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SYNTHESIS, PHYSICOCHEMICAL STUDY AND CRYSTAL STRUCTURE OF BIS-(P-NITROBENZOATE)-DI-(PYRAZINE) NICKEL(II)-DIHYDRATE

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Abstract: *The molecular structure of the new Ni(II) complex of p-nitrobenzoic acid and pyrazine was synthesized and deciphered. It found that the central atom was coordinated by the ligand of p-nitrobenzoic acid according to the monodentate type. Having the basic properties of the pyrazine molecule, it was coordinated by the nickel atom in a donor-acceptor type of bond through donor nitrogen atoms. Two water molecules through donor oxygen atoms were coordinated by nickel and complement its coordination number to six. Pyrazine molecules cross-link para-nitrobenzoate Ni(II) molecules with the help of donor nitrogen atoms and form polymeric molecules.*

Keywords: *polymer molecule, monodentate bond, crystal and molecular structure, pyrazine, aqua complex.*
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Introduction

The most promising area of coordination chemistry is the preparation of new coordination polymers with certain structural and specific functions [1]. They are of practical interest as components for a new generation of functional materials with improved characteristics. Metal-organic coordination polymers exhibit high sorption characteristics, which opens up prospects for their use, for example, in heterogeneous catalysis, in processes of separation of complex mixtures, purification and storage of industrial gases. The presence of magnetic or photoactive centers (e.g., d- and/or f-metal ions, organic radical ligands) in metal-organic polymeric molecules makes it possible to expect that molecular magnets, photomagnetics or photoactive molecules can be used to create new types of data carriers, quantum computers and various magnetic and optical-mechanical devices [2,3].

The key role in the synthesis of coordination polymers is played by the nature of the ligands used, by the choice of suitable solvents based on transition elements and reaction conditions [4].

Organic ligands most often used to obtain coordination polymers with carboxyl groups must have more than one donor center for the coordination of different metal atoms [5].

Bearing in mind the importance of the diversity of coordination of carboxylates and in the composition of the donor nitrogen atom in the pyrazine molecule, we synthesized and deciphered the molecular and crystal structures of pyrazine adducts of Co(II) Mn(II) para-nitrobenzoates [6].

In this work, we synthesized and studied the crystal structures of a new p-nitrobenzoate Ni(II) pyrazine adduct in the (p-nitrobenzoate)$_2$ Ni•$C_4H_4N_2$ composition.

Experimental part

Single crystals for X-ray diffraction analysis were synthesized in the following way:

1.25 g of sodium para - nitrobenzoate was dissolved in hot (50-600C) 50 ml of

distilled water, 0.25 g of pyrazine was added to the solution.

To the resulting solution was added a solution of 2.13 grams of NiSO4·H2O salt. The solution was filtered and left at room temperature in a dark place. After a few days, brown needle-shaped single crystals precipitated.

The crystalline complex was filtered and dried in a desiccator over anhydrous $CaCl_2$.

Elemental analysis of the resulting complex was carried out on a Castech ECS 4010

CHNSO analyzer.

% calculated: C- 42.87; H-3.20; N - 11.13.

$(4\text{-}NO_2\text{-}C_6H_4\text{-}COO)_2Ni\cdot 2C_4H_4N_2$

Found %: C- 43.01; H-3.26; N - 11.06.

An IR spectroscopic analysis of the obtained complex (4000-400 cm-1) was carried out on a Perkin-Elmer-spectrum 100 PI-IR instrument. The absorption bands (sym COO^{-}) in the region of 1650 cm-1, and (sym COO^{-}) in the region of 1540 cm-1 were determined. The absorption bands of the C-NO2 bond appear in the region of 1365 cm-1, coordinated water molecules in the region of 827 cm-1, the N-N bond in the region of 645 cm-1, the Ni-O bond in the region of 552 cm-1.

The thermogravimetric analysis of the complex was carried out in a NETZSCH STA-409 PDPG derivatograph in air.

X-ray diffraction analysis of the single crystal was carried out in an automatic diffractometer XeaLAB AFC 11 (RINC) in the USA at the University of Virginia. The structure was solved using the Olex2 [7], Refine [8], and Shelx [9] programs. Crystallographic parameters are given in Table 1. Coordinates of atoms in Table 2 and the distance between the atoms in Table 3, bond angles in Table 4. Coordinates of hydrogen atoms in Table. 5.

Table 1. Crystallographic data of the Ni(II) complex

CCDC	052318	Cristal size.mm3	0.152×0.050×0,038
Empirical formula	$C_{18}H_{16}N_4NiO_{16}$	Radiation	Cu Kα (λ =1,54184)
Formula weight	253.52	20 range for data collection/°	8.02 to 150.08
Temperature K	294.7 (3)	Index ranges	$-27 \le h \le 27$, $-8 \le k \le 8$, $-15 \le 1 \le 15$
Crystal system	Monoclinic	Reflections collected	17980
Space group	C2/c	Independent reflections	1929 [R_{int} = 0.0182, R_{siqma} = 0.0061].
a/Å	22.0922(2)	Data / restraints/ parameters	929/0/175
b/ Å	6.9939(1)	Goodness – of – fit on F^2	1.087
c/Å	12.3766(1)	Final R indexes [I>=2σ(1)]	R_1 = 0.0259, wR_2 = 0.0712
α/°	90	Final R indexes [all data]	R_1 = 0.0260, wR_2 = 0.0712
β/°	94.586(1)	Largest dff.peak/hole	e $Å^{-3}$ 0.28/ - 0.32
γ/°	90		
Volume/ $Å^3$	1906.19(4)		
Z	4		

Table 2. Atomic coordinates ($\times 10^4$) and their temperature factors.

Atom	a/x	b/x	c/z	$U_{(eq)}$
Ni 1	5000	620.8(5)	2500	22.35912)
O13	41.59	587.3(15)	3082.4(9)	28.2(2)
O14	4630.3(6)	758.9(18)	873.9(10)	34.6(3)
O12	3620.3(5)	1788(2)	1634.7(10)	41.8(3)
N17	5000	-2385(2)	2500	25.2(3)
N18	5000	-3628(2)	2500	25.2(3)
O10	1510.9(7)	-542(2)	5578.9(12)	53.9(4)
N8	1495.3(6)	450(20	4766.3(12)	36.5(3)
O9	1040.8(6)	1287(3)	4391.9(12)	57.7(4)
C5	3106.4(6)	1049(2)	3187.0(12)	24.7(3)
C6	3120.1(7)	178(2)	4198.6(12)	27.7(3)
C2	2057.4(7)	669(2)	4216.7(13)	28.2(3)

Table 3. Distance between atoms, d Å

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ni1	O13	2.0449(10)	O10	N8	1.220(2)
Ni1	O13[1]	2.0449(10)	N8	O9	1.222(2)
Ni1	O14[1]	2.1128(12)	N8	C2	1.4706(19)
Ni1	O14	2.1128(12)	C5	C6	1.391(2)
Ni1	N17	2.1025(17)	C5	C11	1.5102(19)
Ni1	N18	2.1030(17)	C5	C4	1.393(2)
O13	C11	1.2661(18)	C6	C7	1.385(2)
O12	C11	1.2457(19)	C2	C3	1.381(2)
N17	C22[1]	1.3375(17)	C2	C7	1.380(2)
N17	C22	1.3375(17)	C20	C22	1.385(2)
N18	C20[2]	1.3360(17)	C3	C4	1.383(2)
N18	C20[3]	1.3360(17)			

[1]1-X,+Y,1/2-Z; [2]1-X,1+Y,1/2-Z; [3]+X,1+Y,+Z

Table 4. Valence angles.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O13[1]	Ni1	O13	178.69(6)	C20[3]	N18	Ni1	121.64(9)
O14[1]	Ni1	O13	87.56(5)	C20[3]	N18	C20[2]	116.71(18)
O14	Ni1	O13	92.50(5)	O9	N8	O10	123.61(14)
O14	Ni1	O13[1]	87.56(5)	C2	N8	O10	118.13(14)
O14[1]	Ni1	O13[1]	92.50(5)	C2	N8	O9	118.25(14)
O14[1]	Ni1	O14	174.76(7)	C11	C5	C6	120.78(13)
N17	Ni1	O13	89.34(3)	C4	C5	C6	119.53(13)
N17	Ni1	O13[1]	89.34(3)	C4	C5	C11	119.63(13)
N17	Ni1	O14	92.62(4)	C7	C6	C5	120.46(14)
N17	Ni1	O14[1]	92.62(4)	C3	C2	N8	118.62(14)
N18	Ni1	O13	90.66(3)	C7	C2	N8	118.58(14)
N18	Ni1	O13[1]	90.66(3)	C7	C2	C3	122.80(14)
N18	Ni1	O14	87.38(4)	O12	C11	O13	125.66(13)
N18	Ni1	O14[1]	87.38(4)	C5	C11	O13	116.38(13)
N18	Ni1	N17	180.0	C5	C11	O12	117.95(13)
C11	O13	Ni1	125.76(10)	C22	C20	N18[4]	121.68(14)
C22	N17	Ni1	121.67(9)	C20	C22	N17	121.63(14)
C22[1]	N17	Ni1	121.67(9)	C4	C3	C2	118.03(14)
C22[1]	N17	C22	116.65(18)	C2	C7	C6	118.36(14)
C20[2]	N18	Ni1	121.64(9)	C3	C4	C5	120.81(14)

[1]1-X,+Y,1/2-Z; [2]1-X,1+Y,1/2-Z; [3]+X,1+Y,+Z; [4]1-X,-1+Y,1/2-Z

Table 5. Coordinates of hydrogen atoms.

Atom	X	y	z	U(eq)
H14a	4599(11)	-140(40)	560(20)	51.9(4)
H14b	4249(11)	1100(30)	1008(18)	51.9(4)
H6	3482(9)	-270(30)	4518(15)	33.2(4)
H20	5437(9)	-6100(30)	1224(16)	35.2(4)
H22	5462(9)	-2720(30)	1230(16)	35.1(4)
H3	1649(9)	2010(30)	2905(16)	37.5(4)
H7	2613(9)	-590(30)	5400(17)	35.5(4)

Crystal structures are shown in Fig. 1. Fig. 2 shows the polymer structure in the "c" axis.

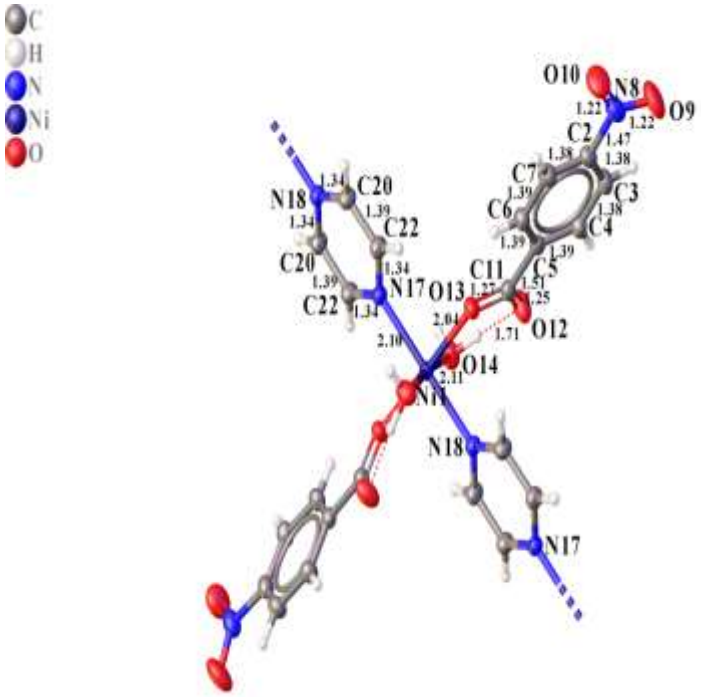

Fig. 1. Crystalline and molecular structure of the Ni(II) complex

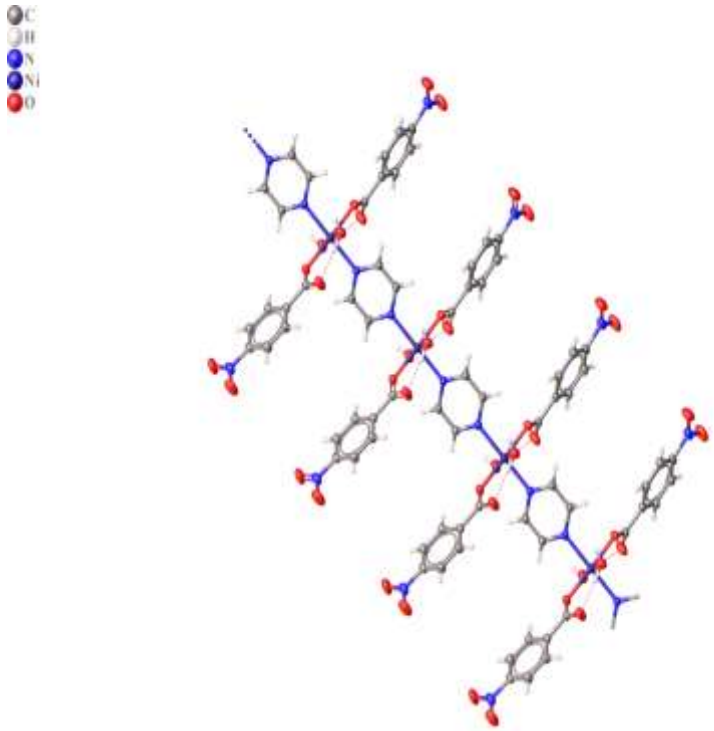

Fig. 2. Polymer structure of the Ni(II) complex along the c-axis.

Discussion

As can be seen from Fig.1, the central Ni (II) atom is coordinated by one oxygen atom of the carboxyl group, according to the monodentate type. The donor nitrogen atoms of pyrazine are coordinated by the Ni (II) atom in accord with the donor-acceptor mechanism.

Two water molecules are coordinated by the central Ni(II) atom through donor oxygen atoms, and the coordination number of the metal is raised to six.

The distance NiC with the oxygen of the carboxyl group will be Ni(1)-O(17)=2.0443 Å, Ni(1)-N(12)= 2.1025 Å, Ni(1)-H2O= 2.1128 Å.

Pyrazine molecules cross-link molecules through donor nitrogen atoms to form a polynuclear polymer along the “b” axis (Fig. 2).

In the polymer molecule, there are strong hydrogen bonds and between the uncoordinated oxygen atom of the carboxyl group and the OH group of the water molecule. And there are also van der Waals bonds between molecules.

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BİS -(p-NİTROBENZOAT)- Dİ -(PİRAZİN) Ni (II) -DİHİDRAT KOMPLEKS BİRLƏŞMƏSİNİN SİNTEZİ, FİZİKİ-KİMYƏVİ ANALİZİ VƏ MOLEKULYAR KRİSTAL QURULUŞU

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Xülasə: *Məqalədə nikel(II) kationunun yeni kompleks birləşməsi bis – (nitrobenzoato),-di (pyrazin) Ni (II) – dihidrat akva kompleksi sintez olunaraq, fiziki – kimyəvi tədqiqatı aparılmış və monokristalları alınaraq avtomatlaşdırılmış difraktometrdə molekulyar və kristal quruluşu açılmışdır. Məlum olmuşdurki, p-nitrobenzoy turşusunda karboksil qrupunun bir oksigeni mərkəzi atomla koordinasiyaya daxil olur. Quruluşa daxil olan pirazin molekulu donor azot atomları vasitəsilə Ni(II) ilə donor – akseptor tipli rabitə yaradır. Eyni zamanda koordinasiyaya daxil olan iki su molekulları Ni atomu ilə rabitə yaradaraq onun koordinasiya ədədini altıya çatdırır. Pirazin molekulları donor azot atomları vasitəsilə molekulları bir – birinə tikərək polimer zəncir əmələ gətirir.*

Açar sözləri: *polmer molekulu, monodentat rabitə, kristal və molekulyar quruluş, pirazin, akva kompleks, p – nitrobenzoat, Ni(II) kompleksi.*

СИНТЕЗ, ФИЗИКО-ХИМИЧЕСКОЕ ИССЛЕДОВАНИЕ И КРИСТАЛЛИЧЕСКАЯ СТРУКТУРА БИС-(n-НИТРОБЕНЗОАТО)-ДИ-(ПИРАЗИН) НИКЕЛЬ(II) –ДИГИДРАТА

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Аннотация: *Синтезирована и расшифрована структура нового комплекса Ni(II) с n-нитробензой кислотой и пиразином. Установлено, что центральный атом координируется лигандом n-нитробензойной кислоты по монодентатному типу. Имеющая основные свойства молекула пиразина координируется атомом никеля по донорно-акцепторному типу связи через донорные атомы азота. Две молекулы воды через донорные атомы кислорода координируются никелем и дополняет его координационное число до шести. Молекулы пиразина с помощью донорных атомов азота сшивают молекулы пара-нитробензоато Ni (II) и образуют полимерные молекулы.*

Ключевые слова: *полимерная молекула, кристаллическая структура, пиразин, аквакомплекс.*