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X-Ray structure of a 1D-coordination polymer of copper(II) bearing pyrazine-2,3-dicarboxylic acid and 2-aminopyrimidine

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Abstract: A new 1D-coordination polymer of Cu(II) ions, $\{(2\text{-apymH})_2[\text{Cu}(\text{pyzdc})_2] \cdot 6\text{H}_2\text{O}\}_n$, (2-apym = 2-aminopyrimidine, pyzdcH₂ = pyrazine-2,3-dicarboxylic acid), was synthesized based on the proton transfer mechanism and characterized by elemental analysis, infrared spectroscopy and single crystal X-ray diffraction. The coordination polymer consists of infinite chains of $[\text{Cu}(\text{pyzdc})_2]^{2-}$ bridged across a double chain running along the *a*-axis and discrete (2-apymH)⁺ fragments. The Cu(II) ion is located on the inversion centre in the basal plane of an elongated octahedron with two oxygen atoms from adjacent (pyzdc)²⁻ ligands occupying the axial positions. The interaction between oxygen atoms of water molecules with the dicarboxylic acid plays an important role in the overall supramolecular assembly.

Key words: copper; pyrazine-2,3-dicarboxylic acid; 2-aminopyrimidine; proton transfer; hydrogen bond; coordination polymer; water cluster.

INTRODUCTION

The field of coordination polymer particles has received much attention in coordination chemistry in recent years owing to their novel and diverse topologies and potential applications in host–guest chemistry, catalysis, biomedical applications, magnetism, and non-linear optics.^{1–4} By selecting appropriate metal ions and organic linkers, coordination polymers with various structures, such as 1D chains ladders,^{5–7} 2D grids⁸ and 3D networks⁹ can be obtained. Polycarboxylic acids represent supramolecular connectors that can generate infinite networks and metal–organic frameworks.¹⁰ The carboxylate group may present various coordination modes, leading to the formation of *mono*-nuclear, *di*-nuclear,

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metal–organic frameworks or coordination polymers.¹¹ In particular, pyrazine-dicarboxylic acids have many different modes of coordination to metal ions. For example, it coordinated to the Cu(II) ion as a monodentate ligand in the [Cu(pyzdc)(H₂O)(en)₂] (en = ethylene diamine) complex.¹² In another instance, pyzdcH₂ behaved as a bidentate ligand *via* the oxygen atom of carboxylate and the nitrogen atom of 1,4-pyrazine ring in the (ampyH)₂[Cu(pyzdc)₂(H₂O)₂]·6H₂O (ampy = 2-amino-4-methylpyridine) coordination compound.¹³ Moreover, pyzdcH₂ is well known to act as a bridging ligand, especially in the design and construction of metal–organic frameworks and coordination polymers.¹¹ It acts as multi-dentate bridges between metal ions forming 1D-network chains. For example, pyzdcH₂ coordinated to the metal ions as a tridentate and tetradentate ligand in {(acrH)₂[Zn(pyzdc)₂]}_n (acr = acridine) and {[Mn(pyzdc)(H₂O)]·2H₂O}_n complexes.^{14–16} In the mentioned complexes, the coordination sites for each (pyzdc)²⁻ are, respectively, three and four O atoms of carboxylate groups and one N atom of the 1,4-pyrazine ring. In this work, the synthesis and identification of {(2-apymH)₂[Cu(pyzdc)₂]·6H₂O}_n by elemental analysis, infrared spectroscopy, and crystal structure determination are described.

EXPERIMENTAL

Materials and physical measurements

All reagents used in the synthesis were purchased from commercial sources and were used as received without further purification. The infrared spectrum in the range (4000–600 cm⁻¹) was recorded on a Buck 500 scientific spectrometer using a KBr disc. Elemental analyses were performed using a Thermo Finnigan Flash-1112EA microanalyzer. The X-ray diffraction studies were performed on a Bruker-APEX diffractometer with a CCD area detector, using Mo K_α-radiation, ($\lambda = 0.71073 \text{ \AA}$), and a graphite monochromator. Frames were collected at $T = 100 \text{ K}$ *via* ω/ϕ -rotation at 10 s per frame (SMART).¹⁷ The measured intensities were reduced to F^2 and corrected for adsorption with SADABS (SAINT-NT).¹⁸ Corrections were made for Lorentz and polarization effects. Structure solution, refinement, and data output were realised with the SHELXTL-NT program package.¹⁹ Non-hydrogen atoms were refined anisotropically. C–H hydrogen atoms were placed in the geometrically calculated positions using a riding model. O–H and N–H hydrogen atoms were localized by difference Fourier maps.

Preparation of {(2-apymH)₂[Cu(pyzdc)₂]·6H₂O}_n (I)

A mixture of pyzdcH₂ (0.18 mmol, 0.030 g) and 2-apym (0.36 mmol, 0.030 g) in water (10 mL) was refluxed for 1 h, then CuCl₂·2H₂O (0.060 mmol, 0.010 g) was added and refluxing was continued for 6 h, whereby a green solution was obtained. This solution gave green needle crystals of **I** in a yield of approximate 60 % (based on copper) after slow evaporation of the solvent at room temperature. Anal. Calcd. for C₂₀H₂₈CuN₁₀O₁₄: C, 34.56; H, 4.03; N, 20.16 %. Found: C, 34.15; H, 3.93; N, 21.05 %; IR (KBr, cm⁻¹): 3400, 1651, 1607, 1554, 1437, 1362, 1283, 1174, 1127, 1060, 975, 880, 842.

RESULTS AND DISCUSSION

*X-Ray crystallographic study of $\{(2\text{-apymH})_2[\text{Cu}(\text{pyzdc})_2]\cdot 6\text{H}_2\text{O}\}_n$ (**1**)*

The crystallographic data of the title compound is given in Table I. The molecular structure of **1** contains a discrete coordination polymer of the $[\text{Cu}(\text{pyzdc})_2]^{2-}$, organic species of $(2\text{-apymH})^+$ and crystallization water molecules in a 1:2:6 molar ratio (Fig. 1). In the polymeric chain of $[\text{Cu}(\text{pyzdc})_2]^{2-}$, the copper ion is six-coordinated showing CuN_2O_4 bound set by two N and four O atoms belonging to two $(\text{pyzdc})^{2-}$ ligands which are related by an inversion centre (the N1-Cu-N1^i bond angle is 180°). This arrangement causes the formation of a distorted octahedral geometry. The equatorial plane around the Cu(II) ion consists of a five-membered chelate ring with N (Cu–N1, 1.991(2) Å) and O (Cu–O1, 1.959(17) Å) as donor atoms while the axial positions are occupied by two oxygen atoms (Cu–O3, 2.427(19) Å) belonging to the remaining carboxylate group. The bonds length in the title compound can be compared with two 1D-coordination polymers, *i.e.*, $\{\text{Cu}(\text{pzdc})(\text{H}_2\text{O})_2\cdot\text{H}_2\text{O}\}_n$ (**a**)²⁰ and $\{[\text{Cu}(\mu\text{-pzdc})(\text{bipy})]\cdot\text{H}_2\text{O}\}_n$ (**b**)²¹ (bipy = bipyridine). The axial bond distance in **1** is

TABLE I. Selected crystallographic data and structure refinement parameters of **1**

Empirical formula	$\text{C}_{20}\text{H}_{28}\text{CuN}_{10}\text{O}_{14}$
Formula weight, g mol ⁻¹	696.07
Temperature, K	293(2)
Wavelength λ , Å	0.71073
Crystal system	Monoclinic
Space group	P21/c
a / Å	6.625 (3)
b / Å	11.600 (5)
c / Å	18.438 (8)
β / °	82.901 (8)
V / Å ³	1395.4 (11)
Z	2
D_c / kg m ⁻³	1657
F_{000}	718
μ / mm ⁻¹	0.87
Crystal size, mm	0.45×0.32×0.26
Space range, °	$2.1 < \theta < 23.4$
Reciprocal lattice segments: h	$-7 \rightarrow 7$,
k	$-12 \rightarrow 12$,
l	$-20 \rightarrow 20$
Reflections collected	11294
Reflection independent	2026
$R_1, wR_2 [I > 2\sigma(I)]$	0.0317, 0.0752
R_1, wR_2 (all data)	0.0350, 0.0770
Goodness-of-fit on F^2	1.061
Largest differences peak and hole, e Å ⁻³	0.31 and -0.29

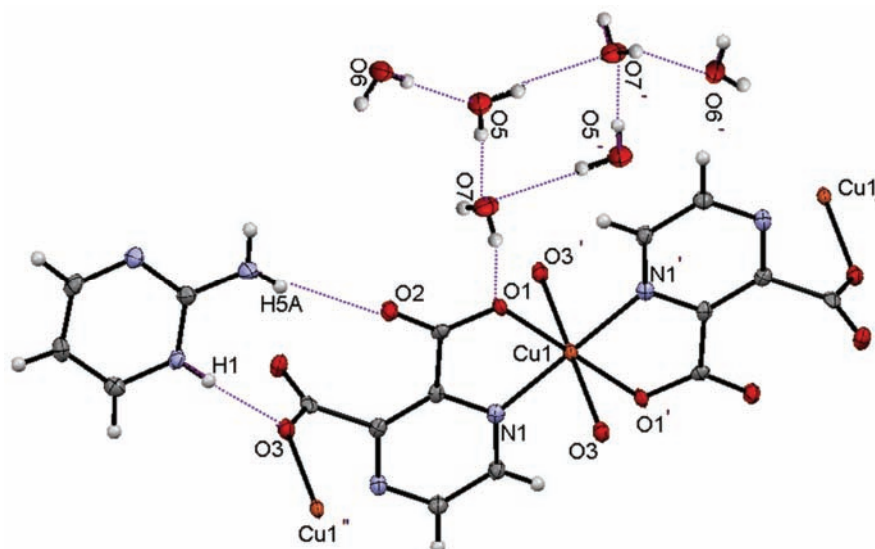


Fig. 1. The coordination environment of the Cu(II) ion with atom numbering, showing displacement ellipsoids at the 50 % probability level. Hydrogen bonds shown as dashed line. Atom symmetry operators: O6, $1-x, -y, 1-z$; O7, $1+x, 1/2-y, 1/2+z$; O5, $1+x, 1/2-y, 1/2+z$; O7', $2-x, -1/2+y, 1.5-z$; O5', $2-x, -1/2+y, 1.5-z$; O6', $2-x, -y, 1-z$; O4, $2-x, -y, 1-z$; O1', $1-x, -y, 1-z$; O3', $1-x, -y, 1-z$; N1', $1-x, -y, 1-z$; Cu1', $1+x, y, z$; Cu1'', $-1+x, y, z$.

longer than in **a** (2.306(3) Å) and **b** (2.151(3) Å), while the equatorial Cu–O bond distance is shorter than the respective bond (1.987(3) and 1.963(3) Å) in **a** and **b**, respectively. In addition to the covalent coordinative bonds in the crystalline network that cause the formation of a 1D-chain-like polymer, cooperatively there are intriguing intermolecular hydrogen bonds that join together to create various motifs and chains of solvent water molecules. The N5–H5A...O2 and N4–H1...O3 interactions between $[\text{Cu}(\text{pyzdc})_2]^{2-}$ polymeric species and protonated moiety resulted in the formation of hetero synthon $R_2^2(11)$. One of the most significant points in this study is the molecules of crystallization water, which play an important role in expanding the title polymer to give a 3D supramolecular architecture. In fact, these water molecules, which are linked by hydrogen bonds to form tapes comprised of an alternating sequence of fused hexamer and tetramer water clusters, act as a gluing factor for connecting adjacent polymeric chains by the establishment of hydrogen bonding interactions.²² In 2006, Castillo and co-workers reported the synthesis of a coordination polymer, $\{(\text{H}_2\text{bpe})[\text{Cu}(\mu\text{-pyzdc})_2] \cdot 2\text{H}_2\text{O}\}_n$, (bpe = 1,2-bis(4-pyridyl)ethylene), that is similar to compound **1**.²³ In both structures, the cations and water molecules are inserted between two parallel arrays of chains giving rise to a pillared structure which acts as a hydrogen-bond donor linking the upper and lower arrays of chains (Fig. 2). However, the difference in reaction conditions and type of the

cationic entities leads to a change in the crystalline network, the packing diagram and the hydrogen bonding interactions. One of the significant differences within **1** in comparison to the Castillo compound is the presence of water clusters in the former and their absence in the latter.

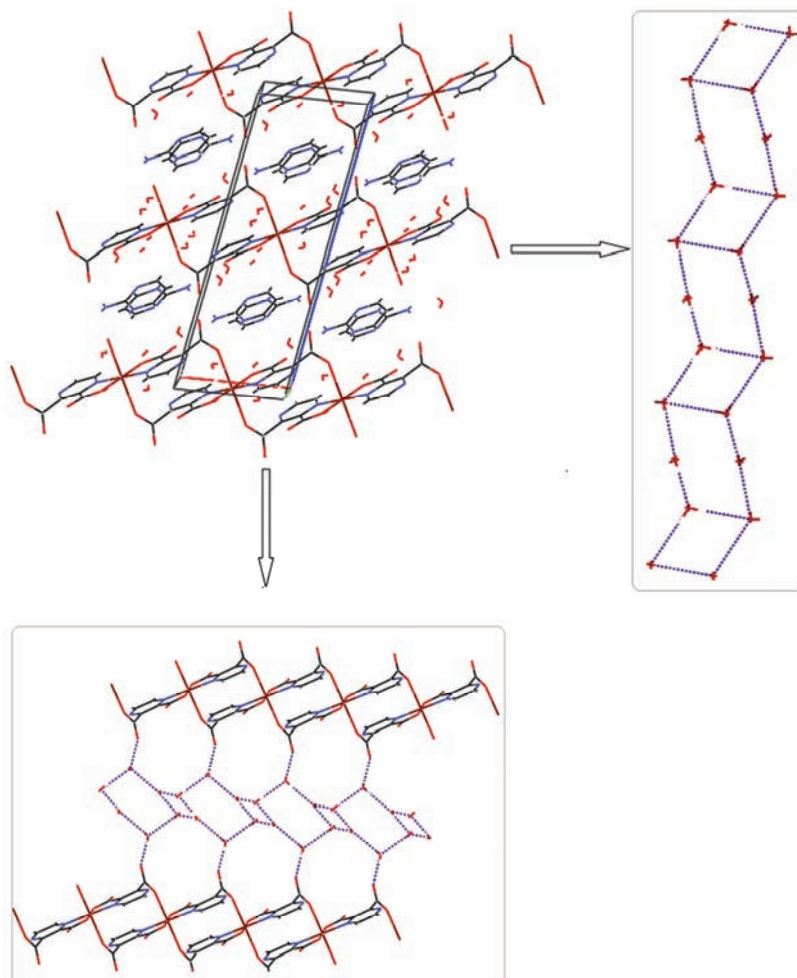


Fig. 2. View of the network including non-coordinated water molecules formed by $\text{N-H}\cdots\text{O}$ and $\text{O-H}\cdots\text{O}$ bonds.

CONCLUSIONS

A new 1D-Cu(II) coordination polymer was synthesized and structurally characterized by means of elemental analysis, infrared spectroscopy and single crystal X-ray diffraction. A novel topological net with channels was prepared by using a flexible ligand. The crystal structure of **1** consists of a 1D-polymer and

shows a coordination number of six for the Cu(II) ions. Presently, other complexes are being explored with much more flexible polycarboxylate ligands and relationships between their coordination mode and the structures obtained *via* the proton transfer mechanism are being studied.²⁴ Many aspects of these categories of coordination polymer with a proton transfer ligand and their complexes, such as their solid phase fluorescence and biological activity, as well as further studies employing SEM and/or TEM techniques with the view of obtaining layered coordination metal–organic frameworks in nano-size regime using sonochemical irradiation, for comparing with the routine methods, remain to be investigated, which are our aims for the near future.

SUPPLEMENTARY DATA

CCDC 785660 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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ИЗВОД

МОЛЕКУЛСКА СТРУКТУРА 1D-КООРДИНАЦИОНОГ ПОЛИМЕРА БАКРА(II) СА ПИРАЗИН-2,3-ДИКАРБОКСИЛНОМ КИСЕЛИНОМ И 2-АМИНОПИРИМИДИНОМ

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На основу протон-трансфер механизма синтетизован је нови 1D-координациони полимер бакар(II) јона, $\{(2\text{-арумН})_2[\text{Cu}(\text{pyzdc})_2] \cdot 6\text{H}_2\text{O}\}_n$, (2-арум = 2-аминопиримидин, $\text{pyzdcH}_2 =$ = пиазин-2,3-дикарбоксилна киселина). За карактеризацију овог полимера употребљени су елементална микроанализа, инфрацрвена спектроскопија и дифракција X-зрака са монокристала. Координациони полимер садржи непрекидне полимерне ланце од $[\text{Cu}(\text{pyzdc})_2]^{2-}$, где су два ланца међусобно мосно повезана дуж *a*-осе, и дискретних $(2\text{-арумН})^+$ фрагмената. Бакар(II) јон се налази у инверзионом центру основне равни издуженог октаедра, док су два кисеоникова атома суседних $(\text{pyzdc})^{2-}$ лиганада у аксијалном положају актаедра. Интеракције између атома кисеоника из молекула воде заједно са дикарбоксилном киселином имају значајну улогу у грађењу супрамолекулске структуре.

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