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DEFECTIVE OCTANUCLEAR NICKEL COMPLEX WITH PYRAZINE AND NAPHTHYRIDINE MODULATED N^2 (PYRAZIN-2-YL)-N^7-(2-(PYRAZIN-2-YLAMINO)-1,8-NAPHTHYRIDIN-7-YL)-1,8-NAPHTHYRIDINE-2,7-DIAMINE LIGAND

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Abstract: *Defective metal string complex with one nickel(II) metal absent in center $[Ni_8(\mu_8\text{-}N_9\text{-}2pz)_4Cl_2](PF_6)_2$ (**2**) was obtained on the basis a pyrazine and naphthyridine-containing triamino ligand N^2-(pyrazin-2-yl)-N^7-(7-(pyrazin-2-ylamino)-1, 8-naphthyridin-2-yl)-1, 8-naphthyridine-2,7-diamine (H_3N_9-2pz) **(1)**. The small J value ($J = –2.96$ cm$^{–1}$) suggests quite a weak magnetic interaction throughout the molecule of complex **2**. The weak magnetic interaction in defective complex indicates that the spin exchange in metal string occurs through the metal core rather than the bridging ligands.*

Keywords: *naphthyridine and pyrazine -modulated oligo-α-pyridylamino ligand, metal–metal interactions, nickel complexes, magnetic properties*
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1. Introduction

In the past decade, numerous metal string complexes (also called "Extended Metal Atom Chain complexes" – EMACs) have been synthesized with various metals (Cu, Rh, Co, Ru, Ni, and Cr) and their magnetic and electronic properties extensively studied [1-6]. The chemistry of metal string complexes is of great interest in the field of molecular wire development [7]. Metal string complexes are known to be valuable for their interesting magnetic properties, as well as superconductivity [8].

The typical structure of this family includes a linear metal chain which is helically wrapped by four deprotonated oligo-α-pyridylamido ligands; all the pyridine nitrogen and amido nitrogen atoms are coordinated to the metal in a *syn* form. The adjacent pyridyl rings are not coplanar due to the repulsion of the b-H atoms, and the dihedral angle between adjacent pyridyl rings is about 45°. The M–M–M angle deviates only slightly from 180°. Recently we have synthesized modified oligo-α-pyridylamido ligands by replacing some of the pyridyl groups in the ligands with nitrogen-rich aromatic pyrazine rings and/or rigid and potentially redox-active naphthyridine groups. Using tuning ligands we have successfully synthesized longest heptacobalt, nonachromium, undecanickel string complexes, as well as 1D, 2D, and 3D copper(II) coordination polymers [3,6,9,10,11]. Also, we have been succesful in desinging a pyrazine- and naphthyridine-modulated ligand, N^2,N^7-di(pyrazin-2-yl)-1,8-naphthyridine-2,7-diamine (H_2dpznda) and a pyrimidine- and naphthyridine-modulated ligand, N^2-(pyrimidin-2-yl)-N^7-(2-(pyrimidin-2-ylamino)-1,8-naphthyridin-7-yl)-1,8-naphthyridine-2,7-diamine (H_3N_9-2pm) that showed the good reactivity and produced interesting defective metal string complexes with one metal lost in the center of metal chain [12,13].

Below is provided a new pyrazine- and naphthyridine-modulated oligo-α-pyridylamino ligand, N^2-(pyrazin-2-yl)-N^7-(7-(pyrazin-2-ylamino)-1,8-naphthyridin-2-yl)-1,8-naphthyridine-2,7-diamine (H_3N_9-2pz) (**1**) and its nickel string complex $[Ni_8(\mu_8\text{-}N_9\text{-}2pz)_4Cl_2](PF_6)_2$ (**2**).

2. Experimental

2.1. Materials and measurements

All reagents and solvents were obtained from commercial sources and used without further purification unless otherwise was provided.

IR spectra were performed from KBr pellets with a Thermo Scientific Nicolet iS 10 FT-IR Spectrometer in the range of 500-4000 cm^{-1}. Absorption spectra were recorded on Shimadzu UVmini-1240 UV-VIS spectrophotometer. Proton NMR spectra recorded in dimethyl sulfoxide-d_6 (DMSO-d_6). All NMR chemical shifts recorded as δ values in parts per million (ppm) and coupling constants (J) are given in hertz (Hz).

2.2. Crystal structure determinations

The chosen crystal was mounted on a glass fiber. Data collection was carried out on a NONIUS KappaCCD diffractometer at 150(2) K using a Mo-Kα radiation (λ = 0.71073 Å) and a liquid nitrogen low-temperature controller. Cell parameters were retrieved and refined using DENZO-SMN software on all reflections. Data reduction was performed on SHELXTL software. Semi-empirical absorption was based on symmetry-equivalent reflections and absorption corrections were applied with the DENZO-SMN program. The structure was solved using SHELXS-97 and refined with SHELXL-97 by full matrix least squares on F2 values [14, 15]. The details of the X-ray diffraction experiment and the main crystallographic data of the nickel-string complex **2** are given below:

Empirical formula $C_{105}H_{85}Cl_2Ni_8N_{45}P_2F_{12}O_{11}$; formula weight = 2903.70; crystal system – monoclinic; space group - P2 (1)/n; a = 23.4552(8), b = 20.5625(7), c = 24.9815(8) Å; α = 90.00; β = 93.7529(18); γ = 90.00°; объем = 12022.7(7) Å^3, Z = 4; density(calculated) = 1.604 мг/м^3; absorption coefficient = 1.387 мм$^{-1}$; crystal size: 0.30x0.10x0.05 мм^3; θ range for data collection ~ 1.52– 25.00˚; reflection collected - 59984, independent reflection - 21182 [R(int) = 0.1144]; R_1-factor = 0.1160, wR2[I >2σ(I)] = 0.2576, R_1 = 0.2866, wR2 = 0.3491; GOF = 1.179.

The *R* factors for **2** are reasonable and acceptable, despite they are higher than usual because (a) the molecule is large and contains solvent (CH_3OH and $(C_2H_5)_2O$)) molecules which escape quickly during the data collection and (b) some atoms were found in disordered positions in every molecule. We carefully examined structures and concluded that the P2 (1)/n option is best.

2.3. Synthesis

N^2-(pyrazin-2-yl)-N^7-(7-(pyrazin-2-ylamino)-1,8-naphthyridin-2-yl)-1,8-naphthyridine-2,7-diamine (1).

A mixture of bis(2-chloro-1,8-naphthyridin-7-yl)amine (7.2 g, 21.0 mmol) [12], 2- aminopyrazine (4.8 g, 50.4 mmol), *t*-BuONa (6.84 g, 70.8 mmol), $Pd_2(dba)_3$ (0.64 g, 4 mol-%, dba = dibenzylideneacetone) and BINAP (1.05 g, 9.6 mol-%, BINAP = 2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl) were placed in a flame-dried flask under argon. The mixture was stirred and refluxed in toluene (350 mL) for 72 h. After cooling to room temperature, the solvent was removed using a rotary evaporator. The mixture was washed with water. The resulting dark solid was recrystallized from dmf/ethyl acetate/methanol (1:20:1) and gave pure H_3N_9-2pz as a light yellow-orange solid. Yield 6.83 g (70 %). IR (KBr) ʋ/cm^{-1}: 3360 w, 3220 m, 3030 m, 1600 s, 1580 s, 1560 m, 1492 s, 1444 s, 1422 s, 1380 m, 1330 s, 1258 m, 1135 m, 840 m, 790 m, 648 w, 444 w; UV/Vis (DMF) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 275 (3.25 × 10^4), 338 (6.10 × 10^3), 352 (1.32 × 10^4); ^{1}H NMR (400 MHz, $(CD_3)_2SO$): δ =10.50 (s, 1H), 10.30 (s, 2H), 8.37–8.35 (d, J = 8.4Hz, 2H), 7.94 (s, 2H), 7.90–7.88 (d, J = 8.4 Hz, 2H), 7.80–7.77 (m, 4H), 6.77–6.74 (m, 4H); MS(FAB): m/z (%) 460 (75) [M]$^+$; Elemental analysis (%) $C_{24}H_{17}N_{11}$ [H_3N_9-2pz] (459.47): calc.: C 62.74, H 3.73, N 33.53; found: C 62.80, H 3.92, N 33.61.

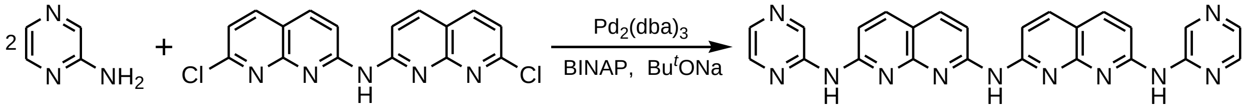
[$Ni_8(\mu_8$-N_9-2pz$)_4Cl_2](PF_6)_2$ (2).

Anhydrous $NiCl_2$ (339 mg, 2.62 mmol), H_3N_9-2pz (500 mg, 1.09 mmol) and naphthalene (60 g) were mixed and heated at ca. 170–180 °C under argon. After 12 h, a solution of potassium *tert*-butoxide (322 mg, 2.87 mmol) in *n*-butyl alcohol (6 mL) was added dropwise. The reaction was continued for another 2 h, and then KPF_6 (610 mg, 3.3 mmol) was added. After that the mixture was left to cool to about 50 °C and then hexane was added to wash out the naphthalene. The solid was extracted with benzene and recrystallized from dichloromethane/diethyl ether solution to give deep brown-purple crystals. Single crystals were obtained by diffusion of diethyl ether into a solution of **2** in CH_2Cl_2/CH_3OH (1:2). Yield: 132 mg (18%). IR (KBr) υ/cm^{-1}: 3450 (w), 1587 (m), 1568 (m), 1492 (s), 1446 (m), 1414 (m), 1328 (s), 1289 (m), 1142 (m), 842 (w), 785 (w), 664 (w), 561 (w) cm^{-1}. UV/Vis (CH_2Cl_2) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 230 (1.41 × 10^5), 268 (1.38 ×10^5), 447 (1.62 × 10^5), 632 (7.24 × 10^3) nm. MS (MALDI): *m*/*z* (%) 2294(48) [M – 2Cl]$^+$. $C_{97}H_{60}Cl_2N_{44}Ni_8P_2F_{12}O$ [**2**·CH_3OH] (2688.19): calcd. C 43.34, H 2.25, N 22.93; found C 43.48, H 2.32, N 22.82.

3. Results and discussion

3.1. Syntheses

The ligand N^2-(pyrazin-2-yl)-N^7-(7-(pyrazin-2-ylamino)-1,8-naphthyridin-2-yl)-1,8-naphthyridine-2,7-diamine (H_3N_9-2pz) **1** was synthesized by palladium-catalyzed cross-coupling of bis(2-chloro-1,8-naphthyridin-7-yl)amine and 2-aminopyrazine, in the presence of catalysts [$Pd_2(dba)_3$, BINAP, Bu^{t}ONa] in refluxing toluene under argon (Scheme 1), and characterized by IR, ^{1}H NMR and MS(FAB).



H_3N_9-2pz (**1**)

$$4H_3N_9\text{-}2pz + 9NiCl_2 \xrightarrow[\text{Naphthaline}]{Bu^tOK,\ KPF_6} [Ni_8(\mu_8\text{-}N_9\text{-}2pz)_4Cl_2](PF_6)_2$$

(**2**)

Scheme 1. Synthesis of H_3N_9-2pz (**1**) and its octanickel complex (**2**).

The defective octanuclear complex [$Ni_8(\mu_8$-N_9-2pz$)_4Cl_2](PF_6)_2$ (**2**) was obtained by the reaction of anhydrous $NiCl_2$ with the H_3N_9-2pz ligand in an argon atmosphere employing naphthalene as solvent and Bu^{t}OK as a base to deprotonate the amine groups.

3.2. Structure

The crystal structure of **2** is shown in Fig. 1. Selected bond distances and angles are shown in Table 1. Complex **2** is dicationic molecule associated with two PF_6^- anions as counter anions. The complex consists of eight nickel (II) atoms in a linear chain with Ni–Ni–Ni angles in the range of 179.0–179.7°. There are four equatorial ligands in a molecule, wrapping around the metal string in a syn–syn form as trianion helixes; the axial chloride ligands are collinear with the Ni_8 axis; the whole length of the Ni_8 chain is 18.3 Å. The nonadentate ligand H_3N_9-2pz is expected to form metal-strings with nine metal centers instead of the octanickel compound **2**. This is a typical example of a nickel-defective metal-string with the absence of one metal atom in the metal-atom chain related to the naphthyridine moiety [13]. It crystallizes in space group $P2_1/n$ of the monoclinic system. In complex **2**, the Ni-Ni distances range from 2.266(2) to 2.400(2) Å, the terminal distance (Ni(1)–Ni(2)) is the longest and the distance of Ni–Ni bonded to naphthyridine units (Ni(3)–Ni(4)) is the shortest. The Ni(3)–Ni(4) distance (2.266(2) Å) is significantly longer than that in defected octanickel complex $[Ni_8(\mu_8\text{-}N_9\text{-}2pm)_4Cl_2](PF_6)_2$ (2.225(9) Å) with pyrimidyl- and naphthyridyl-modulated pentapyridyltetramine ligand (H_3N_9-2pm) [12]. It is important to note that the Ni – Cl distances of complex **2** are also shorter than in case of complex $[Ni_8(\mu_8\text{-}N_9\text{-}2pm)_4Cl_2](PF_6)_2$. Compare with the Ni-Cl bond distance (Ni-Cl=2.3290(3) Å) of the pyrimidyl- and naphthyridine-modulated pentapyridyltetramine ligand complex $[Ni_8(\mu_8\text{-}N_9\text{-}2pm)_4Cl_2](PF_6)_2$, the relatively short Ni-Cl distances (2.298(4) and 2.319(4) Å) of **2**, maybe result from a stronger ligand field providing by the two-pyrazine containing ligand H_3N_9-2pz. This phenomenon was also observed in our previous work with pyrazine-modulated ligands [16]. Two terminal Ni (II) ions bonded with the axial ligands are in a square-pyramidal (NiN_4Cl) environment and exhibit long Ni–N bonds (Ni (1)–N_{av} = 2.091(14) and Ni(8)–N_{av} = 2.075(14) Å), which are consistent with a high-spin Ni(II) configuration. However, all shorter inner Ni–N distances, ranging from 1.889(13) to 1.962(11) Å, indicate Ni (II) with a low spin state S=0.

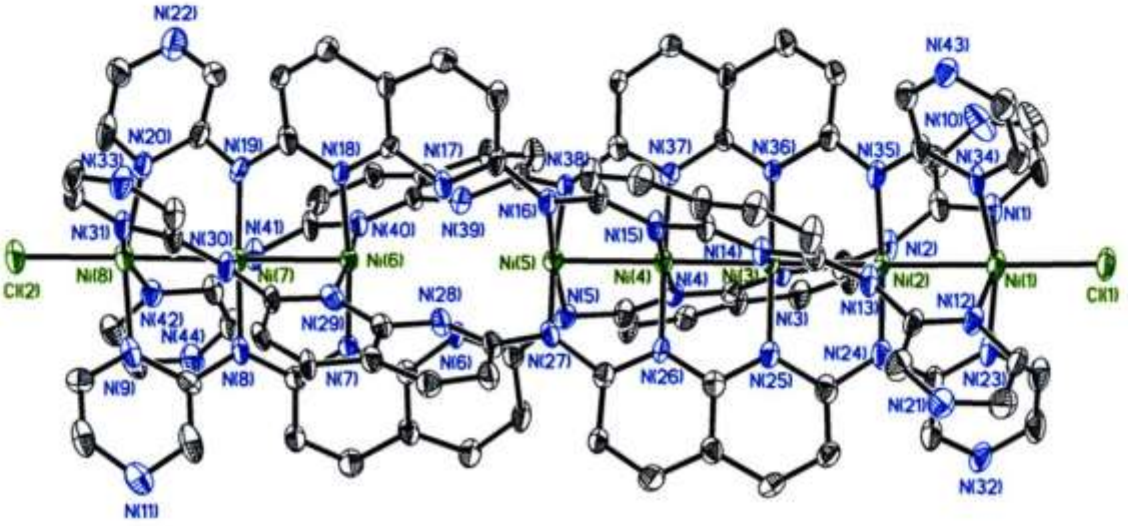


Figure 1. The molecular structure of dicationic complex in $[Ni_8(\mu_8\text{-}N_9\text{-}2pz)_4Cl_2](PF_6)_2$. (**2**). Thermal ellipsoids are drawn at the 20% probability level. The hydrogen atoms have been omitted for clarity.

In our opinion, the defect complex comes from the rigid structure and unsaturated coordination of the supporting ligands of naphthyridines resulting just in one nitrogen atom of each naphthyridine coordinated to the metal atom. As has previously been noted, the electronic structure of EMACs depends on both the metal and ligands [16]. All the known defective metal string complexes, including also complex **2** are very stable although the entire metal core has been off due to the lack of one central metal atom. Therefore it can be assumed that the steric force from four helical wrapping ligands may be responsible for the formation of the metal chain.

Table 1. Selected bond distances (Å) and angles (^{o}) for **2**.

2			
Ni(1)-Ni(2)	2.400(2)	Ni(2)-Ni(3)	2.313(2)
Ni(3)-Ni(4)	2.266(2)	Ni(4)-Ni(5)	2.306(3)
Ni(6)-Ni(7)	2.350(2)	Ni(7)-Ni(8)	2.319(4)
Ni(1)-N_{av}	2.091(14)	Ni(2)-N_{av}	1.891(13)
Ni(3)-N_{av}	1.927(11)	Ni(4)-N_{av}	1.951(11)
Ni(5)-N_{av}	1.952(12)	Ni(6)-N_{av}	1.962(11)
Ni(7)-N_{av}	1.889(13)	Ni(8)-N_{av}	2.075(14)
Ni(1)-Cl(1)	2.298(4)	Ni(8)-Cl(2)	2.319(4)
Cl(1)-Ni(1)-Ni(2)	178.76(17)	Ni(1)-Ni(2)-Ni(3)	179.09(13)
Ni(2)-Ni(3)-Ni(4)	179.42(13)	Ni(3)-Ni(4)-Ni(5)	179.57(12)
Ni(6)-Ni(7)-Ni(8)	179.06(13)	N-Ni(1)-Ni(2)-N	22.97
N-Ni(2)-Ni(3)-N	17.88	N-Ni(3)-Ni(4)-N	14.50
N-Ni(4)-Ni(5)-N	16.07	N-Ni(5)-Ni(6)-N	18.80
N-Ni(6)-Ni(7)-N	23.98		

Ni-N_{av}: average value from the four wrapping ligands.

In our previous work, we reported on a new pyrimidyl and naphthyridine-modulated pentapyridyltetramine ligand (H_3N_9-2pm) and its linear nona- and octanickel chain complexes [12]. However, in the case of H_3N_9-2pz in similar condition to get a suitable single crystal for X-Ray measurement for nonanickel metal string complex was unsuccessful even despite that mass spectrometry analysis clearly shows the formation of this compound (MS (MALDI): m/z (%) 2424 (100) $[M+H]^+$ – parent peak in the mass spectra).

3.3. Magnetic properties

The magnetic susceptibility of complex **2** was measured over a temperature range of 5–300 K. The observed $\chi_M T$ value of **2** at room temperature (300 K) was 2.28 emu K mol^{-1} to comply with high-spin dinuclear nickel(II) complexes (uncoupled spin-only for dinickel compound $\chi_M T$ = 2.00 emu K mol^{-1}) [5,17]. The Ni(II) ions with d^8 electrons are divided into two states, high-spin $S = 1$ and low-spin $S = 0$ configurations. According to the structural analysis of $[Ni_8(\mu_8\text{-}N_9\text{-}2pz)_4Cl_2](PF_6)_2$, both terminal nickel(II) atoms are in spin state $S = 1$ and all other inner nickel(II) atoms are in spin state $S = 0$. When the system was cooled down from room temperature, the $\chi_M T$ value decreased in a very smooth fashion to a value of 1.86 emu K mol^{-1} at 20 K, then declined rapidly to 1.28 at 5 K (Fig.2). This indicates an antiferromagnetic interaction. The experimental results were in excellent agreement with the theoretical analyses, for a dinuclear system deduced from the spin Hamiltonian equation $\boldsymbol{H} = -J\mathbf{S}_1\mathbf{S}_2$ ($S_1 = S_2 = 1$) (eqn. (1) and (2)) [17]. The fitting parameters for **2** are $J = -2.96$ cm^{-1} and $g = 2.008$ with TIP = $8.3\times10^{-4} cm^3 mol^{-1}$.

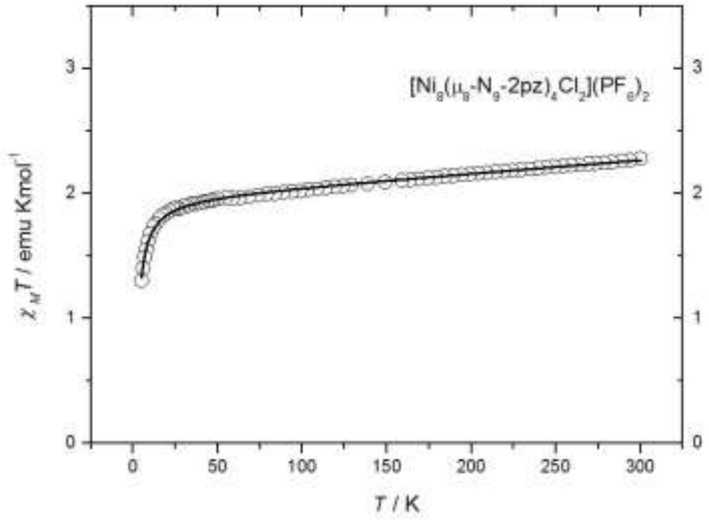


Figure 2. Plots of $\chi_M T$ vs. T for compound **2**. Solid line results from least-squares fit.

The small *J* value suggests quite a weak magnetic interaction throughout the molecule of **2** which is comparable with the magnetic coupling of similar defected octanuclear complex of $[Ni_8(\mu_8\text{-}N_9\text{-}2pm)_4Cl_2](PF_6)_2$ ($J = -1.66$ cm^{-1} and $g = 2.03$, TIP = 1.08×10^{-3} cm^3 mol^{-1}) [12]. In considering that the metal chain is defective due to one missing metal atom, the very weak magnetic interaction indicates that the spin exchange in metal string occurs through the metal core rather than the bridging ligands and is consistent to our previous reports on the nickel string complexes [12,15].

Conclusions

By using naphthyridine and pyrazine modulated novel bridging ligand N^2-(pyrazin-2-yl)-N^7-(7-(pyrazin-2-ylamino)-1,8-naphthyridin-2-yl)-1,8-naphthyridine-2,7-diamine **1**, defective nickel metal string **2** was obtained. The metal chain in **2** is defective because of one missing metal atom to consist of eight nickel atoms in a straight line with a Ni_8 core. The Ni_8^{16+} complex reveals weak antiferromagnetic coupling of *ca.* –2.96 cm^{-1} between two terminal nickel(II) ions of high-spin states ($S = 1$) in line with our previous reports on the defective multi-nickel complexes.

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PİRAZİN VƏ NAFTİRİDİNLƏ MODULLAŞDIRILMIŞ N^2(PİRAZİN-2-İL)-N^7-(2-(PİRAZİN-2-İLAMİNO)-1,8-NAFTİRİDİN-7-İL)-1,8-NAFTİRİDİN-2,7-DİAMİN LİQANDININ DEFEKTLİ SƏKKİZ NÜVƏLİ KOMPLEKSİ

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Yeni pirazin və naftiridinlə modullaşdırılmış N^2(pirazin-2-il)-N^7-(2-(pirazin-2-ilamino)-1,8-naftiridin-7-il)-1,8-naftiridin-2,7-diamin liqandı əsasında, mərkəzində bir nikel atomu itmiş *defektli* $[Ni_8(\mu_8\text{-}N_9\text{-}2pz)_4Cl_2](PF_6)_2$ *(**2**) metal strinq kompleksi sintez olunmuşdur. J kəmiyyətinin kiçik qiyməti (J = –2.96 sm*$^{-1}$*) kompleks molekulunda maqnit qarşılıqlı təsirin kiçik olduğunu göstərir. Defektli metal strinq kompleksdə maqnit qarşılıqlı təsirin zəif olması, metal strinqdə spin mübadiləsinin körpü liqandlarla deyil, metal zənciri boyu getdiyini göstərir.*

Açar sözlər: *naftiridin və pirazinlə modullaşdırılmış oliqo-α-piridilamin liqandı, metal–metal qarşılıqlı təsiri, nikel kompleksləri, maqnit xassələri*

ДЕФЕКТНЫЙ ОКТАЯДЕРНЫЙ НИКЕЛЕВЫЙ КОМПЛЕКС С ПИРАЗИН И НАФТИРИДИН МОДУЛИРОВАННЫМ ЛИГАНДОМ N^2 (ПИРАЗИН-2-ИЛ)-N^7-(2-(ПИРАЗИН-2-ИЛАМИНО)-1,8-НАФТИРИДИН-7-ИЛ)-1,8-НАФТИРИДИН-2,7-ДИАМИН

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Синтезирован новый пиразин- и нафтиридин-модулированный лиганд N^2 *-(пиразин-2-ил)-N*^{7}*-(2-(пиразин-2-иламино)-1,8-нафтиридин-7-ил)-1,8-нафтиридин-2,7-диамин **(1)** и дефектный октаядерный никелевый комплекс **(2)** на его основе. Небольшое значение J (J = –2.96 см – 1) свидетельствует о достаточно слабом магнитном взаимодействии через молекулы комплекса **2**. Слабое магнитное взаимодействие в дефектном комплексе указывает на то, что спиновый обмен в металл стринге происходит через металлическое ядро комплекса, а не через мостиковый лиганд.*

Ключевые слова: *нафтиридин и пиразин-модулированный олиго-α-пиридиламиновый лиганд, металл-металл взаимодействие, никелевые комплексы, магнитные свойства*