Bulletin of Environment, Pharmacology and Life Sciences
Bull. Env. Pharmacol. Life Sci., Vol 5 [3] February 2016: 12-17
©2015 Academy for Environment and Life Sciences, India
Online ISSN 2277-1808
Journal's URL:http://www.bepls.com
CODEN: BEPLAD
Global Impact Factor 0.533
Universal Impact Factor 0.9804

ORIGINAL ARTICLE **OPEN ACCESS**

Synthesis, Physical- And Structure- Chemical of Research Of Coordinating compounds of Diaquo-1,2,4,5 Benzoltetracarbonat Dimedi (II)

B.T. Usubaliev[1],M.K. Munshieva[2],V.H. Nurullayev[3], F. B. AlievaF[2], P. S. Safarova[2]
1.Azerbaijan State Oil and Industry University.Research Institute of "Geotechnical problems of oil, gas and chemistry",Azerbaijan, Baku, 225, D.Alieva ,
e-mail:ubeybala@gmail.com
2. Institute of Catalysis and Inorganic Chemistry after the name of M.F.Naghiyev
National Academy of Sciences of Azerbaijan.
3.(Management Oil Pipelines SOCAR) Candidate of Technical Sciences State Oil Company of the Azerbaijan Republic (SOCAR) Engineer of «Quality Control» Department 28, Khodzhalaave., Baku, Az 1025, Republic of Azerbaijan
E-mail: Veliehet1973@mail.ru

ABSTRACT

Complex compounds of copper (II)1, 2 ,4, 5 – benzoltetracarbonate acid with a porous structure have been synthesized for the first time. Individuality and chemical formula of complex compounds have been determined on the basis of the data of elemental, X-ray, IR spectroscopy and differential-thermal analyses. Also the process of thermal decomposition of the obtained complex has been studied. It is determined that the obtained new product not only misses crystallization molecules, but also two coordinating water molecules. Herewith layered-polymeric structure of the complex compound is preserved.

Key words: *pyromellitic acid, a complex compound, layered-polymeric structure, hydrogen bonds, chelating coordination, decomposition, thermogram, IR spectroscopy, elemental analysis, X-ray, the crystal grid.*

Received 22.12.2015 Revised 31.12.2015 Accepted 10.01.2016

INTRODUCTION

We have previously synthesized and decoded crystal and molecular structure of the decahydrate complex of copper (II) with 1,2,4,5-benzenetetracarboxylic acid [1] (Figure 1).

Central atom is five coordinated. Coordinated polyhedron is square pyramid. The square base of the pyramid has a rare type of distortion -2

tetrahedral, which is also found in the tetragonal pyramid of Cu oktagidratan-hydroxybenzoate of copper (II).

[2]. Just around the center of the plane of the base of the pyramid there is a copper atom with distances Cu - O 1,94 - 2,02 Å. Somewhat unexpected is the bond length Cu - O, regardless of appurtenance of O atoms (acid or water).

The coordination sphere of the copper ion (II) includes an oxygen atom, three-molecules of water and two carboxyl groups of pyromellitic anion acid. All carboxyl groups are monodentate.

The complexes related with coordinating impact of Cu - O, O – a hydroxyl atom of oxygen acid ligand form two-dimensional grid (2D), parallel planes (011) (Figure 1). The composition of the investigated crystal compound other than a water molecule coordination related to the copper atom (coordinating water), also includes a molecule of crystallization water which does not interact with the central atom.

Through the hydrogen bonds covering all the oxygen atoms but one set of 0 (4), the complex is combined into a single unit in the form of a crystal structure.

This difference in the ability of the two bridging oxygen atoms 0 (4),0 (6) with respect to the formation of H-bonds is due to their difference in interaction with the copper atom - the weaker the link Cu – O is, the greater is the probability of H-bonding. The water molecules H2O (1) which are the coordination peak of the pyramid use all four possibilities for the formation of connections, one of which is of Cu – O type, and the other three are of H interaction. This is not the first case of this type of interaction of atoms of oxygen which is most weakly coordinatingly bound to the metal atom. [3] From the analysis of the crystal structure, (Figure 1) it is also seen that a single layer of complexes (light) is slightly displaced in a plane (011) with respect to the other layer of complexes (black). Both layers are linked by hydrogen bonds forming a three-dimensional (3D) structure. Crystallization water molecules play an active role in this interaction. We assumed that in the absence of the crystallization water molecules there would not take place bias of layers. For this purpose, in this study we have investigated and newly synthesized complex 4compound of copper (II) with pyromellitic acid. The main goal of this work is to get nonvalent compounds with different "guest" molecules, as it has, as can be seen from the Figure 1, a porous-layered structure.

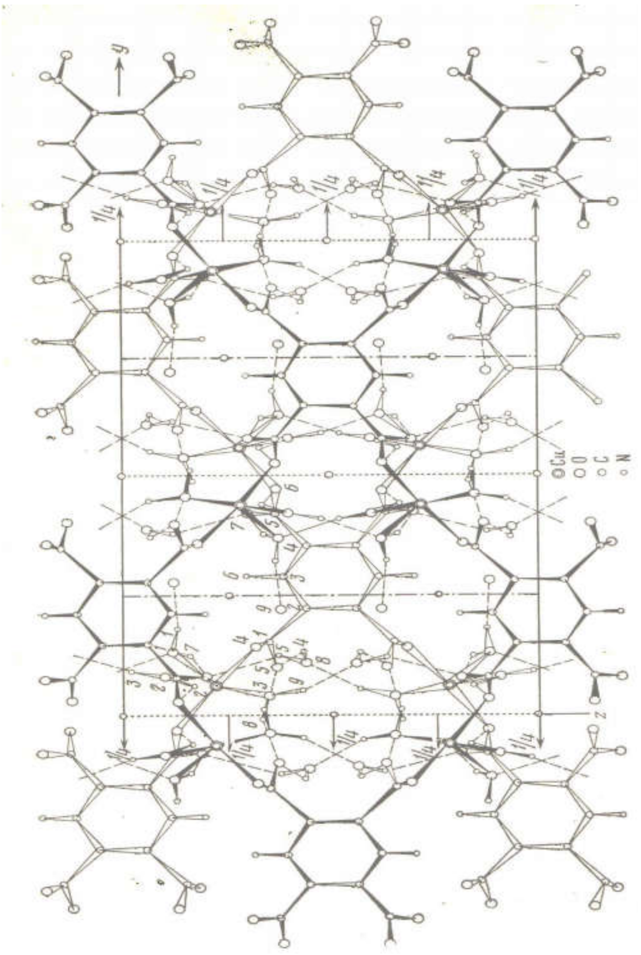


Fig. 1. Crystallic structure of the compound.

Radiograph of the complex compound of copper (II) is shown in Figure 2. As can be seen from the Figure 2, the complex compounds are highly crystalline and have a high symmetry, as maximums are distributed throughout all diffraction patterns. Unit cell parameters of the identified diffraction pattern are calculated: a = 10,68, b = 19,11, c = 11,28Å.

Comparison of the obtained parameters of a new complex compound with the parameters of previously known complex, the crystal structure of which was deciphered [1] (a = 9,679 (5), b = 18,17 (2), c = 12.18 (1) Å, β = 113.32 (5), z = 4, pr.gr A2 / a), revealed that the complex parameters of the new obtained complex differ by 1; 0.94 and 0,9Å consequently.

As it is seen, the parameters of *a* and*b* increase, but parameters of *c* decrease. The Figure 1 shows that the layers in the structure are perpendicular to the axis a, and as compared with the known complex, the axis *a*increases by 1Å. It means that the distance between the layers of the new obtained complex is increased by 1Å. Taking into account that the layers in the known complex are interconnected with hydrogen bonds through crystallization molecules of water, we can conclude that in the new obtained complex they are missing.

EXPERIMENTAL PART

X-ray analysis was performed on the device Commander SampleID (CoupledTwoTheta/Theta) WL 1.54060. The elemental composition of the obtained compound was determined by a gas chromatography analyzer CHN30 E Carlo ERBA. The metal content was calculated from the weight loss curve in count of the oxide obtained after heating on the derivatograph up to 800^{0}C. IR spectra were recorded on the devices SPECORD-MBO in 400 - 4000 sm-1 field. Derivatograms were recorded on derivatographs NETZSCH STA 449F3 STA449F3A-0836-M (heating speed 10 ° C / min, standard Al_2O_3).

Getting the complex. The starting materials were $C_6H_2(COOH)_4$, $CuSO_4 \cdot 5H_2O$, $NaHCO_3$ of qualification 4 (GOST 3759–75). The complexes were obtained by interaction of the sodium salt of pyromellitic acid with copper sulfate (II) in a weak acidic medium (pH = 6.8) at a stoichiometric ratio of 1: 2.

For synthesis of the complex compound of copper (II), 0.254 gr (0,001mol) pyromellitic acid, 0,336 gr (0,004mol) sodium hydrogen carbonate and 0,499 gr (0.002 mol) of copper sulfate (II) with 5 moles of crystallization water were taken. The solution was heated until it boiled and was cooled down till the room temperature. Blue halfcrystalline precipitate dropped from the solution which was filtered and washed for several times with distillated water, and then was dried on filter paper in a room temperature and afterwards in an oven at 1000C. The chemical composition of the complex compound was based on the data obtained from X-ray, elemental, thermogravimetric, and IR spectroscopic analyzes.

RESULTS AND DISCUSSION

The elemental composition of the newly obtained (1) and known (2) complex compounds is listed in Table 1.

Table 1

The results of the elemental analysis of the samples.

p/p	Found. %			Formula	Calculated. %		
	H	C	Me		Me	C	H
1	1,663	29,158	31,012	$Cu_2C_{10}H_6O_{10}$	30,751	29,056	1,453
2	4,023	21,643	22,965	$Cu_2C_{10}H_{22}O_{18}$	22,801	21,544	3,950

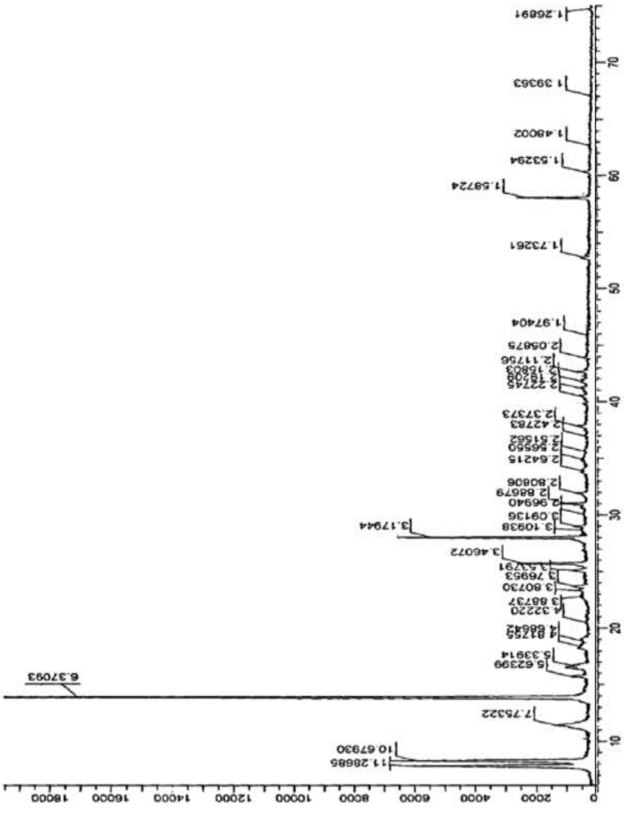


Fig. 2. The diffractogram of the complex compound $Cu_2(C_6H_2(COO)_4)(H_2O)_2$.

The table 1 shows that the elemental composition of the complex compounds 1 and 2 differ from each other. If to draw up a formula on the base of the results of the new obtained compound, it will look like that - $Cu_2(C_6H_2(COO)_4)(H_2O)_2$.

Thus, we can conclude that the obtained complex misses not only crystallization, but also coordination molecules of water. If the results of the elemental analysis will be verified with the results of the other analysis, in particular thermographic and IR spectroscopic analysis, then we can conclude that the two water molecules in the coordination sphere of the central atom are replaced by hydrogen of carboxyl group which has not entered in the coordination. Thus, carboxyl groups of acids will not have monodentate function as in the known complex, and will perform the chelating function.

Thermal analysis. Thermogravigram of a complex compound (1) is shown in Figure 3. Decomposition of the complex compound (1) begins at 140° C in 140 – 192°C temperature range and is accompanied by a shallow but clear endothermic effect with a maximum at 164°C and corresponds to removal of two water molecules. The experimental value of the mass loss is 7.4% (8.71% subtracted). In 192 – 260°C temperature range waterless complex is very steady. Then, in 260 – 6100C temperature range, the decomposition of anhydrous complex starts at a high speed.

The weight loss corresponds to the decomposition and parching of organic part of a molecule. This process is accompanied by an exothermic effect with a maximum of 340; 415; 5600C. The loss of weight is 48.6% (48.9% subtracted). Herewith, the complex nature of DTA shows that in this stage of the process numerous intermediate organic products are formed and burnt out. It can be assumed that these processes are the catalytic processes in which the catalyst is CuO. After complete burnout of the organic part of the complex, at 6100C as a final product of the thermolysis thereremains CuO, as evidenced by X-ray analysis.The loss of weight is 44% (38.5% subtracted). Thus, the results of the thermal analysis show that the chemical formula of the given compound is $Cu_2(C_6H_2(COO)_4)(H_2O)_2$, which is consistent with the formula obtained by elemental analysis. IR spectrum of the studied complex compound is shown in Figure 4.

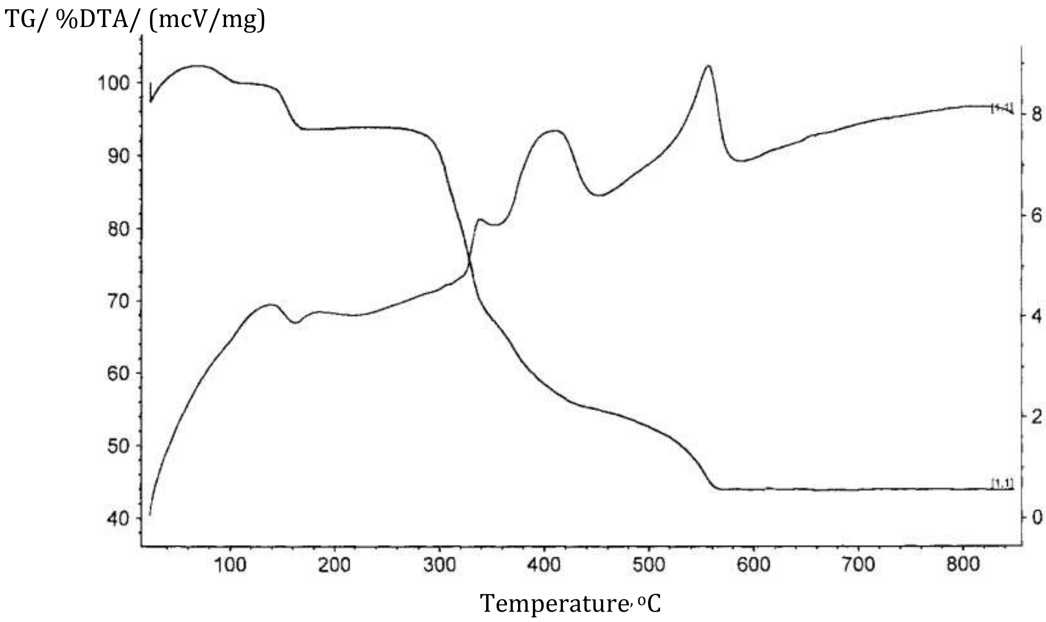
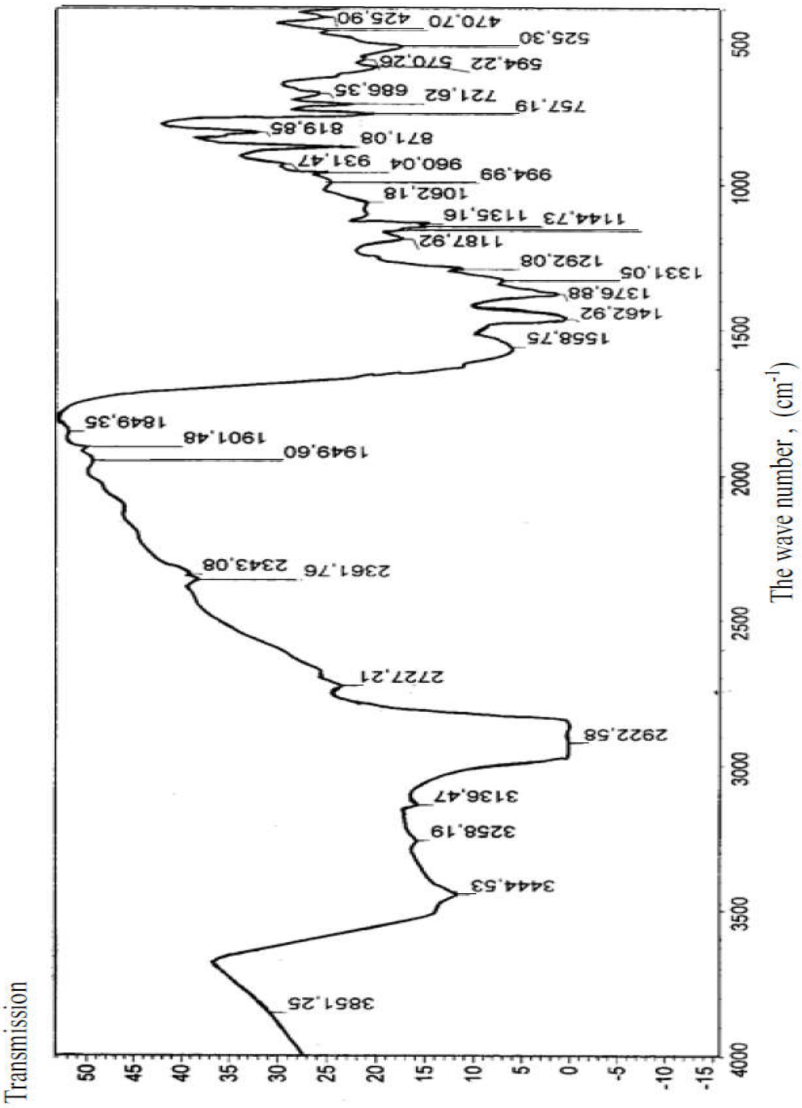


Fig. 3. Thermogravigram of the complex compound $Cu_2(C_6H_2(COO)_4)(H_2O)_2$.

Consistent with the formula obtained by elemental analysis. IR spectrum of the studied complex compound is shown in Figure 4.IR spectroscopic studies have shown that in the spectrum of the complex compound of the copper (II) there are observed absorption bands at 1559, 1376 and 1463, 1331 cm1, which are asym- metrical (ν_a) and symmetrical (ν_s) absorption bands of the carboxyl group of pyromellitic acid anion which indicates that they are coordinated with the central atoms of copper.

The difference between symmetric and asymmetric absorption bands are respectively 182 and 132 cm^1, which shows that carboxyl groups have strong
chelatestructure [4].



$\Delta\nu_{a}-\nu_{s}$

Fig. 4. IR spectrum of the complex compound $Cu_2(C_6H_2(COO)_4)(H_2O)_2$.

The difference between symmetric and asymmetric absorption bands are respectively 182 and 132 cm1, which shows that carboxyl groups have strong chelate structure [4].

As$\Delta\nu_{a}$ - ν_{s}has different values, it may be assumed that the relationship between M-O in one of the carboxyl groups is stronger than the other. Besides it, an absorption band relating to water molecules is observed in the spectrum of the field 3000-3600 cm1. Thus, the results of the spectroscopic studies also confirm the results obtained from the elemental and thermographic analysis. Based on an analysis of the data, an alleged schematic structure of a complex compound of Cu2(C6H2(COO)4)(H2O)$_2$ was drawn up which is represented in Figure 5.

From the alleged pattern it is seen that the central atom of copper (II) is five coordinated as in structure [1]. That is, it is a coordinating polyhedron-tetragonal pyramid.

The square base of the pyramid is a rectangle. Approximately in the center of the plane of the base of the pyramid the copper atom is located. All the oxygen atoms of the carbonyl groups of pyromellitic anion are involved to the coordination of the metal and due to this preserve five coordinated character of copper. The only difference is the fact that it is more ordered. On the vertex of the pyramid there is oxygen of coordinating molecules of water.

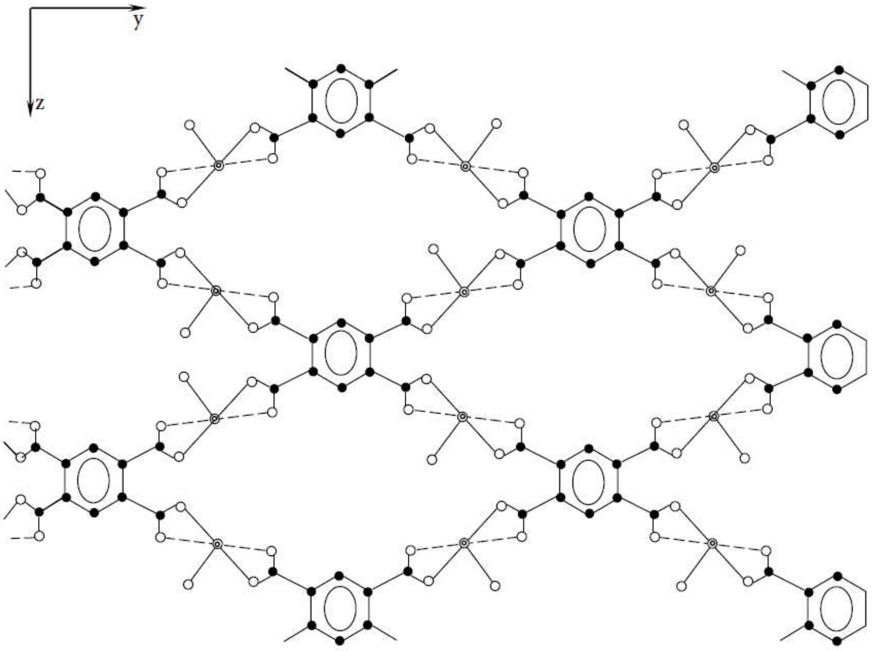


Fig. 5.Alleged schematic structure of the complex compound (along the axis 011).

CONCLUSION

The results of the studies showed that in the obtained new compound there are no crystallization molecules and even two coordinating water molecules. As a result, layered-polymeric structure of the complex compound is preserved.

We assume that, as in this complex there are no crystallization water molecules, insulated crystallographic pores in the crystal will lie above one another and as a result, through columns which are able to involve in themselves neutral organic molecules of different sizes and geometry, will be formed. The interlayer channels in the structure are also able to hold "guest" molecules, as well as clay.

ACKNOWLEDGEMENT

This work was supported by the Science Development Foundetion under the President of the Republic of Azerbaijan Grant № EİF/GAM-3-2014-6(21)-24/09/4 13.

REFERENCES

1. Usubaliev B.T., Shnulin A.N., MamedovKh.S. The crystal and molecularstructure of the decahydrate copper complex with 1,2,4,5-benzoltetracarboxylic acid .// Coordination Chemistry, 1982, vol.8, issue 11, p.1532-1538.
2. Shnulin A.N., MamedovKh.S. Crystallic and molecular structure ofoctahydrate - oxibenzol of copper (II) .// Coordination Chemistry. 1981, vol.7,№10, p.1544-1548.
3. Bellami L. New data on the infrared spectra of complex molecules.Moscow: Mir, 1971, p.505.
4. Nakamoto K. Infrared Spectra and Spectra KR of inorganic and coordinationcompounds. Moscow: Mir, 1991, p. 318.

CITATION OF THIS ARTICLE

B.T. Usubaliev,M.K. Munshieva,V.H. Nurullayev, F. B. Alieva F, P. S. Safarova.Synthesis, Physical- And Structure-Chemical of Research Of Coordinating compounds of Diaquo-1,2,4,5 Benzoltetracarbonat Dimedi (II). Bull. Env. Pharmacol. Life Sci., Vol 5 [1] December 2015: 12-17