

ORIGINAL RESEARCH ARTICLE

Synthesis and structural-chemical studies of adduct of coordination supramolecular porous polymer hexaaquatribenzene-1,2,4,5-tetracarboxyato-tetrairon(III) with dipyridyl

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ABSTRACT

An α, α' -dipyridyl adduct of a complex compound hexaaquatribenzene-1,2,4,5-tetracarboxyato-tetra iron (III) with porous structure was synthesized for the first time. According to the results of elemental, X-ray, IR-spectroscopic and differential-thermal analyses the individuality, chemical formula, thermal destruction, and form of coordination of acidic anion and dipyridyl were established. During interaction of a complex compound with dipyridyl, it completely loses all crystallization molecule of water resulting in a compound with a chemical formula of $\text{Fe}_4(\text{C}_6\text{H}_2(\text{COO})_4)_3(\text{dpy})_2$ (dipyridyl). Using the identification of diffraction pattern the parameters of lattice cell of the complex compound were determined.

Keywords: compound; adduct; thermal destruction; chemical formula; crystal structure

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1. Introduction

We have earlier synthesized and studied supramolecular compounds of copper, zinc, iron (II) and iron (III) benzene-1,2,4,5-tetracarboxylic acid using physical and chemical analyses^[1-5]. The crystal structure of decahydrate compound of copper with benzene-1,2,4,5-tetracarboxylic acid was determined. The blue polycrystalline powder was not dissolved in water, carbon tetrachloride, benzene, acetone and in other neutral organic solvents except tetrahydrofuran (THF).

Monoclinic monocrystals suitable for X-ray structural analysis were obtained by dissolution of a complex compound in THF at 50–60 °C. Determination of a structure of this complex compound showed that crystalline compound contains ten water molecules. Eight of them enter into the coordination of copper atoms (II), but two of them which do not interact with the metal atom, water molecule, combine the complex with hydrogen bonds into a one whole in the form of a crystal structure. The structure of complex compound consists of polymeric layers parallel planes (011). Analysis of a crystal structure showed that one layer of complexes is slightly shifted in a plane (011) to another layer. Layers are linked to each other with hydrogen bonds (**Figure 1**)^[1]. Complexes of other metals are expected to form isostructural series. But results of studies showed that they form isomorphous series.

To detect the structural distinctions of these complexes one of them was dissolved in α, α' -dipyridyl.

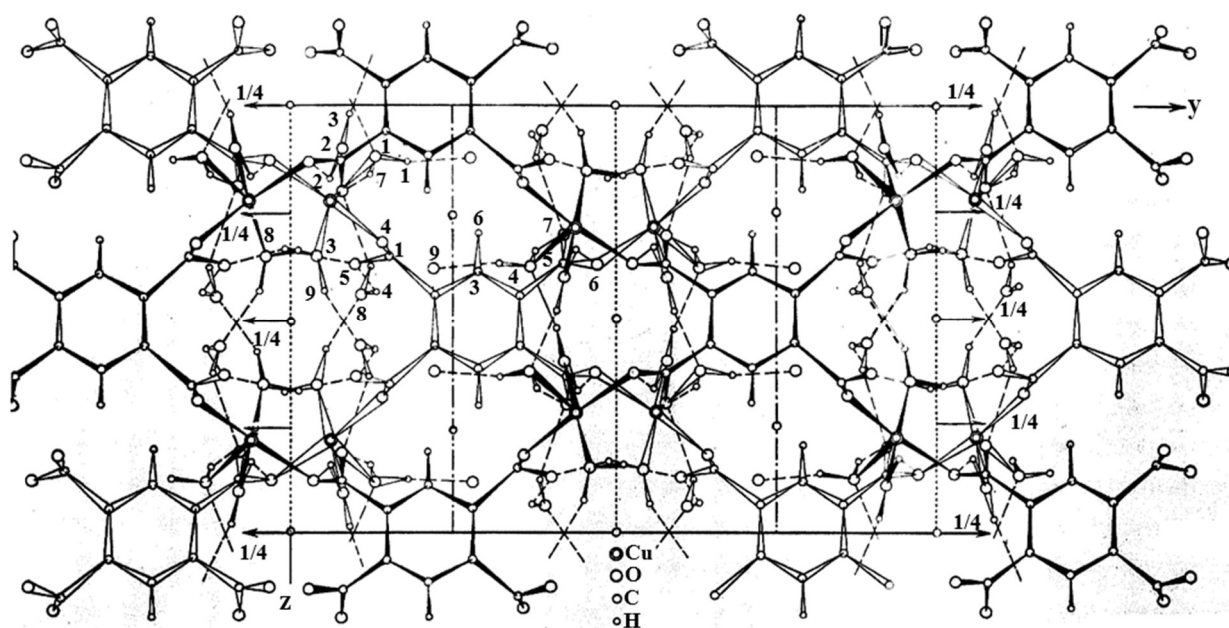


Figure 1. The crystal line structure of the complex compound $[\text{Cu}_2(\text{C}_6\text{H}_2(\text{COO})_4)(\text{H}_2\text{O})_8](\text{H}_2\text{O})_2$.

The results of synthesis, physical and structural-chemical studies of the complex compound tetra α, α' -dipyridyl tribenzene-1,2,4,5-tetracarboxatetra iron (III) were presented in this work.

2. Materials and methods

Elemental composition of the compound was determined by the gas chromatographic method on CHN3OE Carlo ERBA. Metal content was calculated on TG curve (weight loss) per quantity of oxide produced after heating up to 800 °C on derivatograph.

Thermograms were registered on derivatograph NETZCH STA 449 F3 STA 449F3A-0836-M (24/10.0 (k/min.)/800). X-ray phase analysis was performed on Commander Sample ID (coupled Two Thet/Theta) WL/1,54060. IR-spectra were taken on SPECORD-M80 in the range of 4000–400 cm^{-1} .

Synthesis of the compounds

$\text{C}_6\text{H}_2(\text{COOH})_4$ (pyromellitic acid), $\text{FeCl}_3 \cdot 7\text{H}_2\text{O}$, chemically pure NaHCO_3 (GOST 3759-75) were used as primary substances. The synthesis of the complex compound was performed by the known method^[2].

0.762 g (0.003 mol) of pyromellitic acid is taken for synthesis, 100 ml of distilled water is added into it, and then 1.344 g (0.0012 mol) of sodium hydrocarbonate powder is added in portions by heating at 80 °C. After complete dissolution of acid 0.796 g (0.004 mol) of $\text{FeCl}_3 \cdot 7\text{H}_2\text{O}$ salt powder is added to a solution to avoid the formation of hydroxyl complex and heated to boiling.

Dark brown fine thick polycrystalline powder precipitates during the interaction of sodium salt with ferric (III) chloride. The precipitate is filtered hot, and at first, it is washed several times with distilled water, then with benzene and dried on filter paper at room temperature.

The synthesized compound is not soluble in water and neutral organic solvents. To produce monocrystals of this compound it dissolves in water solution of α, α' -dipyridyl in stoichiometric ratio of the complex compound— $\text{Fe}_4(\text{C}_6\text{H}_2(\text{COO})_4)_3(\text{H}_2\text{O})_6$ to α, α' -dipyridyl 1:2, i.e., 1.082 g (1.001 mol) of complex compound dissolves in 32.5 g of 1% water solution of α, α' -dipyridyl and heated up to 80 °C. The reaction goes slowly, and within a day the solution becomes red-crimson. Fine pink monocrystals precipitate in the form of

parallelepiped after two weeks. A chemical formula of the compound was defined according to the results of X-ray phase, elemental, differential-thermal and IR spectroscopic analyses.

3. Results and discussion

3.1. Elemental analysis

Table 1 shows the elemental composition of synthesized compound.

Table 1. Results of elemental analysis of the product.

| Found, % | | | | Elemental composition Calculated,% | | | | |
|----------|--------|------|-------|--|-------|------|-------|------|
| H | C | N | Fe | Fe ₄ C ₅₀ H ₂₂ N ₄ O ₂₄ | Fe | N | C | H |
| 2.03 | 49.842 | 4.69 | 18.63 | | 18.52 | 4.64 | 49.79 | 1.84 |

According to elemental analysis for the compound chemical formula can be expressed as Fe₄(C₆H₂(COO)₄)₃ (dpy)₂.

3.2. X-ray phase analysis

Figure 2 shows X-ray diagram of synthesized compound. As the figure shows the product is highly crystalline and intensive peaks are dislocated at an angle of 0–30° which points to a maximum monoclinic symmetry of crystals. All peaks are identified under maximums of 14.24; 12.86; 11.30 which show that parameters of a lattice cell of this compound make nearly a = 12.86 Å; b = 14.24 Å and c = 11.30 Å.

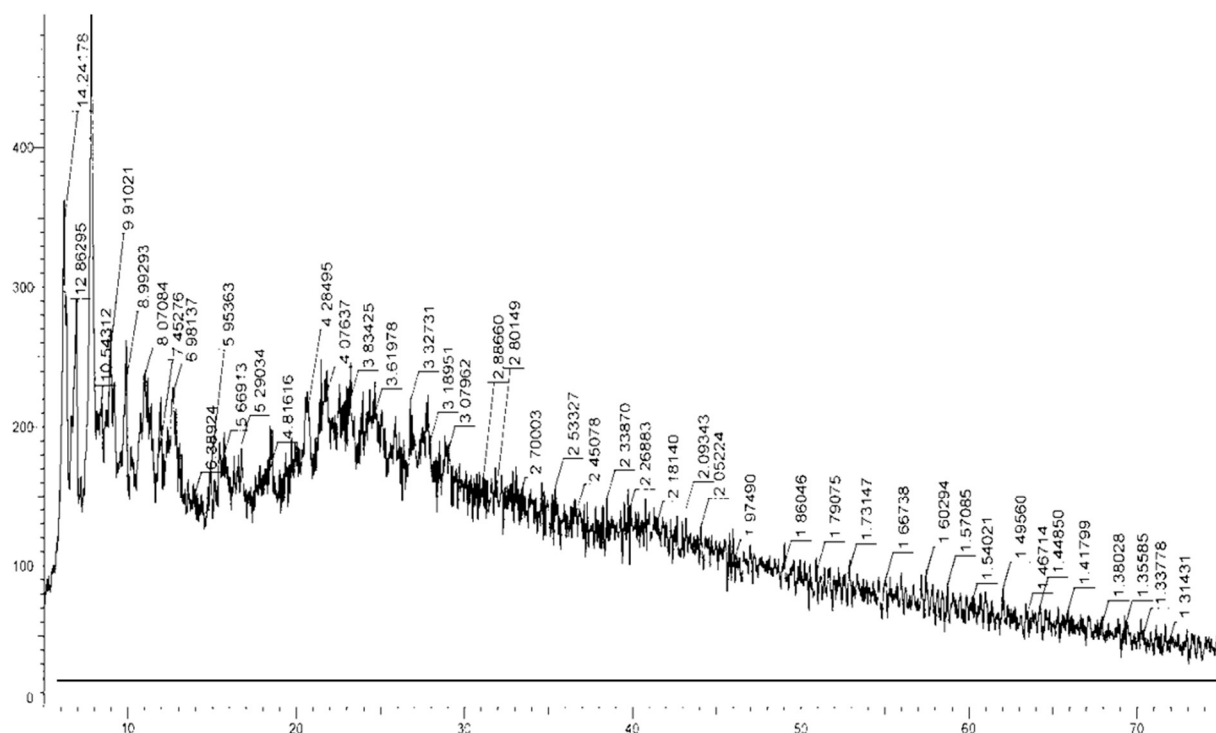


Figure 2. XRD of the synthesized complex of iron (III).

3.3. IR-spectroscopic analysis

IR-spectra of the complex compound was presented in **Figure 3**. As figure shows clear absorption bands which are related to asymmetric valence vibrations of carboxylic groups (C = O) appear in spectrum of 170–1310 cm⁻¹, particularly in 1596 cm⁻¹ and 1574 cm⁻¹, bands in 1377 cm⁻¹ and 1339 cm⁻¹ are related to

symmetric vibrations (C-O) of anion of pyromellitic acid. Value of absorption bands indicates that carboxylic groups are differently linked to central atom. Differential value of $\Delta[v_a(\text{CO}_2) - v_c(\text{CO}_2^-)]$ 219 cm^{-1} and 235 cm^{-1} is higher than in ionic complexes ($\sim 164 \text{ cm}^{-1}$), therefore we can say with certainty that in this complex carboxylic groups are monodentately linked to metals, as in primary complex^[6].

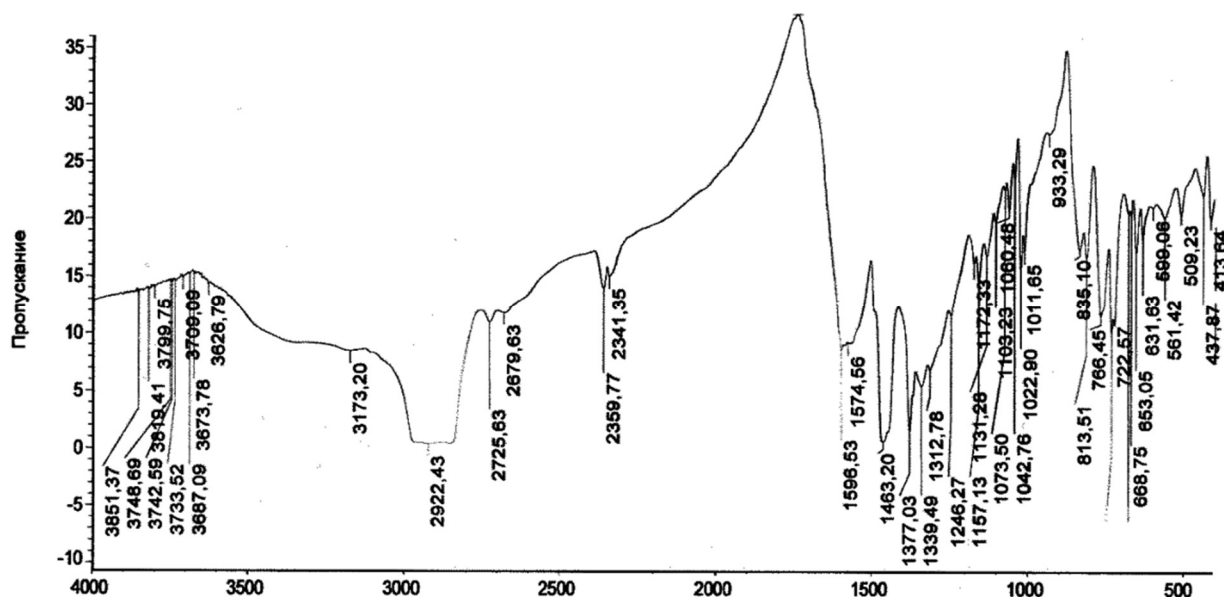


Figure 3. IR—Spectrum of the complex compound of iron (III).

As it is seen from spectrum a wide band relating to asymmetrical and symmetrical vibrations of OH groups of water molecules do not appear in the range of 3600–3200 cm^{-1} ^[7]. This is proof that the complex does not contain crystallization molecules of water. In this spectrum two non-intensive bands in 3105 and 3173 cm^{-1} which are related to dipyrindyl, and more precisely, to bonds M – N, are visible. Bands in high-frequency region are not sensitive to replacement of metal, they are linked to vibrations of aromatic cycle of a ligand. The main attention is given to a low-frequency region where bands of $\nu(\text{MN})$ and other vibrations with metal atom are located. However, it was difficult to assign $\nu(\text{MN})$ empirically, since some vibrations of ligands are located in the same frequency range. Despite aforementioned, the comparison of IR-spectra of the complex compound with IR-spectrum of dipyrindyl (Figure 4) showed that absorption bands in 3053; 3085 and 3149 cm^{-1} in dipyrindyl has considerably increased 3105 cm^{-1} ; 3173 cm^{-1} in the complex.

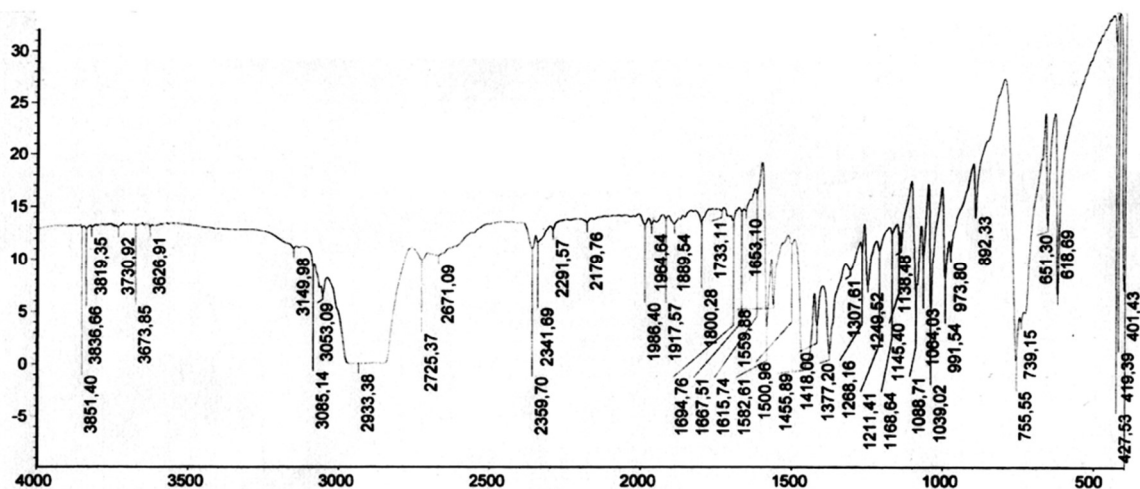


Figure 4. IR—Spectrum of the α, α' -dipyridine.

3.4. Thermogravimetric analysis

Figure 5 shows thermogram of the complex compound. Complex compound is stable up to 165 °C. Beginning from 165 °C clear, shallow wide endothermic effect appears on DTG curve in the range of 165–296 °C with a maximum at 221 °C which conforms to the removal of two dipyriddy molecules. In this stage loss in weight makes 25.2% experimentally (calculated 25.9%). From 296 °C the decomposition of a non-adductive complex by autocatalytic mechanism and burn-out of the organic part of a molecule occur in a wide range of 296–450 °C. These processes are accompanied by an intensive exothermic effect with maximums at 450 °C and 580 °C. In this stage lose in weight makes 47.74% experimentally (calculated 54.23%). Reaction results in the production of Fe₂O₃ as a final product at 784 °C. Residual mass makes 29.06% experimentally (calculated 26.53%).

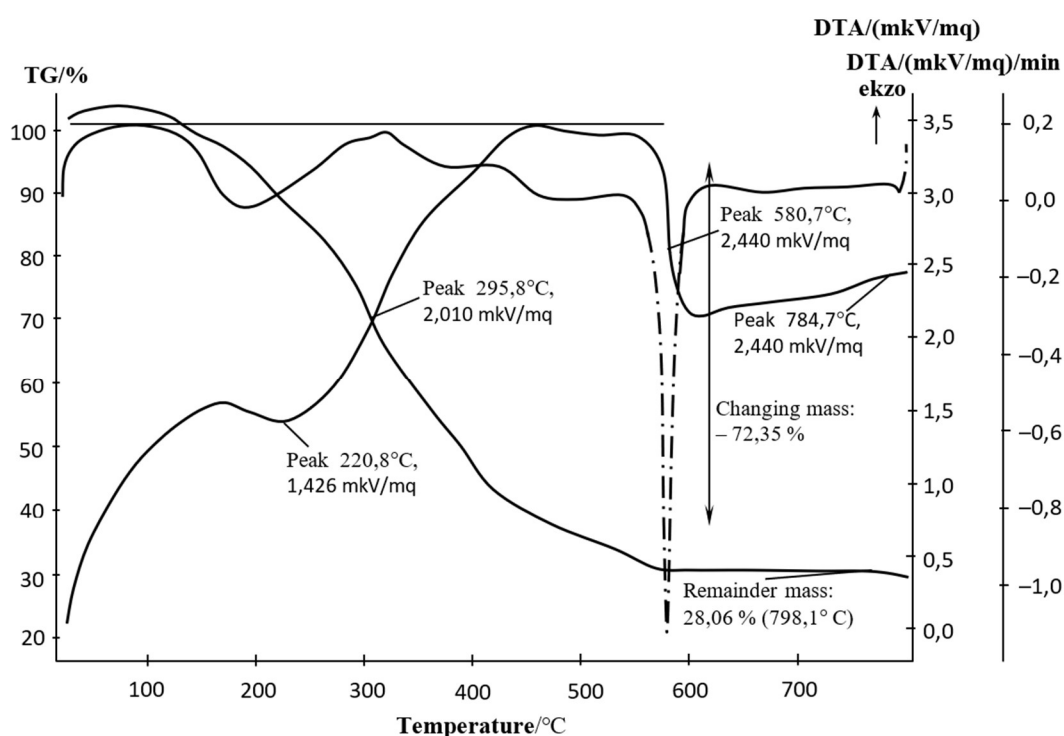
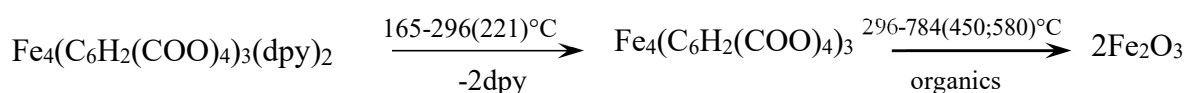


Figure 5. Termogramm complex compound of iron (III).

Thus, chemical formula of Fe₄(C₆H₂(COO)₄)₃ (dpy)₂ based on differential-thermal analysis agrees well with chemical formula obtained in elementary analysis.

Scheme of solid phase transformation of the complex compound is as follows:



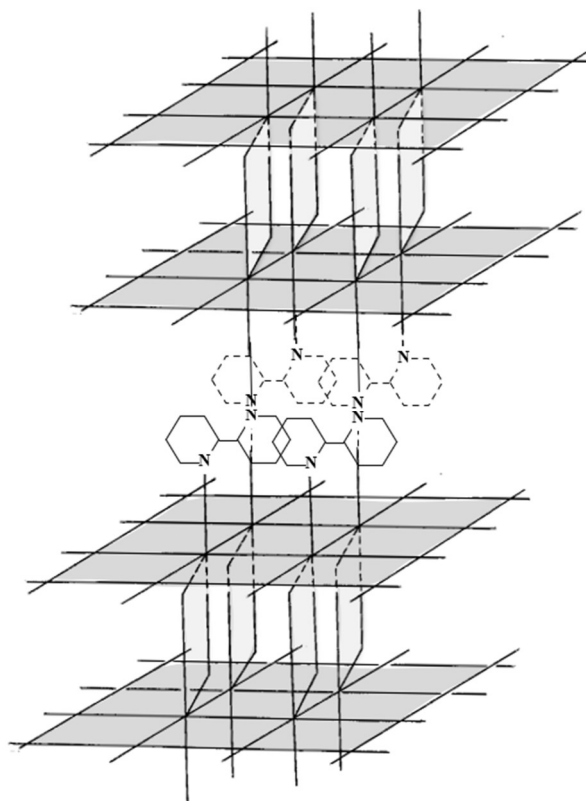
Results of physical and chemical studies showed that α , α' -dipyridyl acts as a pyridine—like in other metal carboxylates^[8,9], i.e., it completely displaces both coordination and crystallization molecules from a crystal lattice.

Comparison of lattice cell parameters of the compound with lattice cells parameters of known complexes of this series and primary complex showed that parameter *a* of this complex, the layers of which are perpendicular to this axis, increased in the size of an aromatic phenyl ring 2.53 Å (**Table 2**). This again confirms that α , α' -dipyridyl enters to the coordination of metal, but the polymeric structure is kept.

Table 2. Parameters of elementary cells of known complexes from this series.

| Complex formulas | a, Å | b, Å | c, Å | Molecular weight | References |
|--|-------|-------|-------|------------------|------------|
| $\text{Cu}_2(\text{C}_6\text{H}_2(\text{COO})_4)(\text{H}_2\text{O})_{10}$ | 9.679 | 18.17 | 12.18 | 557.18 | [1] |
| $\text{Cu}_2(\text{C}_6\text{H}_2(\text{COO})_4)(\text{H}_2\text{O})_2$ | 10.68 | 19.11 | 11.28 | 413.24 | [2] |
| $\text{Zn}_2(\text{C}_6\text{H}_2(\text{COO})_4)(\text{H}_2\text{O})_4$ | 9.78 | 19.70 | 11.76 | 452.92 | [3] |
| $\text{Fe}_2(\text{C}_6\text{H}_2(\text{COO})_4)(\text{H}_2\text{O})_6$ | 10.10 | 18.24 | 11.76 | 469.90 | [4] |
| $\text{Fe}_2(\text{C}_6\text{H}_2(\text{COO})_4)_3(\text{H}_2\text{O})_6$ | 10.33 | 15.92 | 11.21 | 1081.55 | [5] |
| $\text{Fe}_2(\text{C}_6\text{H}_2(\text{COO})_4)_3(\text{dpy})_2$ | 12.86 | 14.24 | 11.30 | 1494 | - |

Thus, the coordination number of iron (III) in the complex corresponds to four, but coordination polyhedron—distorted tetrahedron. The coordination of each iron ion contains three oxygen atoms of three carboxylic groups. Two carboxylic groups have an equatorial position as in the complex^[5] and are linked with metal monodentately, but the third anion has an axial position and acts as a bridge between layers, and double layer two-dimensional dimer is formed. The nitrogen atom of dipyriddy molecule has the second axial position. As the chemical formula of the compound shows, there are two dipyriddy molecules of four iron atoms. This means that the second atom of nitrogen enters to coordination of iron which is in other dimer molecules. Thus, during interaction of complex compound with dipyriddy one pyridine ring turns round in ratio to other ring, and dimer layers are cross-linked to each other with dipyriddy molecules resulting in more firm three-dimensional framework 3D structure. The alleged schematic structure of the complex of iron (III) is shown in **Figure 6**.

**Figure 6.** Alleged schematic structure of the complex of iron (III).

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Conflict of interest

The authors declare no conflict of interest.

References

1. Usubaliyev BT, Shiulin AN, Mammadov KhS. Crystalline and molecular structure of decahydrate complex of copper with 1,2,4,5-benzenetetracarboxylic acid. *Coordination chemistry* 1982; 8(11): 1532–1538.
2. Usubaliyev BT, Munshiyeva MK, Nurullayev VKh, et al. Synthesis, physical and structure-chemical of research of coordinating compounds of diaqua-1,2,4,5-benzotetracarboxylate dicopper (II). *Bull Of Environment, Pharmacology and Life Sciences* 2016; 5(3): 12–17.
3. Usubaliyev BT, Nurullayev VKh, Aliyeva FB, et al. Synthesis and structural-chemical research of coordinating compounds of tetraaqua bisbenzol-1,2,4,5-tetracarboxylate dizinc (II). *Bull of Environment, Pharmacology and Life Sciences* 2016; 5(4): 10–16.
4. Usubaliyev BT, Taghiyev DB, Nurullayev VKh, et al. Structural-chemical research of coordination compounds of hexaaqua-bis benzol 1,2,4,5-tetracarboxylate diiron (II) with a layered-porous structure. *Journal of Nanomaterials and Molecular Nanotechnology* 2017; 6(1): 1–5.
5. Usubaliyev BT, Taghiyev DB, Nurullayev VKh, et al. Synthesis, physical and structure-chemical studies of hexaaqua tribenzene-1,2,4,5-tetracarboxylate iron (III) coordination compound. *Frontiers in Nanoscience and Nanotechnology* 2017; 3(2): 4. doi: 10.15761/fnn.1000152
6. Nakamoto K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*. Mir; 1991; p. 535.
7. Bellamy LJ. *Advances in Infrared Group Frequencies*. Mir; 1971. p. 318.
8. Najafov GN, Shnulin AN, Mammadov KhS. Crystalline structure of molecular complex di-(p-oxybenzoate) tripyridine-Cd (II) and pyridine. *Journal of Structural Chemistry* 1981; 22(3): 106–112.
9. Najafov GN, Usubaliyev BT, Amiraslanov IR, et al. Crystalline structure of bis-pyridine bis-(p-oxybenzoate) zinc (II) dipyridine. *Coordination Chemistry* 1981; 7(5): 770–775.