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SYNTHESIS, STRUCTURE OF THE NI (II) COMPLEX OF 4-HYDROXYBENZOIC ACID

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ABSTRACT: - 4-Hydroxybenzoic acid has antibacterial (against Gram+ve and Gram-ve bacteria), antimicrobial, antimutagenic, blood clot prevention and estrogenic activity. In addition, it is used as a "trap" to study the formation of hydroxyl radicals during cerebral ischemia and reperfusion (restoration of blood flow) and is widely used as a preservative in drugs, cosmetics, pharmaceuticals, food and beverages [1, 2528 p.]. It was found that p-hydroxybenzoic acid increases the resistance of winter wheat (Tritisum aestivum) to external abiotic stress under drought conditions [1, 2528 p.]. Its coordination compounds have been studied for their stimulating properties [2, 588p.].

Aim of the work

Obtaining of the structure a complex combination of pHBA with nickel, studying its composition and structure.

KEYWORDS: Ni complex, single crystal X-ray diffraction, crystal structure, coordination compound.

INTRODUCTION

4-Hydroxybenzoic acid with empirical formula C7H6O3, molecular mass 138.1, melting point 216.2ºC (see Figure 1) from carrot (Daucus carota), oil palm (Elaeis guineensis), grape (Vitis vinifera), yellow leaf tree (Xanthophyllum rubescens), obtained naturally or synthetically from peroba tree (Paratecoma peroba), southern catalpa tree (Catalpa bognonioides), Cuban royal palm (Roystonea regia) [4, 109p.]. Additionally, 4-hydroxybenzoic acid is also found naturally in plants such as Vitex agnus-castus and Hypercium perforatum. It can also be found in coconut fruit and methods of its extraction have also been developed [5, 379p.]. Among Azerbaijani scientists, Rasulov et al. It was announced that p-hydroxybenzoic acid was isolated from the extract of Centaurea polypodiifolia plant [6, 495b.].

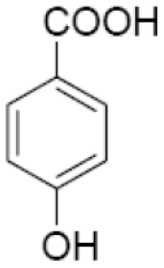

Figure-1
pHBA

The pKa value is equal to 4.58 [7, 17 p.], which shows acidic property. It undergoes reactions typical of organic acids [8, 1255 p.].

METHODOLOGY

During the synthesis of the studied metal complex [Ni(PHBA)(H2O)5](PHBA)(H2O)3, 0.177 g (1.0 mmol) of Ni(CH3OO)2 was dissolved in a small amount of water. 4-Hydroxybenzoic acid (0.276 g, 2 mmol) was dissolved in an equal volume mixture of 2 ml of absolute alcohol and 2 ml of distilled water. After the ligand solution was added dropwise to the Ni(II) salt solution, the color of the obtained solution gradually turned to light green. The resulting solution was stirred on a magnetic stirrer at room temperature for 1 hour. The solution was then left in a beaker with small holes for evaporation at room temperature. After about 3 weeks, single crystals of the complex compound appeared. To determine the crystal structure, data were analyzed on an Oxford diffraction Xcalibur-R SSD diffractometer (CuKa-radiation, λ=1.54184 Å, ω-scanning mode, graphite monochromator) at 293 K. The structure was solved by the direct method using the SHELX-2014 software package. All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed in calculated locations and constrained by isotropic thermal parameters. Drawings of the molecule were created using the MERCURY program [3].

Obtained results: The crystal has an orthorhombic structure and space group Pca2/1. a=7.5845(3), b=11.2963(4), c= 23.9669(7), a, b, g = 90°, and the crystal size is V=2053.41. The complex has a total of 5 intermolecular and 1 internal hydrogen bonds. But the polyhedron was found to be a distorted octahedron. When the valence bond lengths were studied in relation to its spatial structure, the values obtained together with the angles confirmed the distorted structure.

RESULTS AND DISCUSSION

4-Hydroxybenzoic acid is monodentately coordinated to the Ni(II) atom through the O1 oxygen atom in the carboxyl group. At the same time, 5 water molecules are attached to the Ni(II) ion and form an inner sphere. In the outer sphere, one molecule of p-hydroxybenzoic acid and 3 molecules of water

are placed in the carboxylate form (Fig. 2). Since the coordination number of the central atom is equal to 6, the polyhedron of the new complex obtained is an octahedron. The valence bond lengths and angle values given below confirm that the polyhedron is a distorted octahedron. The bond lengths of 5 water molecules bound to the Ni(II) ion are in the range of 2.05-2.098 Å, and the distance between the central atom and the O1 oxygen atom of the carboxyl group of 4-hydroxybenzoic acid is 2.031 Å (Table 1). The valence angles are 46.41 degrees with Ni(II) ion, the distance between O1 oxygen and O11 oxygen, and 44.84 degrees with O10 oxygen. The valence angles between the central atom and water molecules are 43.29-45.43 degrees (Table 2).

The Ni(II) ion has a +2 charge, and the compound is neutralized due to deprotonation of the carboxyl group of 4-hydroxybenzoic acid monodentately attached to it, and para-hydroxybenzoic acid located in the outer sphere being in the carboxylate state.

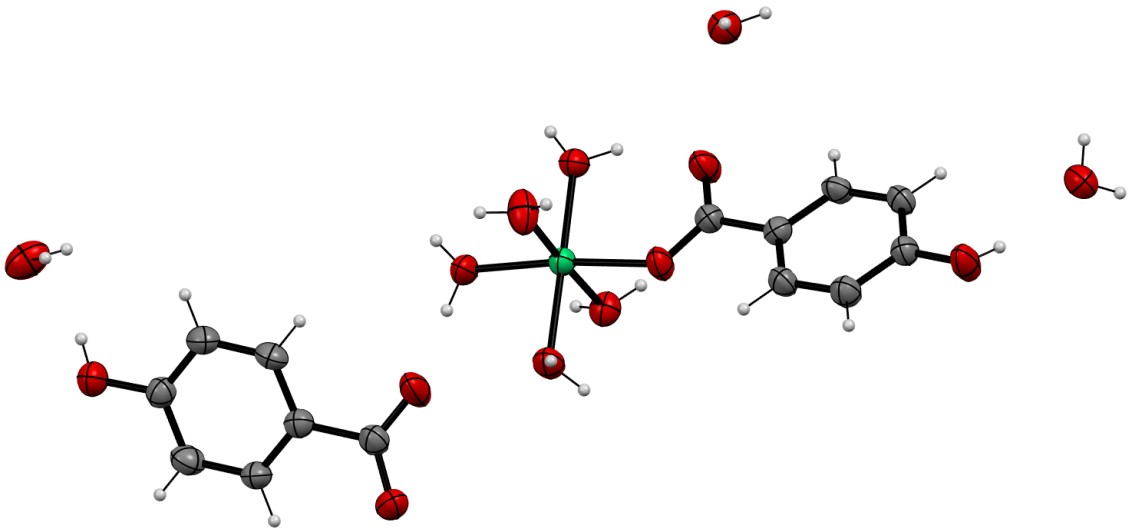

Figure 2. The structure of the [Ni(PHBA)(H2O)5](PHBA)(H2O)3 molecule.

The length of the hydrogen bond between oxygen O9 in the inner sphere and oxygen O5 in the carboxyl group of 4-hydroxybenzoic acid located in the outer sphere is 2.654 A.

The central atom, i.e. O9, O7 attached to the Ni(II) ion, and O5, O6 oxygen of the carboxylate group of 4-hydroxybenzoic acid located in the outer sphere and O13 on the outside interact with water, O2 on the carboxylate group of p-hydroxybenzoic acid on the inner sphere and O12 on the outside, i.e. water molecule intermolecular hydrogen bonds are formed. The complex has a total of 5 intermolecular and 1 internal hydrogen bonds (Table 3).

Compared to the pHBA of the inner sphere, the pHBA of the outer sphere is tilted by 59.1 degrees.

Table 1. Selected bond lengths with metal ions in [Ni(PHBA)(H2O)5](PHBA)(H2O)3

Bond	d, Å	Bond	d, Å

Ni1 – O1	2.031(4)	Ni1 – O10	2.032(5)
Ni1 – O7	2.098(5)	Ni1 – O11	2.060(4)
Ni1 – O8	2.089(5)		
Ni1 – O9	2.050(4)		
Symmetry codes	*(i) -x,-y, z+1/2*	*(ii) x+1/2,-y, z*	*(iii) -x+1/2, y, z+1/2*

Table 2. Selected bond angles of metal ions

Bond	d, Å	Bond	d, Å
O1 -Ni1 -O7	86.06(18)	O8 -Ni1 -O11	88.88(18)
O1 -Ni1 -O8	95.97(17)	O9 -Ni1 -O10	92.91(19)
O1 -Ni1 -O9	174.47(19)	O9 -Ni1 -O11	88.85(17)
O1 -Ni1 -O10	90.33(19)	O10 -Ni1 -O11	177.6(2)
O1 -Ni1 -O11	88.04(18)	O7 -Ni1 -O11	88.62(19)
O7 -Ni1 -O8	176.72(19)	O8 -Ni1 -O9	88.54(17)
O7 -Ni1 -O9	89.30(18)	O8 -Ni1 -O10	89.6(2)
O7 -Ni1 -O10	93.0(2)		
Symmetry codes	*(i) 1-x,y,3/2-z*	*(ii) 1-x,1-y,1-z*	*(iii) x,1-y,1/2+z*

Table 3. Geometry of H-bonds

Bond D–H···A	**Distance, Å**			**AngleD–H···A, degree.**	**Coordinates of atom A**
	D –H	H ···A	D··· A		
O7-H7···O13	0.8600	2.0600	2.861(7)	154.00	-
O8-H8···O2	0.8500	1.8500	2.596(6)	145.00	x,1+y,z
O9-H9···O5	0.8500	1.8200	2.654(7)	165.00	3/2-x,3/2-y,1-z

O10-H10···O4	0.8500	1.9100	2.738(7)	163.00	
O11-H11···O4	0.8500	0.8500	2.818(6)	154.00	
O11-H11···O5	0.8500	2.5400	3.268(6)	145.00	
O12-H12B···O6	0.8500	2.1600	2.796(7)	132.00	
O13-H13A···O6	0.8500	2.0400	2.617(7)	124.00	
O13-H13B···O6	0.8500	2.0700	2.890(7)	162.00	
O14-H14A···O8	0.8500	1.9400	2.774(6)	168.00	
O14-H14B···O4	0.8500	2.0200	2.732(7)	140.00	

RESULTS

For the first time, the [Ni(PHBA)(H2O)5](PHBA)(H2O)3 complex was synthesized and its molecular and crystal structure was determined using a single crystal diffractometer. The crystal has an orthorhombic structure and space group Pca2/1. The complex consists of an inner and outer sphere, three molecules of water. Since the coordination number of the central atom is equal to 6, the polyhedron of the new complex obtained is an octahedron. The complex has a total of 5 intermolecular and 1 internal hydrogen bonds.

REFERENCES

1. Sytar Oksana. Plant phenolic compounds for food, pharmaceutical and cosmetics production. Journal of Medicinal Plants Research 2012; 6(13): 2526–2538. DOI: 10.5897/jmpr11.1695.

2. Ibragimov AB, Ashurov ZM, Zakirov BS. Molecular and crystal structure of a mixed-ligand cadmium complex with p-hydroxybenzoic acid and monoethanolamine. Journal of Structural Chemistry 2017; 58(3): 588–590. DOI: 10.1134/S0022476617030209.

3. C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, Mercury programme, J. Appl. Crystallogr. 41 (2008) 466–470.

4. Kakkar S, Narasimhan B. A comprehensive review on biological activities of oxazole derivatives. BMC Chemistry 2019; 13(3): 109–115. DOI: 10.1186/s13065-019-0531-9.

5. Dey G, Chakraborty M, Mitra A. Profiling C6-C3 and C6-C1 phenolic metabolites in Cocos nucifera. Journal of Plant Physiology 2005; 162(4): 375–381. DOI: 10.1016/j.jplph.2004.08.006.

6. F. A. Rasulov, A. Sh. Ibragimov MBB. Centaurea polypodiifolia. New York 1984; (4): 495–507.

7. Zhang JD, Zhu QZ, Li SJ, Tao FM. Prediction of aqueous pKa values of hydroxybenzoic acid using hydrogen-bonded complexes with ammonia. Chemical Physics Letters 2009; 475(1–3): 15–18. DOI: 10.1016/j.cplett.2009.05.007.

8. Lin CJ, Xu JQ, Zheng YQ, Zhu HL, Xu W. Synthesis, Crystal Structures, and Properties of Two New Cu(II) Complexes with p-Hydroxybenzoic

Acid. Journal of Cluster Science 2015; 26(4): 1253–1265. DOI: 10.1007/s10876-014-0810-5.