UDC 547.853.4

COPPER(II) COMPLEX WITH PYRAZINE- AND TRIAZINE-MODULATED TRIPYRIDYLDIAMINE LIGAND: SYNTHESIS, CRYSTAL STRUCTURE, MAGNETIC, AND ANTIMICROBIAL PROPERTIES

S.Z.Ismayilova[a], M.H.Osmanli[a], R.H.Ismayilov[a*], D.B.Tagiyev[a], M.T.Huseynova[b], K.R.Gahramanova[b], A.A.Medjidov[a], B.Yalcin[c], F.F.Valiyev[d], M.A.Bayramov[e], L.Sh.Guliyeva[a], O.Şahin[f], S.M.Peng[g]

[a]M.Nagiyev Institute of Catalysis and Inorganic Chemistry, Ministry of Science and Education of the Republic of Azerbaijan, Baku, Azerbaijan;
[b]A.Guliyev Institute of Chemistry and Additives, Ministry of Science and Education of the Republic of Azerbaijan, Baku, Azerbaijan;
[c]Department of Chemistry, Marmara University, Istanbul, Türkiye;
[d]"OilGasScientificResearchProject" Institute, SOCAR, Baku, Azerbaijan;
[e]Institute of Radiation Problems, Ministry of Science and Education of the Republic of Azerbaijan, Baku, Azerbaijan
[f]Department of Occupational Health & Safety, Faculty of Health Sciences, Sinop University, TR-57000 Sinop, Türkiye;
[g]Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC.

ismayilovrayyat@gmail.com

Received 24.01.2025
Reviewed 03.03.2025
Accepted 31.03.2025

Using the pyrazine- and triazine-modulated tripyridyldiamine ligand 6-phenyl-N^2,N^4-di(pyrazin-2-il)-1,3,5-triazine-2,4-diamine (H_2dpztzda), a new mononuclear copper(II) complex $[Cu(H_2dpztzda)(NO_3)_2]\cdot 2C_3H_7NO$ 1 has been synthesized, structurally characterized, and its antimicrobial properties studied. According to the single crystal X-ray analysis of complex 1, Cu(II) exhibits five coordination with a distorted trigonal bipyramidal geometry. The "inverted type" of EPR spectra ($g_\perp > g_\parallel \sim g_e$), alongside results from magnetic moment susceptibility and electronic spectrum studies, collectively support this observation. The calculated Addison value for 1 is $\tau_5 = 0.54$, indicating also that the Cu(II) center possesses distorted trigonal bipyramidal geometry. The H_2dpztzda molecule coordinates with the Cu(II) as a tridentate ligand. Complex 1 exhibits two types of hydrogen bonding: classical and non-classical. It has been shown that the interactions involving C-H···π, π-π, and hydrogen bonding significantly influence the crystal packing of synthesised complex 1 and play a crucial role in the formation of supramolecular motifs. The antimicrobial activity of the compounds was evaluated using the traditional well diffusion method. Both compounds (complex 1 and H_2dpztzda ligand) analyzed for antimicrobial activity showed highly effective results against the bacteria *Pseudomonas aeruginosa, Mycobacterium phlei,* and the fungi *Aspergillus niger* and *Penicillium chrysogenum* in lubricants and coolants.

Keywords: *Modulated oligo-α-aminopyridine ligand, Copper complex, Crystal structure, Hydrogen bonds, Spectroscopy, Antimicrobial agents.*

doi.org/10.32737/0005-2531-2025-4-23-33

Introduction

As is known from recent studies, among the numerous chemical compounds whose activity against infectious diseases is investigated, pyrazine- and triazine-based compounds should be specially mentioned. Compounds of the triazine and pyrazine class have demonstrated effective activity as potent antimicrobial inhibitors against a number of bacterial, fungal, and mycobacterial infections [1–4]. In medicinal chemistry, pyrazine and its derivatives are highly valued heterocyclic compounds. Their importance stems from their diverse biological activities, including potent antipyretic, anti-inflammatory, analgesic, anticancer, antibacterial, and antioxidant activities [5, 6]. This

makes them an important component in the design and synthesis of various pharmaceuticals [7]. Pyrazine and its derivatives, containing two nitrogen atoms in their six-membered aromatic ring, have become a new interesting basis for the study and development of antimicrobial properties of chemical substances [8]. The study showed that pyrazine derivatives have potent antimicrobial activity, successfully combating a wide range of bacterial and fungal strains [9]. As the main leader molecule, triazine is highly valued and widely used in the pharmaceutical field. Three different triazine isomers, 1,2,3-triazine, 1,2,4-triazine, and 1,3,5-triazine, are formed due to different mechanisms of nitrogen atom substitution in the aromatic ring. 1,3,5-triazine (s-triazine), characterised by its symmetrical structure, has extensive applications across various fields, including pharmaceuticals, textiles, rubber, and plastics. Substituted 1,3,5-triazine derivatives have become attractive targets in medicinal chemistry because of their significant biological activities, such as antibacterial, antifungal, antimalarial, antitumor, and anti-inflammatory [10–12]. As an essential trace element in biological systems, copper is an important transition metal for human health. In the field of medicinal chemistry, there is a growing interest in copper complexes with potent biological activities such as antibacterial, antiviral, antifungal, and antitumor activity [13]. A recently synthesized new copper (II) complex with neocuproine and triazine exhibits excellent antibacterial and antifungal activity [14]. Due to their ability to function as polydentate heterocyclic ligands, oligo-α-pyridylamines (Scheme 1) are of interest to researchers due to the variety of ways in which they can be coordinated with metals. The elongating metal atom chains (EMAC) are supported by oligo-α-pyridylamine ligands, which adopt a fully syn-configuration critical for linear chain formation. This is in stark contrast to mononuclear complexes, where the same ligands typically favour a fully anti-configuration [15–19]. The dimer of the free ligand contains the oligo-α-pyridylamines in their anti-syn structure [20]. Furthermore, a range of pharmacological effects, such as antibacterial, antioxidant, and anticancer properties, may be anticipated from oligo-α-pyridyl/pyrimidyl/pyrazylamine ligands, and particularly their complexes with transition metals that contain highly biologically active pyridine, pyrimidine, and pyrazine rings. Indeed, our recent studies have shown that the copper(II) and nickel(II) complexes with pyrazine- and pyrimidine-modulated oligo-α-pyridylamino ligands have high biological activity [21–23].

It should be noted that due to the development of modern processing technologies in the last 10 years, high stress, high static and dynamic loads cause heating of deformable materials. This, in turn, leads to deterioration of equipment quality, as well as tool wear. The use of cutting fluids (coolants - CFL) in the machining zone allows for changing the temperature in this zone, reducing it to an acceptable level due to the formation of more vapors. The presence of CFL with lubricating properties reduces friction, wear and abrasion in the machining zone, as well as the likelihood of damage to the surfaces of machined parts and tools. They may contain additives against corrosion, wear and abrasion as well as biocides [24]. Therefore, researchers are actively exploring new antimicrobial compounds as potential solutions. This endeavour highlights the key role of antimicrobial activity screening and evaluation methods, a crucial step in the search for and characterisation of antimicrobial agents [25, 26].

Well diffusion assay is widely used and is one of the effective methods in antimicrobial research to determine the antimicrobial activity of test compounds. This method is based on the diffusion of antimicrobial agents into wells in an agar medium, which inhibits the growth of the test compound inoculated on the surface of the agar By measuring the resulting inhibition zone, which is the area where microbial growth is possessed or inhibited by the agent, the relative effectiveness of the test compound against the constant test determination can be estimated [27, 28].

In this paper, we present our latest research with 6-phenyl-N^2,N^4-di(pyrazin-2-il)-1,3,5-triazine-2,4-diamine (H_2dpztzda) tuning

ligand from tripyridyldiamine – H_2tpda (Scheme 1). We describe the first time the synthesis, crystal structure, magnetic and antimicrobial properties of mononuclear complex $[Cu(H_2dpztzda)(NO_3)_2]\cdot 2C_3H_7NO$ (1) of H_2dpztzda.

Experimental part

Materials and measurements

Metal salt was commercial product of highest chemical grade (Aldrich). Solvents were purified according to standard procedures. Elemental analyses were done with a FLASH EA 1112 SERIES CHNS analyzer. IR spectra were recorded with a Bruker Alpha FTIR spectrometer as KBr discs, in the range of 400-4000 cm^{-1}. Absorption spectra were performed on a SPECORD 50 plus spectrophotometer. EPR spectra were recorded in the solid state with a Bruker BioSpin GmbH spectrometer at X-band microwave frequency. Molar magnetic susceptibility was measured using a SQUID system with a 1000 Oe external magnetic field.

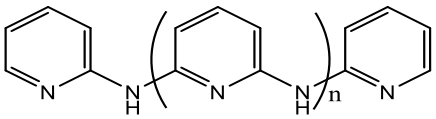
Preparation of compounds

The ligand 6-phenyl-N^2,N^4-di(pyrazin-2-il)-1,3,5-triazine-2,4-diamine (H_2dpztzda) was prepared in good yield by palladium-catalyzed cross-coupling of 6-phenyl-1,3,5-triazine-2,4-diamine and 2-chloropyrazine, and characterized by IR, ^{1}H NMR and MS(FAB) [29, 30].

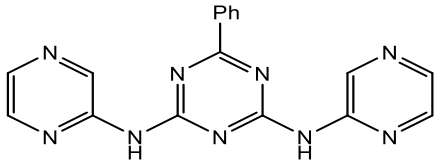
$[Cu(H_2dpztzda)(NO_3)_2]\cdot 2C_3H_7NO$ (1). A mixture containing 0.40 mmol (0.138 g) of H_2dpztzda and 0.44 mmol (0.106 g) of $Cu(NO_3)_2\cdot 3H_2O$ was stirred for 24 hours at room temperature. Following stirring, it was filtered to remove any unreacted starting materials and subsequently concentrated under vacuum. Through slow diffusion of ethyl ether, single crystals of the copper(II) complex, green in color and suitable for X-ray structural investigation, were extracted from the solution after a week (0.095 g, 35% yield). IR (KBr) ν/cm^{-1} 3411 w (NH of DMF), 3223 w(NH), 3097 w(Ar CH), 1650 m, 1629 m, 1590 m, 1556 s, 1457 s, 1438 m (Ar), 1388 s, 1272 s, 1147 s, 1028 s, 838 m, 708 m, 656 w, 518 w, 447 m(Cu-N); UV/Vis (CH_3OH) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 211 (3.50×10^4), 265 (1.22×10^4), 830 (1.12×10^2); elemental analysis (%) $C_{23}H_{27}CuN_{13}O_8$: calc. C 40.80, H 4.02, N 26.89; found: C 40.92, H 4.12, N 26.76.

Crystal structure determinations

The suitable crystals of $[Cu(H_2dpztzda)(NO_3)_2]\cdot 2C_3H_7NO$ (1) was selected for data collection, which was performed on a D8-QUEST diffractometer at 293 K using Mo-Ka radiation (λ = 0.71073 Å). The structure was solved by direct methods using SHELXS-2013 [31] and refined by full-matrix least-squares methods on F2 using SHELXL-2013 [32]. 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 0.93 A and a N-H distance of 0.86 A. The other H atoms were located in a difference map refined freely. Molecular graphics were created using the MERCURY programs [33]. Below are the specifics of the X-ray diffraction experiment and a summary of the crystallographic data for the copper(II) complex 1:



Scheme 1. Oligo-α-pyridylamino ligands (n=0, Hdpa; n=1, H_2tpda)



H_2dpztzda

Empirical formula $C_{23}H_{27}CuN_{13}O_8$; formula weight = 677.11; crystal system – triclinic; space group – P-1; a = 11.1956 (10), b = 11.5094 (10), c = 11.8053 (11) Å; α = 86.265 (2); β = 76.693 (3); γ = 85.755 (2) °; volume = 1474.4 (2) $Å^3$, Z = 2; density (calculated) = 1.525 Mgm^{-3}; absorption coefficient=0.81 mm^{-1}; crystal size: 0.17 × 0.11 × 0.09 mm^3; θ range for data collection 2.3–22.1°; reflection collected - 44537, independent reflection - 6115 [R(int) = 0.057]; R_1 = 0.052, wR_2 = 0.126; GOF = 1.020.

The bactericidal and fungicidal activity of the obtained compounds

Antimicrobial activity of samples was determined by the zonal diffusion method using the following microorganisms: bacteria – Pseudomonas aeruginosa, Mycobacterium phlei; fungi – Aspergillus niger, Penicillium chrysogenum. An assumed test period is 2 days for bacterial development and 3–4 days for fungal development.

Results and discussion

Syntheses and structures

The ligand 6-phenyl-N^2,N^4-di(pyrazin-2-il)-1,3,5-triazine-2,4-diamine (H_2dpztzda) was synthesized according to our previously reported work [29].

The complex $[Cu(H_2dpztzda)(NO_3)_2]\cdot 2C_3H_7NO$ (1) was synthesized by direct reaction of H_2dpztzda with $Cu(NO_3)_2 \cdot 3H_2O$ in methanol. The compound was characterized as mononuclear species by single-crystal X-ray diffraction, elemental analysis, ESR, FTIR and UV-Vis spectra. The crystal structure of 1 is shown in Figure 1, selected bond lengths and angles are collected in the Table 1. Complex 1 crystallizes in P-1 space group of the triclinic system and contents two dimethylformamide (DMF) molecules in the crystal lattice. In compound 1 Cu(II) is five coordinated. It is well known that, the five coordinate Cu(II) atom can have the trigonal bipyramidal (TBP), square pyramidal (SP) or a geometry in between these two extremes. To comprehend the reasons behind deviations from ideal geometries, Addison, Reedijk, and their colleagues first introduced the trigonality parameter τ_5 in 1984 [34]. It is widely acknowledged that τ_5 ranges from 1.00 (τ_5 = 1.00) for an ideal trigonal pyramidal geometry to zero (τ_5 = 0) for a perfect square pyramidal geometry. The calculated Addison value for 1 is τ_5 = 0.54, indicating that the Cu(II) center possesses distorted trigonal bipyramidal geometry. In complex 1, the equatorial plane consists of triazine nitrogen (N6) and two oxygen atoms (O1, O4) from the two monodentate coordinated nitrate groups. Meanwhile, the axial positions are occupied by two nitrogen atoms (N1 and N8) from the two terminal pyrazine rings of the H_2dpztzda ligand. This configuration gives rise to an overall distorted trigonal bipyramidal stereochemistry. In the trigonal plane, the coordination bond distances range from 2.046(2) Å to 2.405(3) Å, and the angle N(1)-Cu(1)-N(8) measures 173.25(11)° (see Table 1). The Cu-$N_{pyrazine}$ apical bond distances are almost equal (Cu(1)-N(1)=1.975(3) Å; Cu(1)-N(8)=1.974(3) Å), and they remain closer to the values previously reported for copper complexes containing nitrogen-containing heterocyclic ligands [15, 19, 35]. In complex 1, the H_2dpztzda coordinates to the Cu(II) ion in an anti-anti-anti-anti conformation as a tridentate ligand.

Complex 1 (Table 2) displays two types of hydrogen bonding: classical and non-classical. The classical hydrogen bonding occurs between amino groups and DMF molecules within the crystal lattice, specifically N(3)···O(7)^{ii} at a distance of 2.795(3) Å and N(7)···O(8) at 2.780(3) Å. The weak C-H···O type hydrogen bonds (ranging from 3.076(5) to 3.374(5) Å) between hydrogen atoms from aromatic groups and oxygen atoms from nitrate anions and DMF molecules in complex 1 play a significant role in influencing crystal packing (Figure 2). The pyrazine, triazine and phenyl groups of the H_2dpztzda in 1 are planar and twisted. The dihedral angle between each pair of neighboring planes is 4.49(2)^o of (Pz(N1)-Tz(N6)), 7.94(2)^o of (Tz(N6)-Pz(N8)) and 2.37(3)^o of (Tz(N6)-Ph(C7)), respectively. Moreover, complex 1 exhibits two intermolecular π-π stacking interactions between pyrazine(Cg(1)/or pirazine(Cg(3) - phenyl(Cg(4) rings, respectively (Table 3). The perpendicular projections of Cg (J) onto ring (I) for two pairs of rings in complex 1 are found to be 3.453 Å and 3.551 Å (Table 3). The crystal packing of synthesized complex 1 [21, 23] is significantly affected by H-bonding, π-π, and C-H···π interactions, which facilitate the formation of supramolecular motifs. These interactions are essential for the establishment of the complex's two-dimensional structure. As observed in most mono- and dinuclear complexes with oligo-α-aminopyridine ligands [21–23, 29, 36, 37], the amino group nitrogen atoms in complex 1 remain uncoordinated to the metal center.

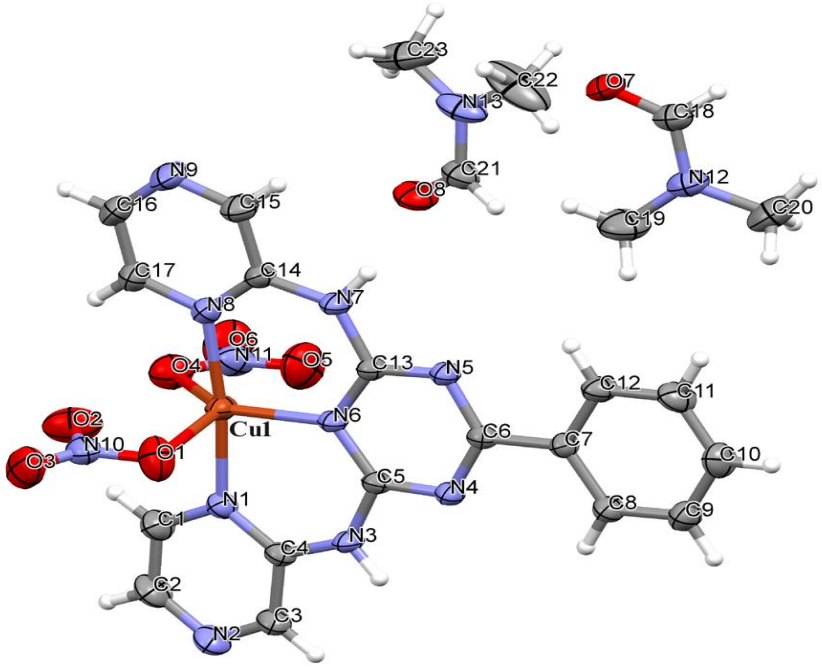


Fig. 1. The molecular structure of complex $[Cu(H_2dpztzda)(NO_3)_2]\cdot 2C_3H_7NO$ **1** showing the atom numbering scheme. Thermal ellipsoids are drawn at the 40% probability level.

Table 1. Selected bond distances (Å) and angles (°) for 1 and 2

1			
Cu(1)–N(1)	1.975(3)	Cu(1)–O(1)	2.405(3)
Cu(1)–N(6)	2.046(2)	Cu(1)–O(4)	2.177(3)
Cu(1)–N(8)	1.974(3)	N(6)–Cu(1)–O(1)	86.86(10)
N(1)–Cu(1)–N(8)	173.25(11)	N(6)–Cu(1)–O(4)	140.62(12)
N(1)–Cu(1)–N(6)	93.35(10)	O(1)–Cu(1)–O(4)	132.47(11)
N(1)–Cu(1)–O(1)	86.41(11)	N(8)–Cu(1)–O(4)	88.21(11)
N(1)–Cu(1)–O(4)	88.22(11)	N(8)–Cu(1)–N(6)	93.04(10)
N(8)–Cu(1)–O(1)	91.78(11)		

Table 2. Hydrogen-bond geometry (Å,°) for complex 1

D-H···A	D-H	H···A	D···A	D-H···A
C2-H2···O3^{i}	0.93	2.46	3.344 (5)	158
C3-H3···O7^{ii}	0.93	2.29	3.076 (5)	142
C15-H15···O8	0.93	2.34	3.106 (5)	140
C16-H16···O6^{iii}	0.93	2.45	3.374 (5)	177
C18-H18···O1^{iv}	0.93	2.60	3.261 (5)	128
C21-H21···O5^{iv}	0.93	2.58	3.228 (5)	127
N3-H3A···O7^{ii}	0.86	1.96	2.795(3)	165
N7-H7···O8	0.86	1.93	2.780(3)	168

Symmetry codes: (i) −x, −y+2, −z+2; (ii) x, y+1, z; (iii) −x, −y+1, −z+2;
(iv) −x+1, −y+1, −z+1.

Table 3. The π···π interactions distances for $[Cu(H_2dpztzda)(NO_3)_2]\cdot 2C_3H_7NO$ (1) (Å)

Cg(1)	Cg(J)	Cg-Cg	Perpendicular distance
Cg(1)	Cg(4)^{i}	3.761 (4)	3.453
Cg(3)	Cg(4)^{ii}	3.750 (3)	3.551

Symmetry codes: (i) 1-x, -y, 1-z; (ii) 1-x, 1-y, 1-z; Cg(1) = N1-C1-C2-N2-C3-C4; Cg(3) = N8-C14-C15-N9-C16-C-17; Cg(4) = C7-C8-C9-C10-C11-C12.

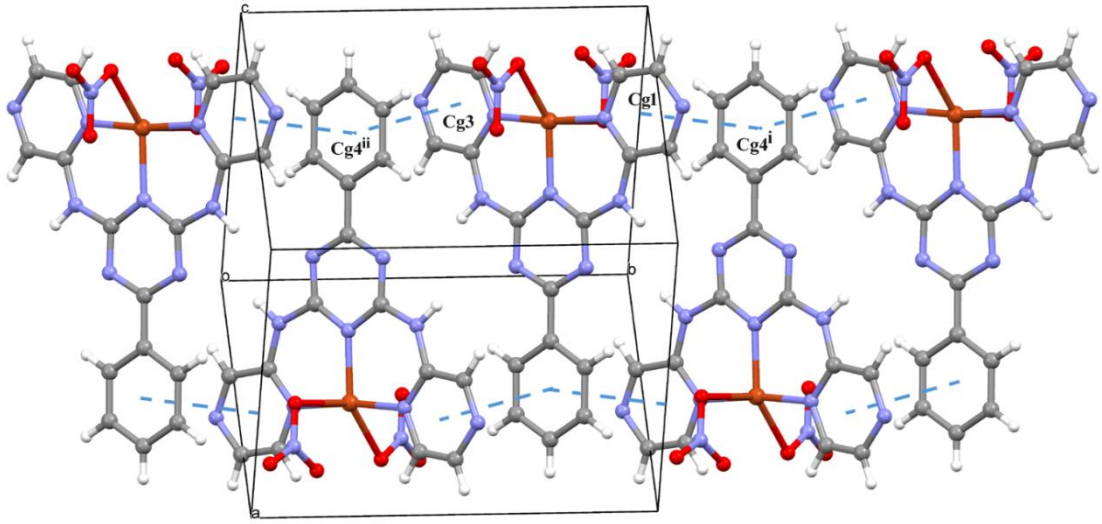


Fig. 2. The formation of a chain along [010] generated by π···π interactions in $[Cu(H_2dpztzda)(NO_3)_2]\cdot 2C_3H_7NO$ **1**. [(i) 1-x, -y, 1-z; (ii) 1-x, 1-y, 1-z].

IR, UV-Vis, EPR spectroscopy and magnetic properties

The stretching vibration of the amide group (N–H) in DMF is indicated by the broad, weak peak observed in the IR spectrum of 1 at 3411 cm^{-1} (Figure 3). The asymmetric and symmetric stretching vibrations of the DMF's methyl group (C–H) are represented by the weak peaks at 2965 cm^{-1} and 2897 cm^{-1}, respectively. The weak band observed at 3223 cm^{-1} is attributed to the NH bonds present in the amine groups of compound 1. Meanwhile, υ(Cu–N) of complex 1 is tentatively identified as the new band detected at 447 cm^{-1}. Compound 1's skeletal vibrations of aromatic rings produce strong absorption bands in the IR spectra located in the 1438–1650 cm^{-1} regions. The monodentate-coordinated NO_3^- anions exhibited strong vibrations at 1467 cm^{-1} for $\nu_{as}(NO_2)$, 1272 cm^{-1} for $\nu_s(NO_2)$, and 1028 cm^{-1} for ν(NO) in complex 1. Similar strong vibrations of coordinated NO_3^- anions have been observed earlier for other copper(II) complexes with pyrazine-modulated oligo-α-aminopyridine ligands [21, 22].

The electronic spectra of trigonal-bipyramidal copper (II) complexes anticipate two spin-allowed transitions in the visible or near-infrared range. It would make sense to attribute the lower energy band to the $d_{xy},d_{x^2-y^2}\rightarrow d_{z^2}$ transitions and the higher energy band to the $d_{xz},d_{yz}\rightarrow d_{z^2}$ transitions based on works [38] that have been discussed in the literature. However, only one broad, unresolved asymmetric peak with a maximum at 830 nm has been identified in the visible region of complex 1's electronic spectra. For certain trigonal-bipyramidal copper(II) complexes, K.D. Karlin et al. previously reported the finding of a single, broad band around 800 nm with a more or less noticeable shoulder [39]. The higher and lower energy bands may be challenging to distinguish due to the very close energies of the d_{xz}, $d_{yz}\rightarrow d_{z^2}$, as well as the $d_{x^2-y^2}\rightarrow d_{z^2}$ transitions. The X-ray structural study also supports the reported result, which is in good agreement with a trigonal-bipyramidal ligand environment of Cu(II) ions in 1.

It is well known that, the Cu(II) polyhedron in pentacoordinated Cu(II) complexes can adopt two distinct geometric arrangements: the trigonal bipyramidal geometry (TBP) with D_{3h} symmetry and the square pyramidal geometry (SP) with D_{4v} symmetry. EPR spectroscopy is a direct and convenient method to elucidate the variations in the geometry of the Cu(II) complex [34, 40]. Figure 4 shows the powder EPR spectrum of the synthesized pentacoordinated Cu(II) complex $[Cu(H_2dpztzda)(NO_3)_2]\cdot 2C_3H_7NO$ at room temperature. It displays the usual anisotropic pattern belonging to the Cu^{2+} ion (S=1/2, I= 3/2).

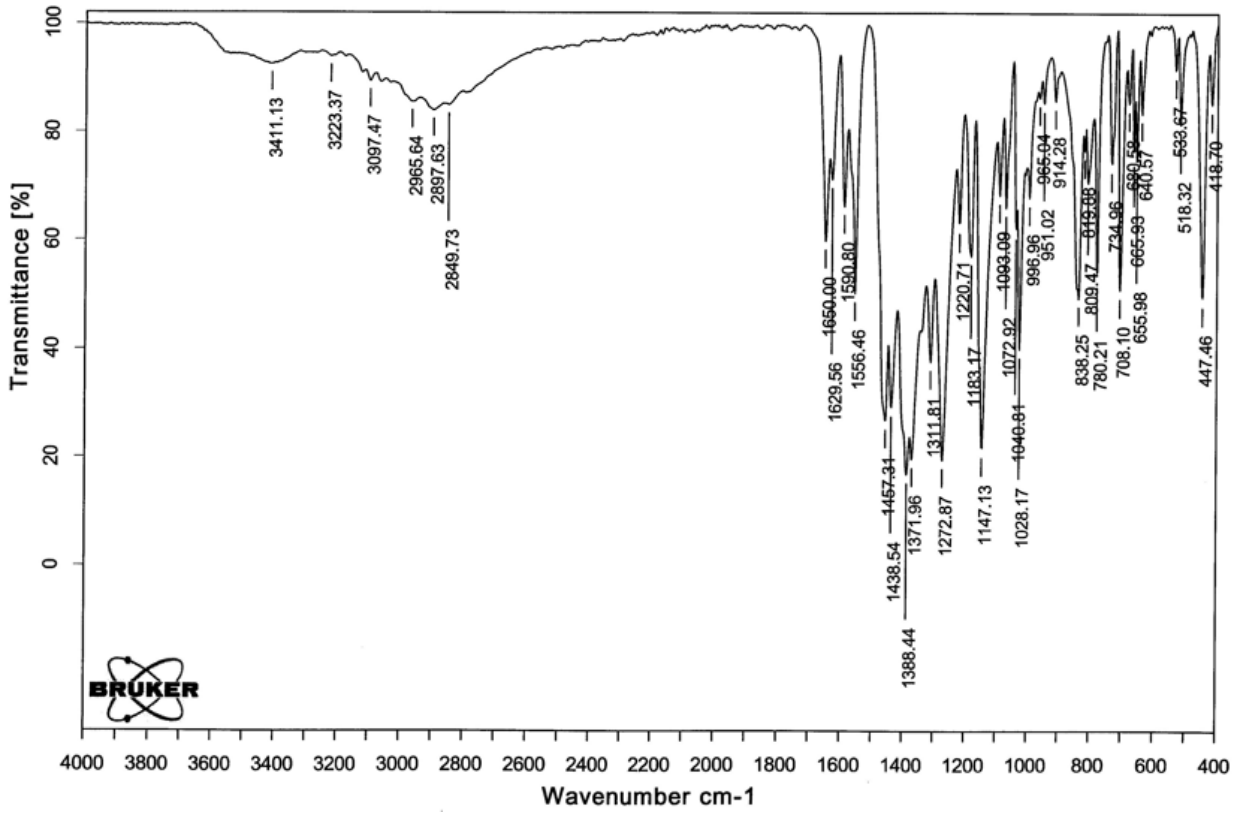


Fig. 3. IR spectra of complex 1.

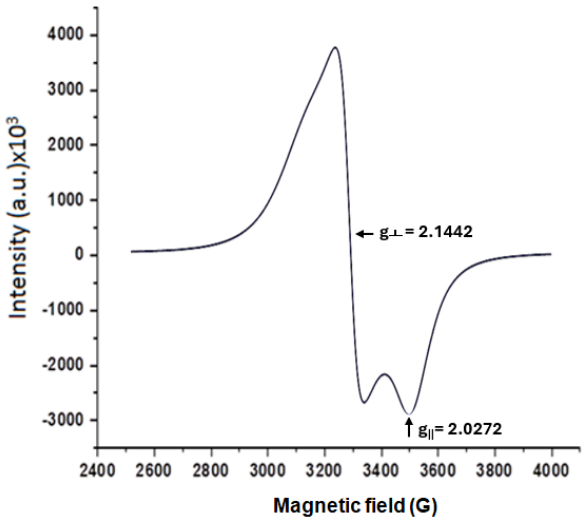


Fig. 4. EPR spectra of powder sample of the copper(II) complex 1 at room temperature.

Both parallel and perpendicular components have been observed in this spectrum. Hyperfine splitting could not be resolved because of line broadening, which originated from spin-orbital and spin-exchange interactions due to the excess concentration of spins. The values of the $g_{\parallel}$ and $g_{\perp}$ components were extracted from the powder spectrum. These parameters have numerical values of $g_{\parallel}$ = 2.0272 and $g_{\perp}$ = 2.1442, respectively. The axial symmetry of the paramagnetic core is shown by these g values. So, according to the order of $g_{\perp} > g_{\parallel} \sim ge$ (with the free electron g value, ge = 2.0023), the Cu(II) ions are arranged in a distorted triangular bipyramidal configuration, 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 (Table 1). At 300 K, compound 1's measured magnetic moment is 1.81 B.M., which is compatible with one unpaired electron in Cu(II) (d^9) and a minor orbital contribution.

Antimicrobial activities

For the primary evaluation of antimicrobial efficacy of the synthesized compounds under LCM conditions, aqueous solutions of the samples were investigated. Sodium pentachlo-

rophenolate was used as a standard antimicrobial reference substance. The antimicrobial properties of the studied compounds (complex 1 and H_2dpztzda ligand) were determined using the zonal diffusion method. Laboratory isolates of bacteria and fungi: Pseudomonas aeruginosa, Mycobacterium phlei, as well as fungi Aspergillus niger and Penicillium chrysogenum, were used to study antibacterial activity.

Meat-peptone agar (MPA) was used to cultivate bacteria, and wort agar (WA) was used to cultivate fungi. As a preliminary step at the start of the experiment, both of the test samples were added to the lubricating and cooling fluid (LCF) in two different mass ratios: 0.5 and 0.25.

The effectiveness of the tested samples as additives against microorganisms is measured by the diameter of the microorganism damage zone (cm): the larger the diameter of the damage zone, the greater the antimicrobial activity of these compounds.

The biocidal activity of the tested compounds compared to the standard (sodium pentachlorophenolate) is presented in Table 4. The sign (+++) in Table 4 indicates the general growth of microorganisms. The results of laboratory tests demonstrate that the synthesized compounds according to Table 4 have significant activity against certain bacteria and fungi (Figure 5). Analyzing the test results, it can be observed that the studied compounds possess bactericidal and fungicidal properties.

Table 4. Determination of antimicrobial properties of synthesized compounds in CFL

№	Compounds	Biocide concentration %	Zone of destruction of microorganisms (cm)	
			Bacteriya (Pseudomonas aeruginosa, Mycobacterium phlei)	Fungi (Aspergillus niger, Penicillium chrysogenum)
1	Complex 1	0.5	2.2–2.4	2.6–2.8
		0.25	1.2–1.2	1.4–1.6
2	H_2dpztzda (Ligand)	0.5	1.6–1.8	2.0–2.0
		0.25	+++	1.2–1.2
3	Standard (sodium pentachlorophenolate)	1.0	1.3–1.4*	1.3–1.4*
4	Check sample -CFL (biocide-free)	–	+++	+++

+++ the overall development of microorganisms

I II

Fig. 5. Laboratory test results displayed in a Petri dish I bacteriy and II fungi.

As shown in Table 4, complex 1 at a concentration of 0.5% exhibits a notable result: 2.2–2.4 cm against bacteria and 2.6–2.8 cm against fungi. It was found that the results of the antimicrobial properties of both of the tested compounds were higher than the standard, sodium pentachlorophenolate.

Conclusions

A new mononuclear copper(II) complex, $[Cu(H_2dpztzda)(NO_3)_2]\cdot 2C_3H_7NO$ 1, was synthesized and structurally characterized. This complex features a symmetrical ligand, 6-phenyl-N^2,N^4-di(pyrazin-2-il)-1,3,5-triazine-2,4-diamine, which is modulated by both pyrazine and triazine groups. X-ray single crystal analysis revealed that in a synthesized mononuclear complex 1, H_2dpztzda acts as a tridentate ligand and coordinates the copper(II) ion in an anti-anti-anti-anti conformation. In 1, the Cu(II) atom is five-coordinated and has distorted trigonal bipyramidal geometry. The results of spectroscopic analysis, including IR, UV-visible, and EPR spectroscopy, as well as magnetic measurements, are in good agreement with the XRD data. Extensive hydrogen bonds, as well as π-π stacking construct the complex 1 into a 2D network and stabilize the crystal packing. Complex 1 and the H_2dpztzda ligand analyzed for antimicrobial activity showed highly effective results against the bacteria *Pseudomonas aeruginosa, Mycobacterium phlei,* and the fungi *Aspergillus niger* and *Penicillium chrysogenum* in lubricants and coolants.

Supplementary material

CCDC 2475261 contains the supplementary crystallographic data for compound 1. This 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

References

1. Hou W., Dai W., Huang H., Liu S.L., Liu J., Huang L.J., Huang X.H., Zeng J.L., Gan Z.W., Zhang Z.Y., Lan J.X. Pharmacological activity and mechanism of pyrazines, Eur. J. Med. Chem. 2023. V. 258. https://doi.org/10.1016/j. ejmech.2023.115544.
2. Miniyar P.B., Murumkar P.R., Patil P.S., Barmade M.A., Bothara K.G. Unequivocal role of pyrazine ring in medicinally important compounds: a review, Mini Rev. Med. Chem. 2013. V. 13. P. 1607–1625. https://doi.org/10.2174/1389557511313110007
3. Tang X., Su S., Chen M., He J., Xia R., Guo T., Chen Y., Zhang C., Wang J., and Xue W. Novel chalcone derivatives containing 1,2,4-triazine moiety: design, synthesis, antibacterial and antiviral activities. RSC Advances. 2019. V. 11. P. 6011–6020.
4. Al-Dahlaki M.H.M., Al-Majidi Suaad M.H. ″Synthesis and study impaction antibacterial, antifungal activity newly pyridazine and 1,2,4-triazine derivatives″ Jour. Chem. Methodologies. 2022. V. 6. P. 269–279.
5. Tantawy E.S., Amer A.M., Mohamed E.K., Abd Alla M.M., Nafie M.S. Synthesis, characterization of some pyrazine derivatives as anti-cancer agents: In vitro and in Silico approaches, J. Mol. Struct. 1210. 2020. 128013. doi.org/10.1016/j.molstruc.2020.128013
6. Choudhary D., Garg S., Kaur M., Sohal H.S., Malhi D.S., Kaur L., Verma M., Sharma A., Mutreja V. Advances in the Synthesis and Bio-Applications of Pyrazine Derivatives: A Review. Polycycl. Aromat. Compd. 2023. V. 43. P. 4512–4578. https://doi.org/10.1080/10406638.2022.2092873
7. Chen G.Q., Guo H.Y., Quan Z.S., Shen Q.K., Li X., Luan T. Natural Products–Pyrazine Hybrids: A Review of Developments in Medicinal Chem. Molecules 2023. V. 28. P. 7440. https://doi.org/10.3390/molecules28217440
8. Ong K.T., Liu Z.Q., Meng G.T. Review on the synthesis of pyrazine and its derivatives, Borneo J. Resour. Sci. Technol. 2017. V. 7. P. 60–75. https://doi.org/ 10.33736/bjrst.591.2017.
9. Huigens R.W., Brummel B.R., Tenneti S., Garrison A.T., Xiao T. Pyrazine and Phenazine Heterocycles: Platforms for Total Synthesis and Drug Discovery. Molecules 2022. V. 27. No 3. P. 1112. https://doi.org/10.3390/molecules27031112
10. Gunasekaran P., Fan M., Kim E.Y., Shin J.H., Lee J.E., Son E.J., Kim J., Hwang E., Yim M.S., Kim E.-H., et al. Amphiphilic triazine polymer derivatives as antibacterial and anti-atopic agents in mice model. Sci. Rep. 2019. V. 9. P. 15161. doi: 10.1038/s41598-019-51561-7.
11. Sharma A., Singh S., Utreja D. ″Recent Advances in Synthesis and Antifungal Activity of 1,3,5-triazines″. Curr. Org. Synth. 2016. V. 13. P. 484–503.

12. Adhikari N., Kashyap A., Shakya A., Ghosh S.K., Bhattacharyya D.R., Bhat H.R., Singh UP. ″Microwave assisted synthesis, docking and anti-malarial evaluation of hybrid PABA-substituted 1,3,5-triazine derivatives″. Journ. Heterocyclic Chem. 2020. V. 57. P. 2389–2399.
13. Qi J., Wang X., Liu T., Kandawa-Schulz M., Wang Y., Zheng X. Synthesis, antiproliferative activity and mechanism of copper(II)-thiosemicarbazone complexes as potential anticancer and antimicrobial agents. J. Coord. Chem. 2020. P. 1–14. doi:10.1080/00958972.2020.1768378
14. Vinayagam V., Prabu S., Rajalakshmi S., Arumugam M.N. Synthesis, characterization, DNA interaction, antimicrobial activity, DFT analysis and molecular docking studies of copper(II) complex with triazine and neocuproine, J. Mol. Struct. 2023. V. 1287. P. 135649 https://doi.org/10.1016/j.molstruc.2023.135649
15. Ismayilov R.H., Valiyev F.F., Tagiyev D.B., Song Y., Israfilov N.V., Wang W.Z., Lee G.H., Peng S.M., Suleimanov B.A. Linear pentanuclear nickel(II) and tetranuclear copper(II) complexes with pyrazine-modulated tripyridyldiamine ligand: Synthesis, structure and properties, Inorg. Chim. Acta. 2018. V. 483. P. 386–391. doi.org/10.1016/j.ica.2018.08.045
16. Ismayilov R.H., Ismayilova S.Z., Tagiyev D.B., Medjidov A.A., Jafarov Y.I., Wang W.Z., Yeh C.Y., Chien S.Y., Lee G.H., Peng S.M. Linear nonanuclear chromium(II) complex with pyrazine-modulated pentapyridyltetraamine ligand: Synthesis, structure and properties, J. M. Struct. 2025. V. 1331. P. 141592. https://doi.org/10.1016/j.molstruc.2025.141592
17. Wang W.Z., Ismayilov R.H., Lee G.H., Huang Y.L., Yeh C.Y., Fu M.D., Chen C.H., Peng S.M. Fine tuning of pentachromium(II) metal string complexes through elaborate design of ligand, New J. Chem. 2012. V. 36. P. 632–637. DOI: 10.1039/c1nj20512a
18. Berry J.F., Cotton F.A., Lu T., Murillo C.A., Wang X. Enhancing the Stability of Trinickel Molecular Wires and Switches: Ni_3^{6+}/Ni_3^{7+}, Inorg. Chem. 2003. V. 42. P. 3595–3601. https://doi.org/10.1021/ic0341486
19. Ismayilov R.H., Valiyev F.F., Israfilov N.V., Wang W.Z., Lee G.H., Peng S.M., Suleimanov B.A. Long chain defective metal string complex with modulated oligo-á-pyridylamino ligand: Synthesis, crystal structure and properties, J. Mol. Struct. 1200 (2020) 126998. (doi.org/10.1016/j.molstruc.2019.126998)
20. Brogden D.W., Berry J.F. Coordination Chemistry of 2,2'-Dipyridylamine: The Gift That Keeps on Giving, Comments Inorg. Chem. 2015. P. 17–37. doi.org/10.1080/02603594.2015.1079522
21. Ismayilov R.H., Valiyev F.F., Tagiyev D.B., Song Y., Medjidov A.A., Fatullayeva P.A., Tüzün B., Taslimi P., Peng C.H., Chien S.Y., Lee G.H., Peng S.M. Trinuclear nickel (II) string complexes and copper (II) coordination polymer with pyrazine modulated unsymmetrical dipyridylamino ligand: Synthesis, structure and bioactivity properties with molecular docking, J. Mol. Struct. 2024. V. 1307. P. 137966. https://doi.org/10.1016/j.molstruc.2024.137966
22. Abbasova G.G., Ismayilov R.H., Tagiyev D.B., Şenol H., Song Y., Medjidov A.A., Huseynova M.T., Fatullaeva P.A., Taslimi P., Sadeghian N., Lee G.H., Peng S.M. Synthesis, characterization, crystal structure, molecular dynamics simulations, MM-GBSA analysis, and bioactivity studies of pyrazine- and pyrimidine-modulated unsymmetrical dipyridylamide complexes, J. Mol. Struct. 2024. V. 1315. P. 138896. doi.org/10.1016/j.molstruc.2024.138896
23. Ismayilova S.Z., Ismayilov R.H., Tagiyev D.B., Şenol H., Medjidov A.A., Huseynova M.T., Yalcin B., Taslimi P., Rasulov N.S., Sadeghian N., Şahin O., Peng S.M., Copper(II) monohelix complexes with pyrazine-modulated long-chain oligo-α-aminopyridine ligand: synthesis, crystal structures, and bioactivity studies, J. Mol. Struct. 2025. V. 1347. P. 143295. https://doi.org/10.1016/j.molstruc.2025.143295
24. Hossain T.J. Methods for screening and evalution of antimicrobial activity: A review of protocols, advantages, and limitations. European Journ. Microbiology and Immunology. 2024. V. 14. No 2. P. 97–115. doi:10.1556/1886.2024.00035.
25. Bauer A.W., Kirby W.M.M., Sherris J.C., Turck M. Antibiotic susceptibility testing by a standardized single disk method. American Journ Clinical Pathology. 1966. V. 45. No 4. P. 493–496.
26. Huseynova M.T. DFT Calculations, Hirshfeld Analysis, Antimicrobial, Antifungal Properties of The Cu(II) Polymeric Complex with Thiosemicarbazone of Glyoxylic Acid. Azerb. Chem. Journ. 2021. No 4. P. 77–81.
27. Tarannum N., Hossain T.J., Ali F., Das T., Dhar K., Nafiz I.H. Antioxidant, antimicrobial and emulsification properties of exopolysaccharides from lactic acid bacteria of bovine milk: insights from biochemical and genomic analysis. LWT. 2023. V. 186. P. 115263 doi.org/10.1016/j.lwt.2023.115263
28. Farzaliyeva A.E., Kahramanova K.R., Magerramov A.M., Mammadov I.G. Study of some N, S, O-containing organic compounds as additives preventing microbiological damage of cutting fluids. Journ. Azerb. Oil Industry. 2023. No 11. P. 57–61. DOI.10.37474/0365-8554/2023-11-57-61.
29. Ismayilov R.H., Synthesis, crystal structure and magnetic properties of copper(II) complex with 6-

phenyl-N^2,N^4-di(pyrazin-2-il)-1,3,5-triazine-2,4-diamine ligand. Chem. Probl. 2009. No 4. P. 619–623.
30. Wagaw S., Buchwald S.L., The Synthesis of Aminopyridines: A Method Employing Palladium-Catalyzed Carbon–Nitrogen Bond Formation, J. Org. Chem. 61. 1996. P. 7240–7241.
31. Sheldrick G.M., A short history of SHELX. *Acta Cryst*. 2008. V. A64. P. 112.
32. Sheldrick G.M., Crystal structure refinement with SHELXL, Acta Cryst. 2015. V.71. P. 3.
33. Macrae C.F., Sovago I., Cottrell S.J., Galek P.T.A., McCabe P., Pidcock E., Platings M., Shields G.P., Stevens J.S., Towler M., Wood P.A., J. Appl. Cryst. 2020. V. 53. P. 226–235.
34. Korkmaz Ş.A., Karadağ A., Yerli Y., Soylu M.S. Synthesis and characterization of new heterometallic cyanido complexes based on $[Co(CN)_6]3^-$ building blocks: crystal structure of $[Cu_2(N\text{-}bishydeten)_2Co(CN)_6]\bullet 3H_2O$ having a strong antiferromagnetic exchange. New J. Chem. 2014. V. 38. P. 5402–5410. DOI: 10.1039/c4nj00737a
35. Ismayilova S.Z., Huseynova M.T., Ismayilov R.H., Medjidov A.A. Synthesis and properties of Cu^{II} complex of benzidine- N,N,N′,N′ tetraacetic acid. Azerb. Chem. Journ. 2024. No 3. P. 69–75. doi.org/10.32737/0005-2531-2024-3-69-75
36. Ismayilova S.Z., Ismayilov R.H., Tagiyev D.B., Yalcin B., Şahin O., Medjidov A.A., Huseynova M.T., Guliyeva L.Sh., Gasimov R.J., Peng S.M. Copper(II) complex of the pyrazine-modulated oligo-α-aminopyridine as a coordination polymers′ promising building block. Chemical Problems. 2025. V. 23. No 4. P. 476–482. doi: 10.32737/2221-8688-2025-4-476-482
37. Ismayilova S.Z. Co(II), Ni(II), Zn(II) and Cu(II) complexes with N,N'-*bis*-(2-hydroxybenzyl)benzidine. Azerb. Chem. Journ. 2019. No 4. P. 94–98. doi.org/10.32737/0005-2531-2019-4-94-99
38. Duggan M., Ray N., Hathaway B.J., Tomlinson G., Brint P., Pelin K., Crystal Structure and Electronic Properties of Ammine[tris(2-aminoethyl)-amine]copper(II) Diperchlorate and Potassium Penta-amminecopper(II) Tris(hexafluorophosphate). J. Chem. Soc., Dalton Trans. 1980. P. 1342–1348. https://doi.org/10.1039/DT9800001342
39. Wei N., Murthy N.N., Karlin K.D. Chemistry of Pentacoordinate $[LCu^{II}\text{-}Cl]^+$ Complexes with Quinolyl Containing Tripodal Tetradentate Ligands L. Inorg. Chem. 1994. V. 33. P. 6093–6100.
40. Valko M., Pelikán P., Biskupič S., Mazúr M. ESR spectra of copper(II) complexes in the solids. Chem. Papers. 1990. V. 44. P. 805–813.

PİRAZİN VƏ TRİAZİN İLƏ MODULLAŞDIRILMIŞ TRİPİDİLAMİN LİQANDI İLƏ MİS (II) KOMPLEKSİ: SİNTEZİ, KRİSTAL QURULUŞU, MAQNİT VƏ ANTİMİKROB XÜSUSİYYƏTLƏRİ

S.Z.İsmayılova, M.H.Osmanlı, R.H.İsmayılov, D.B.Tağıyev, M.T.Hüseynova, K.R.Qəhrəmanova, A.A.Məcidov, B.Yalçın, F.F.Vəliyev, M.A.Bayramov, L.Ş.Quliyeva, O.Şahin, S.M.Peng

Pirazin və triazin ilə modulyasiya edilmiş tripiridildiamin liqandından 6-fenil-N^2,N^4-di(pirazin-2-il)-1,3,5-triazin-2,4-diamindən (H_2dpztzda) istifadə edərək, yeni birnüvəli mis(II) kompleksi $[Cu(H_2dpztzda)(NO_3)_2]\cdot 2C_3H_7NO$ 1 sintez edilmiş, quruluşu müəyyənləşdirilmiş və antimikrob xassələri tədqiq edilmişdir. Monokristal rentgen struktur analizinə əsasən 1 kompleksində Cu(II) beşli koordinasiya olunub və təhrif olunmuş triqonal bipiramidal həndəsi ətrafda yerləşir. Kompleks üçün "ters çevrilmiş tip" EPR spektri ($g_\perp > g_\parallel \sim g_e$), ölçülmüş maqnit nüfuzluluğu və eıektron spektroskopik tədqiqatların nəticələri birlikdə quruluş analizi ilə tam uyğunluq təşkil edirlər. Addison parametrinin hesablanmış qiyməti də (τ_5 = 0,5) Cu(II) mərkəzinin təhrif olunmuş triqonal bipiramidal həndəsi ətrafa malik olduğunu göstərir. H_2dpztzda molekulu Cu(II) ionunu tridentat liqand kimi koordinasiya edir. Kompleks 1 iki növ hidrogen rabitəsi nümayiş etdirir: klassik və qeyri-klassik. Göstərilmişdir ki, C-H···π, π-π və hidrogen rabitələrini əhatə edən qarşılıqlı təsirlər sintez edilmiş kompleks 1-in kristal qablaşdırılmasına(packing) əhəmiyyətli dərəcədə təsir edir və supramolekulyar quruluşun formalaşmasında həlledici rol oynayır. Birləşmələrin antimikrob aktivliyi ənənəvi zonal diffuziya üsulu ilə qiymətləndirilmişdir. Antimikrob aktivliyi üçün təhlil edilən hər iki birləşmə (kompleks 1 və H_2dpztzda liqandı) sürtkü və soyuducu maddələrdə *Pseudomonas aeruginosa, Mycobacterium phlei, Aspergillus niger* və *Penicillium chrysogenum* mikroorqanimlərinə qarşı yüksək effektiv nəticələr göstərmişdir.

Açar sözlər: *Modulyasiya edilmiş oliqo-α-aminopiridin liqandı, Mis kompleksi, Kristal quruluşu, Hidrogen rabitələri, Spektroskopiya, Antimikrob agentlər.*