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# Synthesis and Structure of the Novel Mononuclear Copper(II) Complex of the Unsymmetrical Pyrimidine-Modulated Long-Chain Hexapyridylpentaamine Ligand

Through the pyrimidine-modulated hexapyridylpentaamine ligand $N^2$-(pyridin-2-yl)-$N^6$-(6-((6-((6-(pyrimidin-2-ylamino)pyridin-2-yl)amino)pyridin-2-yl)amino)pyridin-2-yl)pyridine-2,6-diamine ($H_5N_{11}$-tpm), a new mononuclear copper(II) complex $[Cu(H_5N_{11}\text{-tpm})](ClO_4)_2$ (**1**) were synthesized and structurally characterized. The single crystal X-ray analysis showed distorted trigonal bypyramidal geometry (Addison parameter value $\tau = 0.69$) of the complex (**1**), which is well consistent with the "inverted type" of ESR spectra ($g_{\parallel} < g_{\perp}$), measured magnetic susceptibility, and electronic spectroscopy studies. The equatorial copper-nitrogen distances (Cu–N(1) = 2.094(9) Å; Cu–N(5) = 2.045(9) Å; Cu–N(9) = 2.214(9) Å), along with the axial Cu–N distances (Cu–N(3) = 1.999(9) Å and Cu–N(7) = 2.001(9) Å), fall well within the range typically reported for Cu(II) complexes that incorporate this type of ligand. All Cu–N distances are short, ranging from 1.999(9) to 2.094(9) Å, which suggests a strong binding affinity of the chelating ligand. The monohelical $H_5N_{11}$-tpm ligand coordinates with the metal atom, exhibiting an all-anti conformation. The extensive hydrogen bonds were observed between the amino groups and uncoordinated perchlorate anions, resulting in the formation of a three-dimensional network (3D) of the complex. The synthesized complex has high potential for the creation of novel cholinesterase inhibitors since it contains a number of pyridine and pyrimidine rings.

*Keywords:* modulated oligo-α-aminopyridine ligand, long-chain ligand, copper complex, crystal structure, addison parameter, hydrogen bonds, spectroscopy, magnetic measurement

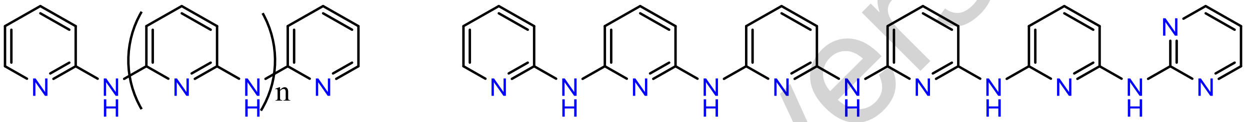
## *Introduction*

Oligo-α-pyridylamine ligands (Scheme 1) have garnered increasing interest over the past three decades due to their ability to synthesize metal string complexes, commonly referred to as "Extended Metal Atom Chain complexes" (EMACs), which have potential molecular electronic device applications, such as single-molecule transistors and molecular wires [1–4]. There are several ways that oligo-α-pyridylamido ligands coordinate with metal atoms. The supporting ligands in EMACs are coordinated to the metal in an all-syn form, while mononuclear complexes were shown to be coordinated in an all-anti form [5–7]. And anti–syn conformation was only observed in the dimers of free ligands [8]. The synthesis of long-chain metal string complexes is very important. This is directly related to their use as molecular wires. It is believed that if a metal-string complex contains 17 metal atoms, it can be described as a 1D (one-dimensional) infinite molecule [9]. However, the synthesis of long-chain metal strings based on traditional oligo-α-aminopyridine ligands is characterized by low yields and instability because of their oxidative decompositions [10].

For the development of oxidative degradation-resistant and extended metal chains, we have recently created a series of modulated oligo-α-pyridylamido ligands. This was achieved by substituting the pyridine rings with nitrogen-rich alternatives such as pyrazine, pyrimidine, and naphthyridine within the oligo-α-pyridylamine ligands (Scheme 1). Using pyrazine-modulated oligo-α-pyridylamine ligands, successfully synthesized heptacobalt and nonachromium EMACs, which are the longest Co(II) and Cr(II) EMAC molecules obtained to date [9, 11].

The introduction of nitrogen-rich aromatic pyrazine rings has enabled ligand molecules to exhibit a variety of coordination modes, making them particularly versatile for the construction of coordination polymers. A series of one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) copper(II) coordination polymers using pyrazine-modulated N, N′-bis(a-pyridyl)-2,6-diaminopyridine ligands has been synthesized and studied [12]. Furthermore, our recent studies have demonstrated that the string complexes of nickel (II), mononuclear complexes, and coordination polymers of copper (II) with pyrazine/pyrimidine-modulated oligo-α-pyridylamino ligands exhibit significant biological activity [4, 7]. Therefore, it is of great interest to synthesize and determine the structure and characteristics of novel copper complexes with pyrazine/pyrimidine-modulated oligo-α-pyridylamine ligands.

In this paper, we present our latest findings in this area. We report, for the first time, the synthesis and characterization of the new mononuclear copper(II) complex, $[Cu(H_5N_{11}\text{-tpm})](ClO_4)_2$ (**1**). This complex is derived from the unsymmetrical pyrimidine-modulated long-chain oligo-α-pyridylamino ligand $N^2$-(pyridin-2-yl)-$N^6$-(6-((6-((6-(pyrimidin-2-ylamino)pyridin-2-yl)amino)pyridin-2-yl)amino)pyridin-2-yl)pyridine-2,6-diamine ($H_5N_{11}$-tpm). The inhibition effect of synthesized complex **1** against AChE and BChE enzymes, as well as the molecular docking and molecular dynamic simulation studies, will be the subject of an upcoming paper.



oligo-α-pyrydlamido ligands $H_5N_{11}$-tpm

n=0, Hdpa; n=4, $H_5$ hexpyrpea

Scheme 1. Oligo-α-pyridylamines and their modulated analogues

## *Experimental*

### *Materials and measurements*

Commercially obtained chemicals and solvents were used without further purification unless otherwise noted. IR spectra were recorded on a Bruker Alpha FTIR spectrometer in the range of 400–4000 $cm^{-1}$. Electronic spectra were recorded on a SPECORD 50 plus spectrophotometer in MeOH using cuvettes of 1 cm path length, and collected data were reported in $\lambda_{max}$/nm. The EPR spectrum of the copper complex was recorded in the solid state on a Bruker BioSpin GmbH spectrometer at room temperature. Elemental analyses were carried out on FlashEA 1112 Series CHNS-O Analyzer. Molar magnetic susceptibility was recorded on a SQUID system with 2 kOe external magnetic field.

### *Preparation of Compounds*

$N^2$-(pyridin-2-yl)-$N^6$-(6-((6-((6-(pyrimidin-2-ylamino)pyridin-2-yl)amino)pyridin-2-yl)amino) pyridin-2-yl)pyridine-2,6-diamine ($H_5N_{11}$-tpm) was synthesized by the palladium-catalysed cross-coupling of 2-aminopyrimidine and $N^2$-(6-bromopyridin-2-yl)-$N^6$-(6-((6-(pyridin-2-ylamino)pyridin-2-yl)amino)pyridin-2-yl)pyridine-2,6-diamine in the presence of catalysts [$Pd_2(dba)_3$, BINAP, $Bu^tONa$] in refluxing benzene under argon, as described in our previously reported work [13, 14]. The work [14] also provides stages for obtaining $N^2$-(6-bromopyridin-2-yl)-$N^6$-(6-((6-(pyridin-2-ylamino)pyridin-2-yl)amino)pyridin-2-yl)pyridine-2,6-diamine (Scheme 1S).

$[Cu(H_5N_{11}\text{-tpm})](ClO_4)_2$ (**1**). A mixture of $H_5N_{11}$-tpm (0.200 g, 0.37 mmol) and $Cu(ClO_4)_2\cdot 6H_2O$ (0.160 g, 0.43 mmol) in methanol (50 mL) was stirred overnight. The solution was then filtered to remove insoluble impurities and concentrated under vacuum. Diffusing ether into the $CH_3OH$ solution provided blue single crystals suitable for X-ray analysis (0.382 g, 47 % yield). IR (KBr) ν/$cm^{-1}$: 3440 w, 3310 w, 3249 w, 3206 w, 3075 s, 1652 s, 1564 s, 1533 m, 1490 s,1467 s, 1448 s, 1409 s, 1426 m, 1211 m, 1140 s, 1041 s, 795 m, 498 w, 431; UV/Vis UV/Vis ($CH_3OH$) $\lambda_{max}$/nm ($\varepsilon$/$dm^3$ $mol^{-1}$ $cm^{-1}$): 206 ($1.23\times10^4$), 272 ($3.37\times10^4$), 330 ($3.10\times10^4$), 475 ($1.05\times10^2$), 635 (54.5), 850 (47.8); Elemental analysis (%) $C_{29}H_{24}Cl_2CuN_{12}O_8$: calc. C 43.38, H 3.01, N 20.93; found: C 43.52, H 3.10, N 20.84.

*Crystal Structure Determinations*

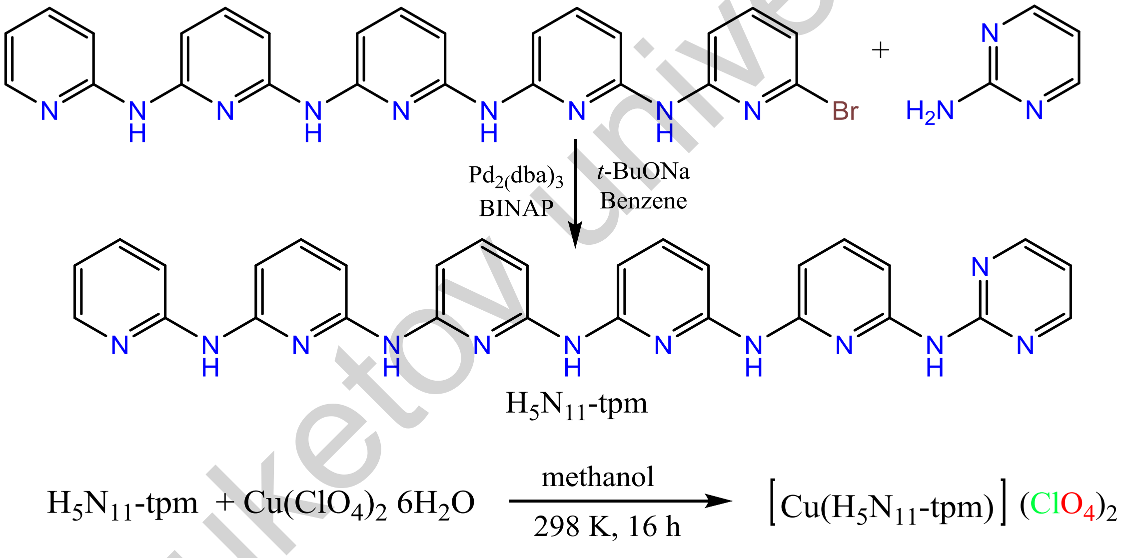
The suitable crystals of $[Cu(H_5N_{11}\text{-tpm})](ClO_4)_2$ (1**)** was selected for data collection, which was performed on a NONIUS Kappa CCD diffractometer at 293 K using Mo-Ka radiation ($\lambda$ = 0.71073 Å). The structure was solved by direct methods using SHELXS-2013 [15] and refined by full-matrix least-squares methods on $F^2$ using SHELXL-2018 [16]. All non-hydrogen atoms were refined with anisotropic parameters. The hydrogen atoms were located from different maps and then refined as riding atoms with a C-H distance of 0.95 A and a N-H distance of 0.88 A. The other H atoms were located in a difference map refined freely. Molecular graphics were created using MERCURY programs. Below are the specifics of the X-ray diffraction experiment and a summary of the crystallographic data for the copper(II) complex **1**:

Empirical formula $C_{29}H_{24}Cl_2CuN_{12}O_8$; formula weight = 803.4; crystal system—orthorhombic; space group—*Pbcn*; *a* = 11.8184(3), b = 20.8835(2), c = 26.3509(7) Å; $\alpha = \beta = 90°$; volume = 6503.7(3) $Å^3$, Z = 8; density (calculated) = 1.640 $g/cm^3$; absorption coefficient = 0.908 $mm^{-1}$; crystal size: $0.17 \times 0.15 \times 0.08$ $mm^3$; $\theta$ range for data collection 1.546–24.122°; reflection collected—18457, independent reflection—4878 [R(int) = 0.0804]; $R_1 = 0.1114$, $wR_2 = 0.2711$; $R_1$(all data) = 0.1465, $wR_2$(all data) = 0.2879; GOF = 1.152.

## *Results and Discussion*

### *Syntheses and Structures*

$N^2$-(pyridin-2-yl)-$N^6$-(6-((6-((6-(pyrimidin-2-ylamino)pyridin-2-yl)amino)pyridin-2-yl) amino) pyridin-2-yl)pyridine-2,6-diamine ($H_5N_{11}$-tpm) was synthesized according to our previously reported work [13].



Scheme 2. The synthesis of $H_5N_{11}$-tpm and its copper(II) complex **1**

The Cu(II) complex **1** was synthesized by treating of pyrimidine-modulated long-chain $H_5N_{11}$-tpm ligand and $Cu(ClO)_2{\cdot}6H_2O$ in methanol. Slow diffusion of the solution with ether gave light blue single crystals suitable for X-ray diffraction. The structure of complex **1** is established by various spectroscopic methods (IR, UV-Vis, ESR) and the single X-ray crystallography. The obtained complex was found to be stable in air and dissolved well in common polar solvents like methanol, dimethyl sulfoxide (DMSO), and dimethylformamide (DMF). According to X-ray diffraction studies complex **1** crystallizes in the orthorhombic crystal system with the Pbcn space group. An ORTEP diagram of **1** including the atomic numbering scheme is depicted in Figure 1, and the important bond lengths and angles in the structure are given in Table 1.

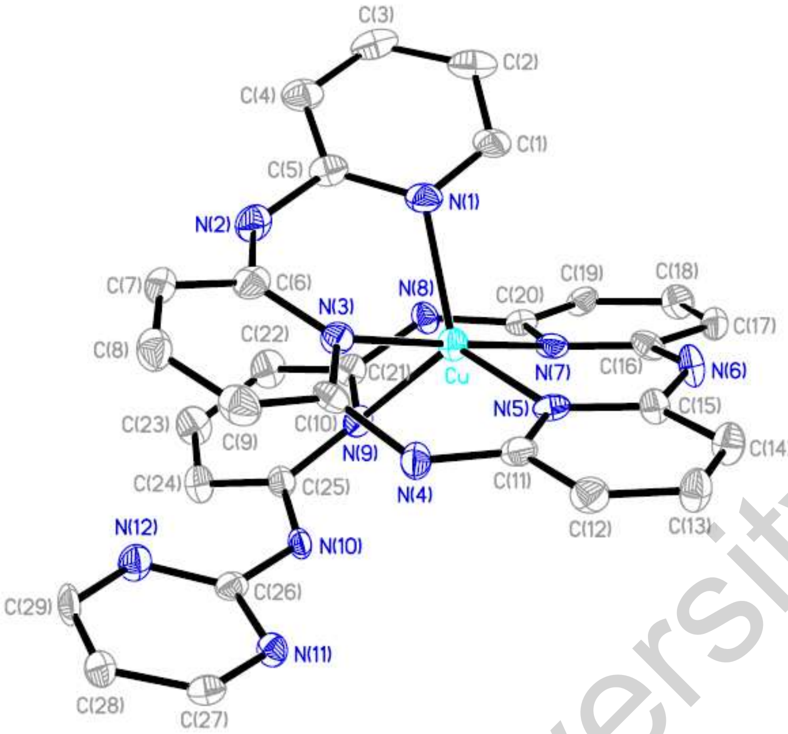


Figure 1. The molecular structure of $[Cu(H_5N_{11}\text{-tpm})](ClO_4)_2$ **1**.
Atoms are drawn at the 50 % probability level and hydrogen atoms are omitted for clarity

Table 1

**Selected bond distances (Å) and bond angles (°) for complex 1**

| Bond lengths for complex 1, Å | | |
|---|---|---|
| Cu–N(1) | 2.094(9) | Cu–N(7) 2.001(9) |
| Cu–N(3) | 1.999(9) | Cu–N(9) 2.214(9) |
| Cu–N(5) | 2.045(9) | |
| Bond angles for complex 1, ° | | |
| N(3)–Cu–N(7) | 173.6(4) | N(3)–Cu–N(1) 88.7(4) |
| N(1)–Cu–N(5) | 132.3(4) | N(3)–Cu–N(5) 93.5(4) |
| N(1)–Cu–N(9) | 100.3(3) | N(3)–Cu–N(9) 89.6(4) |
| N(5)–Cu–N(9) | 127.4(4) | N(7)–Cu–N(5) 92.8(4) |

In this complex the nitrogen atoms of the amino groups are uncoordinated to Cu(II) center. It is noticeable that the uncoordinated amine nitrogen atoms are more characteristic for the coordination polymers and mononuclear Cu(II) complexes of the modulated oligo-α-pyridylamine ligands with perchlorate, nitrate, and chloride anions [4, 12, 17]. However, in all cases known to us, the deprotonation of oligo-α-pyridyl amido ligands modulated with nitrogen-containing heterocycles occurs when they interact with copper(II) acetate. In the process of creating the tetranuclear copper(II) complex $[Cu_4(Hdpzpda)_2(CH_3COO)_6]$ with the $H_2$dpzpda ligand and the copper(II) coordination polymer $\{Cu(mpmpza)(CH_3COO)(H_2O)\}$ with the Hmpmpza ligand, we have previously seen deprotonation of the pyrazine-modulated oligo-α-aminopyridine ligands [6, 7].

The Cu(II) center in complex **1** is five-coordinated and adopts a distorted trigonal bipyramidal geometry by coordinating five pyridine ring nitrogen atoms of $H_5N_{11}$-tpm. The equatorial plane of complex **1** consists of three pyridyl nitrogen atoms (N1, N5, N9), while the axial positions are occupied by two nitrogen atoms (N3 and N7) from the pyridyl rings of the $H_5N_{11}$-tpm ligand (Fig. 2). This arrangement results in an overall distorted trigonal bipyramidal stereochemistry. The trigonality index $\tau$ is calculated by analysing $\alpha$ and $\beta$ (the largest angles around the Cu(II) ion), and it was found to be $\tau = 0.69$ for complex **1**. Since the observed $\tau = 0$ and 1 have been assigned to perfectly square pyramidal and trigonal bipyramidal geometries, the geometry around the Cu(II) center in complex **1** could be described as distorted trigonal bipyramidal. The equatorial copper-nitrogen distances (Cu–N(1) = 2.094(9) Å; Cu–N(5) = 2.045(9) Å; Cu–N(9) = 2.214(9) Å), as well as axial Cu–N distances (Cu–N(3) = 1.999(9) Å and Cu–N(7) = 2.001(9) Å), are well within the range reported for Cu(II) complexes with this type of nitrogen-containing heterocyclic ligand [4, 12, 17, 18]. In complex **1**, except for the Cu–N(9) distance (2.214(9) Å), all Cu–N distances are short, ranging from 1.999(9) to 2.094(9) Å, indicating a strong binding of the chelating ligand.

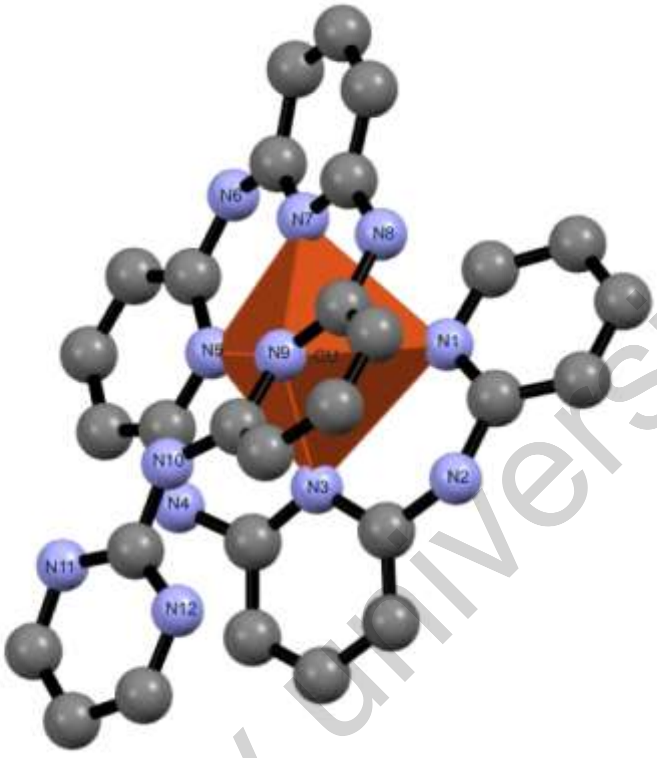


Figure 2. The distorted trigonal bipyramidal geometry environment of Cu(II) in [Cu($H_5N_{11}$-tpm)]$^{2+}$

In complex **1**, the monohelical hexadentate ligand $H_5N_{11}$-tpm coordinates with the metal atom, adopting an all-anti conformation. The pyridyl groups of the ligand are planar, and the dihedral angles between planes Py(N1)-Py(N3), Py(N3)-Py(N5), Py(N5)-Py(N7), Py(N7)-Py(N9), and Py(N9)-Pm(N11) are 25.6(5)°, 20.4(5)°, 11.6(3)°, 27.7(4)°, and 31.9(4)°, respectively. The crystal lattice of compound **1** contains no solvent molecules. Non-coordinated perchlorate ions act as counter-ions within its crystal structure. Complex **1** was found to have extensive intra- (N(3)···N(10) = 3.076 Å, N(1)···N(8) = 2.960 Å) and intermolecular hydrogen bonding. Intermolecular hydrogen bonds (HBs) between the amino group and uncoordinated perchlorate anions (N(6)···O(4) = 2.988 Å and N(8)···O(10) = 2.957 Å) create complex 1's three-dimensional network. These hydrogen bonds are essential for maintaining the system's overall stability.

*IR, UV-Vis, EPR Spectroscopy and Magnetic Properties*

The IR bands associated with the C=C and C=N vibrations in aromatic rings for complex **1** were observed in the range of 1650−1422 cm$^{-1}$. Complex **1** exhibited a series of absorption bands within the range of 3448−3111 cm$^{-1}$, which are characteristic of the N–H bonds present in the amine groups (Fig. 1S and Fig. 2S). The strong bands observed at 1040–1148 cm$^{-1}$ are attributed to the $ClO_4^-$ anions. The Far-IR spectra of compound **1** displayed a band at 431 cm$^{-1}$, which was assigned to the ν(Cu−N) vibration.

The assignment of electronic spectra for Cu(II) complexes has been thoroughly examined in the literature [19–21]. The electronic spectra of complex **1** were recorded at room temperature in a methanol solution, revealing six bands at wavelengths of 206, 272, 330, 475, 635, and 850 nm (Fig. 3). Compared to $H_5N_{11}$-tpm, which exhibited absorption at 210, 260, and 310 nm, the band observed at 475 nm for compound **1**, within the visible region of the electronic spectra, can be attributed to a charge transfer between the ligand and the metal center. Weak, broad bands centered at 635 nm and 850 nm in the electronic spectra of 1 were related to d–d transitions [19]. The result obtained is consistent with a trigonal-bipyramidal ligand environment for

Cu(II) ions in **1**, which is further corroborated by X-ray structural analysis. By comparing the electronic spectra of the complexes in methanol solution and Nujol suspension (in the solid state), it was discovered that their structure remained unaltered (Fig. 3S). Using absorbance spectroscopy, similar findings have already been reached for other Cu(II) complexes [7, 22].

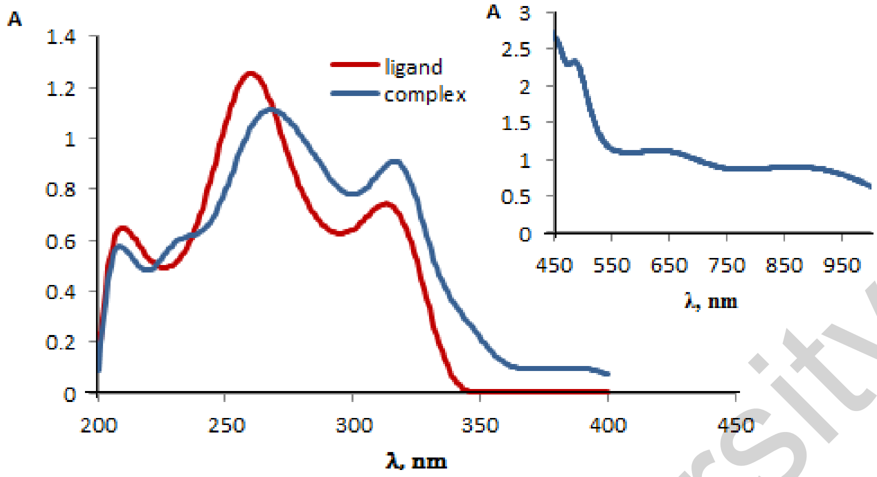


Figure 3. Electronic spectra of the $H_5N_{11}$-tpm ligand
and its Cu(II) complex — $[Cu(H_5N_{11}\text{-tpm})](ClO_4)_2$ **1** in methanol solution

The EPR spectra of complex **1** were recorded at room temperature in the polycrystalline state to analyze the coordination environment surrounding the Cu(II) ion and to determine the geometry of the complex (Fig. 4).

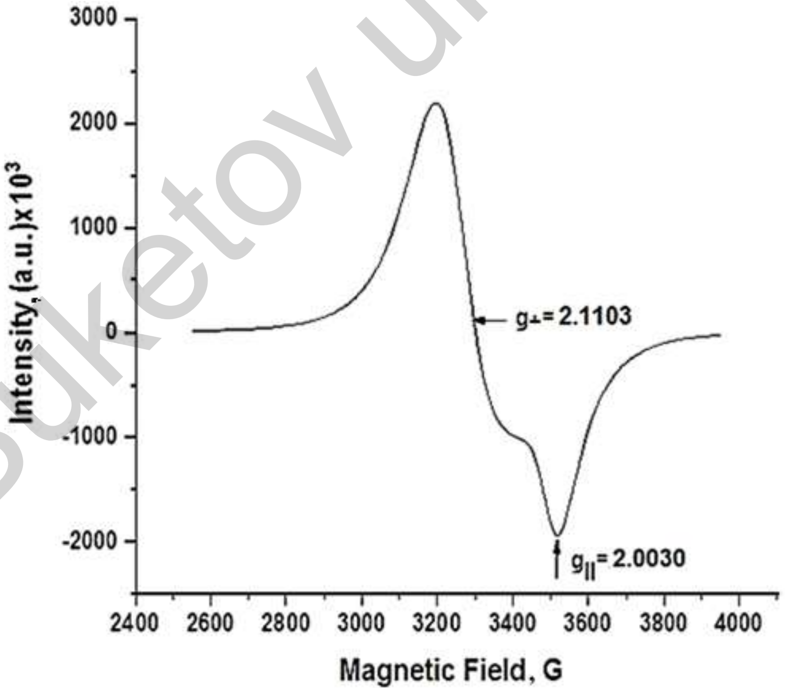


Figure 4. EPR spectrum of powder sample of the Cu(II) complex 1 at room temperature

The EPR spectra of complex **1** displayed a broad signal, with $g_{\parallel}$ recorded at 2.0030 and $g_{\perp}$ at 2.1103, suggesting pentacoordinate geometry around the metal atom. The g parameters indicate that the paramagnetic center shows axial symmetry, characterized by “inverted type” EPR spectra, where $g_{\parallel} < g_{\perp}$. It is well known that for Cu(II)$N_5$ polyhedrons, two different geometric arrangements, the trigonal bipyramidal geometry (TBP) (symmetry $\mathbf{D_{3h}}$) and the square pyramidal geometry (SP) (symmetry $\mathbf{D_{4v}}$), are possible. Square pyramidal geometry is ruled out for pentacoordinate complexes with $g_\perp$ values bigger than $g_\parallel$, which are suggestive of distorted trigonal bipyramidal geometry [23, 24]. So, from the order of $g_\perp > g_\parallel \sim g_e$ (free electron g value, $g_e = 2.0023$), it can be concluded that Cu(II) ion in complex **1** is located in the distorted triangular bipyramid arrangement and the ground state of the unpaired electron is $d_{z^2}$. The results obtained from EPR are in excellent agreement with the single crystal analysis data for complex **1**. The $\mu_{eff}$ value of complex **1** at room temperature (300 K) was 1.80 B.M., slightly higher than the expected spin-only value for a non-interacting Cu(II) ion (1.73 B.M.).

## *Conclusions*

The pyrimidine-modulated long-chain oligo-α-pyridylamino ligand $N^2$-(pyridin-2-yl)-$N^6$-(6-((6-((6-(pyrimidin-2-ylamino)pyridin-2-yl)amino)pyridin-2-yl)amino)pyridin-2-yl)pyridine-2,6-diamine ($H_5N_{11}$-tpm) has been used to synthesize and structurally characterize the novel mononuclear Cu(II) complex. In Cu(II) complex $[Cu(H_5N_{11}\text{-tpm})](ClO_4)_2$ (**1**), $H_5N_{11}$-tpm functions as a pentadentate ligand and coordinates to a metal atom in an all-anti mode as a monohelix. The amino groups' nitrogen atoms are not coordinated to the metal center. The computed Addison parameter value of $\tau = 0.69$ for Cu(II) establishes the distorted trigonal bipyramidal geometry of the copper (II) core in complex **1**. Complex **1** builds extensive hydrogen bonds to construct 3D networks. The synthesized complex has high potential for the creation of novel cholinesterase inhibitors and medications to treat particular illnesses since it contains a number of nitrogen-containing heterocycles, such as pyridine and pyrimidine.

## *Supporting Information*

The Supporting Information is available free at https://ejc.buketov.edu.kz/ejc/article/view/420/320

CCDC 2443681 contains the supplementary crystallographic data for compound **1.** These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk

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## *Author Contributions*

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: ***Sabina Zahid Ismayilova*** data curation, validation, writing-original draft; ***Lala Shahin Guliyeva*** data curation, formal analysis, visualization; ***Rayyat Huseyn Ismayilov*** data curation, conceptualization, visualization, writing-review & editing; ***Dilgam Babir Tagiyev*** conceptualization, supervision, validation; ***Fuad Famil Valiyev*** data curation, formal analysis; ***Bahattin Yalcin*** supervision, validation; ***Ajdar Akber Medjidov*** methodology, supervision; ***Mansura Teyfur Huseynova*** data curation, validation; ***Su-Ying Chien*** data curation, formal analysis, investigation; ***Gene-Hsiatig Lee*** data curation, formal analysis; ***Shie-Ming Peng*** conceptualization, supervision.

## *Conflicts of Interest*

The authors declare no conflict of interest.

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