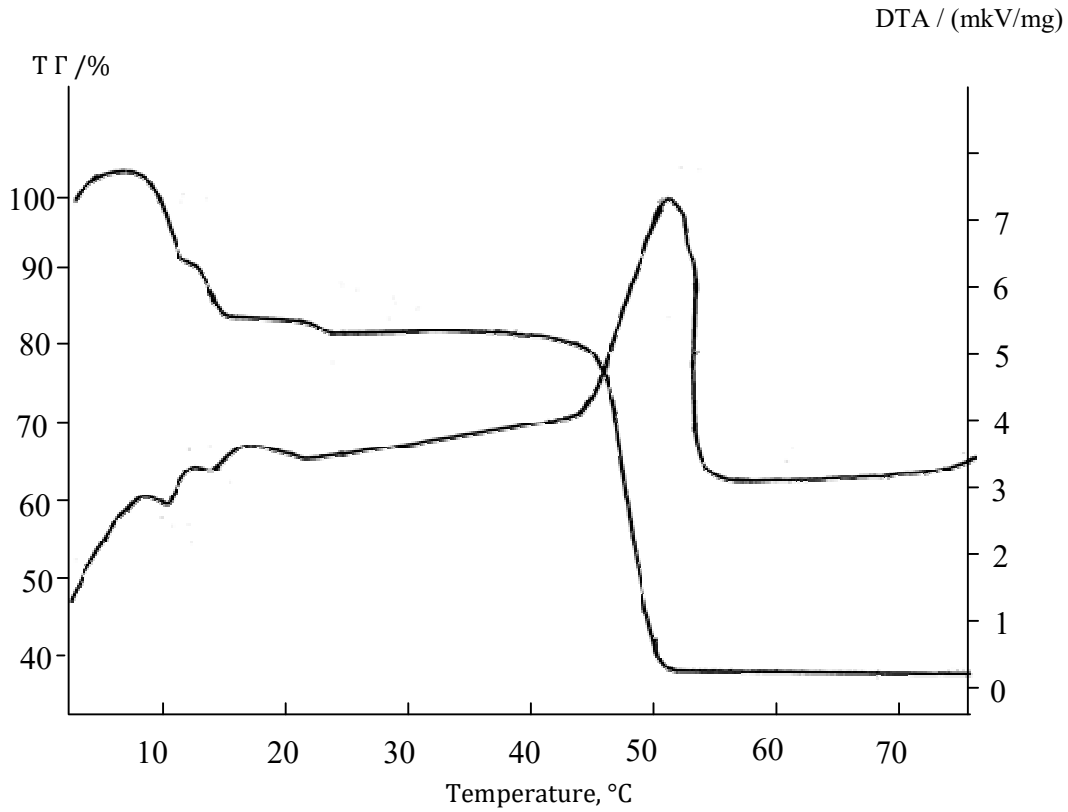

Fig. 3.Thermogravigram of complex compound $Zn_2(C_6H_2(COO)_4)(H_2O)_4$.

Experimental loss value of mass is 8 % (calculated 7.95%). Thereafter, in DTA curve there occurs the second endothermic effect in the temperature range of 138 - 180°C with maximum at 150°C, which corresponds to 1.5 moles of water removal. Experimental loss value of mass is 6% (calculated 5.96%).
Then there occurs the third fuzzy and shallow endothermic effect in the temperature range of 180 - 280°C with maximum at 240°C which corresponds to removal of an additional 0.5 moles of water. Here, experimental weight loss of the mass is 2% (calculated 1.99%). Anhydrous intermediate complex is stable up to 400°C which is extremely rare for complex compounds. At 400°C, first slowly, then with high speed decomposition of anhydrous complex takes place in the temperature range of 400 - 600°C with a single clear exothermic effect with the maximum 520°C. Here the experimental weight loss of the mass is 48% (calculated 48.15%). Since on the curve TG after complete decomposition is not observed weight increase, it can be concluded that oxidation of the zinc ion is due to oxygen atoms of the carboxyl groups. The final product is a ZnO. Experimental mass of the final product is 36% (calculated 35.95%). Below is a diagram of a solid phase transformation of complex compounds:
Since a weight increase is not observed on TG curve after complete decomposition, it can be concluded that oxidation of the zinc ion is due to oxygen atoms of the carboxyl groups. As the final product there remain ZnO. Mass of final experimental product is 36% (calculated 35.95%). Below is a diagram of a solid phase transformation of complex compounds:

$$Zn_2(C_6H_2(COO)_4)(H_2O)_4 \xrightarrow[-2H_2O]{90–138(110°C)} Zn_2(C_6H_2(COO)_4)(H_2O)_2 \xrightarrow[-1,5]{138–180(150°C)}$$

$$Zn_2(C_6H_2(COO)_4)(H_2O)_{0,5} \qquad Zn_2(C_6H_2(COO)_4)2 \qquad ZnO$$

$$\xrightarrow[-0,5\ H_2O]{180–280(240°C)} \qquad \xrightarrow{400–600\ (240°C)}$$

Thus, the result of thermogravimetric study showed that the studied complex has a chemical formula of $Zn_2(C_6H_2(COO)_4)(H_2O)_4$, which is in good agreement with the formula obtained from the elemental analysis.

As it is seen from the Fig. 3, four molecules that are part of the complex compound gradually leave the crystal lattice. This indicates that they are connected with the central atom with different strength, that is, M – O (H_2O) has different values.

Basic thermographic data of the complex compound are shown in table 2.

Table 2: Basic thermographic data of the complex compound

Compound	T_{endo}, °C	T_{endo}^{maks}, °C	T_{ekzo}, °C	T_{ekzo}^{maks}, °C	Mass loss	
					Found out	Calculated
$Zn_2(C_6H_2(COO)_4(H_2O)_4$						
$2H_2O$	90 – 138	110			8,00	7,95
$1,5H_2O$	138 – 180	150			6,00	5,96
$0,5H_2O$	180 – 280	240			2,00	1,99
Anion acids without two oxygen atoms ZnO			400 – 6 00	520	48,00 36,00	48,15 35,95

IR spectroscopic study also indicates that the frequency at 461; 534; 553 and 590 sm^{-1} refers to librational vibrations of water of crystallization or torsional vibrations of water molecules with limited interactions with neighboring atoms (Fig. 4) [7].

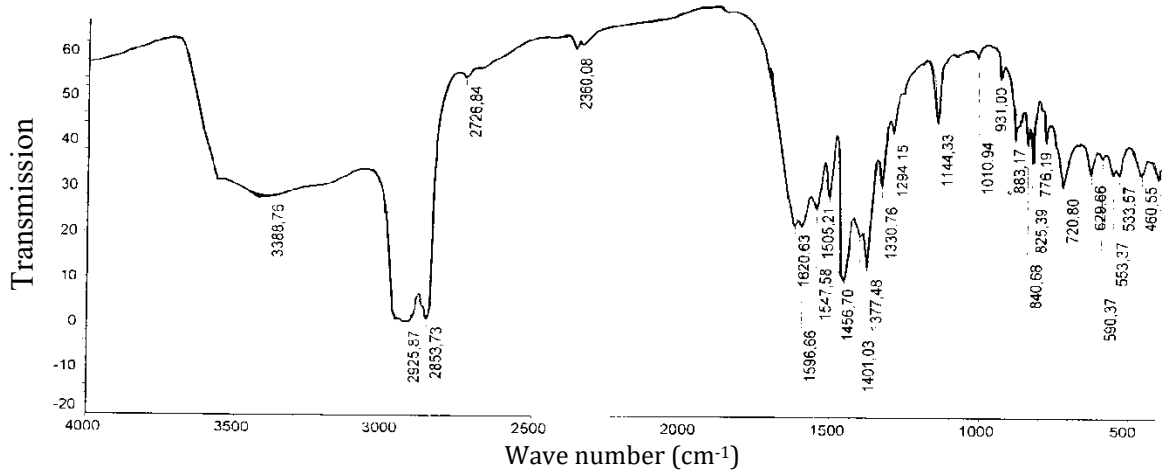

Fig. 4.IR spectrum of the complex compound –$Zn_2(C_6H_2(COO)_4)(H_2O)_4$.

Besides it, absorption bands are observed in IR spectrum of compound at 3550 - 3200 cm^{-1} (symmetric and asymmetric valent vibrations of OH) and at 1630 - 1600 cm^{-1} (deformation vibrations of HOH), which are characteristic for water of crystallization.

Absorption bands at 1597, 1548, 1505 (νa) and 1457, 1401, 1337 cm^1 (νs) refers to the carboxyl group of an acid anion [7]. Value of the difference value Δ (νa- νs) are respectively 140, 146 and 127 cm^1 and it is significantly less than that of ionic compounds, but is in good agreement with the values of bidentate chelate complexes [8].

Thus, the central atom is coordinated to six. Coordination zinc (II) includes four oxygen atoms of two carbonyl groups and two oxygen atoms of water molecules. Coordination polyhedron is octahedron.

Fig. 5 shows the structure of the estimated complex compound. As it is seen from the figure, the structure of the complex compound $Zn_2(C_6H_2(COO)_4)(H_2O)_4$ consists of alternating layers along the axis (011). The structure is porous and the size of pores is approximately 9 x 16 Å, as in [6]. The layers are stitched together due to hydrogen bonds formed by coordination of water molecules in different layers on the tops of octahedra (Fig. 6). It is also possible to assume that the skeleton pores in the structure will be one above the other and, in this case, through columns for the available "guest molecules" will be generated. Thus, one can conclude that a series of non-bonded compounds having practical value can be synthesized on the basis of this compound.

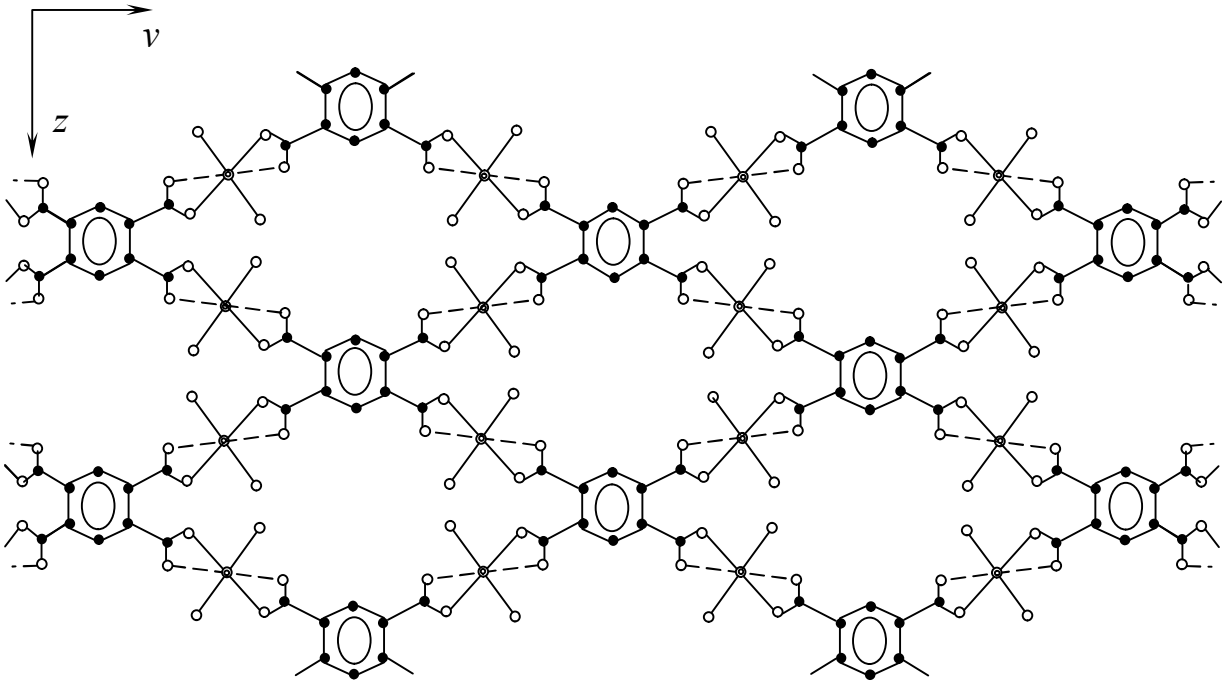

Fig. 5.Alleged schematic structure of the complex compound (along the axis 011).

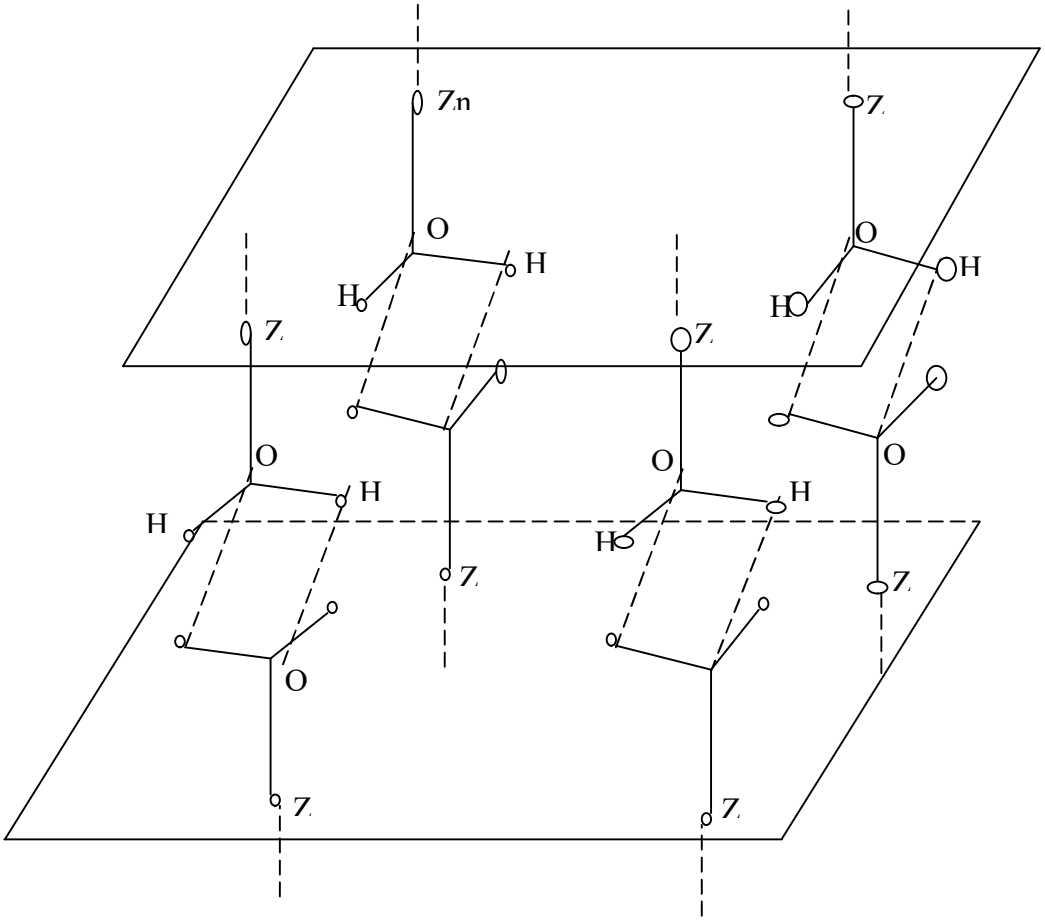

Fig. 6. Stitching of layers through hydrogen bonds in the structure of the complex in structure.

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