



Research Article

Coordination Compounds of Hexaaqua Bisbenzol-1, 2, 4, 5-Tetracarboxylate Diiron (II) with a Layered-Porous Structure, To Reduce Viscosity Crude Oil

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Abstract

The complex compounds of Diiron (II) bisbenzol 1,2,4,5 Tetra carbonate were synthesized for the first time with porous structure. This article presents the results of X-ray diffraction, elemental and IR analyzes of spectroscopic derivatographic complex compound of 1, 2, 4, 5-bis benzene tetra carbonate of Diiron (II). By means of the indicated physical-chemical analyzes the individual coordination form of carboxyl groups, chemical formula and unit cell parameters of the complex compound have been identified. Also, the process of thermal degradation of the studied complex has been studied. It was revealed that the compound after losing six molecules of water is resistant until the temperature 300°C. In all likelihood coordinately related the water molecules form intermolecular hydrogen bonds both with oxygen of the carboxyl groups, and among themselves in all likelihood coordinately related the water molecules form intermolecular hydrogen bonds both with oxygen of the carboxyl groups, and among themselves. Here molecules of coordination water in the different layers play an active role in this interaction. Thus, a two-dimensional structure of a complex compound by means of the hydrogen bonds is transformed into 3D structure.

Keywords: A Layered Porous Structure; Complex Compound; Chemical Formula; Pyromellitic Acid; Thermal Decomposition; IR Spectrum

Introduction

Considerable interest to phthalates and terephthalates of various metals emerging recently is determined with their layered structure and the possibility of wide application. The layered structure of

phthalates and terephthalates allows their use as molecular sieves and adsorbents, and particularly copper terephthalate is used for absorption of N₂, Ar, Xe [1]. Terephthalate of zinc, calcium, and tin is used respectively as an activator of vulcanization in the rubber production, as a lubricant to prevent adhesion of rubber to technological fibers [2] as the capacitive dielectric [3] and terephthalate of ruthenium exhibits semiconductor properties [4,5]. Also, we have synthesized a number of non-bonded compounds on the basis of the complexes of terephthalates of copper, cadmium (II)

obtained in a slightly acid medium with formic acid, [6],

Phthalates and terephthalates of cadmium, nickel (II) with acetic acid and phthalates and terephthalates of cadmium, cobalt, nickel and zinc (II) obtained in a basic medium (pH > 8.5) with acetic acid due to its layered structures [7-10]. The complex compounds of copper (II) has been synthesized with benzene of 1, 2, 4, 5-tetracarboxylic acid (pyromellitic acid) and crystal-crystalline structure [11] have been decrypted (Figure 1). As can be seen from the structure, it also has a polymer-laminate structure with pores of a certain size which are available for self-assembly. That is, a number of non-bonded compounds with various organic molecules of various sizes and geometries can be obtained on its bases. For this purpose, on the basis of pyromellitic acid we obtained a number of complex compounds of various metals [12,13]. This work presents the results of the synthesis, physical-chemical and structural studies of the chemical complex of hexaqua bisbenzene-1, 2, 4, 5-tetracarboxylic Diiron (II). Preliminary studies have shown that they improve the rheological properties of heavy oil.

Experimental Section

The elemental composition of the obtained compound was determined by gas chromatography on an analyzer CHN30E Carlo ERBA. The metal content was calculated from the weight loss curve on quantity of oxide obtained after heating on derivatographic up to 800°C. X-ray diffraction 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 the area of 400-4000 cm⁻¹. Derivatograms were recorded on a derivative graph NETZSCH STA 449F3STA449F3A-0836-M (Range 21/10.0(K/min)/800).

Synthesis of the compound

The starting materials were C₆H₂(COO)₄, (pyromellitic acid), FeCl₂, NaHCO₃ of qualification XCH (GOST 3759-75). Complex compound was obtained by reacting pyromellitic acid sodium salt with iron chloride (II) in a weakly acidic medium. During the reaction, polycrystalline powder of the complex falls abundantly. Polycrystalline powder is heated up to boiling and kept boiling for 15 minutes. Then it was filtered while it was hot and washed for several times with distilled water. First it was dried on a filter paper at a room temperature and then in a drying oven at 50°C. The chemical formula of the complex connections was established on the basis of X-ray diffraction, elemental, TGA and IR spectroscopic analysis.

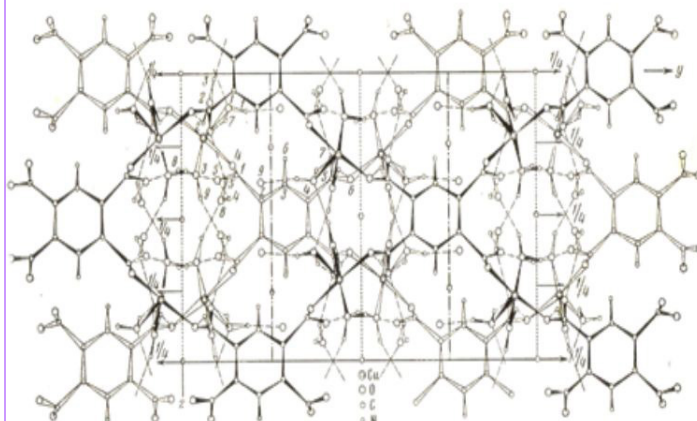


Figure 1: The crystal line structure of the complex compound - [Cu₂ (C₆H₂ (COO)₄ (H₂O)₈)(H₂O)₂]

Discussion of Results

X-ray analysis: (Figure 2) shows the X-ray of the complex compound.

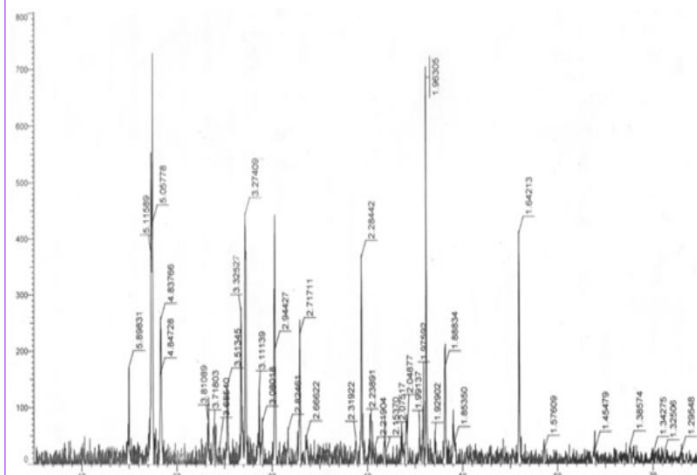


Figure 2: XRD of complex compound of iron (II).

As seen from the radiographs, this compound is highly crystalline and has a high symmetry, as the peaks are located in all corners. The parameters of the elementary cell of the complex compound have been determined with indexing

Diffraction patterns of: a = 10, 1, b = 18, 24, c = 11,76 Å. Comparison of the unit cell parameters of the current complex compound with the parameters of the known complexes

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a = 9,679(5), b = 18, 17(2), c = 12, 18(1) Å [11],
 a = 10, 68, b = 19, 11, c = 11, 28 Å [12],
 a = 9, 78, b = 19, 7, c = 11, 76 Å [13],
 a = 10, 10, b = 18, 24, c = 11, 76 Å [current complex],

It showed that they are isomorphic, but not isostructural. The resulting complex compound is studied with IR spectroscopy methods and differential thermal elemental analysis.

Elemental analysis: Elemental analysis results are presented in (Table 1) According to the results of the elemental analysis of the obtained compound, the following chemical formula can be written - $\text{Fe}_2(\text{C}_6\text{H}_2(\text{COO})_4)(\text{H}_2\text{O})_6$.

Found, %			Formula	Calculated, %		
H	C	Fe		Fe	C	H
3,028	25,582	23,780	$\text{Fe}_2\text{C}_{10}\text{H}_{14}\text{O}_{14}$	23,769	25,561	3,003

Table 1: The results of elemental analysis of synthesized complex

Thermal decomposition

Thermogram of the complex compound of the iron (II) is shown in (Figure 3). Decomposition of the complex compound of hex aqua bis benzene 1,2,4,5 tetra carbonate of Diiron (II) begins at 110°C in the temperature range of 110 - 205°C and is accompanied by a shallow, but a clear endothermic with the peak at 150°C and corresponds to the removal of six molecules of water. As it is seen from the thermo grams of the complex compound (Figure 3), all six water molecules leave the crystal lattice at one stage and are focal points, since their removal temperature is too high. Experimental mass loss value is 24% (calculated 22, 98%).

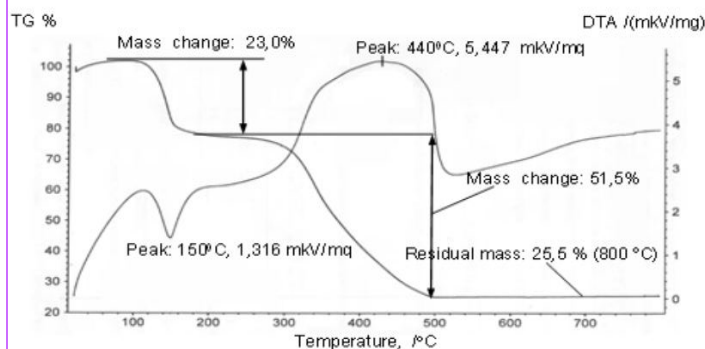


Figure 3: Thermo gram of complex compound of iron (II).

Removal of the water molecules with one precise endothermic effect and a sufficiently high temperature (110 - 205°C) shows

that they are coordinated and quite strongly linked to the central atom. Its zinc analogue has 4 moles of water which are removed step by step (2 mol, 1.5mol and 0,5mol) [13]. Intermediate anhydrous complex is stable up to 300°C which is extremely rare for the complex compounds. At 300°C gradually at 300 - 530°C temperature range decomposition of anhydrous complex and parching of an organic residue with a single precise endothermic effect with a maximum 440°C takes place. Here the weight loss is experimentally 53% (calculated 53, 19%). Since on TG curve after the full decomposition of the complex compound, a slight increase in weight and a good agreement between the experimental and theoretical values is observed, the oxidation of ion (Fe^{2+}) is due to atmospheric oxygen. As the final product Fe O is left. Below, a diagram of a solid phase transformation of the complex compound is given:



Basic thermo graphic data of the complex compound are shown in (Table 2) Thus, the results of thermo gravimetric studies showed that the investigated complex has a chemical formula of $\text{Fe}_2(\text{C}_6\text{H}_2(\text{COO})_4)(\text{H}_2\text{O})_6$ which is consistent with the formula obtained by elemental analysis.

Compounds	Tendo, °C	Tecd, °C	Tekzo, °C,	Tekzo, °C	Weight loss	
					Found %	Calculated%
$\text{Fe}_2(\text{C}_6\text{H}_2(\text{COO})_4) \cdot 6\text{H}_2\text{O}$	110-205	150	300-530	440	23,0	22,98
-6H ₂ O					51,5	49,79
Anion acid Fe O					25,5	27,23

Table 2: Basic thermo graphic parameters of the complex compound.

IR spectroscopic study

IR spectroscopic study also shows the frequencies at 3600-3200 cm^{-1} , in particular at 3416 cm^{-1} which refers to the asymmetric and symmetric vibrations of OH for the water coordination [14] (Figure 4). The absorption bands at 1667, 1586 (ν_a) and 1458, 1376 cm^{-1} (ν_s) refer to the carboxyl groups of pyromellitic acid anion [15]. Significance of difference of the values $\Delta(\nu_a - \nu_s)$ is respectively 209 and 210 cm^{-1} and it is in good agreement with the values of mono dentate complexes and show that all four carboxyl groups bound to the central atom as in the complex [11]. Thus, the central atom is five coordinated. The coordination of the iron (II) includes two oxygen atoms of two carboxylic groups of two different anions and three oxygen atoms of three water molecules.

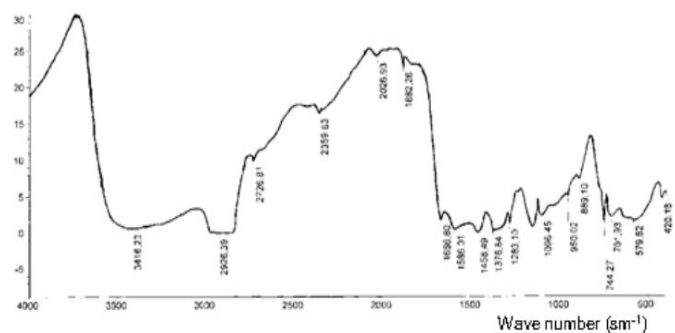


Figure 4: IR spectra of complex compound of iron (II).

The coordination polyhedron is a pyramid. Estimated schematic structure of the complex compound along the axis [11] is shown in (Figure 5). In all likelihood coordinately related the water molecules form intermolecular hydrogen bonds both with oxygen of the carboxyl groups, and among themselves.

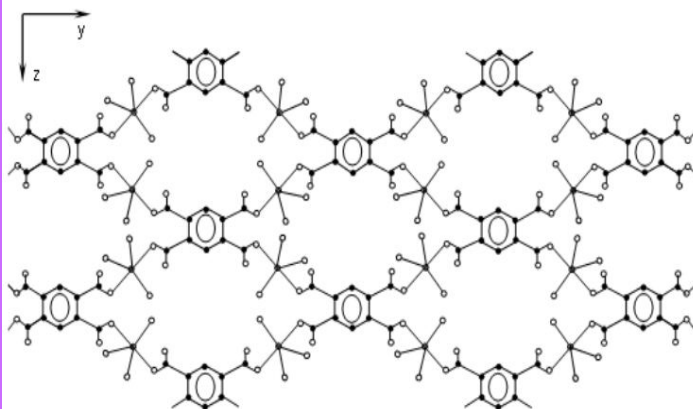


Figure 5: Alleged schematic structure of the complex.

Conclusions

In the crystal, the layers are interconnected with one another also by the hydrogen bonds, since the unit cell parameter (a) which is perpendicular to the layers; slightly ($0,42\text{\AA}$) differs from the parameter (s) of the known complex [11]. Here molecules of coordination water in the different layers play an active role in this interaction. As the unit cell parameter (a) slightly ($0,07\text{\AA}$) differs from the parameter (c) of the known complex, we assume that the layers are slightly displaced relative to each other.

Acknowledgements

Thus, a two-dimensional structure of a complex compound by means of the hydrogen bonds is transformed into 3D structure.

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