

UDC 539.2



## STUDY ON A NEW POLYDENTATE PYRIDYLAMINE AND ITS COMPLEXES: SYNTHESIS, SUPRAMOLECULAR STRUCTURE AND PROPERTIES

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New ligand, N<sup>2</sup>-(6-aminopyridin-2-yl)-N<sup>6</sup>-(pyridin-2-yl)pyridine-2,6-diamine (abbreviated as tripyridyltriamine – H<sub>3</sub>tptra) (1), its protonated analog [H<sub>4</sub>tptra](ClO<sub>4</sub>) (2) and copper(II) (3), nickel(II) (4), iron(II) (5) and cobalt(II) (6) complexes have been synthesized and structurally characterized. The protonated ligand cation (2) exhibits an *anti-anti-syn-anti-syn* conformation. H<sub>3</sub>tptra coordinates to the Cu(II) as a quadridentate ligand in 3. The copper(II) ion is six-coordinated in an elongated octahedral coordination geometry. The perchlorate anions are relatively weakly coordinated in the axial positions. In complexes Ni(II), Fe(II) and Co(II) two ligands are bound directly to the metal ion as tridentate to give a MN<sub>6</sub> chromophore (M-metal atom). Extensive hydrogen bonds are formed and construct the compound 2 into 1D and 3 into 3D supramolecular structure, whereas dimer structure have been found for 4 and 5 complexes through hydrogen bonds. X-band EPR spectra of Cu(II) complex showed well-resolved hyperfine structure resulting from the two paramagnetic isotopes <sup>63</sup>Cu and <sup>65</sup>Cu ( $g = 2.128$  and  $A^0 = 62.7 \times 10^{-4} \text{ cm}^{-1}$ ) and also superhyperfine coupling from four <sup>14</sup>N ( $I = 1$ ) atoms, yielding  $A_{\parallel}^N = 16 \times 10^{-4} \text{ cm}^{-1}$  and  $A_{\perp}^N = 9 \times 10^{-4} \text{ cm}^{-1}$ . The magnetic behavior of 6 obeys the Curie-Weiss law. The best fitting result according to the Curie-Weiss expression leads to a value of  $g = 2.49$  and  $\theta = -3.71 \text{ K}$ .

**Key words:** pyridylamine ligand, transition metal complexes, hydrogen bonds, supramolecular structure.

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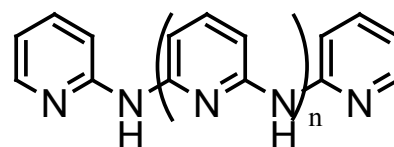
### 1. Introduction

The variety of coordination mode of multidentate ligands is a fascinating topic. Oligo- $\alpha$ -pyridylamino ligands (Scheme 1) have attracted increasing attention over the past two decades owing to their capability to support linear metal chain and lead to so called «Extended Metal Atom Chain» (EMAC) complexes [1–4]. Oligo- $\alpha$ -pyridylamido ligands coordinate to metal atoms in a variety of ways [5,6]. In EMACs the supporting ligands are coordinated to metals in all-*syn* form, whereas all-*anti* form style was observed in mononuclear complexes [1–13]. The free ligands exhibit helical structure, and molecules are paired *via* hydrogen bonds between –NH groups [14].

Compared with oligo- $\alpha$ -pyridylamino ligands of two terminal pyridyl ends (Scheme 1), oligo- $\alpha$ -pyridylamino ligands with even number of pyridyl and amine group (Scheme 2) are more interesting but less studied. With a terminal –NH<sub>2</sub> group at the end, the ligands have more opportunity for the formation of hydrogen bonds, thus are more interesting of building supramolecular architecture. When coordinated to metal to form a metal string complex, the ligand is more negative-charged and produce neutral metal string complexes without axial ligands [7]. The terminal –NH<sub>2</sub> group is active to coordinate even when the ligands react with metal at room temperature. This family of compounds is also important starting materials for the synthesis of long oligo- $\alpha$ -pyridylamino ligands by cross-coupling

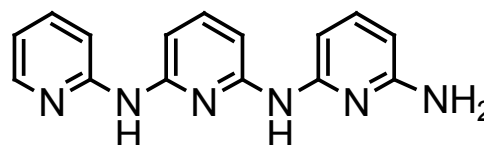
reaction with aryl halide in the presence of palladium catalyst and the appropriate phosphine ligand [15–18]. Here, we report a new synthesized aryl amine ligand, N<sup>2</sup>-(6-aminopyridin-2-yl)-N<sup>6</sup>-(pyridin-2-yl)pyridine-2,6-diamine (H<sub>3</sub>tptra) (1), its protonated analog [H<sub>4</sub>tptra](ClO<sub>4</sub>) (2), copper (II) complex [Cu(H<sub>3</sub>tptra)(ClO<sub>4</sub>)<sub>2</sub>] (3), cobalt (II) complex [Co(H<sub>3</sub>tptra)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (4), nickel (II) complex [Ni(H<sub>3</sub>tptra)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (5) and iron(II) complex [Fe(H<sub>3</sub>tptra)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (6). H<sub>3</sub>tptra is an important intermediate compound for the synthesis of the long-chain oligo- $\alpha$ -pyridylamino ligands and as well as a polydentate nitrogen-heterocyclic ligand (Scheme 2).

Scheme 1. Oligo- $\alpha$ -pyridylamine ligands:



$n = 0$ , Hdpa;  $n = 1$ , H<sub>2</sub>tpda.

Scheme 2. H<sub>3</sub>tptra



## 2. Experimental

### 2.1. Materials and measurements

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

**Caution!** Perchlorate salts are potentially explosive and should only be used in small quantities and handled with the necessary precautions.

Absorption spectra were recorded on JASCO V-550 UV/VIS spectrophotometer. IR spectra were performed from KBr pellets with a Perkin Elmer FT-IR Spectrometer PARAGON 1000 in the range of 400–4000  $\text{cm}^{-1}$ . FAB-MS mass spectra were obtained with a JEOL JMS-700 HF double focusing spectrometer operating in the positive ion detection mode. Elemental analyses were performed on a Perkin-Elmer CHN 2400. Molar magnetic susceptibility was recorded on a SQUID system with 2000 GAUSS external magnetic field. X-band EPR spectra were recorded on a Bruker E500 spectrometer equipped with a Bruker TE102 cavity. Sample temperature at 77 K was maintained using a finger Dewar filled with liquid nitrogen.

### 2.2. Preparation of $N^2$ -(6-aminopyridin-2-yl)- $N^6$ -(pyridin-2-yl)pyridine-2,6-diamine ( $H_3tptra$ ) (1)

The reaction of 6-bromo- $N$ -(pyridin-2-yl)pyridin-2-amine (10.0 g, 0.04 mol) and 2,6-diaminopyridine (5.23 g, 0.05 mol) in the presence of  $Pd_2(dba)_3$  (0.55 g, 1.5 %mol.), BINAP (0.75 g, 3 %mol.) and  $Bu^ONa$  (5.0 g, 0.05 mol) in benzene (300 mL) under an argon atmosphere for 48 h gave a crude product of 1. Purification by column chromatography over silica gel with dichloromethane–acetone (4:1) as eluent gave colorless crystals of 1 after evaporation (7.0 g, 63% yield); IR (KBr)  $\nu/\text{cm}^{-1}$  = 3430 m, 3326m, 3203m, 3134w, 1631s, 1586s, 1523m, 1464s, 1439s, 1361w, 1247m, 1217m, 1143s, 1115s, 1086s, 876w, 776m, 626m, 518w, 457w; UV/Vis ( $CH_3OH$ )  $\lambda_{max}/nm$  ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) = 230 ( $1.19 \times 10^4$ ), 274 ( $1.81 \times 10^4$ ), 341 ( $2.29 \times 10^4$ );  $^1H$  NMR (400 MHz,  $(CD_3)_2SO$ , 25°C):  $\delta$  9.28 (s, 1H, -NH), 8.80 (s, 1H, -NH), 8.19–8.16 (m, 1H, Ar-H), 7.92–7.90 (d,  $J = 8.0$  Hz, 1H, Ar-H), 7.62–7.58 (m, 1H, Ar-H), 7.44–7.40 (t,  $J = 8.0$  Hz, 1H, Ar-H), 7.27–7.17 (m, 2H, Ar-H), 7.08–7.06 (d,  $J = 8.0$  Hz, 1H, Ar-H), 6.84–6.80 (m, 2H, Ar-H), 5.94–5.92 (d,  $J = 8.0$  Hz, 1H, Ar-H), 5.62 (s, 2H, -NH<sub>2</sub>); MS (FAB):  $m/z$  (%) 279 (100)  $[M]^+$ ; EA (%)  $C_{15}H_{14}N_6$ : calc. C 64.73, H 5.07, N 30.20; found: C 64.65, H 4.99, N 29.85.

### 2.3. Preparation of $[H_4tptra](ClO_4)$ (2)

A mixture of  $H_3tptra$  (0.10 g, 0.36 mmol) and  $HClO_4$  (0.04 g, 0.38 mmol)\* was stirred in methanol (50 mL) for 1 h. Then the solution was filtered to remove insoluble impurities. Diffusing ether into the filtrate provided light brown single crystals suitable for X-ray analysis (0.03 g, 22% yield); IR (KBr)  $\nu/\text{cm}^{-1}$  = 3323m, 3244m, 3136w, 3077w, 1638s, 1592s, 1524m, 1491m, 1450s, 1242w, 1143s, 1116s, 1086s, 795m, 627m, 517w, 420w; UV/Vis ( $CH_3OH$ )  $\lambda_{max}/nm$  ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) = 228 ( $1.10 \times 10^4$ ), 262 ( $1.26 \times 10^4$ ), 326 ( $1.38 \times 10^4$ ), 340 (sh) ( $1.24 \times 10^4$ ), 366 (sh) ( $6.50 \times 10^3$ ); EA (%)  $C_{15}H_{15}ClN_6O_4$ : calcd. C 47.56, H 3.99, N 22.19; found: C 47.89, H 3.77, N 22.04.

\* 60% water solution of perchloric acid has been used.

### 2.4. Preparation of $[Cu(H_3tptra)(ClO_4)_2]$ (3)

A mixture of  $H_3tptra$  (0.10 g, 0.36 mmol) and  $Cu(ClO_4)_2 \cdot 6H_2O$  (0.14 g, 0.38 mmol) in methanol (50 mL) was stirred overnight. Then the solution was filtered to remove insoluble impurities. Diffusing ether into the filtrate provided blue single crystals suitable for X-ray analysis (0.11 g, 56% yield); IR (KBr)  $\nu/\text{cm}^{-1}$  = 3431m, 3337m, 3202m, 3132w, 1633s, 1587s, 1522m, 1468s, 1439s, 1368w, 1249w, 1217m, 1170m, 1143s, 1116s, 1086s, 884w, 776m, 627m, 520m, 461w; UV/Vis ( $CH_3OH$ )  $\lambda_{max}/nm$  ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) = 228 ( $1.13 \times 10^4$ ), 246 ( $1.29 \times 10^4$ ), 326 ( $1.23 \times 10^4$ ), 358 ( $8.20 \times 10^3$ ), 538 ( $1.29 \times 10^2$ ); MS (FAB):  $m/z$  (%) 440 (20)  $[M-ClO_4]^+$ , 341 (80)  $[M-2ClO_4]^{2+}$ ; EA (%)  $C_{15}H_{14}Cl_2CuN_6O_8 \cdot 2H_2O$ : calcd. C 31.24, H 3.14, N 14.57; found: C 31.31, H 3.18, N 14.85.

### 2.5. Preparation of $[Ni(H_3tptra)_2](ClO_4)_2$ (4)

A mixture of  $H_3tptra$  (0.05 g, 0.18 mmol) and  $Ni(ClO_4)_2 \cdot 6H_2O$  (0.07 g, 0.19 mmol) in methanol (25 mL) was stirred overnight. Then the solution was filtered to remove insoluble impurities and concentrated to 5 mL under vacuum. Diffusing ether into the  $CH_3OH$  solution provided yellow single crystals suitable for X-ray analysis (0.04 g, 55% yield); IR (KBr)  $\nu/\text{cm}^{-1}$  = 3444 m, 3248 m, 3186 m, 3098 m, 3032 m, 1580 s, 1526 s, 1438 s, 1357 m, 1309 s, 1295m, 1163 m, 885 w, 797 m, 613 w, 516 w; UV/Vis ( $CH_3OH$ )  $\lambda_{max}/nm$  ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) = 222 ( $7.21 \times 10^3$ ), 253 ( $2.61 \times 10^4$ ), 317 ( $2.99 \times 10^4$ ), 364 ( $2.31 \times 10^4$ ), 545 (9.30), 866 (4.37); MS (FAB):  $m/z$  (%) 713 (5)  $[M-ClO_4]^+$ , 613 (5)  $[M-2ClO_4]^{2+}$ ; EA (%)  $C_{30}H_{28}Cl_2N_{12}NiO_8$ : calcd. C 44.25, H 3.47, N 20.67; found: C 44.32, H 3.59, N 20.49.

### 2.6. Preparation of $[Fe(H_3tptra)_2](ClO_4)_2$ (5)

Compound 5 was synthesized using a procedure similar to that for 4 except that  $Fe(ClO_4)_2 \cdot xH_2O$  was used instead of  $Ni(ClO_4)_2 \cdot 6H_2O$  (yield: 42%). IR (KBr)  $\nu/\text{cm}^{-1}$  = 3430s, 3341s, 3202s, 3133m, 1631s, 1586s, 1467s, 1439s, 1143s, 1115s, 1087s, 776m, 627m, 519w, 420w; UV/Vis ( $CH_3OH$ )  $\lambda_{max}/nm$  ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) = 230 ( $3.70 \times 10^4$ ), 251 ( $4.53 \times 10^4$ ), 323 ( $4.27 \times 10^4$ ), 366 ( $3.40 \times 10^4$ ); MS (FAB):  $m/z$  (%) 811 (2)  $[M]^+$ , 611 (20)  $[M-2ClO_4]^{2+}$ ; EA (%)  $C_{30}H_{28}Cl_2N_{12}FeO_8$ : calcd. C 44.41, H 3.48, N 20.72; found: C 44.51, H 3.54, N 20.58.

### 2.7. Preparation of $[Co(H_3tptra)_2](ClO_4)_2$ (6)

Compound 6 was synthesized using a procedure similar to that for 4 except that  $Co(ClO_4)_2 \cdot 6H_2O$  was used instead of  $Ni(ClO_4)_2 \cdot 6H_2O$  (yield: 52%); IR (KBr)  $\nu/\text{cm}^{-1}$  = 3429m, 3337m, 3202m, 3132m, 1632s, 1586s, 1522m, 1487s, 1439s, 1367w, 1249w, 1216m, 1170m, 1143s, 1117s, 1087s, 887w, 776m, 627m, 521w, 461w; UV/Vis ( $CH_3OH$ )  $\lambda_{max}/nm$  ( $\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ ) = 221 ( $1.91 \times 10^4$ ), 254 ( $1.78 \times 10^4$ ), 330 ( $1.70 \times 10^4$ ), 364 ( $9.60 \times 10^3$ ); MS (FAB):  $m/z$  (%) 714 (30)  $[M-ClO_4]^+$ , 614 (50)  $[M-2ClO_4]^{2+}$ ; EA (%)  $C_{30}H_{28}Cl_2CoN_{12}O_8 \cdot H_2O$ : calcd. C 43.28, H 3.63, N 20.19; found: C 43.51, H 3.52, N 20.29.

## 2.8. Crystal structure determinations

The chosen crystals were mounted on a glass fiber. Data collection was carried out on a NONIUS Kappa CCD diffractometer at 150(1) K using a Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) 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 for protonated ligand (2) and on DENZO-SMN software for complexes 3–6. Semi-empirical absorption was based on symmetry-equivalent reflections and absorption corrections were applied with the DENZO-SMN program. All the structures were solved using SHELXS-97 and refined with SHELXL-97 by full-matrix least squares on F2 values [19,20]. The detailed crystal data are listed in table 1.

CCDC reference numbers 757251-757253 for compounds 2, 3, 6 and 1048312-1048313 for compounds 4 and 5, accordingly, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (int.) +44 1223/336 033; email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)].

## 3. Results and discussion

### 3.1. Syntheses and structures

The ligand H<sub>3</sub>tptra 1 was synthesized on the basis of the Buchwald's palladium-catalyzed amination procedures via the coupling of 6-bromo-N-(pyridin-2-yl)pyridin-2-amine and 2,6-diaminopyridine, characterized by IR, <sup>1</sup>H NMR and MS(FAB) (equation (1)). Mononuclear divalent copper, cobalt, nickel and iron complexes 3–6 were synthesized by the direct reaction of metal perchlorate salts and H<sub>3</sub>tptra in methanol. Each complex has been characterized by elemental analysis, EPR, IR, UV/Vis spectroscopy, mass spectrometry, and a magnetic moment measurement. For all complexes 3–6, crystals suitable for single-crystal X-ray diffraction were obtained.

Many attempts to obtain the X-ray crystal structure of free H<sub>3</sub>tptra ligand were unsuccessful because of poor quality of the crystal. Fortunately, the preparation of the single crystal of the protonated ligand 2 was successful. The crystal structure of 2 is shown in figure 1. The protonated cation [H<sub>4</sub>tptra]<sup>+</sup> exhibits an anti-anti-syn-anti-syn conformation. The nitrogen atom in the pyridyl ring (N(1)) was protonated, and formed intramolecular hydrogen bond (N(1)---N(3) = 2.629  $\text{\AA}$ ). Intermolecular hydrogen bonds between protonated

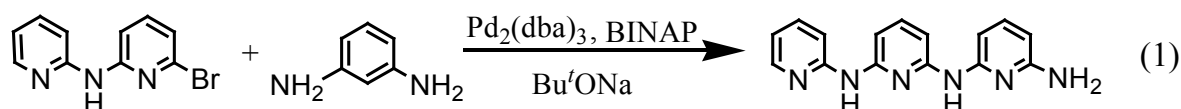
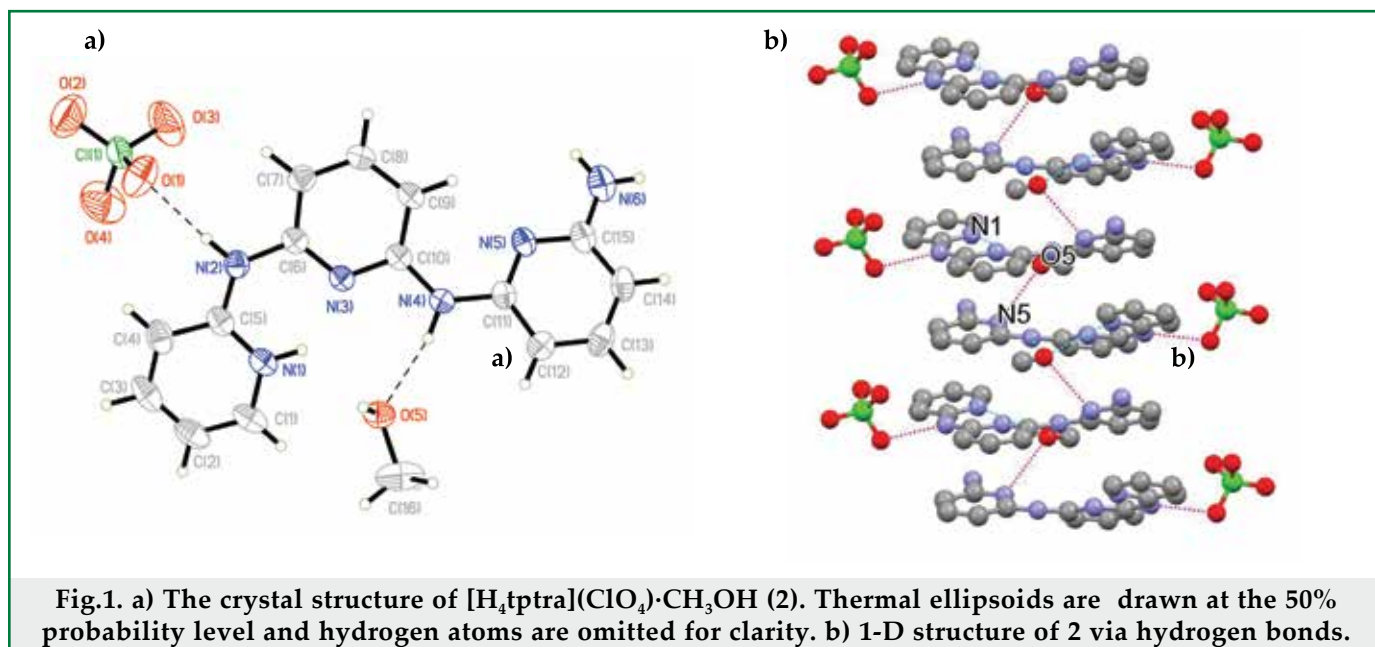


Table 1

Crystal data for 2–6.					
	2 · CH <sub>3</sub> OH	3	4	5	6
Formula	C <sub>16</sub> H <sub>19</sub> N <sub>6</sub> O <sub>5</sub>	C <sub>15</sub> H <sub>14</sub> N <sub>6</sub> Cl <sub>2</sub> O <sub>8</sub> Cu	C <sub>30</sub> H <sub>28</sub> Cl <sub>2</sub> N <sub>12</sub> NiO <sub>8</sub>	C <sub>30</sub> H <sub>28</sub> Cl <sub>2</sub> N <sub>12</sub> FeO <sub>8</sub>	C <sub>30</sub> H <sub>28</sub> Cl <sub>2</sub> N <sub>12</sub> CoO <sub>8</sub>
Formula weight	410.82	540.76	814.25	811.39	814.47
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	P2 <sub>1</sub> /n	C2/c	P-1	P-1	P-1
a (Å)	14.7424(2)	14.1978(2)	8.6075(1)	8.6191(1)	8.6136(1)
b (Å)	6.8906(1)	11.0773(2)	9.8508(1)	9.8300(1)	9.8420(2)
c (Å)	19.2786(3)	13.2554(2)	20.0449(3)	20.1677(3)	20.1157(4)
α (°)	90	90	85.8613(6)	85.7885(6)	85.7323(8)
β (°)	106.8058(6)	110.5867(6)	80.4292(7)	80.3596(6)	80.5515(9)
γ (°)	90	90	75.6152(7)	75.7843(5)	75.5913(7)
V (Å <sup>3</sup> )/Z	1874.75(5)/4	1951.59(5)/4	1622.57(3)/2	1632.07(3)/2	1628.26(5)/2
D <sub>c</sub> (Mgm <sup>-3</sup> )	1.456	1.840	1.667	1.651	1.661
Absorption coefficient (mm <sup>-1</sup> )	0.246	1.454	0.836	0.699	0.764
Crystal size (mm)	0.40×0.18×0.10	0.17×0.30×0.33	0.28×0.17×0.06	0.25×0.07×0.07	0.25×0.12×0.05
θ range for data collection (°)	1.54 – 27.50	2.39 – 27.50	2.06 – 27.50	2.05 – 27.50	1.03 – 27.50
Reflection collected	11239	7306	24906	38475	24141
Independent reflections	4283(R <sub>int</sub> =0.0490)	2244(R <sub>int</sub> =0.0491)	7352(R <sub>int</sub> =0.0905)	7485(R <sub>int</sub> =0.0682)	7380(R <sub>int</sub> =0.0733)
R <sub>p</sub> R <sub>w</sub> (F <sup>2</sup> ) (I > 2σ(I)) <sup>a</sup>	0.0697, 0.1799	0.0395, 0.0964	0.0527, 0.1116	0.0475, 0.1132	0.0530, 0.1253
R <sub>p</sub> R <sub>w</sub> (F <sup>2</sup> ) (all data) <sup>a</sup>	0.1211, 0.2209	0.0587, 0.1059	0.1160, 0.1363	0.0874, 0.1352	0.0953, 0.1538
GOF	1.009	1.057	1.006	1.034	1.072

<sup>a</sup> R<sub>p</sub> =  $\sum |F_o - F_c| / \sum |F_o|$ ; R<sub>w</sub>(F<sup>2</sup>) =  $[\sum W |F_o^2 - F_c^2|^2 / \sum W F_o^4]^{1/2}$





nitrogen atom, amido nitrogen and free methanol molecule ( $N(5) \cdots O(5) = 2.937$ ,  $N(1) \cdots O(5) = 3.047$  and  $N(4) \cdots O(5) = 2.907$  Å) extended the molecules to a one-dimensional supramolecular chain along the b axis. The  $\pi$ - $\pi$  interactions between pyridyl rings of neighbor molecules of the chain through  $N(1)-C(1)-C(2)-C(3)-C(4)-C(5)$  and  $N(5)-C(11)-C(12)-C(13)-C(14)-C(15)$  rings are also observed. Distances between pyridyl rings of  $\pi$ - $\pi$  interactions are ca. 3.52 Å.

The crystal structure analysis show that the ratio of metal to ligand and coordination mode of  $H_3tptra$  in copper(II) complex 3 is totally different than other complexes 4–6. The crystal structures of 3–6 are shown in figures 2, 3, 6 and 7, respectively. The amido groups are not coordinated. Selected bond lengths and angles are listed in table 2.

In complex 3 Cu(II) is in an elongated octahedral

coordination geometry. Three pyridine nitrogen atoms (N1), (N1A), and (N3) and one amino nitrogen atom (N4) from the ligand make up the equatorial plane. The short Cu–N (N is from the pyridine ring) distances in 3, ranging from 1.898(2) to 2.005(3) Å, indicate a strong binding of the chelating ligand. The perchlorate anions are relatively weakly [ $O(1)-Cu$  or  $O(1A)-Cu$  distance 2.428(2) Å] coordinated in the axial positions. The Cu–N and Cu–O distances are well within the range reported for related oligo-pyridylamino complexes [17].  $H_3tptra$  ligand coordinates to the Cu(II) in an anti-anti-anti-anti-syn conformation as a quadridentate ligand.

A zigzag chain structure along c axial was observed through hydrogen bonds between ligand and perchlorate anion ( $N(4) \cdots O(4)$ ). Hydrogen bonds via uncoordinated amido group ( $N(2) \cdots O(3)$ ) further

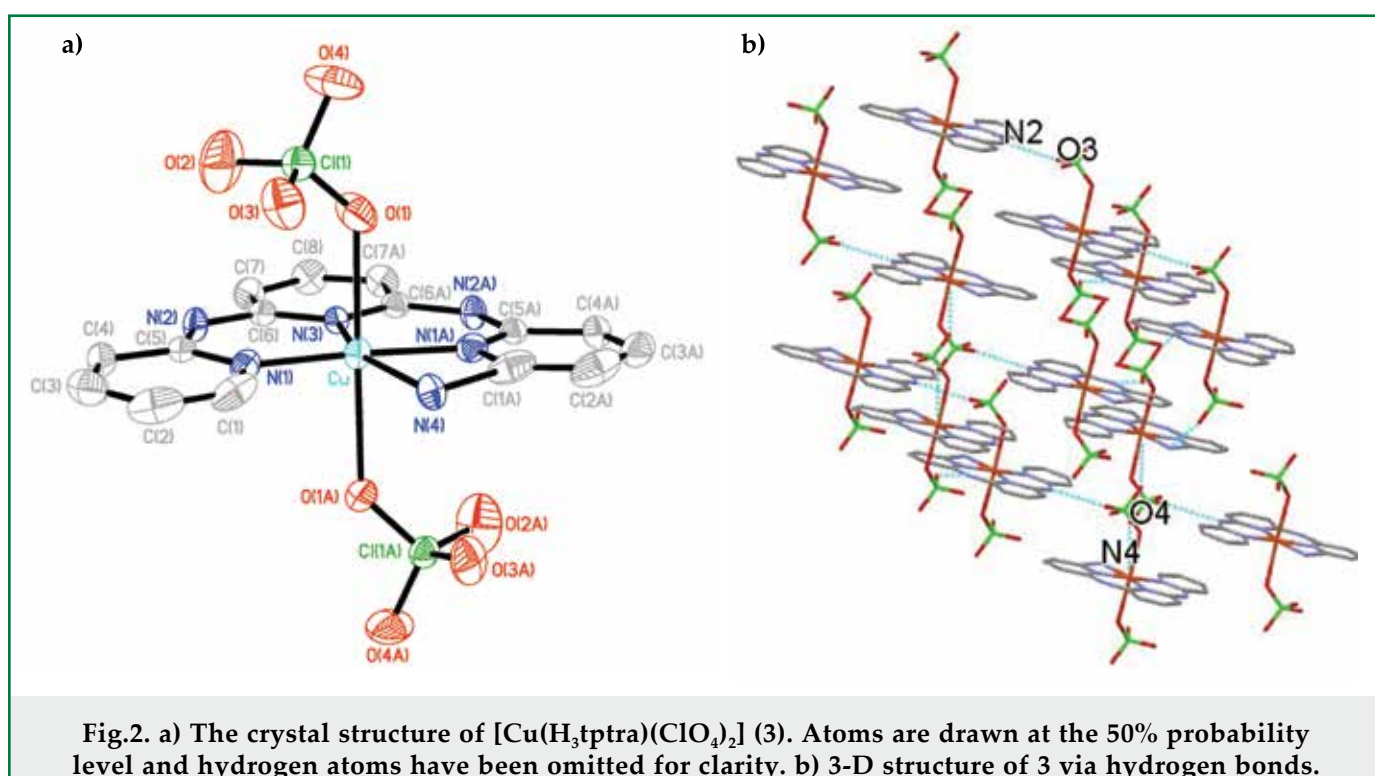


Table 2

## Selected bond distances (Å) and angles (°) for 2–6.

Selected bond distances (Å) and angles (°) for 2–6.			
2			
N(1)–C(5)	1.335(4)	N(3)–C(6)	1.327(4)
N(1)–C(1)	1.379(4)	N(3)–C(10)	1.349(4)
N(2)–C(5)	1.366(4)	N(2)–C(6)	1.395(4)
C(6)–N(3)–C(10)	118.9(3)	N(3)–C(6)–C(7)	123.6(3)
C(11)–N(5)–C(15)	117.6(3)	N(1)–C(5)–C(4)	119.2(3)
C(5)–N(1)–C(1)	122.7(3)	C(2)–C(1)–N(1)	118.7(4)
N(3)–C(10)–C(9)	121.6(3)	N(5)–C(15)–C(14)	122.8(3)
3			
Cu–N(1)	1.898 (2)	Cu–N(4)	2.223(5)
Cu–N(3)	2.005(3)	Cu–O(1)	2.428(2)
N(1A)–Cu–N(1)	169.67(15)	N(1)–Cu–N(4)	106.28(14)
N(3)–Cu–N(4A) <sup>a</sup>	158.46(12)	N(1)–Cu–O(1)	90.19(9)
N(3)–Cu–O(1)	93.10(7)	N(4)–Cu–O(1)	88.85(14)
N(1)–C(1)–C(2)	122.9(3)	N(1)–C(5)–C(4)	120.1(3)
C(6A)–N(3)–C(6)	116.6(3)	N(3)–C(6)–C(7)	122.7(3)
4			
Ni–N(3)	2.054(3)	Ni–N(9)	2.060(3)
Ni–N(1)	2.061(3)	Ni–N(7)	2.070(3)
Ni–N(5)	2.184(3)	Ni–N(11)	2.203(3)
N(3)–Ni–N(9)	177.08(11)	N(3)–Ni–N(1)	87.44(11)
N(3)–Ni–N(9)	95.46(11)	N(3)–Ni–N(7)	93.66(10)
N(9)–Ni–N(7)	86.12(10)	N(1)–Ni–N(7)	87.70(11)
N(3)–Ni–N(5)	86.36(10)	N(9)–Ni–N(5)	90.74(10)
N(3)–Ni–N(5)	173.76(10)	N(7)–Ni–N(5)	93.38(11)
N(3)–Ni–N(11)	94.05(10)	N(9)–Ni–N(11)	86.38(10)
N(1)–Ni–N(11)	88.72(11)	N(7)–Ni–N(11)	171.34(10)
N(5)–Ni–N(11)	91.03		
5			
Fe–N(9)	2.132(2)	Fe–N(3)	2.135(2)
Fe–N(7)	2.145(2)	Fe–N(1)	2.151(2)
Fe–N(11)	2.230(2)	Fe–N(5)	2.245(2)
N(9)–Fe–N(3)	177.00(9)	N(9)–Fe–N(7)	85.11(9)
N(3)–Fe–N(7)	97.47(9)	N(9)–Fe–N(1)	95.09(9)
N(3)–Fe–N(1)	83.57(9)	N(7)–Fe–N(1)	86.56(9)
N(9)–Fe–N(11)	85.37(9)	N(3)–Fe–N(11)	92.09(9)
N(7)–Fe–N(11)	170.34(9)	N(1)–Fe–N(11)	95.91(9)
N(9)–Fe–N(5)	96.11(9)	N(3)–Fe–N(5)	85.48(9)
N(7)–Fe–N(5)	89.00(9)	N(1)–Fe–N(5)	167.55(9)
N(11)–Fe–N(5)	90.39(9)		
6			
Co–N(9)	2.092(2)	Co–N(7)	2.107(3)
Co–N(3)	2.092(2)	Co–N(5)	2.209(3)
Co–N(1)	2.103(3)	Co–N(11)	2.240(3)
N(9)–Co–N(3)	176.81(10)	N(9)–Co–N(7)	85.05(10)
N(9)–Co–N(1)	97.17(10)	N(3)–Co–N(7)	94.49(10)
N(3)–Co–N(1)	85.96(10)	N(1)–Co–N(7)	88.15(10)
N(9)–Co–N(5)	91.26(10)	N(3)–Co–N(11)	95.59(9)
N(3)–Co–N(5)	85.62(10)	N(1)–Co–N(11)	88.02(10)
N(1)–Co–N(5)	171.38(10)	N(7)–Co–N(11)	168.94(10)
N(7)–Co–N(5)	94.38(10)	N(5)–Co–N(11)	90.93(10)
N(9)–Co–N(11)	85.14(9)		

<sup>a</sup>) Symmetry operation for 3:  $A = -x + 1, y, -z + 1/2$ .

constructed the compound 3 to a 3D network (fig.2, table 3).

The nickel, iron and cobalt complexes 4–6 are nearly isostructural, with all crystallizing in the P-1 space group. In each the divalent metal atom is ligated by six pyridine nitrogen donor atoms from two coordinated H<sub>3</sub>tptra ligand. In the complexes 4-6 the nitrogen atoms of amino group are uncoordinated and H<sub>3</sub>tptra ligand coordinates to the metal center in an

anti-anti-anti-anti conformation as a tridentate ligand.

The Ni(II) atom in 4 is six-coordinated in octahedron geometry. The Ni–N distances fall in the range 2.054(3)–2.203(3) Å. These data are consistent with known (NiN<sub>6</sub>) octahedral complexes [21]. In complex 4 the H<sub>3</sub>tptra ligands coordinate to the metal center in an anti-anti-anti-anti conformation.

Hydrogen bonds between uncoordinated perchlorate anion and amido group, N(2)---O(8) and

2			
N(2)---O(1)	2.878	N(5)---O(5)	2.937
N(1)---O(5)	3.047	N(4)---O(5)	2.907
N(1)---N(3)	2.629		
3			
N(4)---O(4)	2.814	N(2)---O(3)	2.937
4			
O(8)---N(2)	2.957	N(1)---N(10)	3.070
O(7)---N(10)	3.046	N(6)---N(11)	3.020
N(8)---O(1)	3.010	N(6)---N(9)	3.019
5			
N(2)---O(1)	3.010	N(6)---O(7)	3.066
N(8)---O(5)	2.955	N(6)---O(9)	3.071
N(5)---N(12)	3.038	N(3)---N(12)	3.094
6			
N(8)---O(2)	3.003	N(6)---N(11)	3.027
N(2)---O(7)	2.954	N(3)---N(12)	3.049
N(6)---N(9)	3.050		

N(10)---O(7), give rise to a dimer structure of 4 (fig.3).

Compound 5 has very similar structure and hydrogen bonding interaction with nickel(II) complex 4 (fig.6, table 3). However, in the case of compound 6, the hydrogen bonding interaction is different than 4 and 5. Hydrogen bonds between coordination cation and two perchlorate anions were observed (N(2)--

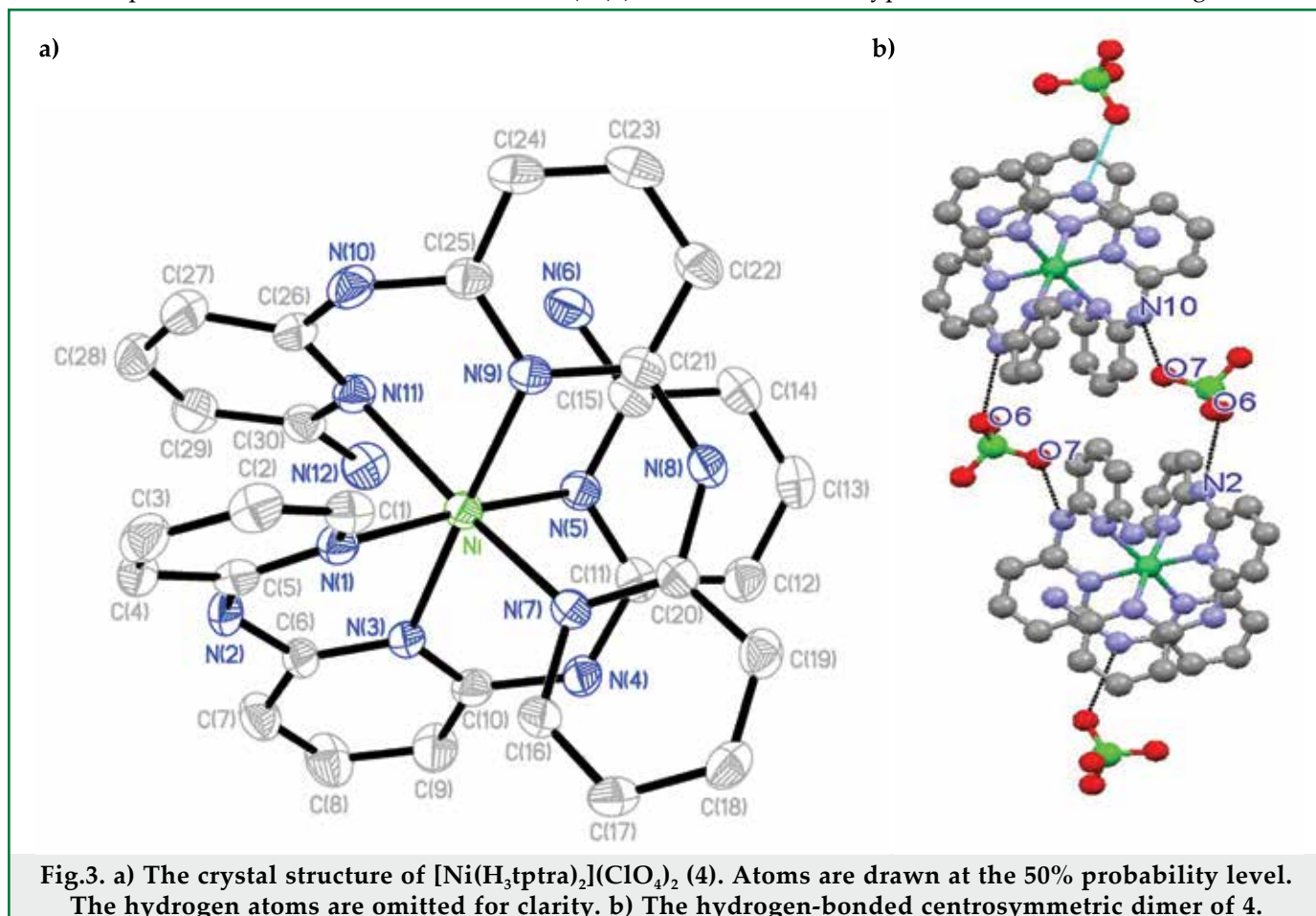
-O(7) and N(8)---O(2)), which construct complex 6 to a neutral monomer (fig.7, table 3).

### 3.2. Spectroscopy

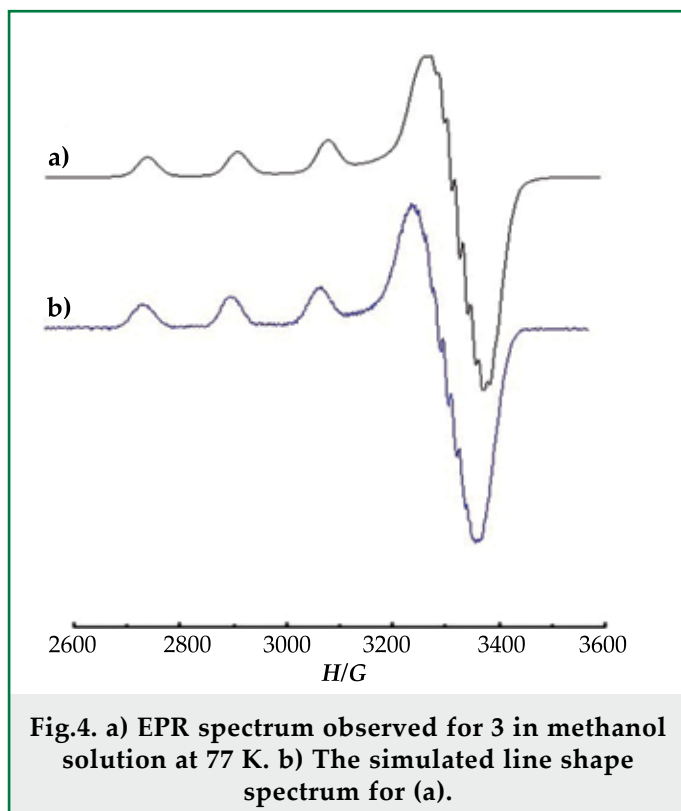
The infrared spectra of the compounds 1–6 contain strong absorption bands in the range 1200–1650  $\text{cm}^{-1}$ , which were assigned to the C–C vibrational modes of the pyridine ring. The N–H stretching bands of the ligand have been observed in the range of 3430–3134  $\text{cm}^{-1}$ . In the complexes 3–6 the nitrogen atoms of the amido groups are uncoordinated to metal centre. Therefore, there are not significant differences between N–H stretching bands of the ligand and complexes 3–6 in the IR spectra. The strong bands at 1087–1170  $\text{cm}^{-1}$  correspond to the  $\text{ClO}_4^-$ .

The UV spectra of complexes 3–6 show strong absorption bands at 228, 246, 326 and 358 nm for complex 3, 222, 253, 318 and 364 nm for 4, 230, 251, 323 and 366 nm for 5 and 221, 254, 330 and 364 nm for 6 respectively. Compared with  $\text{H}_3\text{tptra}$ , which showed absorption at 230, 274 and 341 nm, the bands at 358 nm for 3, 364 nm for 4, 366 nm for 5 and 364 nm for 6 preliminary assigned to a charge transfer between ligand and metal center. Weak, broad band centered at 538 nm in visible part of the electronic spectra of 3 and two broad absorption bands at 545 nm and 866 nm with a small extinction coefficient of  $\sim 9 \text{ M}^{-1}\text{cm}^{-1}$  of compound 4 were related to the d-d transition.

X-band EPR spectra of complexes 3, 4 and 6 were recorded as a polycrystalline powder at room temperature and in methanol solution at room temperature and at 77 K, respectively. The spectra of complexes 4 and 6 are silent. The spectra of 3 showed well-resolved hyperfine structure resulting from the







$^{63}\text{Cu}$  and  $^{65}\text{Cu}$  paramagnetic isotopes (both  $I = 3/2$ ) at 77 K. Three hyperfine lines in the parallel region were observed and the fourth was overlapped with a perpendicular line, yielding  $g_{\parallel} = 2.27$ ,  $g_{\perp} = 2.057$ ,  $\langle g \rangle = 2.128$ ,  $A_{\parallel}^{\text{Cu}} = 169 \times 10^{-4} \text{ cm}^{-1}$ ,  $A_{\perp}^{\text{Cu}} = 9 \times 10^{-4} \text{ cm}^{-1}$ , and  $A^0 = 62.7 \times 10^{-4} \text{ cm}^{-1}$  [calculated from the expression:  $A^0 = (2A_{\perp} + A_{\parallel})/3$ ].

The resulting  $g_{\parallel} > g_{\perp} > g_e$  and  $|A_{\perp}| \ll A_{\parallel} \approx (120 - 200) \times 10^{-4} \text{ cm}^{-1}$  indicated a  $d_{x^2-y^2}$  ground state and agreed with X-ray structure of an elongated octahedral coordination geometry for the Cu(II) ion (fig.4). The spectra at 77 K showed clear superhyperfine coupling from  $^{14}\text{N}$  ( $I = 1$ ), which theoretically produced nine lines from four equivalent nitrogen atoms and yielding  $A_{\parallel}^{\text{N}} = 16 \times 10^{-4} \text{ cm}^{-1}$  and  $A_{\perp}^{\text{N}} = 9 \times 10^{-4} \text{ cm}^{-1}$ . The superhyperfine coupling strongly suggests a large amount of electronic delocalization from d orbitals onto the ligands [22].

### 3.3. Magnetic properties

Magnetic moment at 300 K for 3 is  $1.87 \mu_B$ , which is consistent with one unpaired electron in Cu(II) including a small amount of orbital contribution.

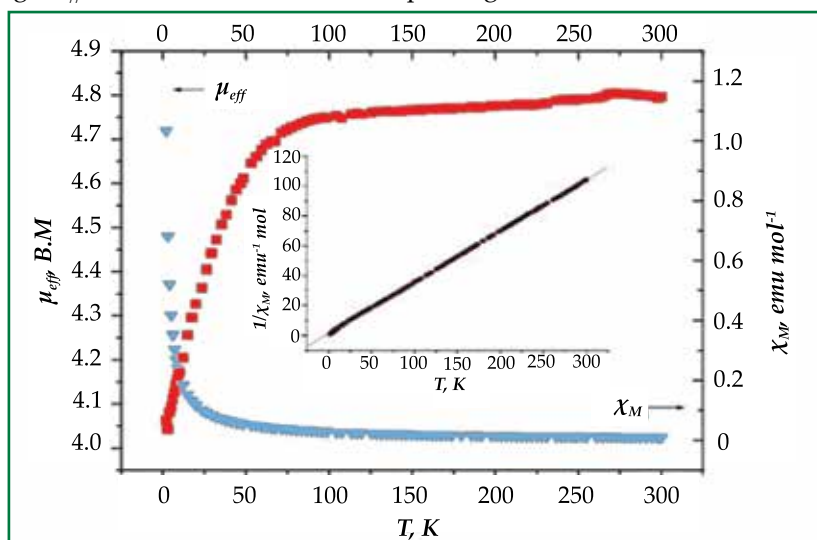
The nickel center in 4 and iron in 5 is high-spin, as demonstrated by the effective magnetic moment value at room temperature ( $\mu_{\text{eff}} = 3.20 \mu_B$  for 4 and  $5.24 \mu_B$  for 5) and metal-ligand distances. Experimental effective magnetic moment is higher than spin-only value ( $\text{Ni}^{\text{II}}: 2.8 \mu_B$ ;  $\text{Fe}^{\text{II}}: 4.9 \mu_B$ ) calculated for the high-spin metal center due to spin-orbit coupling [23].

The temperature-dependent magnetic susceptibilities for 6 were measured in range 2–300 K. The effective magnetic moment at

room temperature is  $4.80 \mu_B$  and much larger than the spin-only value of  $3.87 \mu_B$  for high-spin Co(II) ( $S=3/2$ ). Upon cooling, the  $\mu_{\text{eff}}$  value decreases to  $4.06 \mu_B$  at 2K. The magnetic behavior should be due to a larger orbital contribution arising from the  $^4\text{T}_{1g}$  ground state of Co(II) with an octahedral geometry. An obvious decrease of magnetic moments at low temperature resulted from both zero-field splitting and a weak intermolecular antiferromagnetic interaction [24]. The magnetic behaviour of 6 obeys the Curie-Weiss law. A fit to the Curie-Weiss expression leads to a value of  $g = 2.49$  and  $\theta = -3.71 \text{ K}$  (fig.5).

### 4. Conclusion

A new polydentate pyridylamine ligand  $\text{H}_3\text{tptra}$  and its mononuclear copper(II), nickel(II), iron(II) and cobalt(II) complexes have been synthesized and structurally characterized. The protonated ligand cation 2 exhibits an *anti-anti-syn-anti-syn* conformation. The copper atom in 3 is six-coordinated in elongated octahedral coordination geometry and perchlorate anions are relatively weakly coordinated in the axial positions.  $\text{H}_3\text{tptra}$  coordinates to the Cu(II) in an *anti-anti-anti-syn* conformation as a quadridentate ligand. Extensive hydrogen bonds are formed and construct the protonated ligand 2 into 1D and complex 3 into 3D supramolecular structure. The coordination geometry around metal atom in 4-6 is octahedral with two tridentate coordinated  $\text{H}_3\text{tptra}$  ligand. Dimer structure for 4 and 5 and neutral monomer for 6 have been found through hydrogen bonds. X-band EPR spectra of 3 complex showed well-resolved hyperfine structure resulting from the two paramagnetic isotopes  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$  ( $g = 2.128$  and  $A^0 = 62.7 \times 10^{-4} \text{ cm}^{-1}$ ). The observed superhyperfine coupling from four nitrogen atoms suggests a large amount of electronic delocalization from d orbitals onto the ligands. The temperature-dependent magnetic susceptibility results of 6 showed unquenched spin-orbital coupling from a  $^4\text{T}_{1g}$  ground state of Co(II) with  $g = 2.49$  and the effect of zero-field splitting was observed.



**Fig.5. Temperature-dependent magnetic effective moment (■, left) and molar magnetic susceptibility (▼, right) for  $[\text{Co}(\text{H}_3\text{tptra})_2](\text{ClO}_4)_2$  (6). Inset: Reciprocal dependence of the magnetic susceptibility on temperature. The solid lines result from least-squares fits of Curie-Weiss Law.**

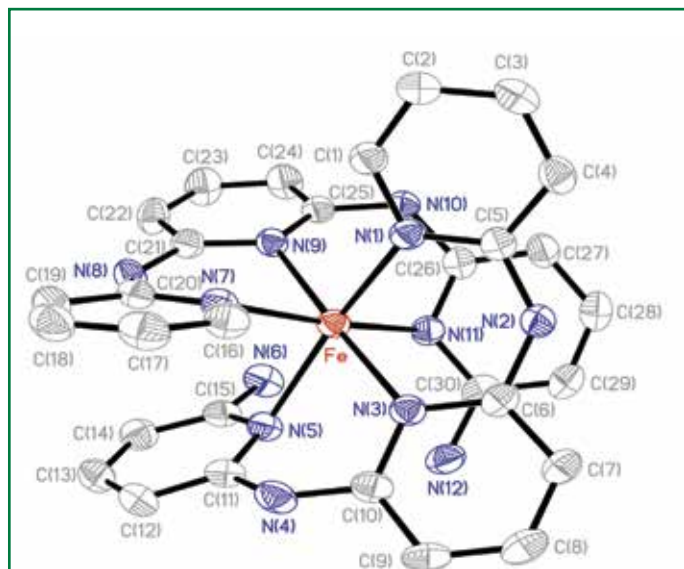


Fig.6. The crystal structure of  $[\text{Fe}(\text{H}_3\text{tptra})_2](\text{ClO}_4)_2$  (5). Atoms are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

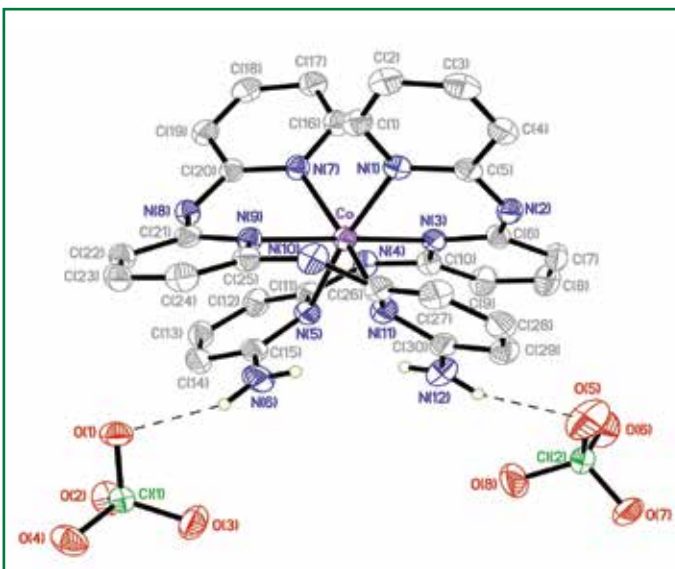


Fig.7. The crystal structure of  $[\text{Co}(\text{H}_3\text{tptra})_2](\text{ClO}_4)_2$  (5). Atoms are drawn at the 50% probability level. The hydrogen atoms are omitted for clarity.

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**Исследование нового полидентат пиридиламина и его комплексов: синтез, супромолекулярное строение и свойств**

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**Реферат**

Синтезирован новый лиганд -  $H_3tptra$  (1), его протонированный аналог  $[H_4tptra](ClO_4)$  (2), комплексы меди(II) (3), никеля(II) (4), железа(II) (5) и кобальта(II) (6) и определено их строение. В комплексе (3),  $H_3tptra$  координируется с Cu(II) как тридентатный лиганд и принимает при этом *анти-анти-син-анти-син* конформацию. В комплексе координационное окружение иона Cu(II) вытянутый октаэдр. Перхлоратные анионы относительно слабо координированы в аксиальных позициях. В комплексах Ni(II), Co(II) и Fe(II) две молекулы лиганда непосредственно связываются с ионом металла как тридентатный ион и образуют хромофору  $MN_6$ . За счет водородных связей соединение(2) 1D и комплекс(3) образуют 3D супромолекулярную структуру. Спектр ЭПР комплекса меди(II) показывает хорошо разрешенную сверхтонкую структуру ( $g = 2.128$ ,  $A^\circ = 62.7 \times 10^{-4} \text{ см}^{-1}$ ) от двух парамагнитных изотопов  $^{63}\text{Cu}$  и  $^{65}\text{Cu}$  (для обеих ядерный спин  $I=3/2$ ). Спектр ЭПР этого комплекса при температуре 77 К также показывает сверхтонкую структуру ( $A_{\parallel}^N = 16 \times 10^{-4} \text{ см}^{-1}$  и  $A_{\perp}^N = 9 \times 10^{-4} \text{ см}^{-1}$ ) от  $^{14}\text{N}(I=1)$ . Определено соответствие магнитное поведение комплекса (6) закону Кюри-Вейса ( $g = 2.49$  и  $\theta = -3.71 \text{ K}$ ).

**Yeni polidentat piridilamin və onun komplekslərinin tədqiqi: sintez, supramolekulyar quruluş və xassələr**

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**Xülasə**

Yeni  $N^2$ -(6-aminopiridin-2-il)- $N^6$ -(piridin-2-il)piridin-2,6-diamin ( $H_3tptra$ ) (1) liqandı, onun protonlaşmış analoqu  $[H_4tptra](ClO_4)$  (2), mis(II) (3), nikel(II) (4), dəmir(II) (5) və kobalt(II) (6) kompleksləri sintez edilib, quruluşları müəyyənləşdirilib. Protonlaşmış liqand kationunun (2) *anti-anti-sin-anti-sin* konformasiyasına malik olduğu tapılmışdır. (3) kompleksində  $H_3tptra$  Cu(II) ionuna kvadridentat liqand kimi koordinasiya olunur. Kompleksdə Cu(II) ionu heksakoordinasiya olunub, dartılmış oktaedrik həndəsi ətrafa malikdir. Perxlorat anionları aksial vəziyyətlərdən zəif koordinasiya olublar. Ni(II), Fe(II) və Co(II) komplekslərində iki liqand molekulu metal ionuna tridentat ion kimi birbaşa bağlanır və  $MN_6$  xromoforunu əmələ gətirir. Hidrogen rabitələrinin hesabına (2) birləşməsi 1D, (3) kompleksi isə 3D supramolekulyar quruluş əmələ gətirirlər. Cu(II) kompleksinin EPR spektri iki  $^{63}\text{Cu}$  və  $^{65}\text{Cu}$  (hər ikisi üçün  $I = 3/2$ ) paramaqnit izotoplarından yaxşı ayırılmış ifrat incə quruluşa malikdir ( $g = 2.128$  və  $A^\circ = 62.7 \times 10^{-4} \text{ sm}^{-1}$ ). Bu kompleksin EPR spektri 77 K temperaturda cütləşməmiş elektronun azot  $^{14}\text{N}(I=1)$  atomları ilə qarşılıqlı təsirindən də həmçinin ifrat incə quruluşa malikdir ( $A_{\parallel}^N = 16 \times 10^{-4} \text{ sm}^{-1}$  və  $A_{\perp}^N = 9 \times 10^{-4} \text{ sm}^{-1}$ ). (6) kompleksinin maqnit xassələrinin Küri-Veyns qanuna tabe olması müəyyən olunub ( $g = 2.49$  və  $\theta = -3.71 \text{ K}$ ).