COPPER(II) COMPLEX OF THE PYRAZINE-MODULATED OLIGO-α-AMINOPYRIDINE AS A COORDINATION POLYMERS' PROMISING BUILDING BLOCK

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Abstract: *Through the pyrazine-modulated tetrapyridyltriamine ligand N^2-(pyrazin-2-yl)-N^6-(6-(pyrazin-2-ylamino)pyridin-2-yl)pyridine-2,6-diamine (H_3pzpz) (**1**), a new mononuclear copper(II) complex $[Cu(H_3pzpz)(NO_3)]\cdot NO_3\cdot 3H_2O$ (**2**) has been synthesized and structurally characterized. The copper(II) atom in complex **2** exhibits a distorted square pyramidal geometry with an Addison parameter value of 0.39 (σ = 0.39). In compound (**2**), H_3pzpz (**1**) acts as a tetradentate N_4-donor ligand and coordinates to the Cu(1) ion in an anti-anti-anti-anti conformation. The single crystal X-ray analysis revealed a distorted square pyramidal geometry of the complex (**2**), which is consistent with the parameters of EPR spectra, measured magnetic moment susceptibility, and electronic spectrum studies. Observed extensive intermolecular hydrogen bond interactions (classical and non-classical) play an important role in the formation of the 3D supramolecular network and crystal packing of this complex. The complex (**2**) has been identified as a promising building block for the construction of coordination polymers.*

Keywords: *Modulated oligo-α-aminopyridine ligand, Copper complex, Crystal structure, Hydrogen bonds, Supramolecular networks.*
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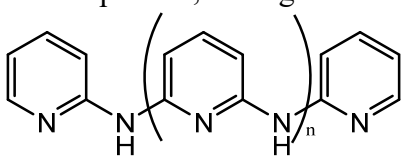
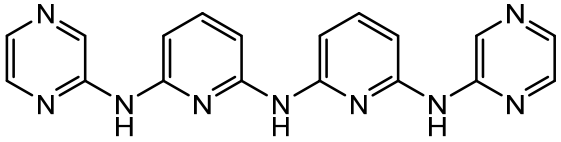
1. Introduction

As a heterocyclic ligand, oligo-α-pyridylamines (Scheme 1) are of great interest due to the variety of coordination modes exhibited by multidentate ligands. Over the past three decades, there has been an increasing focus on these compounds, owing to their ability to support linear metal chains and form so-called "Extended Metal Atom Chain complexes" (EMACs), which have potential applications such as molecular metal wires and switches [1, 2].



oligo-α-pyrydylamido ligands
n=0, Hdpa; n=2, H_3teptra



H_3pzpz

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

There are several ways that oligo-α-pyridylamine ligands can coordinate with metal atoms. While the all-anti form was seen in mononuclear complexes, the oligo-α-pyridylamine ligands in EMACs go through complete deprotonation and bind to the metal center in the all-syn form [3-5]. The dimers are joined by hydrogen bonds between -NH groups, and the free ligands have a double helical structure [6].

In the pursuit of synthesizing oxidative degradation-resistant and longer metal chains, a series of modulated ligands has been recently developed by replacing pyridine rings with nitrogen-rich pyrazine in oligo-α-pyridylamine ligands (Scheme 1) [7-10]. By using the pyrazine-modulated ligands, we have succeeded in synthesizing the heptacobalt and nonachromium EMACs, which are the longest cobalt(II) and chromium(II) EMAC molecules obtained to date [11, 12]. Moreover, the pyrazine ligands exhibit different coordination styles due to additional donor nitrogen atoms in the aromatic ring(s) and are particularly versatile in the construction of coordination polymers. We have synthesized a series of 1-D, 2-D, and 3-D copper(II) coordination polymers and investigated the mechanism of the pyrazine-mediated ferromagnetic interaction [8]. It is noteworthy that our recent studies have demonstrated the high biological activity of nickel(II) EMACs, mononuclear complexes, and coordination polymers of copper(II) with pyrazine-modulated oligo-α-pyridylamino ligands [6, 8]. From this point of view, the synthesis and establishment of the structure and properties of new copper complexes with pyrazine-modulated oligo-α-pyridylamine ligands are of great interest.

In this work, we provide our most recent findings in this field. We present the new mononuclear copper(II) complex $[Cu(H_3pzpz)(NO_3)]\cdot NO_3\cdot 3H_2O$ (**2**) with two-pyrazine-modulated ligand N^2-(pyrazin-2-yl)-N^6-(6-(pyrazin-2-ylamino)pyridin-2-yl)pyridine-2,6-diamine (H_3pzpz) (**1**) [11]. Complex **2** has been identified as a promising building block for the construction of coordination polymers. The bioactivity properties of the synthesized compound **2** will be the subject of an upcoming manuscript, with a focus on the results of a molecular docking analysis.

2. Experimental part

2.1. Materials and measurements. All reagents and solvents were obtained from commercial sources and were used without further purification unless otherwise noted. IR spectra were obtained from a Bruker Alpha FTIR 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 at room temperature on a Bruker BioSpin GmbH radiospectrometer. Elemental analyses were carried out on the FlashEA 1112 Series CHNS-O Analyser. Molar magnetic susceptibility was measured using a SQUID system with a 1000 Oe external magnetic field.

2.2. Preparation of compounds. N^2-(pyrazin-2-yl)-N^6-(6 (pyrazin-2-ylamino)pyridin-2-yl)pyridine-2,6-diamine (**H_3pzpz (1)**) was synthesized via the palladium-catalyzed cross-coupling reaction, as described in our previous reported work [12].

$[Cu(H_3pzpz)(NO_3)]\cdot NO_3\cdot 3H_2O$ (2). A mixture of H_3pzpz **(1)** (0.357 g, 0.001 mol) and $Cu(NO_3)_2\cdot 3H_2O$ (0.266 g, 0.0011 mol) in methanol (25 mL) was stirred at room temperature for 1 day. Then the solution was filtered to remove insoluble impurities and concentrated under vacuum. Slow evaporation of the concentrate after 10 days yielded block-shaped brown single crystals of **2** suitable for X-ray diffraction analysis, which were collected by filtration (0.497 g, 83 % yield); IR (KBr) ν/cm^{-1}: 3399 br., 3327 sh, 3199 sh, 3077 w, 1657 s, 1566 s, 1448 s, 1388 sh, s, 1278 w, 1220 m, 1160 m, 1026 m, 804, 661 w, 561 w, 494w, 434 m; UV/Vis (CH_3OH) λ_{max}/nm ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$): 213 ($1.24\times10^4$), 272 ($1.11\times10^4$), 310 ($1.04\times10^4$), 345 ($1.23\times10^4$), 480 ($1.48\times10^3$), 650 ($6.45\times10^2$); Elemental analysis (%) $C_{18}H_{21}CuN_{11}O_9$: calc. C 36.09, H 3.53, N 25.72; found: C 36.20, H 3.62, N 25.60.

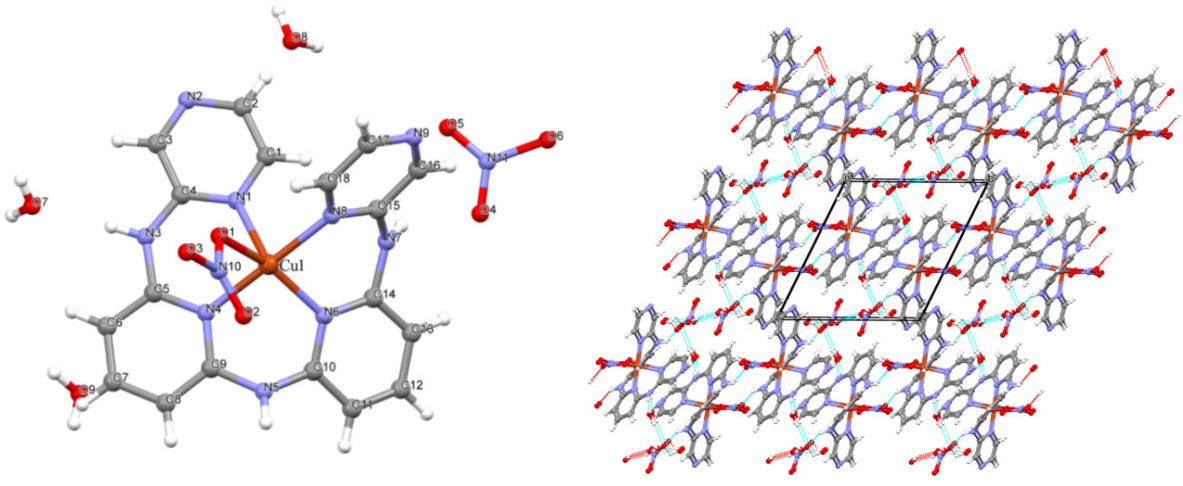
2.3. Crystal structure determinations. The suitable crystals of $[Cu(H_3pzpz)(NO_3)]\cdot NO_3\cdot 3H_2O$ (**2**) were selected for data collection, which was performed on a

D8-QUEST diffractometer at 293 K using Mo-Ka radiation (λ = 0.71073 Å). The structure was solved by direct methods using SHELXS-2013 [13] and refined by full-matrix least-squares methods on F^2 using SHELXL-2013 [14]. 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 Å and an N-H distance of 0.86 Å. 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 **2**:

Empirical formula $C_{18}H_{21}CuN_{11}O_9$; formula weight = 599.00; crystal system – triclinic; space group – *P-1*; *a* = 9.6179 (19), *b* = 12.291 (2), *c* = 12.607 (2) Å; α = 114.611 (5); β = 91.492 (6); γ = 106.846 (5)°; volume = 1278.1 (4) $Å^3$, Z = 2; density (calculated) = 1.556 g/cm^3; absorption coefficient = 0.924 mm^{-1}; crystal size: 0.06 × 0.03 × 0.01 mm^3; θ range for data collection 2.2–24.6°; reflection collected - 20702, independent reflection - 5404 [R(int) = 0.072]; R_1 = 0.0595, wR_2 = 0.1511; GOF = 1.020.

3. Results and discussion

3.1. Syntheses and structures. The interaction of H_3pzpz with $Cu(NO_3)_2{\cdot}3H_2O$ in methanol led to a mononuclear and neutral complex **2** with a higher synthetic yield. Block-shaped brown crystals of complex $[Cu(H_3pzpz)(NO_3)]{\cdot}NO_3{\cdot}3H_2O$ (**2**) crystallize in the triclinic, *P-1* space group. The molecular structure of complex **2** is presented in Fig. 1, and selected bond lengths and angles around the metal center are collected in Table 1. In the crystal lattice of **2**, there are also three water molecules. The coordination geometry around Cu(1) can be described as a distorted square pyramidal geometry (σ = 0.39, where σ = difference between the two largest angles/60; σ = 1 for ideal trigonal–bipyramidal and σ = 0 for ideal square-pyramidal). The distorted basal plane of the Cu(II) center in **2** is defined by the N(4), N(6), and N(8) nitrogen atoms of the heterocyclic aromatic rings of the ligand and the O(1) atom of the monodentate coordinated nitrate anion. The lack of linearity in one of the trans angles, N(6)-Cu(1)-O(1) (155.91(13)°), indicates significant distortion of the basal plane. On the other hand, as would be predicted for a normal square planar geometry, N(1)-Cu(1)-N(6) (179.31(14)°) is nearly linear.



(a) (b)

Fig. 1. (a) The molecular structure of $[Cu(H_3pzpz)(NO_3)]{\cdot}NO_3{\cdot}3H_2O$ (**2**) showing the atom numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. (b) An infinite 3D supramolecular network in (**2**).

The apical position around the Cu(1) ion is occupied by the nitrogen atom (N(1)) from one of the pyrazine rings of the ligand with a relatively long Cu(1)–N(1) = 2.248 (3) Å bond

distance. The axial Cu(1)–N(1) is longer than the other Cu(1)−N bond lengths. A Jahn–Teller distortion, which is typically present in Cu(II) complexes with a d^9 electronic configuration [15], is the cause of the axial Cu–N bond's elongation. The Cu–N distances (Cu(1)–N(4) = 2.007(3)Å; Cu(1)–N(6) = 1.993(3)Å; Cu(1)–N(8) = 2.025(3)Å) are well within the range reported for copper complexes with this type of ligand [3,5]. In compound **2**, the H_3pzpz (**1**) functions as a tetradentate N_4-donor ligand and coordinates to the Cu(1) ion in an anti-anti-anti-anti conformation. In this instance, the ligand's secondary amine groups (-NH) do not coordinate with the metal center.

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

2			
Cu1—O(1)	1.982 (3)	Cu1—N(8)	2.025 (4)
Cu1—N(6)	1.993 (3)	Cu1—N(1)	2.248 (3)
Cu1—N(4)	2.007 (3)		
O(1)—Cu1— N(6)	155.91 (13)	N(4)—Cu1—N(8)	179.31 (14)
N(4)—Cu1—N(1)	85.98 (13)	O(1)—Cu1—N(1)	91.35 (12)
N(8)—Cu1—N(1)	93.37 (13)	N(6)—Cu1—N(1)	112.65 (13)

In the structure of **2**, the nitrate ligand plays an important role in the coordination and supramolecular interactions. The O-N-O angles can be used to determine whether there is any strain in the nitrate anion. In the case of nitrate in complex **2**, the O-N-O angles are in the range of 116.1(4)-122.3(4)°. Similar O-N-O angles have been previously observed for the other distorted square-pyramidal mononuclear copper(II) complexes with pyrazine-modulated oligo-a-pyridylamido ligands [8]. Since the nitrate molecular ion has a trigonal planar geometry and sp^2 hybridization, there seems to be a slight strain in the nitrate anion of **2**.

In **2**, extensive hydrogen bonding was observed between uncoordinated amino groups, nitrate anions, and water molecules, resulting in a complex 3D network (Table 2). In addition to the classical hydrogen bond, complex **2** exhibits non-classical intramolecular (C8-H • • • O2) and intermolecular (C2-H2 • • • O9) hydrogen bond interactions between aromatic hydrogen atoms and oxygen atoms of the monodentate-coordinated nitrate NO_3 group and uncoordinated water molecules, respectively. Both kinds of hydrogen bonding play an important role in the formation of the 3D supramolecular network and crystal packing of this complex. Complex **2** also shows one intermolecular π-π stacking interaction between pyrazine rings (Cg(I) and $Cg(I)^i$) from adjacent molecules, which have π-π interaction distances of 3.9501(8) Å.

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

D–H···*A*	d(*D*–H)	d(H···*A*)	d(*D*···*A*)	∠(DHA)
C2—H2···O9 ^{i}	0.93	2.58	3.200(7)	124
C8—H8···O2 ^{ii}	0.93	2.56	3.283(5)	135
N3—H3A···O7	0.86	1.96	2.820(5)	174
N5—H5···O2 ^{ii}	0.86	2.05	2.822(4)	148
N7—H7A···O4	0.86	2.10	2.810(5)	139

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

3.2. Spectroscopy. The strong absorption bands in the IR spectra of complex **2**, within the range of 1657–1440 cm^{-1}, were assigned to the C=C and C=N vibrations of the pyridyl/pyrazyl groups. The group of bands at 3000–3327 cm^{-1} was assigned to N-H bonds of amine groups and evidenced that the ligand is not deprotonated during complex formation. In the IR spectra of complex 2, the new band observed at 434 cm^{-1} is tentatively assigned to υ(Cu–N), and the broad band at 3399 cm^{-1} is attributed to υ(OH) of the uncoordinated water molecule. The coordinated nitrate anion showed characteristic strong vibrations at 1448 cm^{-1} for $\nu_a(NO_2)$, 1278 cm^{-1}

for $\nu_s(NO_2)$, and 1026 cm^{-1} for $\nu(NO)$ in complex **2**. Conversely, the presence of a pronounced band at 1388 cm^{-1} (manifesting as a shoulder) and a band of medium intensity at 804 cm^{-1} in the IR spectrum signifies the existence of uncoordinated nitrate ions within the complex. The obtained result agrees well with the X-ray crystal structure analysis of this compound. A similar binding style for the NO_3 anion was previously described for other copper(II) nitrate complexes with nitrogen-containing ligands [16].

In the electronic spectra of the H_3pzpz ligand and its copper(II) complex **2**, a number of absorption bands associated with $\pi\rightarrow\pi^*$ and $n\rightarrow\pi$ transitions are observed (Fig. 2). Compared with H_3pzpza, which shows absorptions at 214, 275, and 350 nm, the band at 480 nm for **2** could be assigned to charge transfer between Cu^{2+} and ligand. As demonstrated in Figure 2, complex **2** displays a broad, unresolved, asymmetric weak d-d absorption peak in the visible region of the electronic spectra, with a maximum at 650 nm. It is commonly known that the visible portion of the electronic spectra of trigonal bipyramidal Cu(II) complexes has a single peak with a lower intensity and a higher energy shoulder. Conversely, the opposite absorption pattern, that is, a high energy peak with a low energy shoulder, is typically seen when a Cu(II) ion exhibits square-pyramidal coordination [17]. On the other hand, the presence of a single d-d band at $\lambda > 800$ nm (d_{xy}, $d_{x2-y2}\rightarrow d_{z2}$) is typical for trigonal bipyramidal (TBP) geometry, whereas a broad band in the range 600–650 nm (d_{xz}, $d_{yz}\rightarrow d_{x2-y2}$) is indicative of square pyramidal (SP) geometry [18]. Therefore, the presence of a broad absorption band at around 650 nm in the spectrum of **2** supports the hypothesis of a square pyramidal geometry around Cu(II) centers.

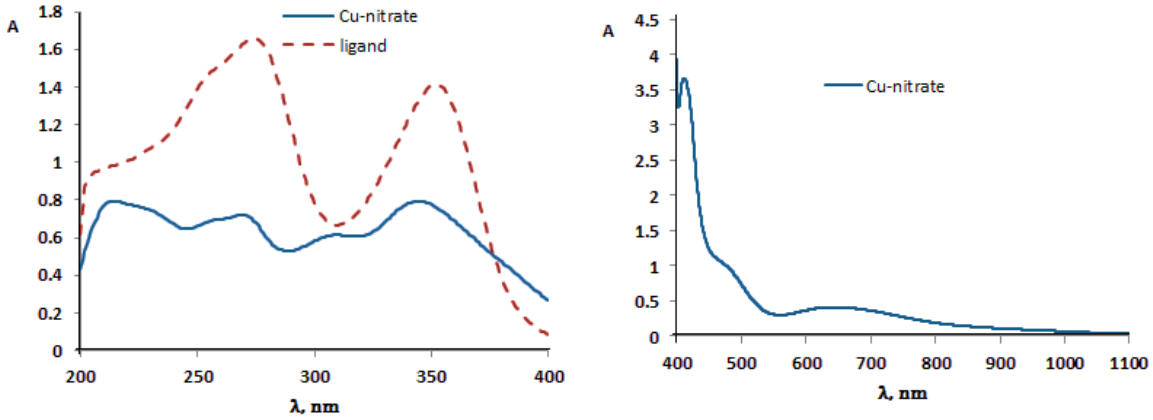


Fig. 2. Electronic spectra of the H_3pzpz (**1**) ligand and its copper(II) complex **2** in methanol solution.

The solid-state EPR spectrum of complex **2** was recorded at room temperature and is of axial symmetry with $g_\perp$=2.0410 and $g_\parallel$=2.3400, which is consistent with the square-based geometries found in the Cu(II) center in the complex [19]. According to the magnetic susceptibility measurements, complex **2** has room-temperature μ_{eff} values of 1.77 BM, confirming the presence of one unpaired electron per Cu^{2+} ion.

Conclusions

A novel copper(II) mononuclear complex $[Cu(H_3pzpz)(NO_3)]\cdot NO_3\cdot 3H_2O$ (**2**) was successfully synthesized and structurally characterized using a symmetrical two-pyrazine-modulated tetrapyridyltriamine ligand N^2-(pyrazin-2-yl)-N^6-(6-(pyrazin-2-ylamino)pyridin-2-yl)pyridine-2,6-diamine (H_3pzpz) (**1**). H_3pzpz coordinates with the Cu(II) as a tetradentate ligand in complex **2** after assuming an all-anti configuration. However, the nitrogen atoms of NH groups of H_3pzpz are not participating in the coordination with the Cu(II) center. In **2**, the geometry of the copper(II) ion was described as a distorted square pyramidal geometry. Extensive hydrogen bonds formed in **2** constructs the complex into a 3D network and stabilize the crystal packing. The ground state is d_{x2-y2}, according to the data acquired from the

electronic spectra and the EPR spectra. This is in agreement with the X-ray structural analysis of the square-pyramidal coordination geometry for the Cu(II) ion. The information from X-ray structure analysis is in good agreement with the results from spectroscopic techniques like infrared, ultraviolet-visible, EPR, and magnetic measurements.

Supplementary material

*CCDC 2422993 contains the supplementary crystallographic data for compound **2**. 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*

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