New copper(II) complexes including pyridine-2,5-dicarboxylic acid: synthesis, spectroscopic, thermal properties, crystal structure and how these complexes interact with purified PON 1 enzyme

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ABSTRACT

We report the synthesis of two square-pyramidal copper(II) complexes, [Cu(2,5-pydc)(2-aepy)(H₂O)]·H₂O, 1, and [Cu(2,5-pydc)(2-ampy)(H₂O)]·H₂O, 2 (2-aepy = 2-(aminoethyl)pyridine, 2-ampy = 2-(aminomethyl)pyridine, 2,5-pydc = pyridine-2,5-dicarboxylic acid or isocinchomeronic acid). The synthesized complexes have been characterized by X-ray diffraction, FT-IR, elemental, and thermal analysis techniques. The crystal structure of 1 was established by X-ray analysis. Powder X-ray diffraction analysis showed that the complexes are pure. The inhibition of human serum paraoxonase 1 (PON 1, EC 3.1.8.1) enzyme with these complexes were investigated. We used diethyl 4-nitrophenyl phosphate as a substrate to measure the paraoxonase activity of PON 1 enzyme spectrophotometrically. Complexes 1 and 2 decreased the in vitro PON 1 activity with different inhibition mechanisms. Complexes 1 and 2 inhibited paraoxonase activity of this enzyme as competitively and noncompetitively, respectively.

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1. Introduction

Self-assembled metal-organic frameworks (MOFs) occur with metal ions and polydentate organic ligands. Metal complexes with pyridine dicarboxylic acid derivatives have been used as model systems for the design of MOFs [1] because formation of hydrogen bonds and n–n stacking interactions are possible. Carboxylates are suitable ligands for building coordination complexes because they contain several coordination sites, demonstrating diverse coordination modes, for example, monodentate, bidentate, tridentate, or bridging [2–4]. Due to the coordination versatility of carboxylate ligands, inorganic supramolecular chemistry is focused on the synthesis and applications of metal-organic frameworks [5–11].

Pyridine-2,5-dicarboxylic acid (2,5-pydc), carrying pyridine ring and carboxyl groups, has been utilized in constructing coordination compounds. Carboxylate groups are in para positions hence may easily coordinate to different metal centers [12–20]. Several monomeric mixed-ligand complexes containing 2,5-pydc have been reported [21–23]. Furthermore, these complexes are finding promising applications in catalysis, antibacterial activity, enzyme inhibition, aqueous solution chemistry, surface chemistry, gas sorption, ion exchange, magnetism, and luminescence [24–36].

As copper is an essential element for humans, several studies deal with the synthesis, characterization, and properties of copper complexes. Cu(II) constitutes an important class of transition metal complexes with regard to biological activity [37]. Therefore, the importance of Cu(II) complexes with polycarboxylic acid and N-containing aromatic ligands have been increasing [2, 4, 12, 13, 23, 24].

Paraoxonase (PON 1) (arilesterase, [EC 3.1.8.1]) is a serum esterase bonded with calcium (Ca$^{2+}$) and synthesized in the liver. The most distinctive feature of this enzyme is hydrolyzing paraoxon [38–41]. Ca$^{2+}$ is required for the enzyme activity and stability. One Ca$^{2+}$ participates directly in catalytic reactions and the other ensures proper conformation of the enzyme active site [42]. PON 1 is released into the blood in humans after synthesis in the liver. It is a protein with a molecular weight of 43 kDa formed of 354 amino acids and physically linked with high-density lipoprotein (HDL) [41, 43–45]. One task of PON 1 is participating in detoxification of organophosphate compounds such as paraoxon and another task is protecting low-density lipoprotein (LDL) from oxidation [46]. PON 1 has antioxidant properties [47]. Therefore, it is thought to play a protective role against development of diseases such as diabetes, cardiovascular disease, sepsis, Alzheimer, and Parkinson [48]. Due to significant effects of PON 1 on people, further study about interactions of PON-drugs or PON-chemicals is required. Many studies on these subjects have been carried out [49–52].

In this study, we described the synthesis, spectroscopic, thermal analysis, powder X-ray diffraction, and crystal structures of neutral copper(II) complexes with pyridine-2,5-dicarboxylic acid in the presence of a nitrogen-donor heterocyclic ligand such as 2-(aminoethyl)pyridine (2-aepy) and 2-(aminomethyl) pyridine (2-ampy). We studied the in vitro effects of [Cu(2,5-pydc)(2-aepy)(H$_2$O)]·H$_2$O, 1, and [Cu(2,5-pydc)(2-ampy)(H$_2$O)]·H$_2$O, 2, on human serum PON 1 enzyme activity.

2. Experimental

2.1. Materials and methods

All reactions were performed with commercially available reagents, used without further purification. DEAE-Sephadex A50, Paraoxone, Sephadex G-200, chemicals for electrophoresis, and protein assay reagents were purchased from Sigma Chem. Co. All other chemicals were analytical grade and obtained from Merck. Fresh human serum was taken from the Blood Centre of the Mengüček Gazi Education and Research Hospital at Erzincan University. Infrared spectra of the complexes were recorded with a Thermo Nicolet 6700 FT-IR spectrophotometer from 4000 to 450 cm$^{-1}$ at a resolution of 4 cm$^{-1}$ using KBr pellets. C, H, and N elemental analyses were performed on a LECO CHNS-932 elemental analyzer. The TG and DTA curves were scanned using a PRIS Diamond TG/DTG apparatus in static air (heating rate: 10 °C min$^{-1}$, platinum crucibles, mass ~10 mg and temperature from 30 to 1000 °C). The powder X-ray diffraction (PXRD) patterns of the complexes were taken at ambient temperatures by use of a
PANalytical Empyrean diffractometer using Ni filtered CuKα radiation (λ = 1.54050 Å; 45 kV and 40 mA). The theoretical PXRD patterns were simulated from single-crystal data using PLATON [53].

2.2. Synthesis

2.2.1. [Cu(2,5-pydc)(2-aepy)(H₂O)]·H₂O (1)

2,5-pydc (0.167 g, 1 mmol) was dissolved in 20 mL water with continuous stirring at 50 °C. Then, 2-aepy (110 μL, 1 mmol) was added in the 2,5-pydc solution. Cu(CH₃COO)₂·2H₂O (0.199 g, 1 mmol) was dissolved in 20 mL water with continuous stirring at 50 °C. The solution of Cu(CH₃COO)₂·2H₂O was added to the first solution. Then, the final solution was stirred for 2 h and filtered. The filtrate was evaporated slowly at room temperature. X-ray quality blue crystals of [Cu(2,5-pydc)(2-aepy)(H₂O)]·H₂O were obtained after a few days.

Yield: 80%; Anal. Calcd for [C₁₄H₁₇N₃O₆Cu]: C, 43.42; H, 4.39; N, 10.86%. Found: C, 43.35; H, 4.42; N, 10.90%.

2.2.2. [Cu(2,5-pydc)(2-ampy)(H₂O)]·H₂O (2)

Complex 2 was prepared following the same procedure for 1 using 2-ampy (0.199 g, 1 mmol) instead of 2-aepy. The solution was left to stand for slow evaporation at room temperature; blue micro-crystals appeared after a few days.

Yield: 90%; Anal. Calcd for [C₁₃H₁₅N₃O₆Cu]: C, 41.84; H, 4.02; N, 11.26%. Found: C, 41.85; H, 4.01; N, 11.28%.

2.3. X-ray crystallography

Diffraction data were collected on a STOE IPDSII image plate detector using Mo Kα radiation (α = 0.71073 Å, T = 293 K). A summary of the key crystallographic information is given in table 1. Data collection: Stoe X-AREA [54]. Cell refinement: Stoe X-AREA [54]. Data reduction: Stoe X-RED [54]. The structure was solved by direct methods using SHELXS-97 [55] and anisotropic displacement parameters were applied.

| Empirical formula | C₁₄H₁₇N₃O₆Cu |
|-------------------|---------------|
| Formula weight    | 386.86        |
| Temperature (K)   | 293           |
| Wavelength (Å)    | 0.71073       |
| Crystal system    | Triclinic     |
| Space group       | P-1           |
| Unit cell dimensions |            |
| a (Å)             | 8.0005(5)     |
| b (Å)             | 9.3289(6)     |
| c (Å)             | 11.6865(8)    |
| α (°)             | 98.868(5)     |
| β (°)             | 109.716(5)    |
| γ (°)             | 105.155(5)    |
| V (Å³)            | 763.83(10)    |
| Z                  | 2             |
| Absorption coefficient (mm⁻¹) | 1.468          |
| Dcalc (mg m⁻³)    | 1.682         |
| Crystal size (mm) | 0.200; 0.407; 0.530 |
| Theta range for data collection (°) | 2.35; 26.50     |
| Measured reflections | 3141        |
| Independent reflections | 2979           |
| Absorption correction | Integration [55] |
| Refinement method  | Full-matrix least-squares on F² |
| Final R indices [F² > 2σ(F²)] | 0.0337 |
| Goodness-of-fit on F² | 1.124         |
to non-hydrogen atoms in a full-matrix least-squares refinement based on $F^2$ using SHELXL-97 [55]. All hydrogens attached to carbon were positioned geometrically and refined by a riding model assigning $U_{iso}$ equal to 1.2 times that of carbon and remaining hydrogens were located from the Fourier difference map.

2.4. Purification and enzymatic activity of PON 1

PON 1 enzyme was purified using ammonium sulfate precipitation by DEAE-Sephadex A-50 anion exchange chromatography and Sephadex G-200 gel filtration chromatography techniques. Purification methods of PON 1 were carried out as previously described [49, 51, 52]. The inhibitory effects of 1 and 2 were tested in vitro. Control activity was considered to be 100% in the absence of complexes. A graph was drawn for each complex concentration against percent activity for each complex (figure 1). $K_i$ values of each complex were determined by selecting three different complex concentrations showing inhibition. Lineweaver-Burk curves were drawn for identifying $K_i$ values and inhibition type (figure 1).

Paraoxonase activity of PON 1 has been identified with paraoxone (1 mM) in 50 mM glycine-NaOH (pH 10.5) buffer including 1 mM CaCl$_2$ at 25 °C. Enzyme activity assay is based on spectrophotometric measurement of p-nitrophenol at 412 nm. The molar extinction coefficient of paranitrophenol ($\varepsilon = 18.290$ M$^{-1}$ cm$^{-1}$ at pH 10.5) is used for calculation of the activity. One enzyme unit is defined as the amount of enzyme that catalyzes hydrolysis of 1 μmol of paraoxon at 25 °C [46].

2.5. Investigation inhibition type of PON 1 inhibition

We investigated the inhibitory effects of different concentrations of 1 and 2, studied three times at each concentration. PON activities were determined at different complex concentrations. Control activity was measured without complex inhibitor and presumed 100%. Percentage activity against complex concentration graphs was drawn for each complex (figure 1). Lineweaver-Burk curves were used for identification of $K_i$ values and inhibition type (figure 1) [56].

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Figure 1. (a) In vitro effect of 1 and 2 at eight concentrations on PON 1 activity. (b) Determination of inhibition types and $K_i$ values for 1 and 2 using Lineweaver-Burk curves.
2.6. Quantitative protein assay
Bradford method was used to carry out quantitative protein assay as in previous studies [49–52].

3. Results and discussion
3.1. Crystal structure of 1
The molecular structure of 1 is shown in figure 2 and selected bond distances and angles are listed in table 2. The complex is mononuclear with 2,5-pydc a bidentate ligand coordinated to Cu(II) through carboxylate oxygen and pyridine nitrogen. In 1, 2-aepy is bidentate via two nitrogens from pyridine ring and NH$_2$; water fills the fifth coordination site. The structure consists of individual [Cu(2,5-pydc)(2-aepy)(H$_2$O)]·H$_2$O molecules, in which the coordination environment of Cu(II) in 1 is square-pyramidal.

The equatorial plane has three nitrogens (N1, N2, and N3) and one carboxylate O1, while the axial position is occupied with the water. The structural distortion index tau (τ) was calculated as 0.10, indicating square-pyramidal geometry. The 2,5-pydc ligands are essentially planar and the torsion angle between C5, C4, C7, and O4 in 2,5-pydc is 14.70° for 1.

The crystal structure is stabilized with strong intermolecular and intramolecular hydrogen bonding. The hydrogen bonds between carboxylic oxygen and water ligand (O5–H5A⋯O4 [2.774 Å], O5–H5B⋯O3

![Figure 2. The molecular structure of 1 showing the atom numbering scheme.](image)

| Bond distances (Å) | Angles (°) |
|--------------------|------------|
| Cu1–N1             | 2.0499(14) | O1–Cu1–N3  | 170.32(7) |
| Cu1–N2             | 2.0206(15) | O1–Cu1–N2  | 87.56(6)  |
| Cu1–N3             | 1.9902(15) | N2–Cu1–N3  | 93.07(6)  |
| Cu1–O1             | 1.9660(13) | O1–Cu1–N1  | 81.43(6)  |
| Cu1–O5             | 2.2354(15) | N1–Cu1–N3  | 95.88(6)  |
|                   |            | N1–Cu1–O5  | 89.92(6)  |
|                   |            | N2–Cu1–O5  | 102.56(6) |
|                   |            | N3–Cu1–O5  | 93.86(6)  |
|                   |            |            | 164.12(6) |
|                   |            |            | 95.43(6)  |
|                   |            |            | 93.86(6)  |
|                   |            |            | 102.56(6) |
|                   |            |            | 89.92(6)  |
[2.779 Å] and N3–H3B⋯O3 [3.055 Å]) link individual [Cu(2,5-pydc)(2-aepy)(H2O)]·H2O molecules, leading to an infinite linear chain along the crystallographic [0 1 0] direction. (In figure 2, oxygen of the aqua ligand and uncoordinated water are depicted pink and orange, respectively). As seen in figure 3(a) and (b), strong intermolecular hydrogen bonding between uncoordinated water (O6), carboxylic O2 and O3, and nitrogen of 2-aepy ligand (N3) play a crucial role to connect linear chains.

Figure 3. (a) Hydrogen bonds formed by water molecules, (b) A view of the three-dimensional framework along the b axis.
In addition to strong intermolecular interactions, weak π⋯π ring interactions coexist in the structure (C6–O2⋯Cg1 [Cu1, O1, C6, C1, N1]). These interactions are significant for holding layers together in the solid state and reinforcing the 3D framework (figure 4). All of these interactions stabilize this arrangement and are given in table 3. The interactions in this study are consistent with those obtained for copper-dicarboxylic acid complexes reported [5, 6, 22].

The Cu-N12,5-pydc (2.0499(14) Å) bond distance is longer than corresponding values in [Cu(pydc)(H2O)(4-meim)2]·H2O (2.004(2) Å) [57], ([Cu(μ-pydc)(im)2]·2H2O)6 (2.023(2) Å) [57], ([Cu(μ-pydc)(H2O)(dmpy)])n (1.983(7) Å) [57], [Cu(pydc)(deen)(H,2O)]2H2O (2.028(2) Å) [22], [Cu(pydc)(H2O)]n (1.958(2) Å) [3], (dma)2[Cu(pydc)]2 (1.965(2) Å) [58], [Cu4(L)[py]] (average 1.980(3) Å) [59] and (H2ben)2[Cu2(μ-pydc)4(H2O)4] (1.986(1) Å) [60]. The Cu–O1 2,5-pydc (1.9660(13) Å) bond distance is slightly shorter than corresponding values in [Cu(pydc)(H2O)(4-meim)2]·H2O (1.984(2) Å) [57], ([Cu(μ-pydc)(im)2]·2H2O)n (1.977(2) Å) [57], and ([Cu(μ-pydc)(H2O)(dmpy)])n (1.980(4) Å) [57]. But Cu–O1 2,5-pydc bond distance is slightly shorter than in [Cu(pydc)(deen)(H2O)]2H2O (1.953(1) Å) [22], [Cu(pydc)(H2O)]n (1.936(2) Å) [3] and (dma)2[Cu(pydc)]2 (1.952(2) Å) [58], which are similar to a corresponding value in [Cu4(L)[py]] (average 1.960(3) Å) [59] and (H2ben)2[Cu2(μ-pydc)4(H2O)4] (1.958(1) Å) [60], where pydc, 4-meim, im, dmpy, deen, L, and H2ben are pyridine-2,5-dicarboxylate, 4-methylimidazole, imidazole, 3,4-dimethylpyridine, N,N-diethylethlenediamine, pyridine-2,5-dicarboxylate, and 1,4-butanediamine.

### 3.2. FT-IR

FT-IR spectra are given in figure S1. The broad bands at 3445–3392 and 3340 cm⁻¹ correspond to υ(OH) of water for 1 and 2, respectively. The absorptions at 3236 and 3133 cm⁻¹ for 1 and 3233, and 3108 cm⁻¹ for 2 are assigned to antisymmetric and symmetric N–H stretching vibration of 2-aepy and 2-ampy, respectively. The weak bands around 3080–3040 cm⁻¹ are assigned to aromatic υ(CH) of phenyl rings. The relatively weak bands between 2967 and 2853 cm⁻¹ are assigned to aliphatic υ(CH) vibration of ligands.

FT-IR spectrum of 2,5-pydc shows the main absorption at 1704 cm⁻¹ corresponding to C=O stretch of COOH group. In 1 and 2, this band disappeared [61] and new carboxylate bands occurred in the

![Figure 4. A view of the 3D supramolecular network of 1.](image-url)
spectra. This situation indicates that 2,5-pydc participates in coordination with carboxylate O. If 2,5-pydc was bound to copper via nitrogen of pyridine, the pyridine ν(C=C) and ν(C=N) vibrations of free ligand at 1626, 1590, 1537, and 1404 cm⁻¹ shift to higher wavenumbers. In the FT-IR spectra of complexes, the peaks at 1654, 1592, 1566, and 1487 cm⁻¹ for 1 and the peaks at 1645, 1592, 1557, and 1481 cm⁻¹ for 2 can be assigned to pyridine ν(C=C) and ν(C=N) vibrations indicating that 2,5-pydc bonded to copper through pyridine N [62, 63]. The FT-IR spectra of complexes demonstrate characteristic bands of carboxyl group at 1611 (1) and 1603 (2) cm⁻¹ for the antisymmetric stretch and at 1346 (1) and 1348 (2) cm⁻¹ for the symmetric stretch, respectively. The Δν[ν_{asym}(COO) – ν_{sym}(COO)] value is often used for determining coordination mode of carboxylate [64]. These values (265 cm⁻¹ for 1 and 255 cm⁻¹ for 2) are consistent with monodentate (>200 cm⁻¹) carboxylate ligand. The absorption bands at 1281, 1065, and 782 cm⁻¹ are due to ν(C–O) and δ(O–C–O) vibrations of 2,5-pydc ligand [22]. The absorptions at 524 and 528 cm⁻¹ correspond to Cu–O vibration and the bands observed at 421 and 422 cm⁻¹ are attributed to the Cu–N for vibration of 1 and 2, respectively [23, 37]. Characteristic IR bands of 1 were in parallel to those obtained for 2. These results demonstrated that 1 and 2 have similar coordination and structures. Also, the infrared spectra of 1 are consistent with its structural characteristic as determined by single crystal X-ray diffraction. IR data of 1 and 2 were compatible with previous studies [2, 37, 65].

### 3.3. Thermal analyses

Decomposition of 2 is similar to that of 1. The differences in temperatures and mass losses are listed in table 4. The thermal behavior of 1 was followed to 1000 °C in a static atmosphere of air, decomposing in three steps. The first step between 30 and 130 °C corresponds to loss of two water molecules; one of them is coordinated and the other is non-coordinated for 1. The endothermic peak occurs at 113 °C for 1 in DTA (DTG_max: 112 °C). The observed mass loss of 9.10% agrees with the calculated mass loss of 9.30%. Degradation of coordinated 2,5-pydc occurs in the second stage (130–291 °C, exothermic DTA peak at 248 °C, DTG_max: 247 °C) with a mass loss of 41.90% (calcd 42.70%). The last exothermic step (DTA: 353 °C) between 291 and 420 °C corresponds to removal of 2-aepy (DTG_max: 357 °C, found 31.10%, calcd...
31.50%). The total observed 82.10% mass loss agrees well with the calculated mass loss of 83.50%; the final product obtained is CuO.

Complex 2 decomposes in three steps. The first step at 30–110 °C is assigned to loss of two water molecules with a mass loss of 9.70% and a calculated value of 9.65%. The endothermic peak occurs in DTA at 87 °C (DTGmax: 87 °C). The second step occurring between 110 and 270 °C corresponds to loss of 2-ampy representing a mass loss of 29.20% with a calculated value of 29.00% (exothermic DTA peak at 256 °C; DTGmax: 251 °C). The last exothermic steps at 292, 335, and 357 °C are from degradation of 2,5-pydc (270–372 °C, DTGmax: 289, 328 and 351 °C, DTA 292, 335 and 357 °C) with a mass loss of 43.70% (calcd 44.30%). The final thermal product obtained is CuO.

3.4. Powder X-ray diffraction

Figures S2 and S3 show the powder X-ray diffraction patterns of 1 and 2 with sharp peaks (figures S2(a) and S3), confirming the crystalline phase. In addition, the single crystal X-ray diffraction data of 1 was compared with computer simulated pattern. The experimental PXRD pattern is compatible with the simulated pattern, indicating phase purity of 1 (figure S2(a) and (b)).

3.5. Inhibition of PON 1

PON 1 was purified from human serum as in our previous study [49–52]. The in vitro effects of 1 and 2 on paraoxonase activity of PON 1. IC50 values were determined as 0.437 and 0.338 mM, respectively. The effect of several metal ions (copper, cobalt) and calcium on purified paraoxonases was elaborated in previous studies. These values obtained in this study were compatible with these studies [66, 67]; Ki values were 0.218 and 0.434 mM, respectively. Both complexes also decreased the in vitro PON 1 activity. While the inhibition mechanism of 1 was competitive, the mechanism of 2 was noncompetitive.

In a study of the active site of PON, some histidine residue as His154 was considered to be more important, not for PON 1 activity but for protein folding or stability of PON 1 [68]. Looking at the active site of the enzyme, it is seen that the catalytic Ca2+ was connected to His (115 and 134) amino acids. In this study, we interacted 1 with enzyme in vitro and saw that it inhibited competitively paraoxonase activity of this enzyme. Therefore, we believe that complex 1 interacts with the active site of the enzyme. This interaction may be between the catalytic Ca2+ in the active site of the enzyme with a free carboxyl group of 1 (figure 5). Complex 2 may be attached to a region outside the active site of the enzyme because they inhibit enzyme noncompetitively.

![Figure 5. Schematic representation for the interaction of 1 with the paraoxonase 1 active site.](image)
4. Conclusion

Two new copper(II) complexes containing pyridine-2,5-dicarboxylic acid – 2-(aminoethyl)pyridine or 2-(aminomethyl)pyridine ligands have been synthesized and characterized by spectroscopic, thermal, and X-ray diffraction techniques. The purities of the complexes were confirmed by elemental analysis and powder X-ray diffraction patterns. Single crystal X-ray diffraction studies revealed that 1 has a square-pyramidal geometry. The IR spectra suggest that carboxylate is monodentate. This coordination mode is supported with X-ray diffraction data. Thermal stability of 1 and 2 are to 112 and 87 °C, respectively, before the onset of decomposition which subsequently occurs in three steps. Thermal analysis data and characteristic IR vibrational bands of 1 were similar to those obtained for 2. These results demonstrated that 1 and 2 have similar coordination mode and structure. Complexes 1 and 2 decreased the in vitro PON 1 activity with different inhibition mechanisms. Complex 1 inhibited competitively, whereas 2 inhibited noncompetitively paraoxonase activity of this enzyme. These complexes might be a potential drug to be used in diseases associated with high HDL after pharmacokinetics studies are done.

Supplementary material

Supplementary data CCDC-1435092 contain the supplementary crystallographic data for 1. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or Email: deposit@ccdc.cam.ac.uk

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Disclosure statement

No potential conflict of interest was reported by the authors.

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