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Crystal structure of *catena*-poly[aqua[(μ_2 -4,5-dicarboxylato-2-(2-carboxylatophenyl)imidazol-1-ido- $\kappa^4 N, O, O': N'$)](μ_2 -4,4'-bipyridine- $\kappa^2 N: N'$)]dicopper(II)], $C_{22}H_{14}Cu_2N_4O_7$

<https://doi.org/10.1515/ncrs-2019-0887>

Received December 6, 2019; accepted January 18, 2020; available online March 26, 2020

Abstract

$C_{22}H_{14}Cu_2N_4O_7$, monoclinic, $P2_1/n$ (no. 14), $a = 7.7885(4)$ Å, $b = 14.9974(8)$ Å, $c = 17.7464(10)$ Å, $\beta = 102.184(2)^\circ$, $V = 2026.22(19)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0357$, $wR_{ref}(F^2) = 0.0936$, $T = 300(2)$ K.

CCDC no.: 1978691

A part of the polymeric title structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All reagents were purchased from commercial sources and used without further purification. A methanol solution (2 mL) of 2-(2-carboxylphenyl)-1H-imidazole-4,5-dicarboxylic acid (CPhH₄IDC, 0.05 mmol) and 4,4'-bipyridine (0.05 mmol) was added dropwise to an aqueous solution (2 mL) of

Table 1: Data collection and handling.

Crystal:	Green block
Size:	0.19 × 0.17 × 0.14 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	2.16 mm ⁻¹
Diffractometer, scan mode:	Bruker D8 Venture Photon, φ and ω
θ_{max} , completeness:	27.6°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	18388, 4590, 0.033
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 3501
$N(param)_{refined}$:	316
Programs:	SHELX [1], Bruker [2, 3]

$Cu(NO_3)_2 \cdot 3H_2O$ (0.05 mmol), then 1 mL dimethylformamide was added to the above mixture. The resulting solution was placed in a 25 mL Teflon-lined stainless steel reactor, which was sealed and heated to 393 K for 72 h. After the mixture was cooled to room temperature at a rate of 5 K h⁻¹, green crystals of the title compound were obtained (yield 53%, based on Cu).

Experimental details

Hydrogen atoms bound to C atoms were positioned geometrically and refined as riding atoms, with C–H = 0.93 Å. Water H atoms were found according to the residual electron-density peaks around the water O atom and the directions of hydrogen bonds, and were then locked in position and included with O–H = 0.85 Å. All H atoms were refined with $U_{iso}(H) = 1.2 U_{eq}(C)$ and $1.5 U_{eq}(O)$.

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Cu1	−0.01549(5)	0.78163(2)	0.40649(2)	0.03277(12)
Cu2	0.36285(5)	0.43343(2)	0.42669(2)	0.03650(12)
N1	0.1042(3)	0.66840(14)	0.42948(13)	0.0269(5)
N2	0.2469(3)	0.53878(14)	0.44283(13)	0.0266(5)
N3	0.4722(3)	0.32443(15)	0.41233(14)	0.0321(5)
N4	0.8689(3)	−0.09902(15)	0.40118(16)	0.0368(6)
O1	−0.0601(3)	0.75939(13)	0.51917(13)	0.0415(5)
O2	−0.0101(3)	0.65640(15)	0.61277(13)	0.0457(6)
O3	0.1658(3)	0.51509(15)	0.63626(12)	0.0432(5)
O4	0.3074(3)	0.42437(14)	0.57187(13)	0.0430(5)
O5	0.1576(3)	0.82396(14)	0.34898(16)	0.0524(7)
O6	0.4416(3)	0.82363(16)	0.35081(16)	0.0536(6)
O7	−0.2564(3)	0.72464(14)	0.33902(13)	0.0439(5)
H7A	−0.351604	0.754206	0.331865	0.066*
H7B	−0.280104	0.673136	0.354035	0.066*
C1	0.0032(4)	0.68709(19)	0.54818(18)	0.0326(6)
C2	0.0993(4)	0.63460(17)	0.50043(15)	0.0259(6)
C3	0.1872(3)	0.55490(16)	0.50921(16)	0.0254(6)
C4	0.2246(4)	0.49292(19)	0.57514(17)	0.0330(7)
C5	0.1933(4)	0.60918(16)	0.39632(16)	0.0265(6)
C6	0.2300(4)	0.61848(19)	0.31925(18)	0.0348(7)
C7	0.2224(5)	0.5421(2)	0.2728(2)	0.0494(9)
H7	0.185955	0.488332	0.290213	0.059*
C8	0.2675(6)	0.5453(3)	0.2022(2)	0.0632(11)
H8	0.259577	0.494543	0.171577	0.076*
C9	0.3253(6)	0.6257(3)	0.1769(2)	0.0615(11)
H9	0.359103	0.628172	0.129695	0.074*
C10	0.3329(5)	0.7016(2)	0.2213(2)	0.0494(9)
H10	0.372511	0.754673	0.203829	0.059*
C11	0.2818(4)	0.6998(2)	0.29220(18)	0.0364(7)
C12	0.2943(4)	0.7878(2)	0.33492(19)	0.0386(7)
C13	0.5415(4)	0.30177(19)	0.35193(18)	0.0353(7)
H13	0.536393	0.343010	0.312382	0.042*
C14	0.6200(4)	0.22033(18)	0.34544(18)	0.0355(7)
H14	0.666890	0.207766	0.302558	0.043*
C15	0.6284(4)	0.15751(18)	0.40343(17)	0.0305(6)
C16	0.5568(4)	0.18153(19)	0.46574(18)	0.0377(7)
H16	0.559744	0.141512	0.506027	0.045*
C17	0.4817(4)	0.26390(19)	0.46837(19)	0.0382(7)
H17	0.435270	0.278263	0.511013	0.046*
C18	0.7098(4)	0.06840(18)	0.40097(17)	0.0327(6)
C19	0.7574(5)	0.0344(2)	0.3368(2)	0.0550(10)
H19	0.736626	0.067044	0.291217	0.066*
C20	0.8361(6)	−0.0485(2)	0.3395(2)	0.0571(11)
H20	0.867711	−0.069565	0.295059	0.069*
C21	0.8200(8)	−0.0671(3)	0.4624(3)	0.0894(18)
H21	0.837875	−0.102264	0.506535	0.107*
C22	0.7442(7)	0.0153(3)	0.4650(2)	0.0843(17)
H22	0.716080	0.035022	0.510612	0.101*

Comment

Aromatic polycarboxylic acid, like benzenedicarboxylic acid, benzenetricarboxylic acid, benzenetetracarboxylic acid, imidazole-4,5-dicarboxylic acid, and their derivatives, have been widely used in the synthesis of new coordination complexes since they have various coordination modes to form diverse structures and can act as hydrogen-bond acceptors and donors in the assembly of final structures [4–10]. 4,4'-Bipyridine has also been used extensively as ligand for the construction of complexes [11, 12]. Furthermore, the combination of aromatic polycarboxylic acid and *N*-heterocyclic ligands is a good choice for the construction of complexes [13–15]. In this study, by employing 2-(2-carboxylphenyl)-1*H*-imidazole-4,5-dicarboxylic acid (CPhIDC) and 4,4'-bipyridine (bipy) as ligands to react with Cu(NO₃)₂ · 3H₂O, we have successfully obtained a new complex [Cu₂(CPhIDC)(bipy)(H₂O)].

The asymmetrical unit of the title structure contains two crystallographically distinct Cu^{II} cations, one tetra-anionic CPhIDC^{4−} ligand, one 4,4'-bipyridine ligand and one coordination water molecule. Each Cu1 ion is coordinated by two N atoms from CPhIDC^{4−} and 4,4'-bipyridine and by three O atoms from one CPhIDC^{4−} and one water molecule, resulting in an irregular O₃N₂ coordination environment. The Cu1–O distances range from 1.960(2) to 2.177(2) Å and the Cu1–N bond lengths are 1.939(2) and 1.997(2) Å, respectively; these values are comparable to distances reported in the literature Cu^{II} complexes [16, 17]. The Cu2 ion is two-coordinated by N atoms from CPhIDC^{4−} and 4,4'-bipyridine with the N2–Cu2–N3 angle of 177.41(10)°. The Cu2–N bond lengths are 1.872(2) and 1.885(2) Å, which are slightly shorter than those of Cu1–N. Cu1 and Cu2 ions are connected by CPhIDC^{4−} and 4,4'-bipyridine alternately to form one-dimensional chain along the *b* direction. There are two kinds of O–H...O hydrogen bonds between coordination water molecules and carboxylate groups. In addition, there are weak π–π stacking interactions between the N1/N2/C2/C3/C5 imidazole ring and the N3/C13/C14/C15/C16/C17 pyridine ring, with a centroid-centroid distance of 3.7485(2) Å, and π–π stacking interactions between the N3/C13/C14/C15/C16/C17 pyridine ring and C6–C11 benzene ring, with a centroid-centroid distance of 3.7838(2) Å, which are in the range for common π–π interactions [18–20]. Adjacent chains are linked by the aforementioned hydrogen bonds and π–π interactions, leading to a three-dimensional supramolecular architecture in the solid state.

Acknowledgements: This study was supported by Science and Technology Innovation Talents of Henan University of Chinese Medicine (2014XCXRC04) and Henan University of

Chinese Medicine, Provincial Scientific Research Business (2014KYYWF-QN03).

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