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SYNTHESIS, CRYSTAL STRUCTURE, SPECTRAL AND MAGNETIC PROPERTIES OF MONONUCLEAR COPPER(II) COMPLEX WITH PYRAZINE-MODULATED 2,2'-DIPYRIDYLAMINE

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New copper(II) complex $[\text{Cu}(\text{Hppza})(\text{CH}_3\text{COO})_2] \cdot 2\text{H}_2\text{O}$ was synthesized via the interaction of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ with the unsymmetrical pyrazine-modulated dipyridylamine ligand – Hppza. The crystal structure, spectral and magnetic properties of this complex are determined. It was found that the coordination polyhedron of the copper(II) ion in this complex is an elongated octahedron, in the equatorial plane of which there are two nitrogen atoms from Hppza ligand and two oxygen atoms from two carboxylate anions. The formation of intermolecular hydrogen bonds has been observed.

Keywords: pyrazine-modulated oligo- α -pyridylamine ligand, copper complex, hydrogen bonds, supramolecular structure.

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Introduction

Oligo- α -pyridylamines are convenient ligands for the synthesis of linear with metal strings complexes (also called "Extended Metal Atom Chain complexes" – EMACs) [1, 2]. In turn, the chemistry of metal string complexes is of great interest in the field of molecular wires, which have potential use in various types of electronic devices [3]. Recently, we have synthesized a series of pyrazine-modulated analogues of oligo- α -pyridylamines. Using tuning ligands we have successfully synthesized first stable reduced pentacobalt, longest heptacobalt and nonchromium string complexes [4–6]. Moreover, pyrazine-modulated oligo- α -pyridylamines possessing a large number of donor nitrogen atoms in the ar-

omatic cycle showed a unique ability in the formation of 1D, 2D, and 3D-coordination polymers [7, 8]. A correlation was found between the structure and magnetic properties of copper (II) coordination polymers with symmetric and asymmetric pyrazine-modified tripyridylamine ligands [8]. It should be noted that the interaction of other copper(II) salts (except perchlorate) with pyrazine-substituted ligands have been partially studied.

This paper describes the synthesis, structure and magnetic properties of a mononuclear complex of copper(II) $[\text{Cu}(\text{Hppza})(\text{CH}_3\text{COO})_2] \times 2\text{H}_2\text{O}$ with a pyrazine-modulated ligand N-(pyridin-2-yl) pyrazin-2-amine ligand(Hppza) (Scheme 1).

Scheme 1. Oligo- α -pyridylamine and pyrazine-modulated oligo- α -pyridylamine ligands.

Experimental part

Materials and measurements

All reagents and solvents were obtained from commercial sources and were used without further purification unless otherwise noted. The preparation of N-(pyridin-2-yl) pyrazin-2-amine ligand (Hppza) was carried out according to the literature [9].

IR spectra were performed from KBr pellets with a Thermo Scientific Nicolet iS 10 FTIR Spectrometer in the range of 500–4000 cm^{-1} . Absorption spectra were recorded on JASCO V-550 UV/VIS spectrophotometer. Molar magnetic susceptibility was recorded on a SQUID system with 2000 Gauss external magnetic field. Elemental analyses were performed on a Perkin-Elmer CHN 2400.

Preparation of

[Cu(Hppza)(CH₃COO)₂·2H₂O (1)

A mixture of Hppza (0.172 g, 0.001 mmol) and Cu(CH₃COO)₂·H₂O (0.199 g, 0.001 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 CH₃OH solution provided rod shape green single crystals suitable for X-ray analysis (0.273 g, 70% yield); IR (KBr) ν/cm^{-1} = 3456 m, 3396 m, 3073 w, 2965 w, 2883 w, 1656 m, 1612 w, 1566 s, 1525 m, 1483 s, 1430 m, 1343 w, 1274 w, 1239 w, 1209 w, 1159 m, 1072 w, 1035 w, 936 w, 892 w, 829 w, 791 w, 691 w, 677 w, 515 w; UV/Vis (CH₃OH) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) = 208 ($4.49 \cdot 10^4$), 252 ($5.54 \cdot 10^4$), 296 ($4.04 \cdot 10^4$), 338 ($4.96 \cdot 10^4$), 390 sh ($1.40 \cdot 10^4$), 674 (33); EA (%) C₁₃H₁₄N₄CuO₄. Calculated: C 44.13, H 3.99, N 15.83; found C 44.23, H 4.08, N 15.74.

Crystal structure determinations

Single crystal X-ray diffraction study of **1** was carried out on a BRUKER SMART Apex CCD at 150 K using a MoK α - radiation ($k = 0.71073 \text{ \AA}$) and a liquid nitrogen low-

temperature controller. Cell parameters were retrieved and refined using the Bruker SAINT software on all reflections. Data reduction was performed on the Bruker SAINT software. Semiempirical absorption corrections were applied. All the structures were solved by using the SHELXLS-97 [10] and refined with SHELXLS-97 [11] by full-matrix least squares on F² values. The details of the X-ray diffraction experiment and the main crystallographic data of the nickel-string complex **1** are given below.

Empirical formula C₁₃H₁₈CuN₄O₆; molecular weight = 389.85; crystal system – monoclinic; space group – *P2 (1)/n*; $a = 6.8483(4)$, $b = 22.7486(14)$, $c = 10.5203(7) \text{ \AA}$; $\alpha = 90.00^\circ$; $\beta = 100.031(1)^\circ$; $\gamma = 90.00^\circ$; $V = 1613.90(17) \text{ \AA}^3$, $Z = 4$; density(calculated) = 1.604 Mg/m^3 ; absorption coefficient = 1.391 mm^{-1} ; crystal size: 0.60·0.20·0.10 mm^3 ; θ range for data collection $\sim 1.79\text{--}27.50^\circ$; reflection collected - 12363, independent reflection – 3704 [$R_{\text{int}} = 0.0297$]; R_1 -factor = 0.0322, $wR_2[I > 2\sigma(I)] = 0.0803$, $R_1 = 0.0363$, $wR_2 = 0.0825$; GOF = 1.059.

Results and discussion

The ligand Hppza was synthesized as previously reported, on the basis of the Buchwald's palladium-catalyzed procedures [9], and characterized by IR, ¹H NMR and MS (FAB). The Cu(II) mononuclear complex **1** was synthesized by the direct reaction of metal salt and Hppza in methanol (Scheme 2). The green rod shape single crystals suitable for X-ray diffraction analysis were obtained by vapors diffusion of ether into the methanol solution.

Figure 1 shows the crystal structure of complex [Cu(Hppza)(CH₃COO)₂·2H₂O **1**. Some selected bond distances and angles are listed in Table 1. The complex crystallizes in the monoclinic system with *P2(1)/n* space group.

Scheme 2.

The crystal structure of $[\text{Cu}(\text{Hppza})(\text{CH}_3\text{COO})_2]$ in **1**. Atoms are drawn at the 50% probability level and hydrogen atoms are omitted for clarity; (b) 3D network of **1** constructed through hydrogen bonds. Hydrogen bonds are indicated with green lines.

Selected bond lengths ($\text{\AA}$) and angles ($^\circ$) for complex **1**

Cu–N(1)	1.9911(16)	Cu–O(1)	2.0059(14)
Cu–N(3)	1.9689(16)	Cu–O(3)	1.9697(14)
Cu–O(2)	2.4605(16)	Cu–O(4)	2.4305(15)
N(1)–Cu–O(1)	156.59(6)	N(3)–Cu–O(3)	157.74(7)
N(1)–Cu–O(4)	113.73(6)	N(3)–Cu–O(2)	105.36(6)
N(1)–Cu–O(3)	96.33(6)	N(3)–Cu–O(1)	91.38(6)

The structure of complex **1** surely indicates that in the complex metal is present in the +2 oxidation state. According to X-ray diffraction studies, in complex **1**, Hppza coordinates to Cu(II) as a bidentate ligand with nitrogen atoms of pyrazine and pyridine in *anti-anti* conformation, and the amino nitrogen atom is free. The coordination geometry of the complex is an elongated octahedron. Two nitrogen atoms from Hppza with the Cu–N(1) = 1.9911 (16) and Cu–N(3) = 1.9689 (16) $\text{\AA}$ distances build an equatorial plane together with the two oxygen atoms from two carboxylate anions. Remaining oxygen atoms (O(2) and O(4)) from two carboxylate anions weakly coordinate with Cu and occupy the axial positions in an average Cu–O distance of 2.4455 $\text{\AA}$. The short Cu–N distances in **1**, with an average value of 1.980 (16) $\text{\AA}$ indicate a strong binding of the chelating ligand. The Cu–N and Cu–O distances are well within

the range reported for the copper(II) complexes of oligo- α -pyridylamino ligands and their pyrazine-modulated analogues [12,13]. There are two uncoordinated water molecule also present in the lattice of complex **1**.

The formation of intermolecular hydrogen bonds is observed in the case of complex **1**. Moreover, the presence of intermolecular hydrogen bonds between the uncoordinated amine NH group of the ligand, the oxygen atoms of the carboxylate anions and water molecules such as N(2) $\cdots$ O(6) (2.770 $\text{\AA}$), O(1) $\cdots$ O(5) (2.850 $\text{\AA}$), O(4) $\cdots$ O(5) (2.736 $\text{\AA}$), and O(2) $\cdots$ O(6) (2.790 $\text{\AA}$) leads to the formation of a 3D supramolecular structure (Figure, 1b). The crystal packing of the Cu(II) complex is stabilized by the π – π interactions between the aromatic rings, with the shortest inter-planar ring-ring distances being 3.43 $\text{\AA}$.

In the IR spectra of the complex $[\text{Cu}(\text{Hppza})(\text{CH}_3\text{COO})_2] \cdot 2\text{H}_2\text{O}$, the strong absorption bands observed at 1566 and 1483 cm^{-1} which were assigned to the asymmetrical and symmetrical bands of the carboxylate group respectively. The smaller separation of the asymmetric and symmetric stretching frequencies ($\Delta\nu = \nu_{\text{asym}} - \nu_{\text{sym}} = 83 \text{ cm}^{-1}$) indicates the bidentate nature of coordination of the carboxylate group [14].

In the electronic spectrum of a methanol solution of the copper(II) complex **1**, absorption bands are observed at 208, 252, 296, 338 and 674 nm. Comparison of these bands with ligand absorption bands allows us to assign the band at 674 nm, located in the visible region of the spectrum, to the $d-d$ transition. This band with a relatively low molar extinction coefficient ($\epsilon = 33$) may indicate the octahedral structure (elongated octahedron) of the synthesized complex.

The magnetic moment at 300 K for **1** is 1.80 μB , which is consistent with one unpaired electron in $\text{Cu}(\text{II}) (d^9)$ including a small amount of orbital contribution.

Thus, the interaction of $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ with Hppza ligand was studied and new copper(II) mononuclear complex was synthesized. The crystal structure, spectral and magnetic properties of this complex are determined. It was shown that the coordination polyhedron of the copper(II) atom in complex **1** is an elongated octahedron. The formation of intermolecular hydrogen bonds has been detected.

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**PİRAZİNLƏ MODULYASIYA EDİLMİŞ 2,2'-DİPİRİDİLAMİNİN BİRNVƏLİ MİS(II) KOMPLEKSİNİN
SİNTEZİ, KRİSTAL QURULUŞU, SPEKTRAL VƏ MAQNİT XASSƏLƏRİ**

F.F.Vəliyev

$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ -in pirazinlə modulyasiya edilmiş dipiridilamin ligandı – $[\text{Cu}(\text{Hppza})(\text{CH}_3\text{COO})_2] \cdot 2\text{H}_2\text{O}$ ilə qarşılıqlı təsirindən yeni mis (II) kompleksi **1** sintez edilmişdir. Bu kompleksin kristal quruluşu, spektral və maqnit xüsusiyyətləri təyin edilmişdir. Müəyyən edilmişdir ki, bu kompleksdə mis (II) ionunun koordinasiya polyhedronu, ekvatorial müstəvisində Hppza liqandının iki azot atomu və iki karboksilat anionunun iki oksigen atomu olan dartılmış bir oktahedrondan ibarətdir. Molekullarası hidrogen rabitələrinin əmələ gəlməsi aşkar edilmişdir.

***Açar sözlər:** pirazinlə modullaşdırılmış oligo- α -aminopiridin liqandı, mis kompleksi, hidrogen rabitəsi, supramolekulyar quruluş.*

**СИНТЕЗ, КРИСТАЛЛИЧЕСКАЯ СТРУКТУРА, СПЕКТРАЛЬНЫЕ И МАГНИТНЫЕ СВОЙСТВА
МОНОЯДЕРНОГО КОМПЛЕКСА МЕДИ(II) С ПИРАЗИН- МОДУЛИРОВАННОГО
2,2'-ДИПИРИДИЛАМИНА**

Ф.Ф.Валиев

Новый комплекс меди (II) $[\text{Cu}(\text{Hppza})(\text{CH}_3\text{COO})_2] \cdot 2\text{H}_2\text{O}$ был синтезирован взаимодействием $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ с несимметричным пиразин-модулированным дипиридиламиновым лигандом - Hppza. Определены кристаллическая структура, спектральные и магнитные свойства этого комплекса. Было обнаружено, что координационный полиэдр иона меди(II) в этом комплексе представляет собой вытянутый октаэдр, в экваториальной плоскости которого находятся два атома азота лиганда Hppza и два атома кислорода двух анионов карбоксилата. Обнаружено образование межмолекулярных водородных связей.

***Ключевые слова:** пиразин-модулированный олиго- α -аминопиридиновый лиганд, комплекс меди, водородные связи, супрамолекулярная структура.*