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**Experimental study of the system Nickel(II) benzoate and 2,2'-
bipyridine**
(Small research project)

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1 INTRODUCTION

At present, the compounds of Nickel(II) are subject of many studies in various fields of science. In the field of biology Ni is interesting because many Ni enzymes are in primitives species and they do important functions in diverse metabolic processes, such as energy metabolism and virulence [Alfano, 2020].

Besides, the nickel is a 3d transition metal with many uses in the field of catalysis, e.g. it catalyses the hydrogenation of nitriles and alkynes a really interesting reaction for the industries [Sharma, 2020].

If we talk about the environment, the nickel could be an interesting element to study because of there are some Ni complexes that can act like a catalyst for water splitting and CO₂ reduction [Wang, 2019]. If this study goes further, we could improve the environment, decrease global warming since we could have a source of clean energy.

Nickel(II) complexes are also studied in the field of magnetism since it can form quite interesting molecular magnets. One of the combinations with Ni(II) in complexes in the formation of 3d / 4f heterometallic complexes because they allow this ion to exhibit magnetic anisotropy. [Chakraborty, 2019].

Previously Anna Vráblová (née Ščerbová) *et al.* [Ščerbová, 2015] have prepared and studied nickel benzoate trihydrate. Its crystal structure is formed of infinite positively charged chains built up of Ni(II) atoms which are triply bridged by benzoate and aqua ligands. At the same time it is known that bpy coordinates mostly as a chelating bidentate ligand. As a continuation of the work of Vráblová *et al.* the aim of this project is to investigate the possibilities to prepare complexes by using a combination of benzoate anion and a blocking ligand bpy, to isolate the formed solid products, and to identify them by chemical analyses and IR spectroscopy.

In this thesis the following abbreviations are used:

bpy / 2,2' bpy	2,2'-bipyridine
bz	benzene
cinn	cinnamato
DABPH	2,6-diacetylpyridine-bis(benzoic acid hydrazone)
DMGH dmgh	dimethylglyoximato
en	1,2-diaminoethane, ethylenediamine
Et ₂ O	ether
mal	maleato
mpcm	methyl-3-pyridylcarbamate
ppds	phenylphosphinediyl)dibenzenesulfonato
tcdp	tetracyano-2-(dicyanomethylene) propane-1,3-diide(2-)

2 THEORETICAL PART

2.1 Nickel(II) as central atom

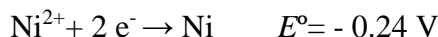
Nickel (Ni) is a transition metal whose atomic number is 28 and is located in group 10 of the periodic table. It also has 5 different isotopes which makes it have a weight around 58.69 u. It has an electronic configuration [Ar] 4s² 3d⁸. Some important properties of nickel are reflected in the following Table 1.

Table 1: Some properties of Nickel [Greenwood, 1984]

Property	Ni
Atomic number	28
Number of isotopes	5
Atomic weight (g/mol)	58.69
Electronic configuration	[Ar] 3d ⁸ 4s ²
Electronegativity	1.8
Metal radius (12 coordinate) (pm)	124
MP/°C	1455
BP/°C	2920
ΔH_{fus} (kJ* mol^{-1})	17.2 (± 0.3)
ΔH_{vap} (kJ* mol^{-1})	375 (± 17)
Density (20°C) (g* cm^{-3})	8.908
Electrical resistivity (20°C) ($\mu\text{ohm*cm}$)	6.84

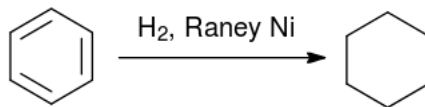
Nickel is the seventh most abundant transition element and about 10 per cent of the core is Nickel and, in the crust, there is only 80 ppm of Ni. In nature we can find it in elemental form alloyed with iron or in combination with Arsenic, Antimony or Sulphur (e.g.: NiS, NiAs₂, NiSbS) [Cotton, 1999].

The nickel has a silver colour, it is quite resistant to air and water at normal temperatures. However, when the air is heated the nickel is pyrophoric if it is very finely divided. Ni is ferromagnetic and slightly electropositive



We have said that Ni is resistant to air or water under standard conditions but this element tends to react with B, Si, P, S and halogens (although very slow with Fluor). It has low acid resistance and oxidizes easy but it does not happen with HNO₃ because passivation occurs [Cotton, 1999].

The main uses of nickel are the coating of metals to protect it from corrosion (Fe, Al, Cu, Steel) and to catalyze reactions. A typical reaction in which Ni in the form of Raney-Ni is used, is the next hydrogenation reaction where the benzene is reduced to cyclohexane [Wade, 2004].



The oxidation states of nickel vary from -1 to 4+, with 2+ being the most common. Oxidation states 0 and 1+ have little interest and oxidation states 3+ and 4+ are rare/very rare, resp. In addition, nickel is an element with a great variety of coordination numbers and with interesting stereochemistries. In the next Table 2 are shown some examples of Nickel compound with various oxidation states and stereochemistries.

Table 2: Overview of Nickel compounds in various oxidation states and stereochemistries [Greenwood, 1984; Cotton, 1999].

Oxidation State	Coordination Number	Stereochemistry	Ni
-1	4	?	[Ni ₂ (CO) ₆] ²⁻
0 (d ¹⁰)	3	Planar	[Ni(P(OC ₆ H ₄ -2-Me ₃) ₃) ₃]
	4	Tetrahedral	[Ni(CN) ₄] ⁴⁻
1 (d ⁹)	4	Tetrahedral	[NiBr(PPh ₃) ₃]
2 (d ⁸)	3	Trigonal planar	[Ni(NPh ₂) ₃] ⁻
	4	Tetrahedral	[NiCl ₂ (PPh ₃) ₂]
		Square planar	[Ni(CN) ₄] ²⁻
	5	Trigonal bipyramidal	[Ni(PPhMe ₂) ₃ (CN) ₂]
		Square pyramidal	[Ni(CN) ₅] ³⁻
	6	Octahedral	[Ni(bpy) ₃] ²⁺
		Trigonal prismatic	NiAs
	7	Pentagonal bipyramidal	[Ni(DAPBH) ₂ (H ₂ O) ₂] ²⁺
3 (d ⁷)	4	Square planar	-
	5	Trigonal bipyramidal	[NiBr ₃ (PEt ₃) ₂]
	6	Octahedral	[NiF ₆] ³⁻
4 (d ⁶)	6	Octahedral	K ₂ [NiF ₆]

From coordination chemistry point of view the most abundant and important oxidation state

of nickel is $2+ (d^8)$ which will be discussed here in more details. Coordination number rarely exceeds 6 and principal stereochemistries are octahedral or square-planar.

There are four types of Ni(II) complexes as to their stereochemistry (Figure 1):

- Octahedral: which are paramagnetic due to presence of 2 unpaired electrons in $(t_{2g})^6 (e_g)^2$ orbitals. They are green to blue.
- Tetrahedral: which are paramagnetic due to presence of 2 unpaired electrons in $e^4 t_2^4$ orbitals. They are green to blue.
- Square planar: in these complexes all electrons in d-orbitals are paired and this means that such complexes are diamagnetic. They are commonly red to yellow.
- Five-Coordinate Nickel (II) Complexes: these can be trigonal bipyramidal or square pyramidal

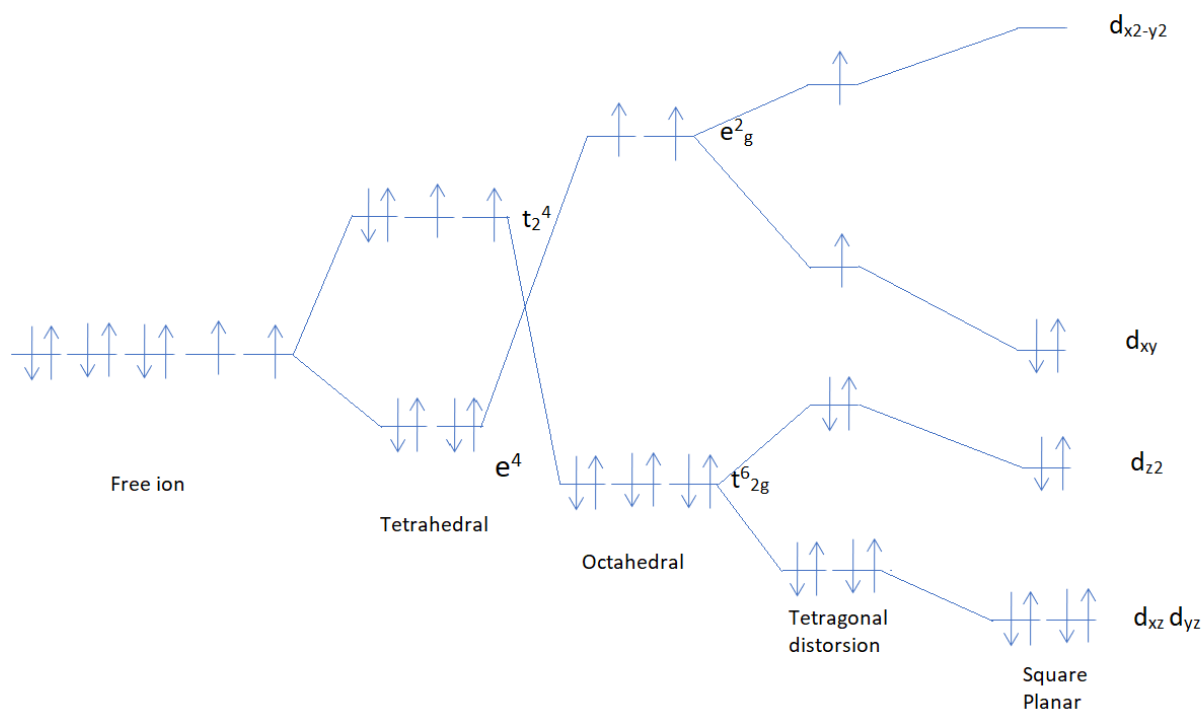


Figure 1: The splitting of the d-orbitals in Ni(II) (d^8) for various stereochemistries [Greenwood, 1984]

Octahedral complexes: The aqueous complex of Ni(II) contains $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ complex cations with octahedral coordination of the Ni(II) atoms and it exhibits bright green color. Normally, for the nickel (II) to form octahedral complexes the ligands must be neutral and N-donors (like amines) or O-donors (like DMSO). These ligands displace part or all of the water molecules of the previously named complex cation. The complexes with amines are of a purple or blue color because the orbitals are closer, the electronic transition is lower, absorbs low energies and emits large wavelengths [Greenwood, 1984]

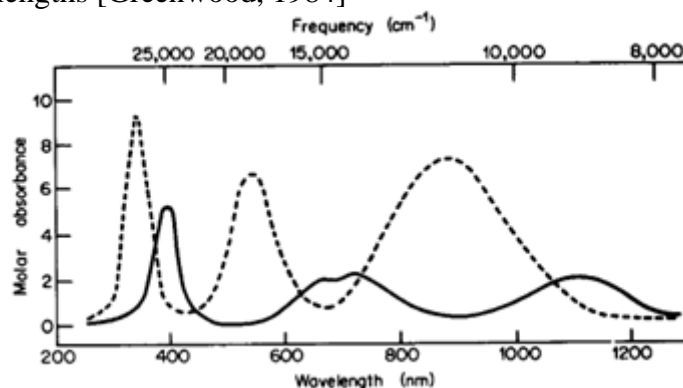


Figure 2: Absorption spectra of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ (solid curve) and $[\text{Ni}(\text{en})_3]^{2+}$ (dashed curve) [Cotton, 1999]

In the previous graphics we can see 3 absorption bands which are characteristic for nickel (II) octahedral complexes. These are shown in the next Table 3.

Table 3: Approximate bands of Octahedral Nickel (II) Complexes [Cotton, 1999]

Spectra of Octahedral Nickel (II) Complexes		
Approximate band positions (cm^{-1})		
Transition	$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Ni}(\text{en})_3]^{2+}$
${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$	9.000	11.000
${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$	14.000	18.500
${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{P})$	25.000	30.000

If we focus on the orbitals we can see in them that there are 2 unpaired electrons which will make the octahedral complexes paramagnetic and their magnetic moment will be from the range 2.9-3.4 BM depending on the orbital contribution.

Tetrahedral Complexes. Moving on to the issue of Ni tetrahedral there are different types: $[\text{NiX}_4]^{2-}$, $[\text{NiX}_3\text{L}]^-$, $[\text{NiX}_2\text{L}_2]$, and $[\text{Ni}(\text{L-L})_2]$ where X is halide ligand, L is neutral ligand such as PPh_3 and L-L is a bidentate chelate type ligand. The only strictly tetrahedral complexes are $[\text{NiX}_4]^{2-}$, the others for different distortions have slight deformations of a real tetrahedron [Cotton, 1999]. These complexes having a symmetry T_d and a d^8 configuration have an absorption band in the region of the visible light (15000 cm^{-1}). This is the reason why these complexes are bluish-green.

Finally, supposedly the magnetic moment in a real tetrahedral complex of Ni (II) should be 4.2 BM. As we know perfection does not exist and there are always slight distortions or displacements. Therefore, if a complex is regular, it will have an angular momentum between 3.5-4 BM and if it is irregular 3 - 3.5 BM [Greenwood, 1984].

Planar Complexes (D_{4h}). Often the Ni(II) compounds are square planar due to their d^8 configuration and the ligands make the $d_{x^2-y^2}$ orbital have a very high energy and being anti-binding orbital and this orbital is empty. It also helps planarity if these ligands are small. Almost all square complexes are diamagnetic with a reddish, yellow or brown colour due to the absorption bands situated between $450\text{-}600\text{ cm}^{-1}$. Most important compound is $\text{K}_2[\text{Ni}(\text{CN})_4]$. Another interesting complex is $[\text{Ni}(\text{DMGH})_2]$ because it is a compound that in solid state is formed by molecules stacked on top of each other with $\text{Ni}\cdots\text{Ni}$ interactions of 320 pm and when dissociated, square-plane monomers occur.

Five-Coordinate Nickel (II) Complexes. These can have trigonal-bipyramidal (D_{3h} , high-spin) or square-pyramidal (C_{4v} , low-spin) geometry. The symmetry cannot be the full D_{3h} because normally there is a tripod ligand such as pp3 (alanyl-pyridoxal-5'-phosphate) and there are, with few exceptions, low-spin like $[\text{Ni}(\text{Me}_6\text{tren})\text{Br}]^+$ (diamagnetic). There are low-spin five coordinate Ni(II) complexes with $[\text{NiL}_5]^{2+}$ and $[\text{NiL}_3\text{X}_2]$ compositions (X = halogen L= phosphine or arsine type ligand).

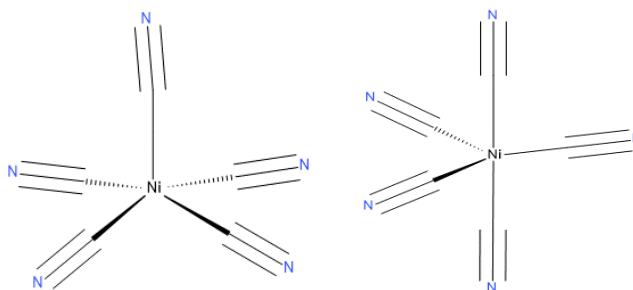


Figure 3: Structure of square pyramidal (left) and trigonal bipyramidal (right) coordination for $[\text{Ni}(\text{CN})_5]^{3-}$ anion

2.2 Characterization of 2,2'-bipyridine as ligand

2,2'-bipyridine (C₁₀H₈N₂) is an important neutral ligand for transition metal ions and its complexing properties are due to the fact that it is a bidentate ligand although it can also act as a monodentate or bridging ligand as well as. Some physical properties 2,2'-bipyridine are given in Table 4.

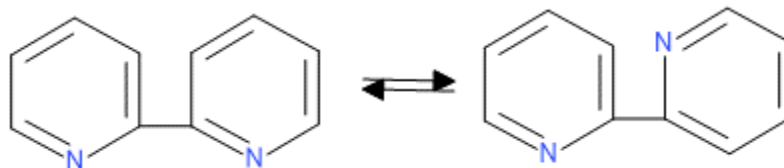


Table 4: Selected physical properties of 2,2'-bipyridine [Haynes, 2011].

Property Name	Property Value
Molecular Weight	156.184 g/mol
Melting Point	69.9 (0.2) ° C
Boiling Point	273 (10) ° C
Density	1.3 ± 0.1 g/cm ³
Colour	White to Light Beige Solid
Solubility	sl H ₂ O; vs EtOH, Et ₂ O, C ₆ H ₆

The crystal structure of 2,2'-bipyridine was reported [Kuhn, 2002] and it is shown on figure 4. As can be seen on this figure the 2,2'-bipyridine molecule is in *trans* conformation as expected.

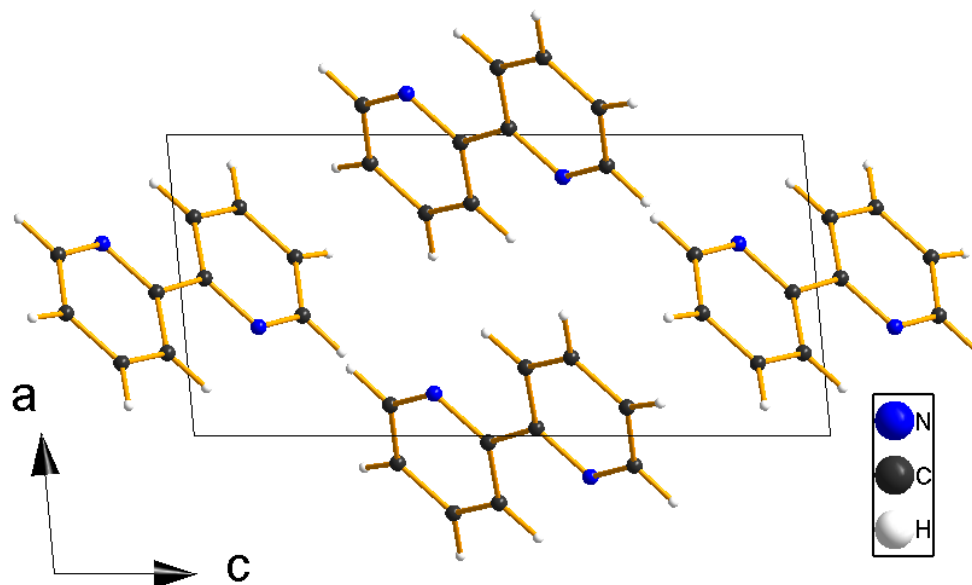


Figure 4: Crystal structure of 2,2 bipyridine [Kuhn, 2002].

2,2'-bipyridine can also exist in monoprotonated form Hbpy^+ , e.g. in $(\text{Hbpy})_2(\text{tcdp})$ (GUHYEP) [Setifi,2015], or in diprotonated form $\text{H}_2\text{bpy}^{2+}$: such form was found for example in 2,2'-bipyridine-1,1'-di-ium dibromide $(\text{H}_2\text{bpy})\text{Br}_2$ (BIPYBR01) [Ali, 2012] or 2,2'-bipyridinium hexafluorosilicate [Gulmeboldt, 2014] (WOC SOY) [Fig. 5]. A search in CSD database [Groom, 2016] has shown that there are 135 compounds containing Hbpy^+ and 63 containing $\text{H}_2\text{bpy}^{2+}$ cations.

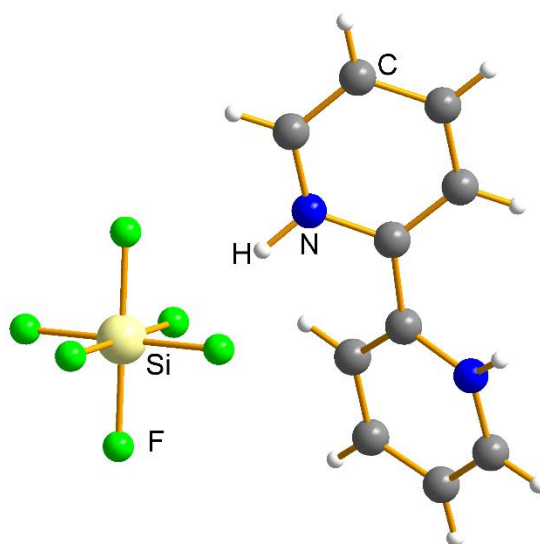


Figure 5: Structure of 2,2'-bipyridinium hexafluorosilicate [Gulmeboldt, 2014].

As already mentioned above, 2,2'-bipyridine can act as a ligand in coordination compounds. The most common coordination mode is chelating bidentate; such coordination fashion of bpy was found in more than 10000 complexes and 621 complexes with Nickel as central atom. We note that in such a way can be coordinated to the central atom one, two or three bpy ligands. As an example of chelate bonding can be mentioned the complex $[\text{Ni}(\text{bpy})_2(\text{mal})] \cdot 7.34\text{H}_2\text{O}$ (AGOYEB) [Pavlová, 2008].

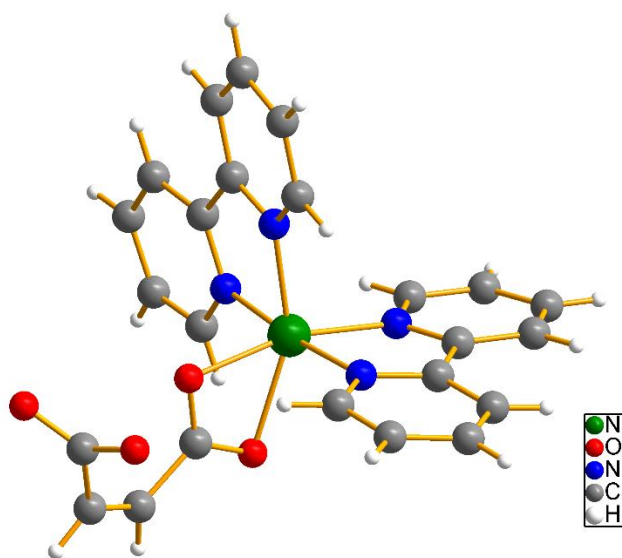


Figure 6: View on the molecular structure of complex $[\text{Ni}(\text{bpy})_2(\text{mal})] \cdot 7.34\text{H}_2\text{O}$ [Pavlová, 2008].
Water molecules are omitted for clarity.

As an another example of chelate coordination of bpy we can display the structure of $[\text{Ni}(\text{bpy})_3]^{2+}$ cation in $[\text{Ni}(\text{bpy})_3] [\text{Mo}(\text{CN})_8] \cdot 12\text{H}_2\text{O}$ complex (AGADAO) [Korzeniak, 2008] (Fig. 7).

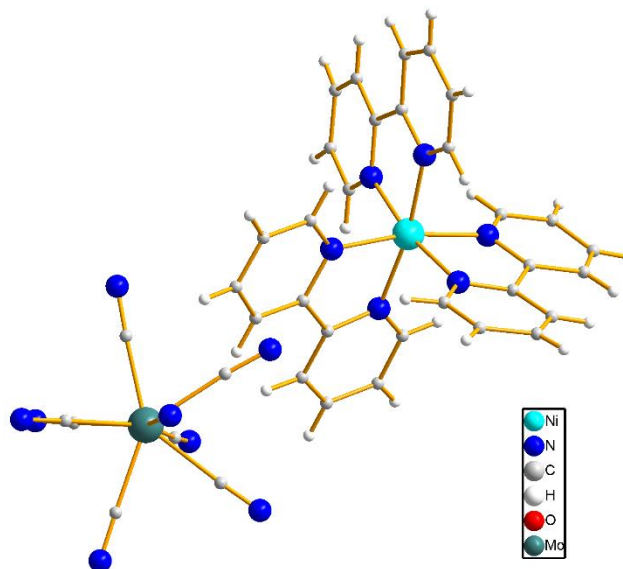


Figure 7: Structure of the $[\text{Ni}(\text{bpy})_3]^{2+}$ cation in $[\text{Ni}(\text{bpy})_3][\text{Mo}(\text{CN})_8] \cdot 12\text{H}_2\text{O}$ [Korzeniak, 2008].
(Water molecules are omitted)

Finally, we have to mention other bonding possibilities for bpy ligand. Its use as a bridging ligand was reported in 27 compounds. We note that bpy acts like a bridge only in complexes containing as central atoms Ag, Pt, Pd and In. As an example we can mention $[\text{Ag}(\text{bpy})](\text{ClO}_4)$ (MAXZOB) [Bookmaker, 2005]. Its structure is depicted on figure 9. Another example is $[\text{Ag}(\text{bpy})](\text{BF}_4)$ (BOYGEC) [Hung-Low, 2009].

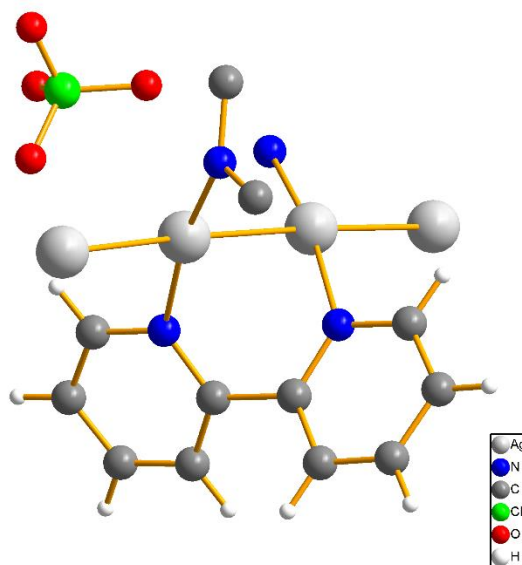


Figure 8: View on the structure of $[\text{Ag}(\text{bpy})](\text{ClO}_4)$ [Bookmaker, 2005].

Other rare coordination behavior of bpy is when it acts as a monodentate ligand; only 8 hits for such bonding were found in CSD. As an example can be mentioned $[\text{Pt}(\text{bpy})_2(\text{ppds})_2] \cdot 5.5\text{H}_2\text{O}$ complex (JOCNUM) [Lo, 2014]. We note that the Pt-N bonding distances are from the range 2.049 - 2.092 Å while the non-bonding distance between Pt central atom and uncoordinated N atom from bpy is 2.75 Å.

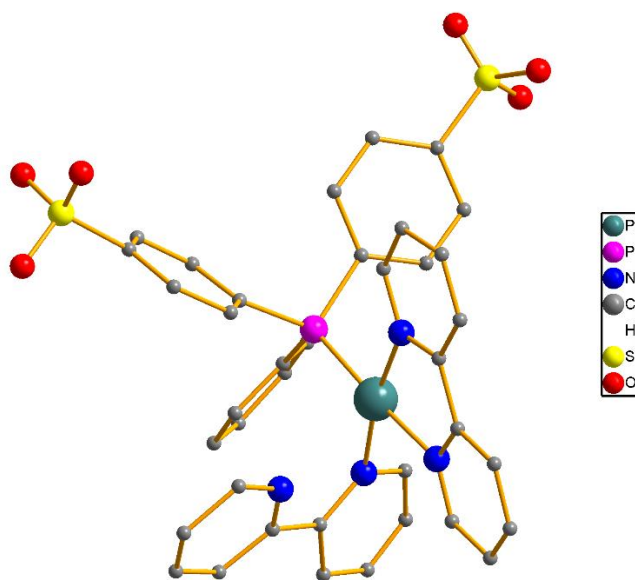


Figure 9: View on the structure of $[\text{Pt}(\text{bpy})_2(\text{ppds})_2] \cdot 5.5\text{H}_2\text{O}$ [Lo, 2014]

2.3 Characterization of benzoate anion as ligand

Benzoic acid is a mildly strong aromatic acid. It is white crystalline powder, very soluble in alcohol, ether, and benzene. There are some derivatives of benzoic acid that the people use it such as sodium benzoate to keep food or benzyl benzoate used as a miticide [JORGE, 2003].

Benzoate anion [Fig. 11] is the conjugate base of benzoic acid, comprising a benzoic acid structure with a proton missing to give a charge of -1. It has a role as a human xenobiotic metabolite and a plant metabolite. [<http://www.chemspider.com/Chemical-Structure.237.html>].

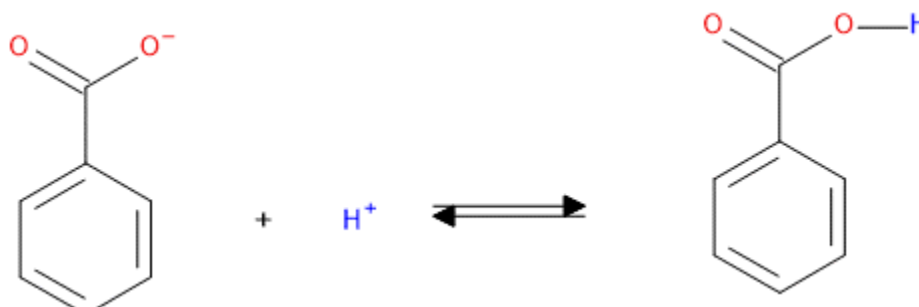


Figure 10: Ionization of benzoic acid

Table 5: Some Chemical and Physical properties of Benzoic acid
[Haynes, 2011]

Property Name	Property Value
Molecular Weight	121.124 g/mol
Density	1.2659 g/cm ³
Solubility	S1 H ₂ O vs EtOH, Et ₂ O; s, C ₆ H ₆
Melting Point	122.35 °C
Boiling point	250.2 (0.6) °C

Benzoate anion can be coordinated to the central atom(s) by various modes and in the next text we will focus our attention to complexes of Ni(II) with Benzoate anion.

We can find in CSD a total of 155 compounds with Ni and benzoate anion in different forms. The most frequent bonding fashions of benzoate ligand are depicted on Figure 11:

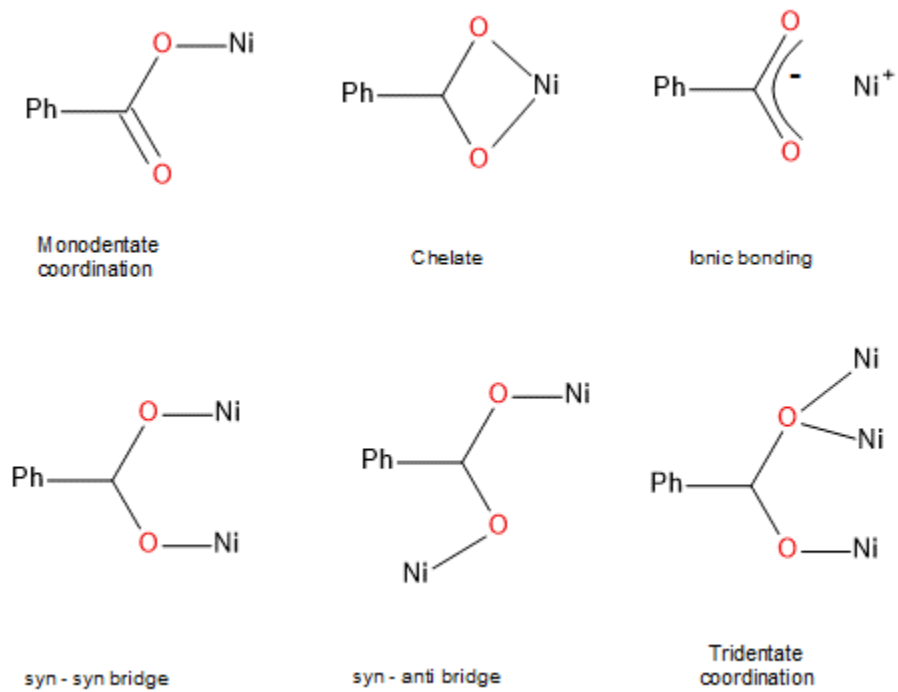


Figure 11: Different bonding fashions of Benzoate anion like ligand.

The first bonding mode of the benzoate ligand is monodentate there are so many examples but a clear example is LEQKIE.

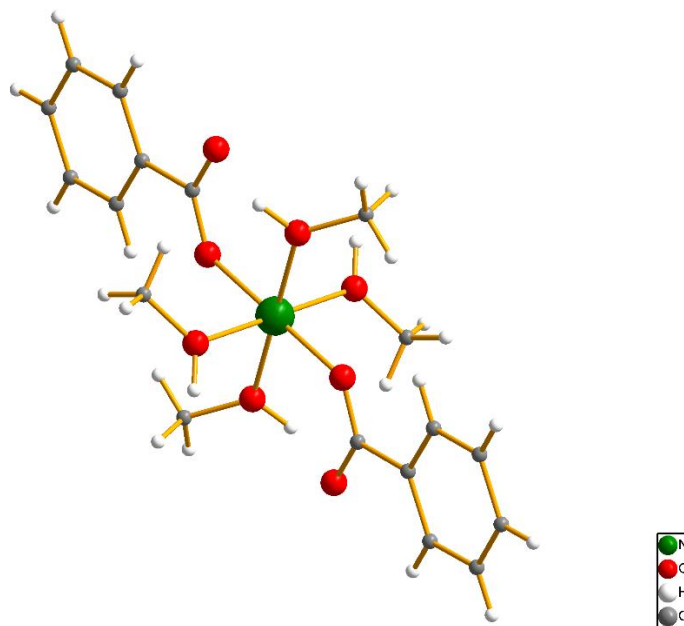


Figure 12: Benzoate anion like monodentate ligand in bis(benzoato)-tetrakis(methanol)-nickel(ii)
[Datchuk, 2017]

We can see in the Figure 13 how benzoate ligand acts like a monodentate ligand forming a bond with Nickel.

Another mode of coordination is a benzoate like a chelate. Its Refcode is BZONNI and it was synthesized by Hursthouse in 1977 [Hursthouse, 1977].

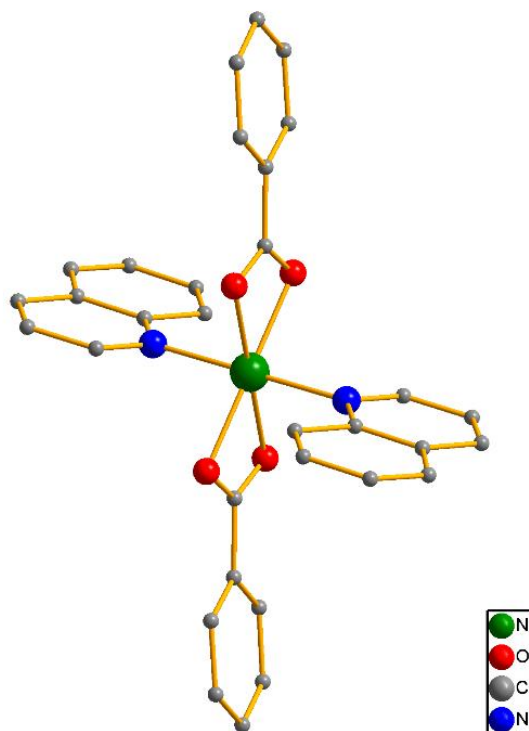


Figure 13: bis (Benzoato-O,O')-bis(quinoline)-nickel(ii) [Hursthouse, 1977]

In the next Figure 14 we can see an ionic bonding of benzoate anion. The compound is tris(2-phenylacetohydrazide)-nickel(ii) bis(benzoate) - REXPUI and is depicted without H₂O [Koksharova, 2017].

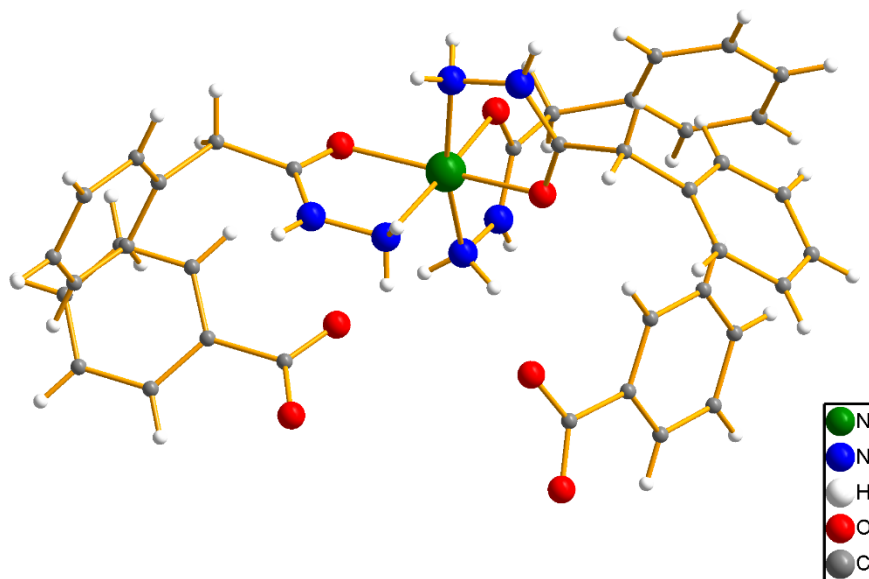


Figure 14: tris(2-phenylacetohydrazide)-nickel(ii) bis(benzoate) without H₂O molecules
[Koksharova, 2017]

The next bonding fashion of the benzoate ligand is when it acts as *syn-syn* bridge. ABIZUI is its ref-code and the structure is depicted on the next figure 15 [Kounavi, 2010].

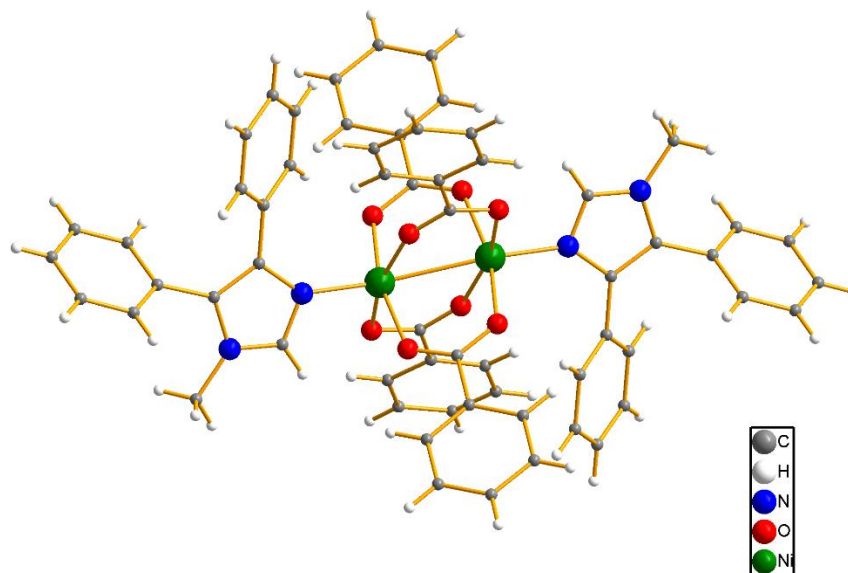


Figure 15: Structure of the cationic part of tetrakis(μ 2-Benzoato)-bis(1-methyl-4,5-diphenyl-1H-imidazole)-dinickel(ii) acetonitrile solvate [Kounavi, 2010].

Syn-anti bridge its really similar like the *syn-syn* bridge but the main difference is that in the case of *syn-syn* bridging the metallic atoms are relatively closely placed while in the case of

syn-anti bridging the two metallic atoms are placed at much longer distance. In CSD database we could not find any example with Ni and benzoate anion with *syn-anti* bridging; the reason may be in interplay of the benzoate ligand conformation and some steric requirements. However, we found an example with Zn, cinn and mpcm ligands (Fig. 16) [Zeleňák, 2006].

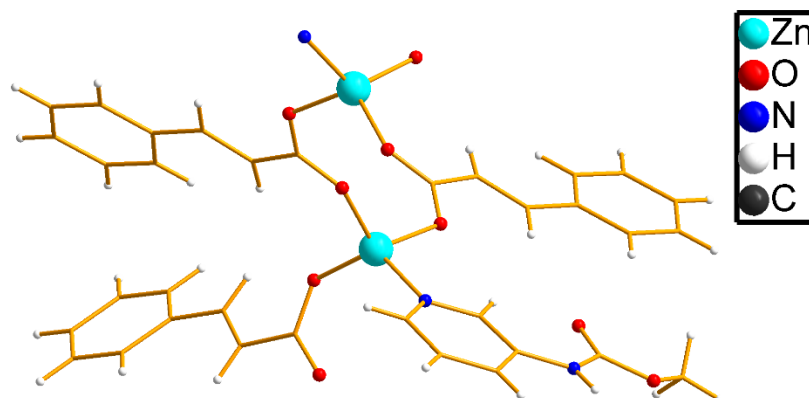


Figure 16: View on the crystal structure of $[\text{Zn}(\text{cinn})_2(\text{mpcm})]_n$ complex [Zeleňák, 2006]

The next compound represents an example in which benzoate anion acts as a tridentate ligand. Its ref-code is DAVYIJ [Gavrilenko, 2005] and you can see the compound without acetonitrile solvate molecule on Fig. 17.

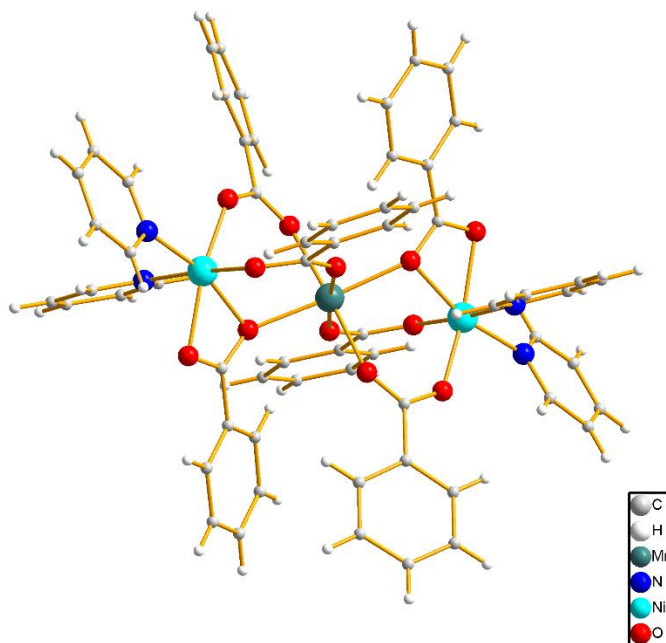


Figure 17: View of the structure of bis(μ_2 -Benzoato-O,O,O')-tetrakis(μ_2 -benzoato-O,O')-tetrapyrindinemanganese-di-nickel [Gavrilenko, 2005]

There is reported an another bonding fashion of benzoate anion but without Nickel. This is the *anti-anti* bridging fashion (see Figure 18) which was rarely reported but it is interesting bonding fashion.

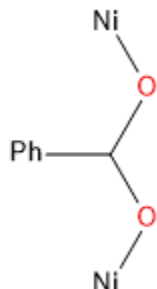


Figure 18: Scheme of the theoretically possible *anti-anti* bridging fashion of benzoate anion with Ni.

This *anti-anti* bonding fashion was observed in complex $[\text{Cu}_2(\text{phen})_2(\mu\text{-O}_2\text{CH})_2(\text{O}_2\text{CH})_2]_n$. The structure consists of four independent polymeric chains of $[\text{Cu}_2(\text{phen})_2(\mu\text{-O}_2\text{CH})_2(\text{O}_2\text{CH})_2]$ with asymmetric bidentate bridge. The neighbouring Cu atoms are linked by carboxylato group in *anti-anti* configuration and all Cu(II) ions exhibit distorted square-pyramidal geometry. [Boonmak, 2008]

3 EXPERIMENTAL PART

3.1 Materials used

We used Filter flask, Büchner funnel, Hirsch funnel, Erlenmeyer flask, beaker and magnetic stirrer with heating.

The chemicals were obtained from commercial sources and they are gathered in the next Table 6.

Table 6: Chemicals used in experiments.

Name	Mw(g/mol)	Purity(%)	Density(g/cm ³)	State
NaOH	39,997		2,13	Solid
NiSO ₄ ·6 H ₂ O	262,85		2,07	Solid
Benzoic acid	122,12		1,27	
2,2'-bpy	156,188			Solid
EtOH	4,06	99%	0,78	Liquid
Ba ²⁺	137,327			Liquid
Water	18		1	Liquid

3.2 Syntheses

Within the experimental part we have done syntheses with four different molar ratios of Ni, benzoate anion and 2,2- bipyridine:

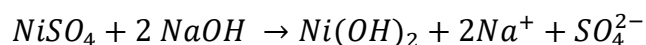
- 1- 1 of Nickel: 2 of benzoate anion: 0 of 2,2- bipyridine (1:2:0). Its name will be AW1
- 2- 1 of Nickel: 2 of benzoate anion: 1 of 2,2- bipyridine (1:2:1). Its name will be AW2
- 3- 1 of Nickel: 2 of benzoate anion: 2 of 2,2- bipyridine (1:2:2). Its name will be AW3
- 4- 1 of Nickel: 2 of benzoate anion: 3 of 2,2- bipyridine (1:2:3). Its name will be AW4

We have worked simultaneously with the above mentioned four systems. The experimental work was done in the following steps.

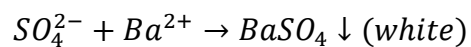
1st step includes the preparation of a 1 M solution of NaOH for the next reactions steps. During the 2nd step we have prepared four solutions, each by dissolving 657 mg of NiSO₄·6 H₂O (2,5mmol) in 15 ml of distillate H₂O.



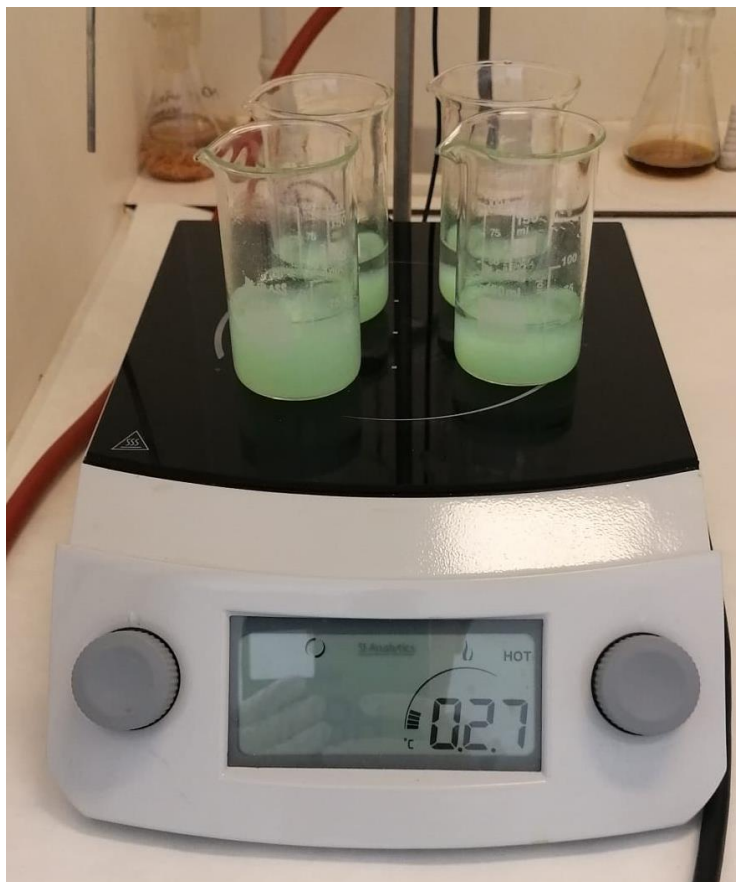
As the 3rd step we added to each solution 8 ml of prepared 1 M solution of NaOH with the aim to prepare Ni(OH)₂ as starting material according to the reactions:



Within the 4th step the formed precipitate was decanted with warm water in order to remove soluble Na₂SO₄. The presence of SO₄²⁻ anions was checked by addition of Ba²⁺ ions according to the reaction



It was necessary to do the decantation several times to rinse out the Na₂SO₄ thoroughly, till the precipitation reaction was negative.



As the 5th step we weighed 611 mg of benzoic acid (5 mmol) for all the four systems and dissolved it in 25 ml of EtOH, consequently we added the obtained ethanolic solution into the prepared Ni(OH)₂. We have obtained a green precipitate (see the upper photo).

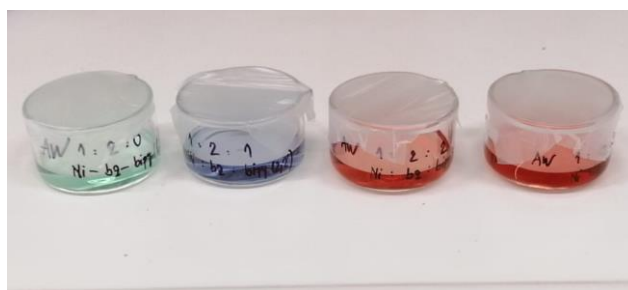
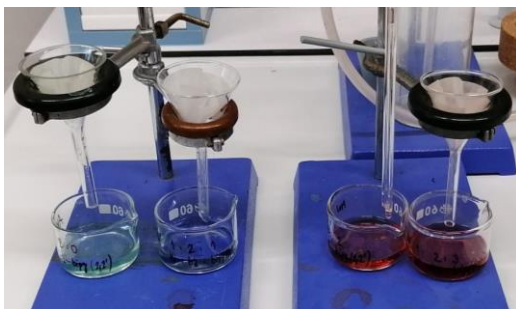
The 6th step consists of adding the appropriate amount of solid 2,2'-bpy into the three reaction mixtures, namely 390 mg of 2,2'-bpy (2.5mmol) was used to prepare the ratio 1:2:1 in **AW2**, 781 mg of 2,2'-bpy (5mmol) was used to prepare the ratio 1:2:2 in **AW3**, and 1171 mg of 2,2'-bpy (7.5mmol) was used to prepare the ratio 1:2:3 in **AW4**. After dissolving the added 2,2'-bpy, we have obtained different coloured reaction mixtures (as the following photos describe).

As the 7th step we have slowly heated the open beakers with the solutions till the temperature of 60° C during 30 minutes, to reduce the volume of the solution for more rapid crystallization.



You can see the colour changes with the amount of 2,2'-bpy we used.

8th step was the final step formed by filtration of the prepared solutions. The obtained solutions were left aside for crystallization.



After two-three weeks the products **AW1**, **AW2**, **AW3** and **AW4**, respectively occurred, and were collected by filtration and dried on air. The synthetic procedures were repeated twice.

In the 1st series we obtained the following results:

- The weight of the green microcrystalline powder **AW1** was 152 mg (first filtration). The attempts to recrystallize **AW1** from EtOH, MeOH or acetone in order to obtain single crystals were unsuccessful.
- The weight of the blue powder of **AW2** was 103 mg and by further crystallization of the filtrate we obtained 22 mg of crystals after first filtration.
- The obtained colour of the solution **AW3** (pink) was different from that expected (violet) so this synthesis was repeated (see below).
- **AW4** separated in the form of pink powder and its weight was 715 mg.

In the 2nd series of **synthetic experiments** we have obtained following results:

- We filtrated product **AW1** and obtained 45 mg of green microcrystalline powder (first filtration). The inspection of the obtained solid after first filtration under optical microscope indicated that the solid was contaminated by few white crystals of benzoic acid. Green product was cleaned mechanically under microscope and these was used for further analyses as **AW1**. The same product **AW1** separated from the filtrate by further crystallization (second filtration, weight 34 mg).
- As the result of synthetic procedure **AW2** we have obtained light blue solution from which nice green needles separated (Fig. 18). The first filtration yielded 288 mg of **AW2** and the second filtration yielded additional 274 mg of crystals of **AW2** (Figure 18). These were used for CHN analysis and X-ray structure analysis.

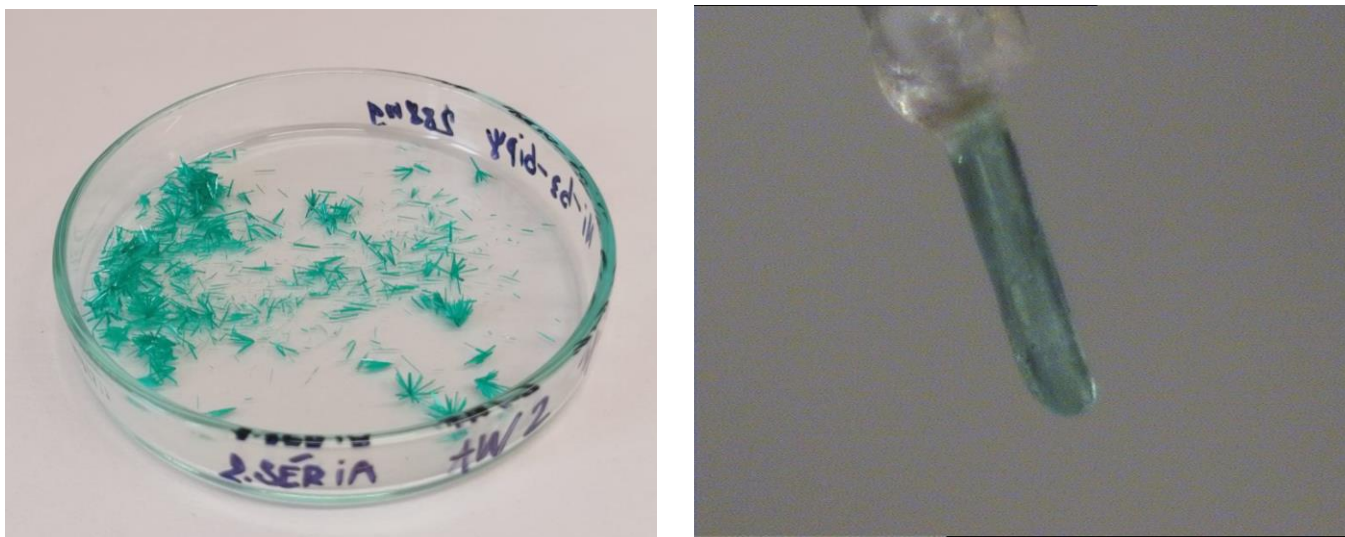


Figure 18: Green single crystals of **AW2**

From the above described synthetic procedures (solution method, diffusion method) aimed to isolate **AW3** and **AW4** we have not obtained single crystals. So we have done the syntheses using solvothermal method (in autoclave, Fig. 19) as follows: the reaction mixture was put in the autoclave, sealed, heated slowly to 110 °C and kept at this temperature during 7 days. After that time the autoclaves were slowly cooled to RT, opened and the formed solutions were left aside for crystallization. From the solution of **AW3** some crystals separated which, however, were by IR spectrum identified as **AW2**. In the case of the second solution (**AW4**) a solid separated which was by IR spectrum identified as **AW4** prepared by solution method (see above).



Figure 19: Different views on the autoclaves used for syntheses.

3.3 Chemical analysis

CHN analyses of some samples were carried out on an Elementar vario MICRO analyser. The results are gathered in Table 6

Table 7: CHN analyses of AW1, AW2 and AW4

Formula	Colour / form / yield	C [%]	H [%]	N [%]
		Calc. / Exp.	Calc. / Exp.	Calc. / Exp.
$\text{Ni}(\text{C}_6\text{H}_5\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (AW1)	Light green microcrystals solid	47,37/46,48	4,54 / 4,52	0 / 0
$[\text{Ni}(\text{C}_6\text{H}_5\text{COO})_2(\text{bpy})]$ (AW2)	Green needles	63,07/62,78	3,97 / 3,89	6,13 / 5,85
$[\text{Ni}(\text{bpy})_3](\text{C}_6\text{H}_5\text{COO})_2 \cdot 5\text{H}_2\text{O}$ (AW4)	Red solid	61,48 / 61,8	5,16 / 4,98	9,78 / 9,54

3.4 IR spectroscopy

Infrared spectra of the prepared samples were measured on a spectrometer FT-IR Nicolet 6700 Thermo Scientific by KBr technique (2:200) as well as by ATR method (Smart Orbit™), in both cases in the range of wavenumbers 4000 – 400 cm^{-1} .

IR spectrum of **AW1 Ni(C₆H₅COO)₂·3H₂O** is shown on Figure 19.

IR (cm⁻¹): 3054w, 2905br, 1674w, 1594s, 1548s, 1495s, 1421m, 1382m, 1301w, 1137w, 1070s, 1028m, 1020w, 1002w, 985w, 935m, 849w, 830w, 802w, 710s, 682s, 667w, 618s, 542w, 503m, 426w.

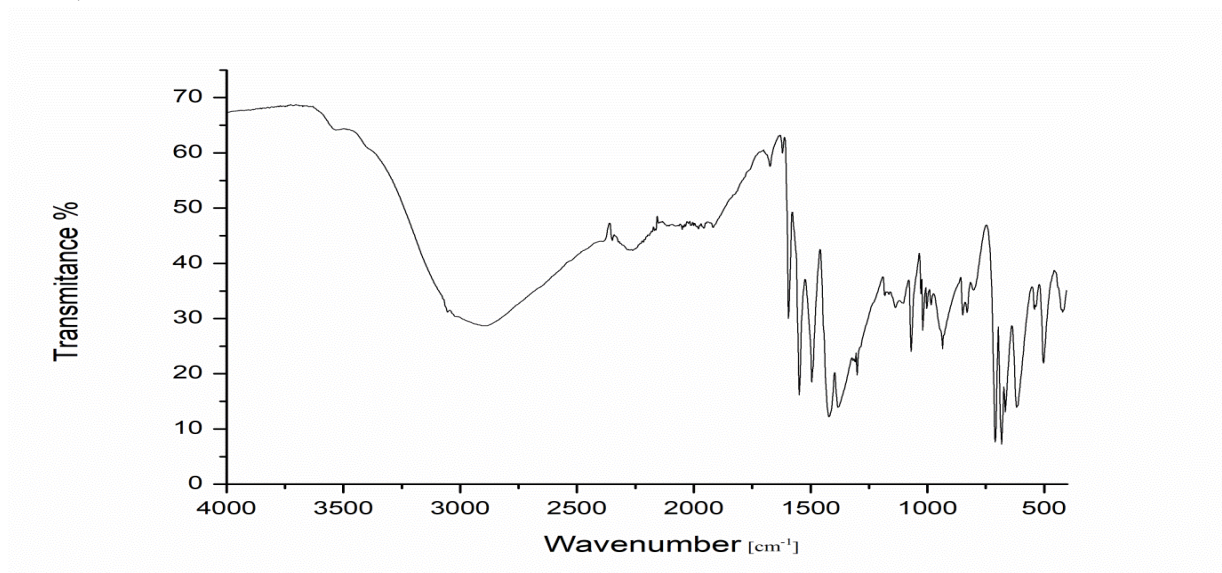


Figure 19: IR spectrum of microcrystalline solid **AW1**.

IR spectrum of **AW2 [Ni(C₆H₅COO)₂(bpy)]** is shown on Figure 20.

IR (cm⁻¹): 3112w, 3069w, 1593s, 1574w, 1564w, 1521s, 1498w, 1472m, 1442w, 1415s, 1313m, 1263w, 1252m, 1221w, 1169w, 1154w, 1114w, 1102w, 1073m, 1054w, 1043w, 1026m, 973w, 945m, 907w, 857s, 824w, 769s, 733w, 723s, 685s, 656w, 636w, 617w, 551w, 519m, 477s, 421s.

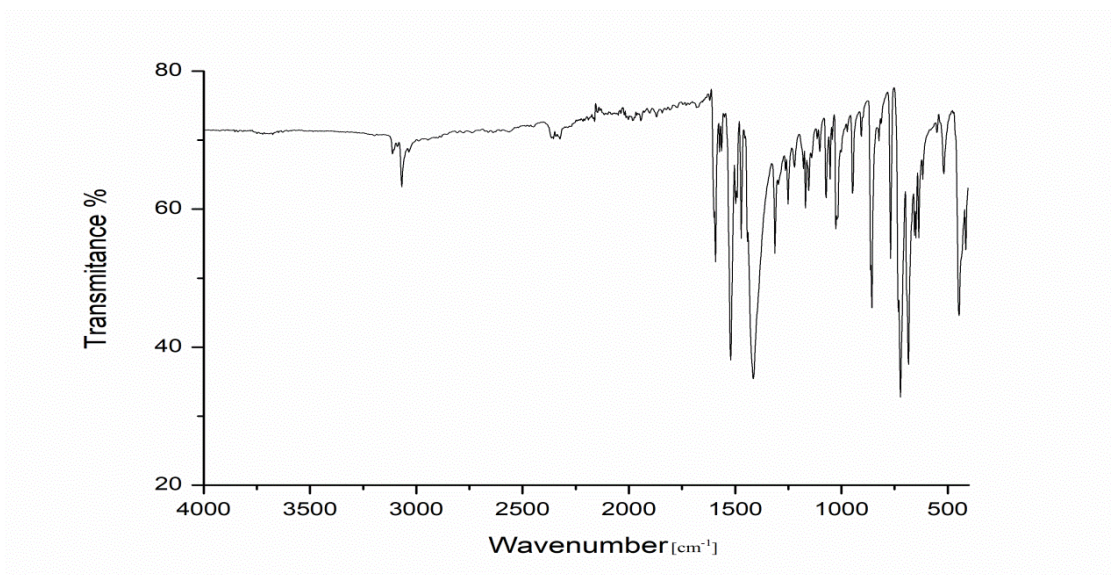


Figure 20: IR spectrum of microcrystalline solid **AW2**.

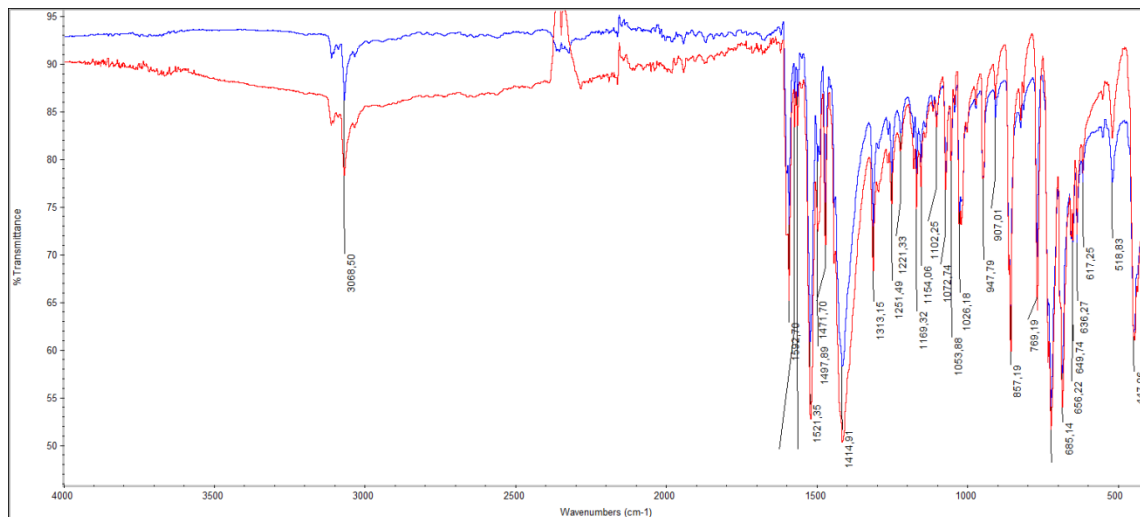


Figure 21: Comparison of the IR spectra of **AW3** and **AW4**.

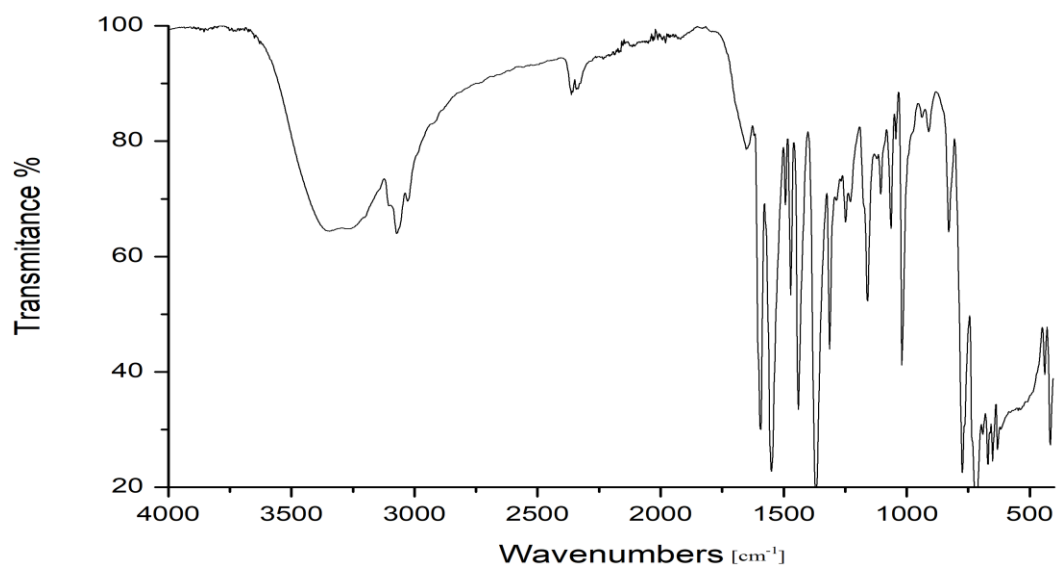


Figure 22: IR spectrum of solid product **AW4**.

It was successfully measured also the IR spectra of **AW4** depending on the growing temperature, in range of 30 – 170 °C. This measurement is shown on the Figure 23, where as we can see, the intensity of the absorption band arising from $\nu(\text{OH})$ stretching vibration from water molecules decreases with growing temperature due to dehydration. Different coloured lines represent different temperatures used during measurement.

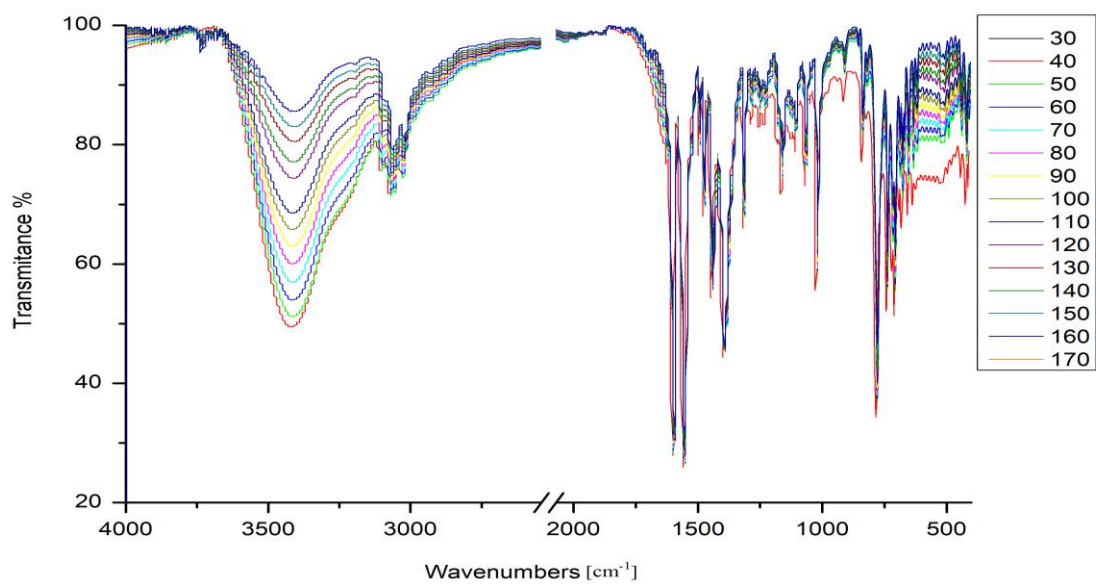
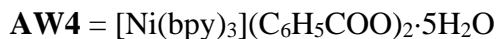
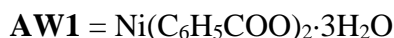


Figure 23: Temperature dependence of IR spectrum of **AW4**. The colour of the lines corresponds to the temperature given on the right side of the figure.

RESULTS AND DISCUSSION

We have studied four different systems based on Ni(II), benzoate anion and bpy with different molar ratios, namely from 1:2:0 to 1:2:3. We have also investigated the properties of the different complexes that we have synthesized. We have used for syntheses mostly mild solution conditions and in two cases also the autoclave method.

As the results of our synthetic experiments we have isolated and identified by CNH analyses and IR spectroscopy three solid products **AW1**, **AW2** and **AW4**. Their formulas are:



By comparison with the literature it became clear that **AW1** is the simplest complex and its formula is $\text{Ni}(\text{C}_6\text{H}_5\text{COO})_2 \cdot 3\text{H}_2\text{O}$. This complex was already prepared and studied by Vráblová *et al.* [Ščerbová, 2015].

Product **AW2** was prepared in the form of nice crystals of needle shape (see above Fig. 18). These were examined by prof. Falvello from University in Zaragoza and the obtained crystal data are gathered in Table 8. The structure is formed of $[\text{Ni}(\text{C}_6\text{H}_5\text{COO})_2(\text{bpy})]$ complex molecules, in which the Ni(II) atom is hexacoordinated by 2 ligands of benzoate anion and one of 2,2'-bipyridine. All ligands are of chelating type, the benzoate anions have two bonds O-Ni and the 2,2'-bipyridine have two bonds N-Ni (Fig. 24). The bond distances within the coordination sphere of Ni(II) are gathered in Table 9. As can be seen from this Table the Ni-N bonds are from the range 2.029(3)-2.049(3) Å while the Ni-O bonds are somewhat longer; they are from the range 2.054(2)- 2.157(3) Å. The bite angles within the chelate rings are 79.53(13) for the chelate ring with bpy ligand, while the bite angles within chelate rings with benzoate anion exhibits values of 62.72(9) and 62.64(9) °. These geometric parameters are close to the corresponding values found by Baruah [2007]: Ni-N are from the range of 2.03 – 2.05 Å, N-O are from the range 2.05 – 2.15 Å and the bite angles are 79.48 ° of chelate ring with bpy ligand and within chelate rings with benzoate anion the values are 62,53 and 62,57 °.

We were unsuccessful in preparation of the expected product **AW3** for molar ration 1 of Ni: 2 of benzoic acid: 2 of bpy. The product obtained from this system was in fact the product **AW2**.

The product **AW4** was identified as $[\text{Ni}(\text{bpy})_3](\text{C}_6\text{H}_5\text{COO})_2 \cdot 5\text{H}_2\text{O}$ and it seems it is a new compound not described in the literature. This represents a good step for the investigation of this type of complex. Unfortunately, we were not able to prepare it in the form of single crystals so here a further effort should be done in the future.

Table 8 Comparison of crystal data of [Ni(C₆H₅COO)₂(bpy)] for our sample AW2 and that published one [Baruah, 2007].

Sample	AW2	Published [Baruah, 2007]
Empirical formula	C ₂₄ H ₁₈ N ₂ Ni O ₄	C ₂₄ H ₁₈ N ₂ Ni O ₄
Molar mass [g/mol]	457.11	457.11
Crystal System	Monoclinic	Monoclinic
Space group	P 2 ₁ /n	P 2 ₁ /n
<i>a</i> [Å]	7.4309(2)	7.4322(2)
<i>b</i> [Å]	16.7209(6)	16.7224(4)
<i>c</i> [Å]	17.3510(7)	17.3528(4)
α [°]	90	90
β [°]	101.420(4)	101.3810(10)
γ [°]	90	90
Dimensions [Å ³]	2113.20(13)	2114.27(9)
Z	4	4
Absorption Coefficient [mm ⁻¹]	0.951	0.951
Form, colour,	Needle, green	Not given
Crystal size [mm]	0,498 x 0,09 x 0,082	Not given
Temperature [K]	294(2)	296(2)
Radiation MoK _α [Å]	λ = 0.71073	λ = 0.71073
Θ range for data collection [°]	4,605 – 27,101	not given - 29.09
Index ranges	-9 ≤ <i>h</i> ≤ 9, -21 ≤ <i>k</i> ≤ 21, -22 ≤ <i>l</i> ≤ 22	-9 ≤ <i>h</i> ≤ 9, -22 ≤ <i>k</i> ≤ 19, -23 ≤ <i>l</i> ≤ 21
Reflections collected/ unique	14337/14337	
GooF (S)	1.034	1.031
Final <i>R</i> indices [<i>I</i> > 2s(<i>I</i>)]	<i>RI</i> = 0.0523, <i>wR2</i> = 0.1143	<i>RI</i> = 0.0298
<i>R</i> indices (all data)	<i>RI</i> = 0.1017, <i>wR2</i> = 0.1229	<i>RI</i> = 0.0432
Largest diff. peak and hole [e Å ⁻³]	-0.279 ; 0.547	Not given

Table 9. Selected Bond lengths [Å] and angles [°] for **AW2**

Ni(1)-N(1)	2.029(3)
Ni(1)-N(2)	2.049(3)
Ni(1)-O(4)	2.054(2)
Ni(1)-O(1)	2.077(2)
Ni(1)-O(2)	2.148(2)
Ni(1)-O(3)	2.157(3)
N(1)-Ni(1)-N(2)	79.53(13)
O(1)-Ni(1)-O(2)	62.64(9)
O(4)-Ni(1)-O(3)	62.72(9)

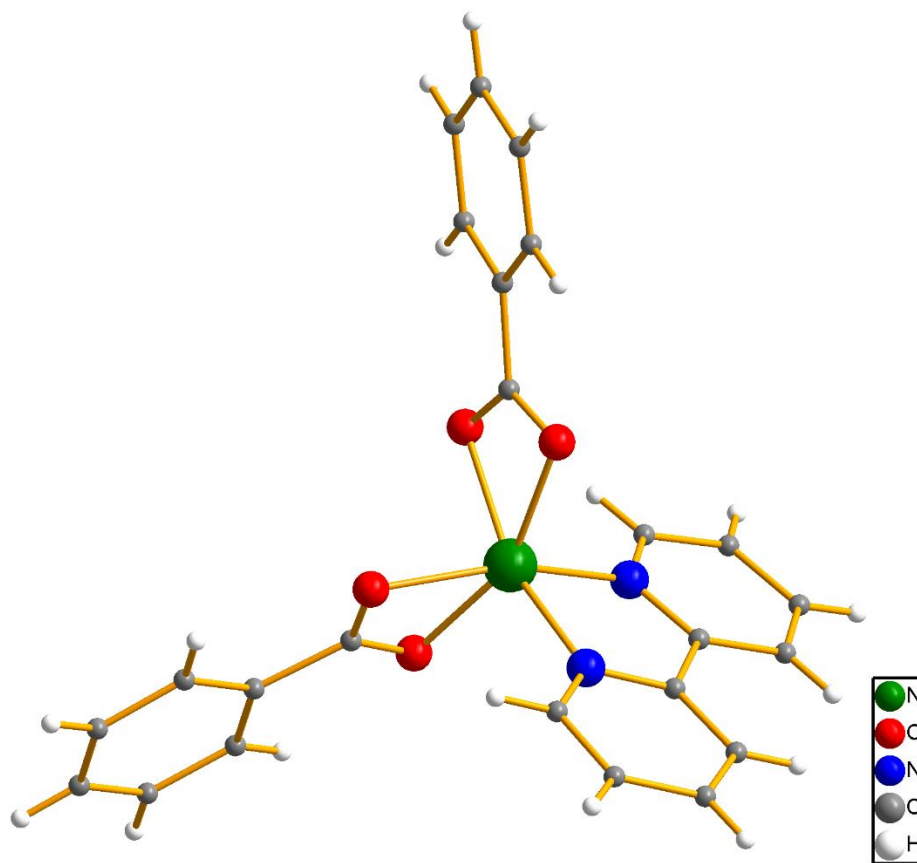


Figure 24: Molecular structure of compound **AW2**. Its formula is $[\text{Ni}(\text{C}_6\text{H}_5\text{COO})_2(\text{bpy})]$

Conclusion

The results obtained can be gathered in the following points:

1. Within the theoretical part we have described the coordination chemistry of Ni(II) as central atom along with the properties and bonding possibilities of benzoate anion and bipyridine as ligands.
2. Within the experimental part we have studied the aqueous-ethanolic systems based on Ni(II) carbonate with benzoic acid and bipyridine with different molar ratios 1:2:0, 1:2:1, 1:2:2, 1:2:2.
3. As the results of our synthetic experiments we have prepared three complexes, namely $\text{Ni}(\text{C}_6\text{H}_5\text{COO})_2 \cdot 3\text{H}_2\text{O}$, $[\text{Ni}(\text{C}_6\text{H}_5\text{COO})_2(\text{bpy})]$ and $[\text{Ni}(\text{bpy})_3](\text{C}_6\text{H}_5\text{COO})_2 \cdot 5\text{H}_2\text{O}$ and we have identified these compounds by chemical analyses and IR spectroscopy. The third compound has not been documented up to now, that is, we have synthesized it for the first time.
4. The complex $[\text{Ni}(\text{C}_6\text{H}_5\text{COO})_2(\text{bpy})]$ was prepared in the single crystal form. Its crystal structure is molecular with two chelating benzoate and one chelating bpy ligand coordinated to the Ni atom.

6 Literature

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