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**ABSTRACT**

of the dissertation for the degree of Doctor of Philosophy

**SYNTHESIS OF METAL STRING COMPLEXES AND  
COORDINATION POLYMERS WITH MODULATED  
OLIGO- $\alpha$ -AMINOPYRIDINE LIGANDS  
AND RESEARCH OF BACTERICIDES, CORROSION  
INHIBITORS, HIGH THERMAL CONDUCTIVITY FLUIDS  
PREPARED ON THEIR BASIS**

Specialty: 2314.01 – Petrochemistry  
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The work was performed at "Analytical research" laboratory of the "OilGasResearchProject" Institute of the State Oil Company of the Republic of Azerbaijan.

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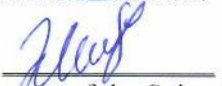
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## GENERAL DESCRIPTION OF THE WORK

### **The current state of the problem and its relevance.**

Although the first metal-string complex was synthesized in 1968, its exact structure based on X-ray structural analysis was determined only in 1991<sup>1</sup>. It is from this time that special attention is paid to this modern and rare family of coordination compounds. The reason for this is that metal-strings have a high potential in the preparation of molecular wires (nanowires) and nano-sized devices, as well as nano/microfluids and catalysts with high thermal conductivity, as well as being a model system for studying the interaction between metals in multinuclear complexes.

Until now, metal-string complexes of Ni, Co, Cu, Cr, Ru, Rh transition metals with three to eleven cores have been synthesized with oligo- $\alpha$ -aminopyridine ligands and their modulated analogues, their structure has been determined, magnetic, electrochemical, etc. properties were studied. For all metal-string molecules, it is characteristic that four deprotonated ligand anions located in the equatorial position, all of which have syn-type conformation, wrap around the metal chain, and at this time the M-M-M angle deviates very slightly by 180<sup>0</sup>. The charge of the molecule is balanced by ligands located in the axial position.

The study of metal-strings has shown that the structure and properties of these compounds depend on the nature of both the metal and the ligand. Despite the fact that nickel-strings obtained on the basis of oligo- $\alpha$ -aminopyridines do not contain Ni-Ni bonds within their molecules, there is a strong metal-metal interaction in the molecules of Cr(II) and Co(II) strings of these ligands.

In the last 15 years, pyrazine, pyrimidine, picoline, etc. oligo- $\alpha$ -aminopyridines modulated with and Ni(II), Co(II) and Cr(II) string complexes based on them were obtained and studied.

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<sup>1</sup>Adulchecha, S. Crystal structure and electronic properties of tetrakis[ $\mu_3$ -bis(2-pyridyl)amido]dichlorotrinickel(II)-water-acetone(1/0.23/0.5)/ S.Adulchecha, B.Hathaway // J. Chem. Soc., Dalton Trans., – 1991. - p. 993-998.

The conducted studies prove that the metal strings synthesized with modulated ligands are significantly different from the metal strings obtained with primary ligands in terms of their oxidation-reduction properties, and their properties are directly dependent on the nature of the ligand. On the basis of modulated ligands, long-chain seven-core cobalt (Co7), nine-core chromium (Cr9), eleven-core nickel (Ni11) strings, which were previously impossible to synthesize, were obtained, their structures were determined, and their magnetic and electrochemical properties were studied.

It is known that compounds containing a hetero atom (N, O, S) with a free electron pair and also having  $\pi$ -bonds and their transition metal complexes are highly effective biocides and corrosion inhibitors for light steel, copper and zinc in acidic environments. are done. Also, in recent years, colloidal dispersed systems obtained by dispersing nanoparticles in liquids - nanofluids are used for cooling various microelectronic devices, as antifreezes in machine building, for increasing oil production in the oil industry, etc. has been identified as having important potential applications.

Taking into account the above, the synthesis of new oxidation-stable metal-string and other types of metal complexes based on modulated oligo- $\alpha$ -aminopyridine ligands, the determination of their structure, the study of their magnetic and electrochemical properties, and the identification of potential applications are undoubtedly an urgent issue.

**Object and subject of the research.** The object of the research is the synthesis of oligo- $\alpha$ -pyridylamine compounds with symmetric and unsymmetric structure modulated by pyrazine, pyrimidine and naphthyridine using palladium catalytic system; purchase of their oxidation-resistant nickel-strings and other types of metal complexes; as well as the study of the structure, magnetic and electrochemical properties of those complexes. Its subject is the preparation of reagents with high inhibitory and biocidal properties, as well as microfluids with high thermal conductivity based on the obtained compounds.

**Purpose and objectives of the research.** It consists of the synthesis of new metal-string and other metal complexes based on

the modulated oligo- $\alpha$ -aminopyridine compounds, the study of the structure and properties of these complexes, as well as the determination of potential applications. To achieve this goal, the following issues were resolved:

- Synthesis of new pyrazine-modulated N-(pyridin-2-yl)pyrazin-2-amine (Hppza) and mononuclear complex of copper(II), coordination polymer and trinuclear string complexes of nickel(II) based on it, structure and properties of the obtained complexes study of its properties;
- Synthesis and study of tetranuclear Cu(II) and pentanuclear Ni(II) complexes with linear structure based on N,N'-di(pyrazin-2-yl)pyridine-2,6-diamine (H2dpzpd);
- New pyrazine-modulated N2(pyrazin-2-yl)-N7-(2-(pyrazin-2-ylamino)-1,8-naphthyridin-7-yl)-1,8-naphthyridin-2,7-diamine (H<sub>3</sub>N<sub>9</sub>-2pz) compound and based on it, synthesis of defective octanickel string, study of its structure, magnetic and electrochemical properties;
- Modulated N2-(pyrimidin-2-yl)-N7-(2-(pyrimidin-2-ylamino)-1,8-naphthyridin-7-yl)-1,8-naphthyridin-2,7-diamine (H<sub>3</sub>N<sub>9</sub>-2pm), synthesis of defective octanuclear Ni(II) string complex and study of its structure, magnetic and electrochemical properties;
- Investigation of inhibitory and bactericidal properties of reagents prepared on the basis of N,N'-di(pyrazin-2-yl)pyridine-2,6-diamine compound and its metal complexes;
- Inhibitory and bactericidal properties of reagents based on N-(pyridin-2-yl)pyrazin-2-amine and its trinuclear Ni(II) strings;
- Preparation of microfluids with high thermal conductivity based on trinuclear nickel(II) strings of N-(pyridin-2-yl)pyrazin-2-amine and their investigation by hot wire (wire) method;

**Research methods.** In dissertation work modern research methods for studying the composition, structure and properties of synthesized compounds (IR-, Electron-, <sup>1</sup>H NMR- and Mass-spectroscopy; elemental analysis; determination of molar magnetic permeability using a SQUID device; X-ray structural analysis ; cyclic

voltammetry, etc.) widely applied. Various physical research methods were also used to determine thermal conductivity, rheology, surface tension coefficient and stability of liquids..

**The main provisions defended:**

- Synthesis of symmetric and unsymmetrical oligo- $\alpha$ -pyridylamine compounds modulated by pyrazine, pyrimidine and naphthyridine.
- Synthesis and research of nickel-strings and other types of metal complexes based on modulated oligo- $\alpha$ -pyridylamine compounds;
- Thermophysical properties of microfluids prepared on the basis of trinuclear nickel-string complexes modulated with pyrazine;
- Corrosion inhibitors and biocide properties of reagents based on N,N'-di(pyrazin-2-yl)pyridin-2,6-diamine, N-(pyridin-2-yl)pyrazin-2-amine compounds and their metal complexes.

**Scientific novelty of the research.**

- N-(pyridin-2-yl)pyrazin-2-amine, an unsymmetrical analogue of di(2-pyridin)amine modulated by pyrazine, and based on it a mononuclear complex of copper(II), a coordination polymer and a trinuclear of nickel(II) string complexes were synthesized. The structure of the complexes was determined by X-ray structural analysis. The obtained trinuclear nickel-strings were determined to be more resistant to oxidation than the corresponding complexes of the original (unmodulated) ligand;
- On the basis of N,N'-di(pyrazin-2-yl)pyridine-2,6-diamine modulated by pyrazine, the synthesis of tetranuclear complexes of copper(II) with a linear structure and string-type pentanuclear complexes of nickel(II) was carried out . The structure of both complexes was determined by X-ray structural analysis, and their magnetic and electrochemical properties were thoroughly studied. The synthesized pentanuclear nickel-string proved to be the most resistant to oxidation among all pentanuclear nickel-strings obtained on the basis of primary and modulated oligo- $\alpha$ -aminopyridine

ligands;

- highly stable defect based on pentapyridyltetraamine with pyrazine and naphthyridine, as well as pyrimidine and naphthyridine modulated analogs ( $H_3N_9-2pz$  and  $H_3N_9-2pm$ ), missing one nickel atom in the metal framework  $[Ni_8(\mu_8-N_9-2pz)_4Cl_2](PF_6)_2$  and  $[Ni_{8.33}(\mu_8-N_9-2pm)_4(NCS)_2](PF_6)_2$  octanuclear string complexes were synthesized and their structures were determined. By magnetic measurements, it was proved that the spin exchange in these strings goes along the metal chain and not with bridging ligands;
- corrosive bacteria (sulfate reducing bacteria - SRB, Thion bacteria - TB) of reagents prepared on the basis of modulated N,N'-di(pyrazin-2-yl)pyridine-2,6-diamine and its copper(II), nickel(II) complexes, hydrocarbon oxidizing bacteria - KOB) has been determined to have high biocidal properties and also a corrosion protection effect.
- Reagents based on N-(pyridin-2-yl)pyrazin-2-amine and its trinuclear nickel(II) strings were found to have high biocidal properties against corrosion-causing bacteria (SRB, TB, KOB) and also corrosion protection effect.
- By adding microcrystals of trinuclear nickel-strings -  $[Ni_3(\mu_3-ppza)_4X_2]$  ( $X=Cl, NCS$ ) to Glycerin-Water solution (base liquid), microfluids with high thermal conductivity were prepared. It was determined that the thermal conductivity of the " $Ni_3(\mu_3-ppza)_4(NCS)_2$ -glycerin-water" system, determined by the "hot wire" method, increased by 80% compared to the base liquid;;

### **Theoretical and practical value of the work.**

- defective octanuclear complexes obtained on the basis of pyrazine-modulated oligo- $\alpha$ -pyridylamine compounds are very important for understanding the mechanism of magnetic interaction in nickel-strings and show the theoretical importance of the work. As for the practical importance of the research, the following can be noted:

- the use of microfluids with high thermal conductivity, made on the basis of trinuclear nickel-string  $[Ni_3(\mu_3-ppza)_4Cl_2]$

microcrystals, in thermal cooling systems (cooling devices, engine systems) has a wide perspective;

- Reagents prepared on the basis of N,N'-di(pyrazin-2-yl)pyridine-2,6-diamine, its tetranuclear copper(II) and pentanuclear nickel-string as highly effective biocides in the fight against corrosion and inhibitors with a high corrosion protection effect can be used.

### **Approval and application.**

The main results of the dissertation were presented and discussed at the following international and national scientific conferences: 1st International Turkic World Conference on Chemical Sciences and Technologies (1st ITWCCST), October 27 – November 1, 2015, Sarajevo Bosnia-Herzegovina; Book of Abstracts, V.1, OR-58; 2nd International Turkic World Conference on Chemical Sciences and Technologies (2nd ITWCCT), 26-30 October 2016, Skopje, Macedonia; Book of Abstracts, V.2 (PO-93, p. 244; PO-147, p. 298); The International Scientific Conference "Chemistry of Coordination Compounds: actual problems of analytical chemistry" dedicated to the 85th anniversary of the Academician Rafiga Alirza gizi Aliyeva (November 16-17, 2017, Baku).

**The name of the organization where the dissertation work was carried out.** The presented dissertation work was carried out in the "Analytical research" laboratory of the "Oil and Gas Research Project" Institute of the State Oil Company of the Republic of Azerbaijan.

### **Personal participation of the author.**

All results reflected in the dissertation were obtained by the author himself. Setting up the problem and conducting tests, systematization, interpretation and generalization of the results were performed with the direct participation of the author.

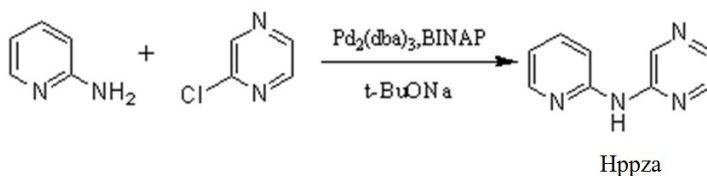
**Scope and structure of work.** Dissertation introduction, 4 chapters, 36 figures, 20 schemes, 17 tables, results and 202 references, without tables, figures, and references, from Introduction 10722, 1st chapter 47209, 2nd chapter 38839, 3rd chapter 46156, chapter 4 28775, Conclusions 3094, total 174795 characters



## MAIN CONTENTS OF THE WORK

### N-(pyridin-2-yl)pyrazin-2-amine compound and its complexes.

Unsymmetrical N-(pyridin-2-yl)pyrazin-2-amine (Hppza) compound 1, with the help of palladium catalytic system [Pd<sub>2</sub>(dba)<sub>3</sub>, BINAP, Bu<sup>o</sup>ONa] in inert medium, in boiling toluene 2- obtained from the interaction of aminopyridine with chlorpyrazine (Scheme 1).

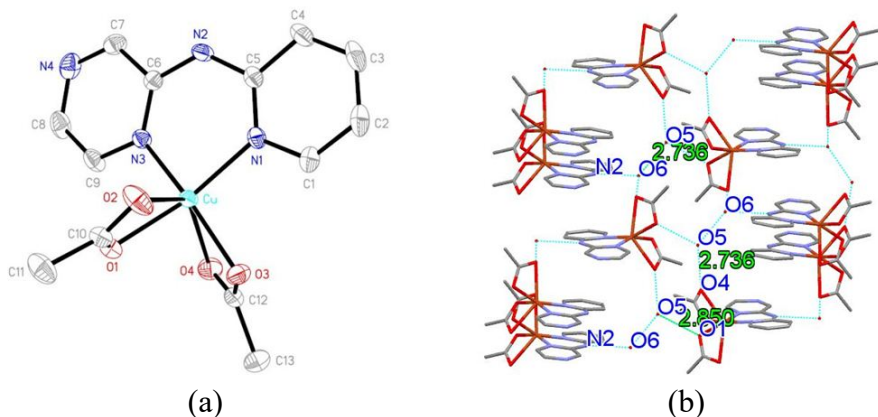


### Scheme 1. Synthesis of N-(pyridin-2-yl)pyrazin-2-amine.

[Cu(Hppza)<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>](H<sub>2</sub>O)<sub>2</sub>(2) and [Cu(Hppza)<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>]<sub>n</sub>(CH<sub>3</sub>OH)<sub>n</sub> (3) complexes with Hppza ligand Cu(CH<sub>3</sub>COO)<sub>2</sub>H<sub>2</sub>O at room temperature synthesized by direct interaction in methanol. Depending on the reaction conditions and the ratio of the ligand to the metal salt, copper(II) mononuclear complex 2 or coordination polymer 3 was obtained. Complex 2 crystallizes in the monoclinic system with space group P2(1)/n. According to the results obtained from the X-ray structure analysis, Hppza is coordinated to the Cu(II) ion as a bidentate ligand through nitrogen atoms of pyrazine and pyridine in the complex. At this time, Hppza adopts an anti-anti type conformation. The nitrogen atom of the amino group of the ligand does not coordinate with the metal atom. In this complex, the Cu(II) ion is located in an extended octahedral environment. The two nitrogen atoms of the Hppza ligand form the equatorial plane with Cu-N(1) = 1.9911 (16) and Cu-N(3) = 1.9689 (16) Å bonds, and also the two oxygen atoms of the two carboxylate groups. The remaining two oxygen atoms (O(2) and O(4)) of the carboxylate anions occupy the axial position by weakly coordinating with the copper(II) ion. At this time, the average value

of the Cu-O distance is 2.4455 Å (Figure 1(a)).

Cu-N<sub>med</sub> = 1.980 (16) Å distances indicate strong bonds between the chelate ligand and the metal ion in complex 2, and the Cu-N and Cu-O distances agree with the distances previously observed for Cu(II) complexes of oligo- $\alpha$ -pyridylamines modulated with pyrazine.

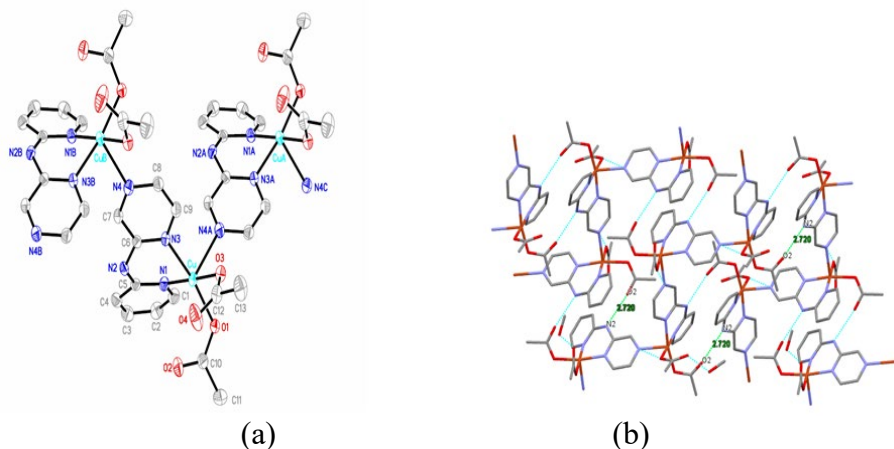


**Figure 1. (a) Crystal structure of [Cu(Hppza)(CH<sub>3</sub>COO)<sub>2</sub>] complex 2. The probability of thermal ellipsoids is at 50% and hydrogen atoms are not shown for clarity; (b) 3D structure formed by complex 2 through hydrogen bonds. Hydrogen bonds are shown with green lines**

Formation of intermolecular hydrogen bonds was observed in complex 2. The non-coordinated NH group of the ligand is formed between the oxygen atoms of the carboxylate anions and the water molecules N (2)  $\cdots$  O (6) (2.770 Å), O (1)  $\cdots$  O (5) (2.850 Å), O (4)  $\cdots$  O (5) (2.736 Å) and O ( 2)  $\cdots$  O (6) (2.790 Å) intermolecular hydrogen bonds lead to the formation of a three-dimensional structure (3D) for this complex (Figure 1(b)).

The value of the effective magnetic moment ( $\mu_{\text{eff}}$ ) of the complex at room temperature (300 K) is slightly higher (1.80 B.M.) than the expected spin-only value (1.73 B.M.) for the non-interacting Cu(II) ion and is similar to that observed for similar compds.

Complex 3 consists of a polymer chain with a one-dimensional zigzag structure (Figure 2).

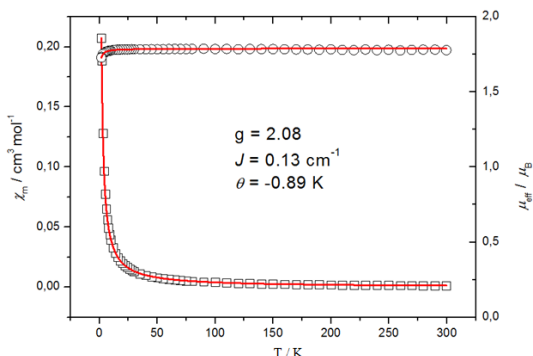


**Figure 2. (a) ORTEP image of zig-zag chain structure in  $[\text{Cu}(\text{Hppza})_2(\text{CH}_3\text{COO})_2](\text{CH}_3\text{OH})_n$  complex, (b) hydrogen bonds in complex 3. For clarity, hydrogen atoms are not shown and the probability of thermal ellipsoids is 50%**

In this complex, the Cu(II) atom is five-coordinated and is located in a tetragonal-pyramidal geometric environment. The Cu(II) ion coordinates with the nitrogen atom (N(1) and N(3)) belonging to the same Hppza ligand molecule (N(1) and N(3)) and the two oxygen atoms of the two carboxylate anions (O(1) and O(3)) to form the equatorial plane. Both carboxylate molecules coordinated to the metal center are in the cis- state. The N(4) nitrogen atom from another ligand is weakly coordinated with Cu(II), therefore it is characterized by a long Cu-N distance (Cu - N (4) = 2.307 (2) Å) and occupies an axial position in the complex. In the complex, the Hppza molecule is coordinated to the Cu(II) ion as a tridentate ligand and connects the coordinated units into an infinite 1D zigzag chain through bridging pyrazine rings. Adjacent ligands are located in a zigzag chain almost perpendicular to each other (Cu-Cu-Cu = 99,56°).

The magnetic permeability ( $\chi_M$ ) of complex 3 was measured in the temperature range of 2-300 K. The determined value of the effective magnetic moment ( $\mu_{\text{eff}}$ ) at room temperature is slightly higher than the value calculated for pure spin magnetism ( $\mu_{\text{eff}} = 1.73$  B.M.) and is 1.78 B.M. is equal to The effective magnetic moment of

the complex gradually increases as the temperature decreases, reaches its maximum value at a temperature of 100 K, and then decreases to 1.73 B.M at a temperature of 2 K. gets equal value. This case proves that there is a ferromagnetic interaction between the magnetic centers for the Cu(II) complex. It was determined that the magnetism of the 3-coordination polymer occurs due to two types of magnetic interactions, namely weak intramolecular ferromagnetic interactions and small interchain antiferromagnetic interactions (Figure 3).

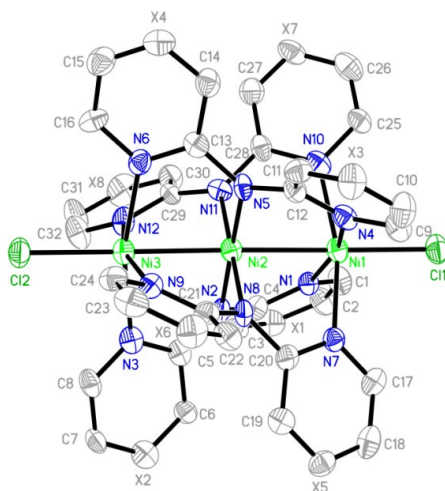


**Figure 3. Temperature dependence of effective magnetic moment  $\mu_{\text{eff}}$  ( $\circ$ , right ordinate) and magnetic permeability  $\chi_M$  ( $\square$ , left ordinate) in  $[\text{Cu}(\text{Hppza})_2(\text{CH}_3\text{COO})_2](\text{CH}_3\text{OH})_n$  (3) complex. The solid line is derived from least-squares processing of experimental results using the ferromagnetic model applied to 1D systems**

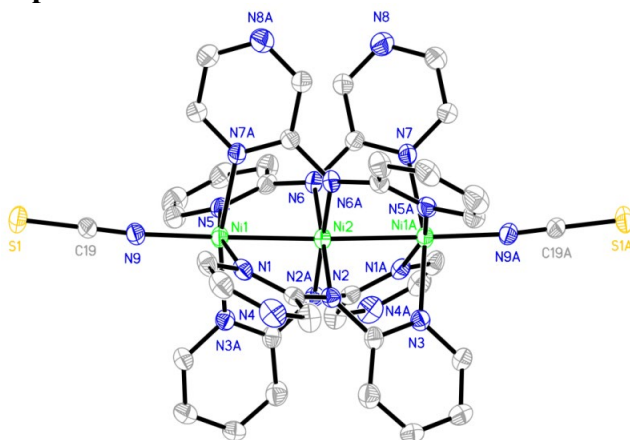
$[\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2]$  complex (4) was synthesized from the reaction of Hppza ligand with anhydrous  $\text{NiCl}_2$  at high temperature (200-215°C). At this time, naphthalene was used as a solvent and  $\text{Bu}'\text{OK}$  base was used to deprotonate amino groups. Complex  $[\text{Ni}_3(\mu_3\text{-ppza})_4(\text{NCS})_2]$  (5) was obtained from complex 4 by axial ligand substitution.

The crystal structures of trinuclear nickel strings 4 and 5 are shown in Figures 4 and 5, respectively. Similar to other metal-strings of oligo- $\alpha$ -pyridylamine ligands, in these nickel-strings the trinickel linear metal chain is helically wound with four deprotonated tridentate ppza- ligands. In this case, ppza<sup>-</sup> ligand anions take syn-syn

type conformation. All nickel(II) ions and axial ligands are approximately collinear, and the Ni–Ni–Ni angle is in the range 177.99(7)–178.93(10)°.



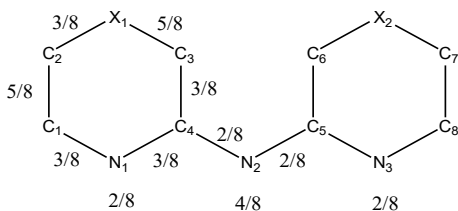
**Figure 4. Crystal structure of  $[\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2]$  (4) nickel string. For clarity, hydrogen atoms are not shown and the probability of thermal ellipsoids is 30%.  $\text{X} = \frac{1}{2} \text{N} + \frac{1}{2} \text{C}$**



In complexes **4** and **5**, the coordination environment of the internal nickel atom is planar square, which proves that Ni(II) is in the low spin state ( $S=0$ ). In addition, the two terminal nickel atoms with an approximately square pyramidal configuration are characterized by a long Ni-N bond distance ( $\sim 2.10 \text{ \AA}$ ), indicating that they are located in a high spin state ( $S = 1$ ). The average values of Ni-Ni distances in complexes **4** and **5** are 2.437(2) and 2.411(7)  $\text{\AA}$ , respectively.

The distribution of the negative charge in the binding ppza- ligand anion and the arrangement of  $\pi$ -bonds were calculated based on the theoretical analysis of the resonance structures (Scheme 2).

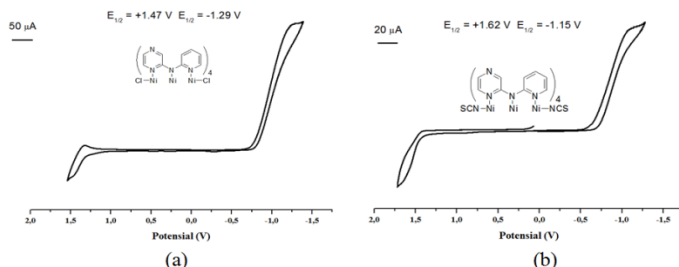
For the bond lengths, it was found that there is a very good agreement between the results obtained from X-ray structural analysis and theoretical calculations. In both nickel-strings **4** and **5**, the terminal nitrogen atom was found to have the least negative charge density and, accordingly, the terminal Ni - N bond distance was the longest. It was found that the density of negative charge on amino nitrogen atom N(2) is greater than the density of negative charge on aromatic nitrogen atoms (N(1) and N(3)) Ni(2)-N(2) bond Ni(1) -N(1) and Ni(3)-N(3) leads to shorter bonds. The same trend was also observed for C - C and C - N bonds.



**Scheme 2. Distribution of negative charge in ppza<sup>-</sup> ligand anion and design of  $\pi$ -bonds. For complexes **4** and **5**, each aromatic ring has a 50% probability of having nitrogen and carbon atoms:  $X = \frac{1}{2} N + \frac{1}{2} C$ .**

Cyclic voltammograms of complexes **4** and **5** in  $\text{CH}_2\text{Cl}_2$  solutions containing 0.1 M TBAP in the range of  $-1.25 - (+) 2.0 \text{ V}$  showed that these complexes, due to their electrochemical nature, are different from the unsubstituted ligand Hdpa complexes  $[\text{Ni}_3(\mu_3\text{-dpa})_4\text{X}_2]$  ( $X=\text{Cl}, \text{NCS}$ ) differ sharply. Thus, while a reversible

oxidation-reduction pair ( $E_{1/2} = +0.105$  V) was determined in the cyclic voltammogram of the  $[\text{Ni}_3(\mu_3\text{-dpa})_4\text{Cl}_2]$  complex, under appropriate conditions, for complex 4, both of which are irreversible, one oxidation ( $E_{1/2} = +1.47$  V) and a reduction ( $E_{1/2} = -1.29$  V) half-wave was observed. Substitution of chloride axial ligand with  $\text{NCS}^-$  led to anodic shift of oxidation ( $E_{1/2} = +1.62$  V) and reduction ( $E_{1/2} = -1.15$  V) half waves in complex 5 (Figure 6).

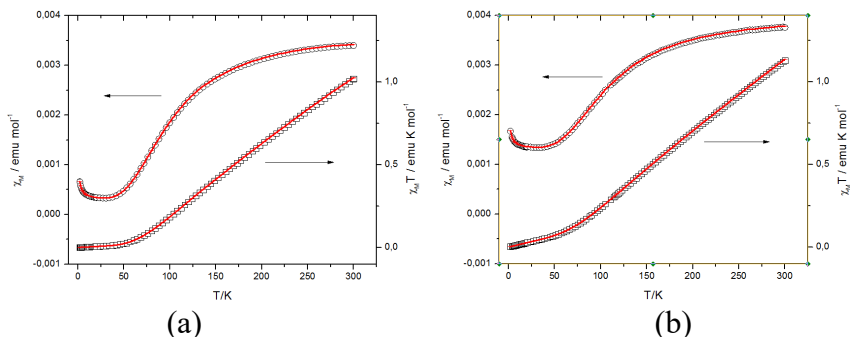


**Figure 6. Cyclic voltammograms of  $[\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2]$  (a) and  $[\text{Ni}_3(\mu_3\text{-ppza})_4(\text{NCS})_2]$  (b) complexes in  $\text{CH}_2\text{Cl}_2$  solution containing 0.1M TBAP**

Thus, replacing the pyridine ring with pyrazine in the Hppza ligand makes trinuclear nickel strings more resistant to oxidation. This is directly related to the fact that pyrazine is more electronegative than pyridine.

It was determined that the magnetic properties determined for nickel-strings 4 and 5 in the temperature range of 2–300 K are similar, and the molar magnetic permeability ( $\chi_M$ ) of both complexes has a maximum value of 300 K. The  $\chi_{MT}$  product for nickel-strings 4 and 5 is 1.02 and 1.12  $\text{emu K mol}^{-1}$  ( $\text{emu} = \text{cm}^3$ ) at room temperature, respectively, and decreases continuously as the temperature decreases, indicating antiferromagnetic interactions between  $\text{Ni}(\text{II})$  ions with magnetic centers. shows that there is an effect (figure 7). For both complexes, the results obtained from magnetic measurements and X-ray structural analysis were found to be in agreement with each other: two antiferromagnetically interacting, high-spin, square-pyramidal geometry detailed paramagnetic  $\text{Ni}(\text{II})$  ions are believed to be at the ends of the metal chain and one low-spin diamagnet, and the square-planar  $\text{Ni}(\text{II})$  ion

is located in the center of the chain.



**Figure 7.**  $\chi$ MT ( $\square$ , right ordinate) and molar magnetic permeability  $\chi$ M ( $\square$ , left ordinate) for  $[\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2]$  (a) and  $[\text{Ni}_3(\mu_3\text{-ppza})_4(\text{NCS})_2]$  (b) complexes ordinate) temperature dependence. The solid red line is obtained from processing the results using the least squares method

The best overlap of experimental and theoretical curves of  $\chi$ MT temperature dependence is  $g = 2.21$ ,  $J = -199.0 \text{ cm}^{-1}$  for complex 4 ( $\text{TIP} = 4.06 \times 10^{-6} \text{ cm}^{-1} \text{ mol}^{-1}$ ), and for 5  $g = 2.20$ ,  $J = -178.0 \text{ cm}^{-1}$  ( $\text{TIP} = 3.11 \times 10^{-3} \text{ cm}^{-1} \text{ mol}^{-1}$ ) values were observed. This proves that there is a strong antiferromagnetic interaction between the high-spin terminal nickel atoms.

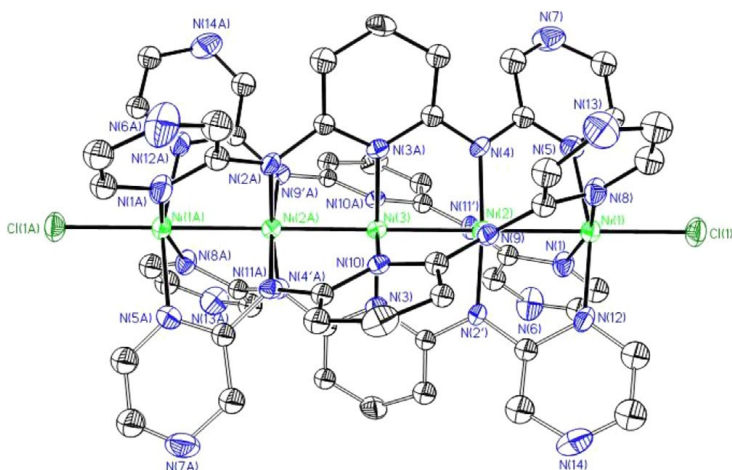
The values obtained for the interaction constants ( $J$ ) and  $g$ -factors for both complexes are in agreement with the values obtained for the initial Hdpa and the corresponding trinuclear nickel-strings of both pyridine rings substituted with pyrazine (Hdpza) ligands (for 4:  $g = 2.067$ ,  $J = -218.2 \text{ cm}^{-1}$ ; for 5:  $g = 2.154$ ,  $J = -200.5 \text{ cm}^{-1}$ ; for  $[\text{Ni}_3(\mu_3\text{-dpza})_4(\text{NCS})_2]$ :  $g = 2.188$ ,  $J = -218.4 \text{ cm}^{-1}$ ) are comparable. Thus, the similarity of the interaction constants ( $J$ ) in trinuclear nickel-strings based on ligands with different electron configurations proves once again that the mechanism asserting that the interaction between the magnetic centers in these compounds occurs through the central metal atom is correct.

### **Pentanuclear nickel-string and tetranuclear copper(II) complexes of N,N'-di(pyrazin-2-yl)pyridine-2,6-diamine.**

Five-nuclear nickel-string  $[\text{Ni}_5(\mu_5\text{-dpzpd})_4\text{Cl}_2]$  (6) was



synthesized by interaction of H<sub>2</sub>dpzpd<sub>a</sub> ligand with anhydrous NiCl<sub>2</sub> in boiling naphthalene. The structure of complex 6 is similar to the structure of pentanuclear nickel-strings obtained on the basis of primary and modulated oligo- $\alpha$ -pyridylamines. It was determined that the complex crystallizes in the orthorhombic system and has the space group Pbc<sub>a</sub>. It was also determined that the molecule has twofold symmetry and 50% disorder for the helical set of four dpzpd<sub>a</sub><sup>2-</sup> ligand anions (Figure 8).

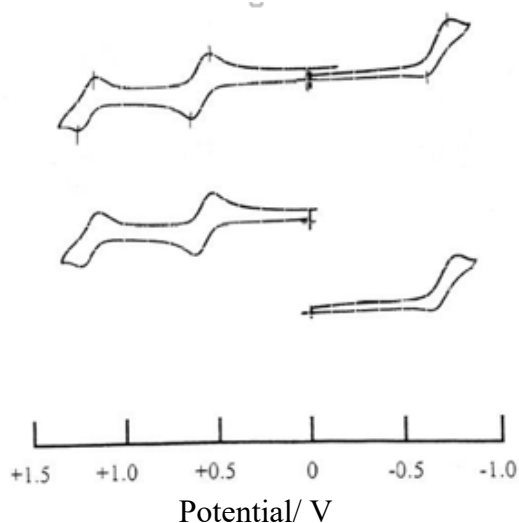


**Figure 8. Crystal structure of the complex [Ni<sub>5</sub>(μ<sub>5</sub>-dpzpd<sub>a</sub>)<sub>4</sub>Cl<sub>2</sub>] (6). For clarity, hydrogen atoms are not shown and the probability of thermal ellipsoids is 50%**

Two types of Ni-Ni distances were determined for complex 6 as in other pentanuclear nickel-strings of oligo- $\alpha$ -pyridylamine ligands. For this nickel-string, the length of the internal Ni-Ni distances was determined to be about 0.08 Å shorter than the terminal Ni-Ni distances. The Ni-Cl bond length of 2.3209 (15) Å in nickel-string 6 was found to be shorter than the Ni-Cl = 2.364 (3) Å distance observed for the unsubstituted ligand complex [Ni<sub>5</sub>(μ<sub>5</sub>-tpda)<sub>4</sub>Cl<sub>2</sub>], and this case contains two was hypothesized to be the result of the pyrazine-bearing H<sub>2</sub>dpzpd<sub>a</sub> ligand creating a stronger ligand site. It was also determined that complex 6 has two types of Ni-N distances: the terminal Ni(1) atom is located in a square-

pyramidal geometry, has a longer Ni-N<sub>med</sub> bond (2.097(5)Å) and is located in a high spin (S = 1) state. ; and the three internal nickel atoms are located in a planar-square environment, characterized by short Ni-N<sub>med</sub> distances (1.892 (9) – 1.902 (4) Å) and because of this, they are in a low spin (S = 0) state.

The study of the electrochemical properties of string 6 was carried out in the presence of TBAP electrolyte in the range -1.0 – (+)1.5 V in dichloromethane solution. In the cyclic voltammogram of this complex, it was determined that there are two rotating oxidation-reduction pairs. One of them is attributed to the rotary oxidation half-wave E<sub>1/2</sub> = +1.206 V, and the other E<sub>1/2</sub> = - 0.680 V to the rotary reduction half-wave (Figure 9).



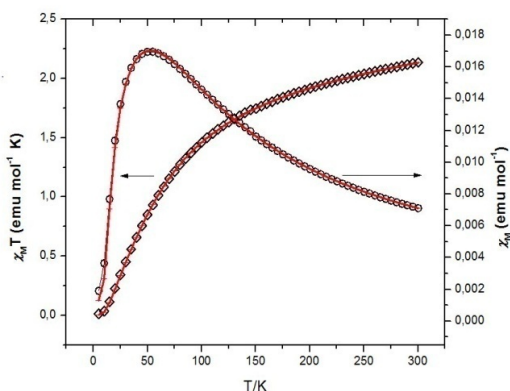
**Figure 9. Cyclic voltammogram of [Ni<sub>5</sub>(μ<sub>5</sub>-dpzpda)<sub>4</sub>Cl<sub>2</sub>] (6) complex in CH<sub>2</sub>Cl<sub>2</sub> solution containing 0.1 M TBAP: bottom: in the range 0 – (-1.0) V; in the middle: in the range of 0 – (+ 1.5 V); above: in the range -1.0 – (+1.5 V)**

However, in the cyclic voltammogram of the known primary ligand complex [Ni<sub>5</sub>(μ<sub>5</sub>-tpda)<sub>4</sub>Cl<sub>2</sub>] under suitable conditions, only one oxidation peak E<sub>1/2</sub> = +0.65 V was determined. Thus, replacement of the terminal pyridine rings of the primary H<sub>2</sub>tpda ligand with electron-withdrawing pyrazine rings complicates the

oxidation of the nickel-string  $[\text{Ni}_5(\mu_5\text{-dpzpd})_4\text{Cl}_2]$  obtained on the basis of this ligand in the 500 mV configuration. That is, the new nickel-string obtained is more resistant to oxidation.

According to the conducted comparative electrochemical studies, the newly synthesized nickel-string 6 is the most resistant compound against oxidation among all five-nuclear nickel strings obtained on the basis of primary and modulated oligo- $\alpha$ -aminopyridine ligands.

Magnetic permeability ( $\chi M$ ) measurements for polycrystalline nickel-string 6 were performed in the temperature range of 5-300 K (Figure 10). The observed effective magnetic moment ( $\mu_{\text{eff}}$ ) for this complex at room temperature is 4.12 B.M. is equal, which is typical for the magnetic moments of dinuclear high-spin nickel(II) complexes ( $\mu_{\text{eff}} = 4.0$  B.M. for pure spin magnetism).

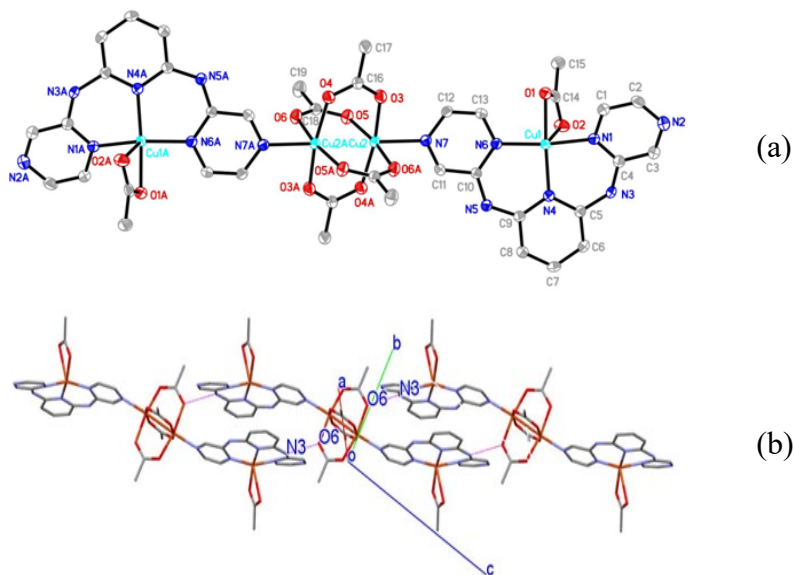


**Figure 10. Temperature dependence of  $\chi MT$  ( $\square$ , left ordinate) and molar magnetic permeability  $\chi M$  ( $\circ$ , right ordinate) for the  $[\text{Ni}_5(\mu_5\text{-dpzpd})_4\text{Cl}_2]$  complex. The solid red line is obtained from processing the results using the least squares method**

The gradual decrease of the  $\chi MT$  product for string 6 as the temperature decreases proves the antiferromagnetic interaction between the spin centers ( $S=1$ ). The best agreement of the experimental data on the temperature dependence of  $\chi MT$  with the theoretical curves occurs at  $g = 2.12$ ,  $J = -51.0 \text{ cm}^{-1}$  ( $\text{TIP} = 8.16 \times 10^{-4} \text{ cm}^{-1} \text{ mol}^{-1}$ ), which indicates that two high-spin indicating a relatively strong antiferromagnetic interaction between the terminal

nickel atoms. The value of interaction constant ( $J$ ) and  $g$ -factor found for this complex is  $[\text{Ni}_5(\mu_5\text{-tpda})_4\text{Cl}_2]$  ( $J = -33.5 \text{ cm}^{-1}$ ,  $g = 2.17$ ) synthesized on the basis of ligands with different electronic configurations. ,  $[\text{Ni}_5(\mu_5\text{-dmpdda})_4(\text{NCS})_2]$  ( $J = -30.8 \text{ cm}^{-1}$ ,  $g = 2.08$ ) and  $[\text{Ni}_5(\mu_5\text{-pppmda})_4\text{Cl}_2]$  ( $J = -51.6 \text{ cm}^{-1}$ ,  $g = 2.07$ ) is almost identical to those parameters determined for pentanuclear nickel-strings. This once again proves that the magnetic interaction in oligonickel-strings occurs along the metal chain and not with the equatorial ligands.

The tetranuclear linear complex of copper(II)  $[\text{Cu}_4(\text{Hdpzpd})_2(\text{CH}_3\text{COO})_6]$  (7) was synthesized from the interaction of  $\text{H}_2\text{dpzpd}$  ligand with  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  in methanol (Figure 11).

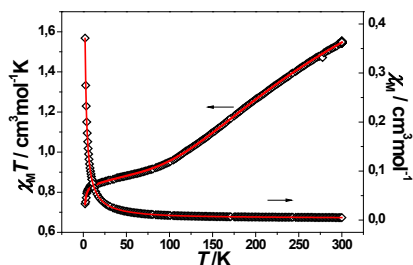


**Figure 11. (a) Molecular structure of  $[\text{Cu}_4(\text{Hdpzpd})_2(\text{CH}_3\text{COO})_6]$  complex (7). For clarity, hydrogen atoms are not shown and the probability of thermal ellipsoids is 50%; (b) 1D structure formed by complex 7 via hydrogen bonds**

It was determined that this dark green complex does not contain solvent molecules in its crystal lattice and consists of a linear

chain of four copper atoms with an acetate dimer in the center of its molecule. (Figure 11). Cu-N distances determined in the complex in the range of 1.936–1.979 Å (Cu-N<sub>med</sub> = 1.958 Å) are typical for complexes formed by copper(II) with nitrogen donor ligands. Intermolecular hydrogen bonding leads to the formation of a 1D structure of the complex (Figure 11(b)). Also, in the 1D supramolecular structure of the compound, it was determined that there is a strong  $\pi$ - $\pi$  mixing effect (3.19 Å) between the pyridine and pyrazine rings..

The magnetic permeability ( $\chi_M$ ) for complex 7 was measured in the temperature range of 2-300 K. The value of  $\chi_{MT} = 1.55 \text{ cm}^3 \text{ K mol}^{-1}$  determined for the complex at a temperature of 300 K is very close to the value of  $\chi_{MT} = 1.50 \text{ cm}^3 \text{ K mol}^{-1}$  characteristic of four high-spin isotropic Cu(II) ( $S=1/2$ ,  $g=2.0$ ). The value of  $\chi_{MT}$  decreases gradually when the system is cooled from 300 K to 80 K, and then slowly to 10 K. This case indicates that there is an antiferromagnetic interaction between the magnetic centers (Figure 12).



**Figure 12.** Temperature dependence of the molar magnetic permeability  $\chi_{MT}$  (left ordinate) and  $\chi_M$  (right ordinate) for the  $[\text{Cu}_4(\text{Hdpzpd})_2(\text{CH}_3\text{COO})_6]$  complex. The solid red line is obtained from processing the results using the least squares method

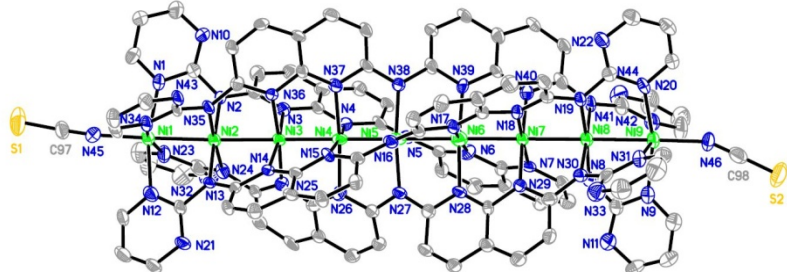
When comparing the experimental and theoretical dependences of  $\chi_{MT}$  on temperature for 7, the curve based on the experimental results best coincides with the theoretical curve  $J_1 = 10.64 \text{ cm}^{-1}$ ,  $J_2 = -175.36 \text{ cm}^{-1}$  (strong antiferromagnetism between the copper(II) atoms of the acetate dimer interaction) and  $g = 2.11$  ( $\text{TIP} = 9.7 \times 10^{-}$

4 cm<sup>3</sup> mol<sup>-1</sup>) values were found. The temperature-independent paramagnetism (TIP) correction was determined using the PHI program.

The tetranuclear Cu(II) complex is the first of its type formed by modulated N,N-bis( $\alpha$ -pyridyl)-2,6-diaminopyridine ligands with copper(II).

**N2-(pyrimidin-2-yl)-N7-(2-(pyrimidin-2-ylamino)-1,8-naphthyridin-7-yl)-1,8-naphthyridine -2,7-diamine (H<sub>3</sub>N<sub>9</sub>-2pm) defective nickel-string complex of the ligand.**

[Ni<sub>18.33</sub>(N<sub>9</sub>-2pm)<sub>4</sub>(NCS)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> nickel-string (**8**) was synthesized from the interaction of anhydrous NiCl<sub>2</sub> with H<sub>3</sub>N<sub>9</sub>-2pm ligand (Figure 13)..



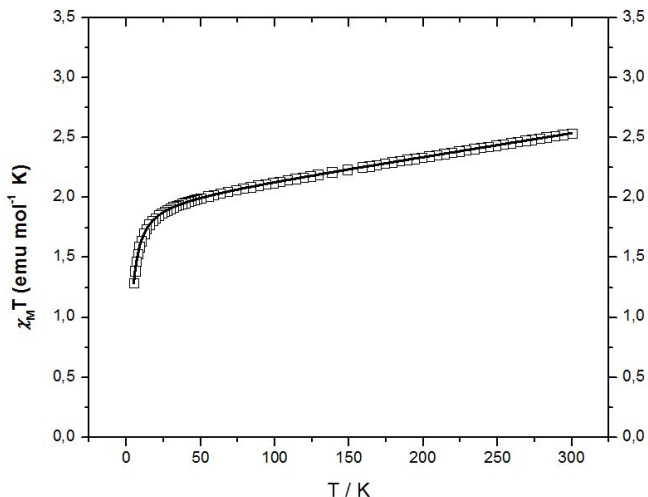
**Figure 13. Crystal structure of [Ni<sub>18.33</sub>(N<sub>9</sub>-2pm)<sub>4</sub>(NCS)<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>(**8**) dication complex. Ni(4) atom placement probability is equal to 0.33. The probability of thermal ellipsoids is 50%**

**8** is a dication-type complex, it holds two PF<sub>6</sub><sup>-</sup> anions as counterions in its molecule; Ni-Ni-Ni angles are located in the range of 177.39-179.90°; the four equatorial ligands wrap around the metal chain in syn-syn fashion as a trianion helix; nitrogen atoms of thiocyanate axial ligands are collinear with the Ni<sub>18.33</sub> axis; the total length of the nickel(II) chain is 18.27 Å.

In string **8**, the Ni-Ni distances range from 2.045 (4) to 2.3996 (15) Å. The terminal Ni(1) – Ni(2) distance was determined to be the longest. The Ni(3)-Ni(4) (2.195 (4) Å) and Ni(4)-Ni(5) (2.045 (4) Å) distances are not typical for this type of complexes and are explained by the defect nature of the compound. The terminal nickel(II) ions

are located in a square-pyramidal NiN<sub>4</sub>N environment, have long Ni–N distances (Ni(1) – N<sub>med</sub> = 2.071 (8) and Ni(9) – N<sub>med</sub> = 2.072 (8) Å) and are high spin (S= 1); The shorter Ni-N distances in the range of 1.900 (7) –2.002 (8) Å prove that the internal nickel(II) ions are in the low spin state (S=0)..

The molar magnetic permeability ( $\chi_M$ ) of complex **8** was measured in the temperature range of 5-300 K and under a magnetic field of 2000 Q (Figure 14).



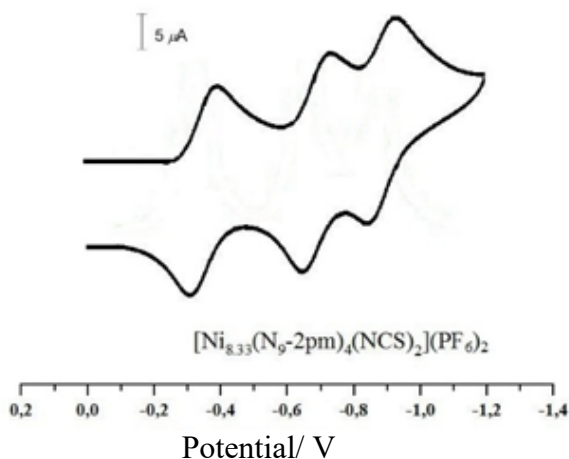
**Figure 14.**  $\chi_M T$  temperature dependence for the  $[\text{Ni}_{8.33}(\text{N}_{9-2\text{pm}})_4(\text{NCS})_2](\text{PF}_6)_2$  complex. The solid line is derived from processing the results using the least squares method

The  $\chi_M T$  value for this complex is 2.56 emu K mol<sup>-1</sup> at room temperature. The obtained value is in agreement with known results for magnetic permeability of similar defect line systems where both terminal nickel atoms are in high spin (S=1) and other nickel atoms are in low spin (S=0) state. The gradual decrease of the  $\chi_M T$  value when the system is cooled (1.80 emu K mol<sup>-1</sup> at 15 K) proves the existence of a weak antiferromagnetic interaction between the magnetic centers (Fig. 14).

The best agreement of theoretical curves with experimental data was observed at  $g = 2.003$  and  $J = -2.90 \text{ cm}^{-1}$  (TIP correction =  $8.8 \times 10^{-4} \text{ emu mol}^{-1}$ ). A small negative value of the interaction

constant ( $J$ ) indicates a weak magnetic interaction between the two terminal nickel(II) ions. The value of  $J$  observed for this complex is very close to the value of the interaction constant ( $J = -1.66 \text{ cm}^{-1}$ ) determined for another defective nickel(II) string synthesized previously based on  $\text{H}_3\text{N}_9\text{-2pm}$  ligand. The result obtained from the magnetic measurements is of great importance and is a direct evidence that the interaction between the magnetic centers in metal-strings occurs along the metal chain and not with the connecting ligands.

The cyclic voltammogram of complex **8** was measured in the range of  $-1.4 \text{ V} - (+) 0.2 \text{ V}$  in the presence of  $0.1 \text{ M}$  TBAP electrolyte. In the cyclic voltammogram,  $E_{1/2} = -0.35, -0.69$  and  $-0.88 \text{ V}$  (compared to  $\text{Ag}/\text{AgCl}$ ) three rotary reduction half-waves are observed (Fig. 15).



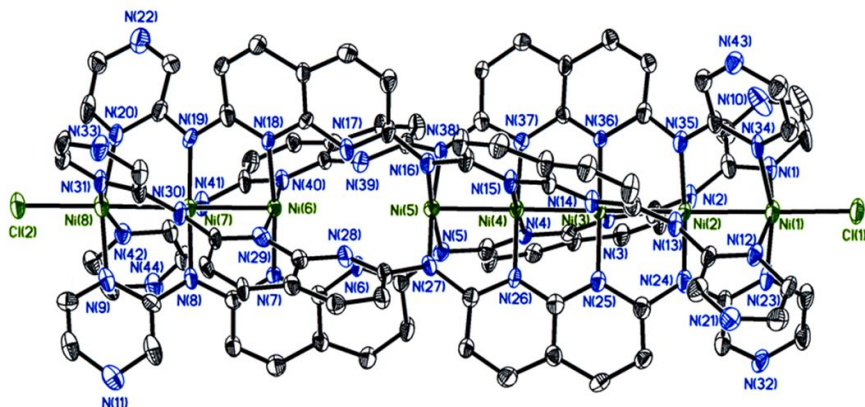
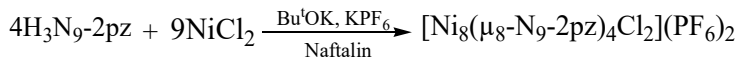
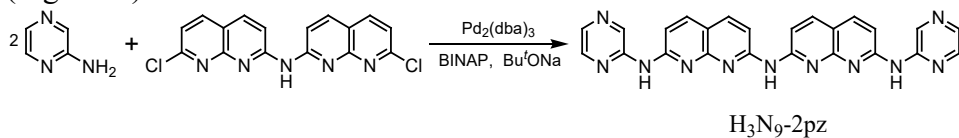
**Figure 15.** Cyclic voltammogram of  $[\text{Ni}_{8.33}(\text{N}_9\text{-2pm})_4(\text{NCS})_2](\text{PF}_6)_2$  complex in  $\text{CH}_2\text{Cl}_2$  solution containing  $0.1 \text{ M}$  TBAP, in the range  $0.2 - (-1.4) \text{ V}$

The obtained results show that reduction is easy and oxidation is difficult for complex **8**. It is believed that the indicated properties of oligo- $\alpha$ -pyridylamine ligands modulated by pyrazine and pyrimidine are directly related to electron acceptor properties of pyrazine and pyrimidine.



**N2-(pyrazin-2-yl)-N7-(2-(pyrazin-2-ylamino)-1,8-naphthyridin-7-yl)-1,8-naphthyridin-2,7-diamine(H<sub>3</sub>N<sub>9</sub>-2pz)  
octanuclear nickel-string complex of the ligand**

The new ligand H<sub>3</sub>N<sub>9</sub>-2pz (**9**) was prepared by the interaction of bis(2-chloro-1,8-naphthyridin-7-yl)amine with 2-aminopyrazine in freshly distilled anhydrous toluene in the presence of a palladium catalyst, and <sup>1</sup>H NMR, IR- and Mass- was characterized by spectroscopy (FAB) methods. The octanickel [Ni<sub>8</sub>(μ<sub>8</sub>-N<sub>9</sub>-2pz)<sub>4</sub>Cl<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub> (**10**) string was synthesized from the interaction of the H<sub>3</sub>N<sub>9</sub>-2pz ligand with anhydrous NiCl<sub>2</sub> in an argon atmosphere (Figure16).



**Figure 16.** Molecular structure of the dication complex [Ni<sub>8</sub>(μ<sub>8</sub>-N<sub>9</sub>-2pz)<sub>4</sub>Cl<sub>2</sub>](PF<sub>6</sub>)<sub>2</sub>. Thermal ellipsoids were drawn with 20% probability. Hydrogen atoms are not shown to make the structure clearer

Complex **10** is a typical representative of metal-strings in

which a metal atom has been lost in the part of the metal chain connected to the naphthyridine.

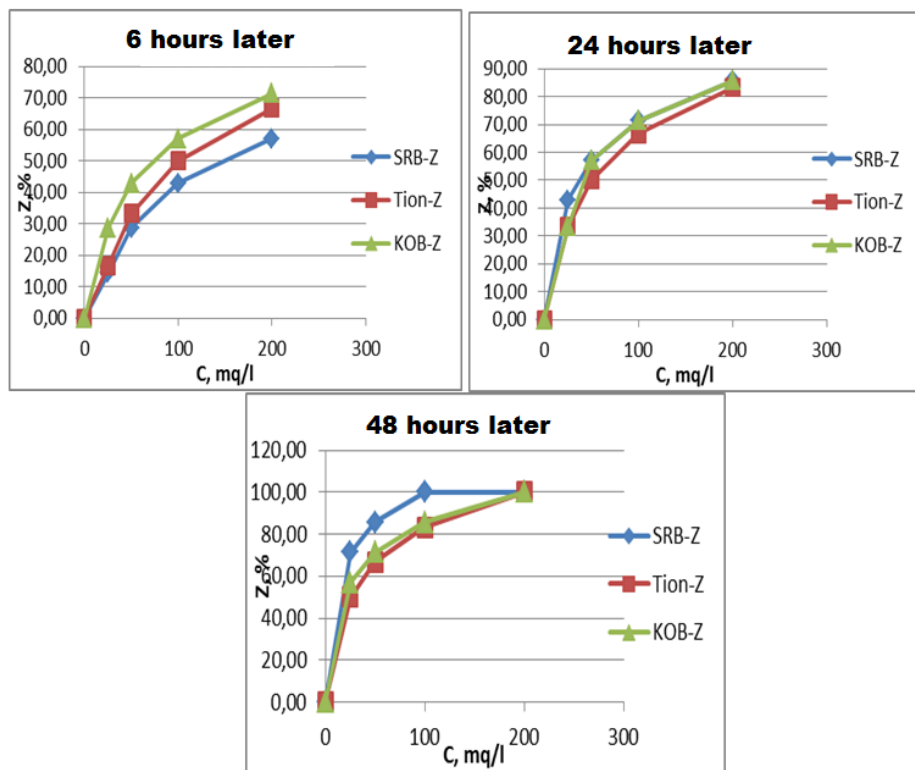
### **Inhibitory and bactericidal properties of reagents prepared on the basis of N,N'-di(pyrazin-2-yl)pyridin-2,6-diamine, N-(pyridin-2-yl)pyrazin-2-amine compounds and their metal complexes**

Evaluation of the biocidal properties of the complexes against planktonic bacteria was carried out based on their solutions with concentrations of 25, 50, 100 and 200 mg/dm<sup>3</sup> calculated on the pure substance. Using the serial dilution method, the amount of living bacteria was determined by selecting an incubation period of 15 days for sulfate-reducing bacteria (SRB) and 30 days for other bacteria. From the obtained results, it was determined that [Ni<sub>5</sub>(μ<sub>5</sub>-dpzpd<sub>a</sub>)<sub>4</sub>Cl<sub>2</sub>] reagent has a higher bactericidal property than [Cu<sub>4</sub>(Hdpzpd<sub>a</sub>)<sub>2</sub>(CH<sub>3</sub>COO)<sub>6</sub>]. Thus, while the rate of 100% destruction of sulfate-reducing bacteria by [Cu<sub>4</sub>(Hdpzpd<sub>a</sub>)<sub>2</sub>(CH<sub>3</sub>COO)<sub>6</sub>] reagent in the same time interval was observed at its concentration of 50 mg/l, for [Ni<sub>5</sub>(μ<sub>5</sub>-dpzpd<sub>a</sub>)<sub>4</sub>Cl<sub>2</sub>] reagent, this result was twice it was found to occur at low concentration, i.e. 25 mg/l (Figure 17). It was determined that the order of decreasing effectiveness of reagents is Ni<sub>5</sub> > Cu<sub>4</sub> > N<sub>5</sub>.

The higher effect of the nickel-string complex compared to H<sub>2</sub>dpzpd<sub>a</sub> is explained by its higher lipophilicity (hydrophobicity). Due to its high lipophilicity, the [Ni<sub>5</sub>(μ<sub>5</sub>-dpzpd<sub>a</sub>)<sub>4</sub>Cl<sub>2</sub>] complex can easily cross the lipid membrane and block the metal binding sites of enzymes of microorganisms. It is believed that, like other metal complexes, the [Ni<sub>5</sub>(μ<sub>5</sub>-dpzpd<sub>a</sub>)<sub>4</sub>Cl<sub>2</sub>] string also affects the cellular respiration process, hinders the synthesis of proteins and prevents the further development of the organism by slowing down the normal processes taking place in the cell.

Analogous results were observed in reagents prepared on the basis of N-(pyridin-2-yl)pyrazin-2-amine and its nickel strings. Thus, while Hppza and [Ni<sub>3</sub>(μ<sub>3</sub>-ppza)<sub>4</sub>Cl<sub>2</sub>] reagents 100% destruction rate of sulfate-reducing bacteria in the same time interval was observed for Hppza at its concentration of 100 mg/l, for [Ni<sub>3</sub>(μ<sub>3</sub>-ppza)<sub>4</sub>Cl<sub>2</sub>]

reagent two was found to occur at low concentrations, i.e. 50 mg/l. 100% protective effect against Thione and Carbon oxidizing bacteria (COB) was also determined at lower concentration of  $[Ni_3(\mu_3\text{-ppza})_4Cl_2]$  reagent.



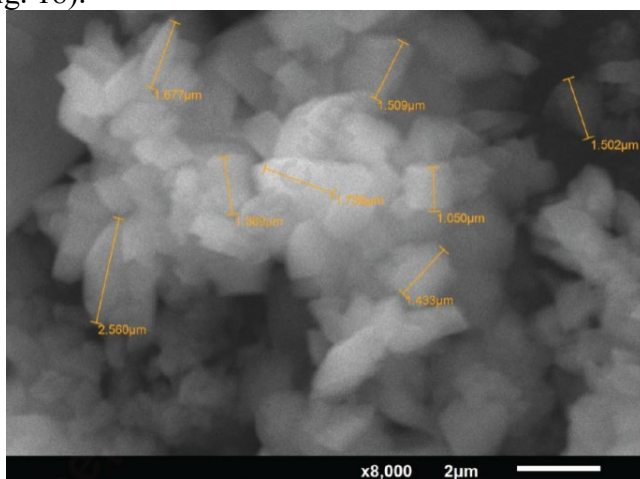
**Figure 17. Dependence of the concentration of  $[Ni_5(\mu_5\text{-dpzpd}a)_4Cl_2]$  reagent killing rates on relevant bacteria in formation water samples at different times**

The comparative analysis of the corrosion protection effects of the investigated compounds was carried out based on the experiments carried out at concentrations of 30, 60, 120, 250, 500 mg/dm<sup>3</sup> calculated on the pure substance. Determination of corrosion protection effects (Z,%) on St20 steel samples at 500 mg/l and 1000 mg/l concentrations of hydrogen-sulfide in a model water

solution of compounds,  $[\text{Ni}_5(\mu_5\text{-dpzpd})_4\text{Cl}_2]$  reagent  $[\text{Cu}_4(\text{Hdpzpd})_2(\text{CH}_3\text{COO})_6]$  was determined to have a higher protective effect than the reagent.

### **Thermophysical properties of microfluids based on pyrazine-modulated trinuclear nickel-string complexes.**

The stability, thermal conductivity, rheology, surface tension and surface tension of microfluids " $\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2$  - water - glycerol" and " $\text{Ni}_3(\mu_3\text{-ppza})_4(\text{NCS})_2$  - water - glycerol" prepared on the basis of newly synthesized trinuclear  $\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2$  and  $\text{Ni}_3(\mu_3\text{-ppza})_4(\text{NCS})_2$  strings, using the "Hot wire method" freezing temperature has been thoroughly investigated. A number of measured parameters of these microfluids (stability, thermal conductivity, density, etc.) were compared with the properties of corresponding nano- and microfluids previously prepared on the basis of Cu, Al, Ni nanoparticles and microparticles of pentanuclear  $\text{Ni}_5(\mu_5\text{-pppmda})_4\text{Cl}_2$  string. The formation of clusters of  $\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2$  nickel-string particles in the base liquid, the size of which is determined by the floating conditions, is evident from the SEM image (Fig. 18).

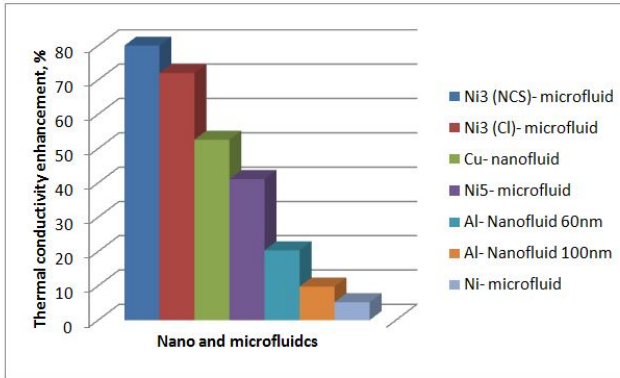


**Figure 18. SEM image of  $\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2$  nickel-string particles in base liquid**

The density determined for  $\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2$  microparticles

from calculations based on SEM studies ( $\rho_m=1.638 \text{ g/cm}^3$ ) coincides with the known density of this complex ( $\rho_m=1.644 \text{ g/cm}^3$ ).

Compared to the base fluid, 80% of the increase in thermal conductivity for the "Ni<sub>3</sub>( $\mu_3$ -ppza)<sub>4</sub>(NCS)<sub>2</sub> - water - glycerol" system containing 5 parts by volume of microparticles/nanoparticles, "Ni<sub>3</sub>( $\mu_3$ -ppza)<sub>4</sub>Cl<sub>2</sub> - water - glycerol" system 72% for "Cu - water - glycerol" system, 53% and 47% for "Ni<sub>5</sub>( $\mu_5$ -pppmda)<sub>4</sub>Cl<sub>2</sub> - water - glycerol" system. The increase in thermal conductivity of similar systems made on the basis of aluminum nanoparticles (50-70 nm) and polycrystalline nickel microparticles is relatively small and is in the order of 20% and 5%, respectively (Fig. 19). The high increase in thermal conductivity of the microfluid based on Ni<sub>3</sub>( $\mu_3$ -ppza)<sub>4</sub>X<sub>2</sub> microparticles is explained by the high stability of the microparticles in the base fluid. This stability is directly related to the low density of Ni<sub>3</sub>-microparticles and the ability to form hydrogen bonds with water molecules.



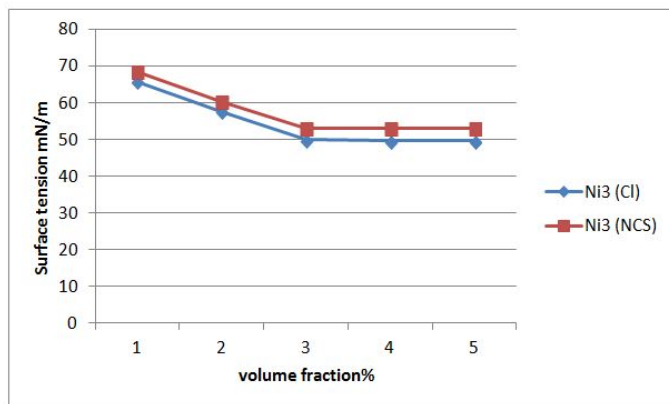
Nano and microfluidics	Ni <sub>3</sub> (NCS)	Ni <sub>3</sub> (Cl)	Cu	Ni <sub>5</sub>	Al (60 nm)	Al (100 nm)	Ni
Thermal conductivity, %	80	72	52.6	41.1	20.26	9.8	5.23

**Figure 19. Increase in thermal conductivity for various nano- and microfluids with a particle volume content of 5%**

It was determined that when the base fluid is Newtonian, the addition of Ni<sub>3</sub>( $\mu_3$ -ppza)<sub>4</sub>Cl<sub>2</sub> microparticles changes its rheological behavior to pseudoplastic.

As for the surface tension, its value decreases slightly as the

density of  $\text{Ni}_3(\mu_3\text{-ppza})_4\text{X}_2$  metal-string particles in the system increases and remains stable starting from 3% density (Figure 20).



Microfluidics	1%	2%	3%	4%	5%
Ni3(Cl)	65.8mN/m	57.6 mN/m	49.9 mN/m	49.6 mN/m	49.6 mN/m
Ni3(NCS)	68.4 mN/m	60.4 mN/m	53.2 mN/m	53 mN/m	53 mN/m

**Figure 20. Dependence of surface tension ( $\gamma_l$ ) on volume density of microparticles for " $\text{Ni}_3(\mu_3\text{-ppza})_4\text{X}_2$  - water - glycerol" microfluidic systems**

The lowest freezing temperature for the microfluidic systems " $\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2$  - water - glycerol" and " $\text{Ni}_3(\mu_3\text{-ppza})_4(\text{NCS})_2$  - water - glycerol" containing 5% by volume of microparticles, respectively -  $41^\circ\text{C}$  and  $-46^\circ\text{C}$  were determined, which proves that these systems have potential applications as coolants in small engine systems.

## RESULTS

1. For the first time, N-(pyridin-2-yl)pyrazin-2-amine (Hppza), a pyrazine-modulated asymmetric analog of di(2-pyridin)amine (Hdpa) and its mononuclear complex with copper(II), a coordination polymer with a one-dimensional zigzag structure and trinuclear string complexes with nickel(II) were synthesized. The structure of the complexes was determined by X-ray structural analysis. Electrochemical studies proved that the obtained trinuclear nickel-

strings  $[\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2]$  and  $[\text{Ni}_3(\mu_3\text{-ppza})_4(\text{NCS})_2]$  are more resistant to oxidation than the corresponding primary ligand complexes. [5,8,10]

2. Nickel(II) pentanuclear string and copper(II) linear tetranuclear complexes were synthesized for the first time on the basis of ligand  $\text{N,N}'\text{-di}(\text{pyrazin-2-yl})\text{pyridine-2,6-diamine}$  ( $\text{H}_2\text{dpzpd}$ ), in which the terminal pyridine rings were replaced by pyrazine. The structure of both complexes was determined by X-ray structural analysis, and their electrochemical and magnetic properties were thoroughly studied. The Cu(II) complex formed by  $\text{N,N-bis}(\alpha\text{-pyridyl})\text{-2,6-diaminopyridines}$  (PMN5) with symmetric and unsymmetric structures modulated by pyrazine, pyrimidine, and picoline was found to be the first such complex with copper(II). The nickel-string  $[\text{Ni}_5(\mu_5\text{-dpzpd})_4\text{Cl}_2]$  synthesized by electrochemical studies was proved to be the most resistant complex against oxidation among all five-nuclear nickel-strings based on oligo- $\alpha$ -aminopyridine ligands. [1,7]

3. Pyrimidine- and naphthyridine-modulated  $\text{H}_3\text{N}_9\text{-2pm}$  and pyrazine- and naphthyridine-modulated  $\text{H}_3\text{N}_9\text{-2pz}$  analogs of pentapyridyltetraamine were synthesized and based on them, one nickel atom was lost in the stable metal chain  $[\text{Ni}_{18}(\mu_8\text{-N}_9\text{-2pz})_4\text{Cl}_2](\text{PF}_6)_2$  and Octanuclear nickel strings  $[\text{Ni}_{18.33}(\mu_8\text{-N}_9\text{-2pm})_4(\text{NCS})_2](\text{PF}_6)_2$  were obtained. The structure of the complexes was determined by X-ray structural analysis. The results obtained from the magnetic measurements for these complexes confirmed the correctness of the mechanism, which claims that the magnetic interaction in nickel-strings occurs by means of metal atoms arranged along the chain. [3,6,9]

4. Made on the basis of modulated  $\text{N,N}'\text{-di}(\text{pyrazin-2-yl})\text{pyridin-2,6-diamine}$  ( $\text{H}_2\text{dpzpd}$ ),  $\text{N}(\text{pyridin-2-yl})\text{pyrazin-2-amine}$  ( $\text{Hppza}$ ) compounds and their metal complexes it was determined that the reagents have high biocide properties against corrosion-causing bacteria (sulfate-reducing-, thione- and hydrocarbon-oxidizing bacteria) and also a corrosion protection effect. [4]

5. Newly synthesized  $[\text{Ni}_3(\mu_3\text{-ppza})_4\text{X}_2]$  ( $\text{X} = \text{Cl}, \text{NCS}$ ) by adding microcrystals of nickel-strings to the base fluid (glycerol-

water) with high thermal conductivity " $\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2$  - water - glycerin" and " $\text{Ni}_3(\mu_3\text{-ppza})_4(\text{NCS})_2$  - water - glycerol" microfluids were prepared. When the amount of  $[\text{Ni}_3(\mu_3\text{-ppza})_4\text{X}_2]$  microparticles in microfluids is 5% by volume, their thermal conductivities determined by the "hot wire" method compared to the base fluid " $\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2$  - water - glycerin" and " $\text{Ni}_3(\mu_3\text{-ppza})_4(\text{NCS})_2$  - water - glycerol" systems were determined to be 72 and 80% higher, respectively. Both microfluids were found to have low freezing point ( $-41^\circ\text{C}$  and  $-46^\circ\text{C}$ ) and surface tension (50 mN/m to 53 mN/m) relative to the base fluid. As a reason for the high thermal conductivity of " $\text{Ni}_3(\mu_3\text{-ppza})_4\text{X}_2$ -glycerin-water" microfluids, nickel-string microparticles have been shown to be more stable in the base fluid than metal nanofluids due to hydrogen bonds. [6].

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1. Ismayilov, R. Linear pentanuclear nickel(II) and tetranuclear copper(II) complexes with pyrazine-modulated tripyridyldiamine ligand: Synthesis, structure and properties / R.H.Ismayilov, F.F.Valiyev, D.B.Tagiyev, You.Song, N.V.Israfilov, W.Z.Wang, G.H.Lee, S.M.Peng, B.A.Suleimanov// *Inorg. Chim. Acta*, -2018, v.483, -p.386–391, <https://doi.org/10.1016/j.ica.2018.08.045>
2. Suleimanov, B. Thermal-conductivity enhancement of microfluids with  $\text{Ni}_3(\mu_3\text{-ppza})_4\text{Cl}_2$  metal string complex particles / B.A.Suleimanov, H.F.Abbasov, F.F.Valiyev, R.H.Ismayilov, S.M.Peng // *Journal of Heat Transfer.*, January -2019, Vol.141/ 012404-1 – 012404-6
3. Ismayilov, R. Long chain metal string complex with one missed nickel atom: synthesis, crystal structure and properties / R.H.Ismayilov, F.F.Valiyev, N.V.Israfilov, W.Z.Wang, G.H.Lee, S.M.Peng, B.A.Suleimanov// *Chemical Problems*, -2019, v.17, -p.185-192
4. Vəliyev, F. *N,N'*-di(pirazin-2-il)piridin-2,6-diamin liqandı və onun metal kompleksləri əsasında hazırlanmış reagentlərin inhibitor və bakterisid xassələrinin tədqiqi // -Bakı: Neft



- təsərrüfatı jurnalı, - 2020. №8, - s.46-52.
5. Valiyev, F. Synthesis, crystal structure, spectral and magnetic properties of mononuclear copper(II) complex with pyrazine-modulated 2,2'-dipyridylamine // Azerbaijan Chemical Journal, -2020, 2, -p.78-82
  6. Ismayilov, R. Long chain defective metal string complex with modulated oligo- $\alpha$ -pyridylamino ligand: Synthesis, crystal structure and properties / R.H.Ismayilov, F.F.Valiyev, N.V.Israfilov, W.Z.Wang, G.H.Lee, S.M.Peng, B.A.Suleimanov // J. Mol. Struct. -2020, v.1200, -p.126998 <https://doi.org/10.1016/j.molstruc.2019.126998>
  7. Ismayilov, R., Valiyev, F., Wang, W., Lee, G.H., Peng, S.M. Linear pentanuclear nickel(II) complex with pyrazine-modulated tripyridyldiamine ligand//1st International Turkic World Conference on chemical Sciences and Technologies// Sarajevo, -Oct. -2015,-p.58
  8. Ismayilov, R., Valiyev, F., Wang, W., Lee, G.H., Peng, S.M. Linear trinuclear nickel (II) complexes and 1D zigzag chain copper (II) coordination polymer with pyrazine-modulated unsymmetrical N-(pyridin-2-yl)pyrazin-2-amine ligand //2<sup>nd</sup> International Turkic World Conference on chemical Sciences and Technologies, -Skopje, Macedonia, -26-30<sup>th</sup> October, -2016, -p.244
  9. Ismayilov, R., Valiyev, F., Wang, W., Lee, G.H., Peng, S.M., Suleimanov, B.A. Linear octanuclear nickel complex with pyrazine and naphthyridine modulated N<sup>2</sup> (pyrazin-2-yl)-N<sup>7</sup>-(2-(pyrazin-2-ylamino)-1,8-naphthyridin-7-yl)-1,8-naphthyridine-2,7-diamine ligand // 2<sup>nd</sup> International Turkic World Conference on chemical Sciences and Technologies, -Skopje, Macedonia, -26-30<sup>th</sup> October, -2016, -p.298
  10. Ismayilov, R., Valiyev, F., Israfilov, N., Wang, W., Lee, G.H., Peng, S.M., Suleimanov, B.A. 1-D zigzag chain copper(II) coordination polymer and mononuclear copper(II) complex with N-(pyridine-2-yl)pyrazin-2-amine ligand // Chemistry of coordination compounds: Actual problems of analytical chemistry. Materials of the Internationals Scientific Conference

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