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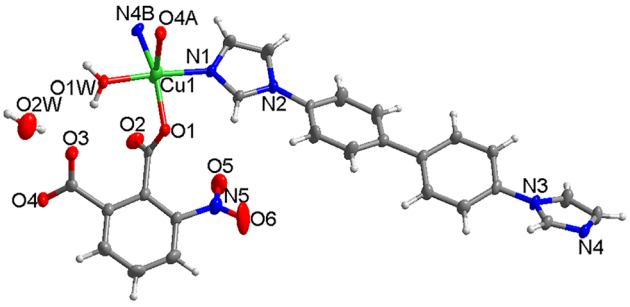
The crystal structure of poly[aqua-(μ_2-4,4′-bis(imidazolyl)biphenyl-κ^2N:N')-(μ_2-3-nitrobenzene-1,2-dicarboxylato-κ^2O:O')]copper (II) hydrate, $C_{26}H_{21}N_5O_8Cu$



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Abstract

$C_{26}H_{21}N_5O_8Cu$, monoclinic, $P2_1/c$ (no. 14), a = 17.2262(10) Å, b = 7.3474(3) Å, c = 21.1086(11) Å, β = 111.498(6)°, V = 2485.8(2) Å^3, Z = 4, $R_{gt}(F)$ = 0.0629, $wR_{ref}(F^2)$ = 0.1433, T = 293(2) K.

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Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Blue block
Size:	0.37 × 0.34 × 0.33 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.94 mm^{-1}
Diffractometer, scan mode:	SuperNova, ω
θ_{max}, completeness:	25.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	25925, 4609, 0.089
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3869
$N(param)_{refined}$:	361
Programs:	Bruker [1], Olex2 [2], SHELX [3, 4]

Source of material

All chemicals were of reagent grade and used as received without further purification. The 4,4′-bis(imidazolyl) biphenyl was obtained from Jinan Henghua Technology Co., Ltd.. The 3-nitrobenzene-1,2-dicarboxylic acid was purchased from Beijing Bailingwei Technology Co., Ltd.. Other chemical reagents were obtained from the Tianjin Deen Chemical Reagent Co., Ltd.. The mixture of 3-nitrobenzene-1,2-dicarboxylic acid ($H_2$3-Nbdc 21.3 mg, 0.1 mmol), 4,4′-bis(imidazolyl)biphenyl (bibp, 28.6 mg, 0.1 mmol), $Cu(OAc)_2{\cdot}4H_2O$ (20.3 mg, 0.1 mmol), EtOH (2 mL) and H_2O (4 mL) was placed in a 23 ml Teflon-lined autoclave at 393 K for four days, then cooled to room temperature. Blue block crystals were obtained in ca. 58% yield. **Elemental analysis** calcd. (%) for $C_{26}H_{21}N_5O_8Cu$: C, 52.48; H, 3.56; N, 11.77 Found: C, 52.42; H, 3.74; N, 11.62.

Experimental details

Using Olex2 [2]. The structure was solved with the SheLXT [3] structure solution program and refined with the SheLXL [4] refinement package. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. The U_{iso} of the H-atoms were constrained to 1.2 times U_{eq} of their bonding carbon atoms with C–H = 0.93 Å (aromatic) and 1.5 times U_{eq} for the hydrogen atoms at water with O–H = 0.85 Å.

Comment

The aromatic 1,2-benzenedicarboxylic acids are widely used constructing coordination polymers (CPs) with interesting structures and properties not only because of their diversities coordination modes (monodentate, bridging, chelating), but also because of their strong thermal and chemical stabilities.

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

Atom	x	y	z	U_{iso}*/U_{eq}
Cu1	0.15767 (3)	0.40843 (6)	0.49484 (2)	0.02090 (17)
C1	0.2736 (2)	−0.0474 (5)	0.60176 (18)	0.0205 (8)
C2	0.2237 (3)	−0.1863 (5)	0.61101 (19)	0.0237 (9)
C3	0.2571 (3)	−0.3136 (6)	0.6623 (2)	0.0350 (11)
H3	0.2235	−0.4082	0.6666	0.042*
C4	0.3384 (3)	−0.3035 (7)	0.7068 (2)	0.0423 (12)
H4	0.3589	−0.3874	0.7420	0.051*
C5	0.3894 (3)	−0.1681 (6)	0.6988 (2)	0.0347 (11)
H5	0.4447	−0.1590	0.7285	0.042*
C6	0.3567 (3)	−0.0458 (5)	0.64573 (19)	0.0244 (9)
C7	0.2357 (2)	0.0982 (5)	0.54786 (19)	0.0230 (9)
C8	0.1312 (3)	−0.1947 (5)	0.56855 (19)	0.0240 (9)
C9	0.2643 (3)	0.6549 (7)	0.4432 (3)	0.0517 (15)
H9	0.2205	0.6909	0.4041	0.062*
C10	0.3444 (3)	0.7116 (8)	0.4613 (3)	0.0556 (17)
H10	0.3654	0.7905	0.4371	0.067*
C11	0.3334 (3)	0.5279 (6)	0.5374 (2)	0.0257 (9)
H11	0.3470	0.4577	0.5767	0.031*
C12	0.4744 (2)	0.6604 (5)	0.56325 (19)	0.0227 (9)
C13	0.5267 (3)	0.7401 (7)	0.5354 (2)	0.0378 (11)
H13	0.5069	0.7679	0.4892	0.045*
C14	0.6091 (3)	0.7794 (7)	0.5758 (2)	0.0372 (11)
H14	0.6441	0.8298	0.5558	0.045*
C15	0.6400 (3)	0.7448 (5)	0.64522 (19)	0.0236 (9)
C16	0.5877 (3)	0.6597 (7)	0.6713 (2)	0.0425 (13)
H16	0.6076	0.6305	0.7173	0.051*
C17	0.5058 (3)	0.6151 (7)	0.6315 (2)	0.0416 (12)
H17	0.4723	0.5549	0.6508	0.050*
C18	0.7262 (3)	0.7990 (6)	0.68939 (19)	0.0240 (9)
C19	0.7676 (3)	0.9366 (6)	0.6696 (2)	0.0310 (10)
H19	0.7410	0.9944	0.6280	0.037*
C20	0.8475 (3)	0.9901 (6)	0.7102 (2)	0.0305 (10)
H20	0.8736	1.0844	0.6963	0.037*
C21	0.8883 (3)	0.9030 (5)	0.77151 (19)	0.0226 (9)
C22	0.8487 (3)	0.7664 (6)	0.7927 (2)	0.0280 (9)
H22	0.8758	0.7083	0.8341	0.034*
C23	0.7686 (3)	0.7158 (6)	0.7521 (2)	0.0295 (10)
H23	0.7422	0.6240	0.7670	0.035*
C24	1.0065 (3)	0.9623 (5)	0.87996 (19)	0.0236 (9)
H24	0.9795	0.9277	0.9090	0.028*
C25	1.0311 (3)	1.0175 (7)	0.7869 (2)	0.0333 (10)
H25	1.0252	1.0276	0.7414	0.040*
C26	1.0991 (3)	1.0595 (6)	0.8418 (2)	0.0321 (10)
H26	1.1488	1.1055	0.8404	0.039*
Cu1	0.15767 (3)	0.40843 (6)	0.49484 (2)	0.02090 (17)
N1	0.2577 (2)	0.5376 (4)	0.49077 (16)	0.0241 (7)
N2	0.3883 (2)	0.6299 (4)	0.52229 (17)	0.0244 (8)
N3	0.9721 (2)	0.9567 (5)	0.81159 (16)	0.0233 (7)
N4	1.0841 (2)	1.0240 (4)	0.90034 (15)	0.0225 (7)
N5	0.4148 (2)	0.0848 (5)	0.63521 (19)	0.0356 (9)
O1	0.23246 (17)	0.2575 (4)	0.57209 (13)	0.0242 (6)
O1W	0.06542 (17)	0.2820 (4)	0.51083 (14)	0.0273 (7)
H1WA	0.0153	0.3134	0.5032	0.041*
H1WB	0.0764	0.1692	0.5171	0.041*
O2	0.2087 (2)	0.0575 (4)	0.48755 (14)	0.0365 (8)
O2W	−0.0406 (2)	0.0301 (6)	0.61584 (17)	0.0583 (11)
H2WA	−0.0057	0.0243	0.5960	0.088*
H2WB	−0.0865	0.0106	0.5831	0.088*
O3	0.09033 (19)	−0.0537 (4)	0.56467 (16)	0.0357 (8)
O4	0.10246 (18)	−0.3459 (4)	0.54288 (15)	0.0319 (7)
O5	0.4051 (2)	0.1294 (5)	0.57752 (17)	0.0484 (9)
O6	0.4727 (3)	0.1381 (7)	0.6843 (2)	0.0919 (18)

The nitro-1,2-benzenedicarboxylates are widely used as O-donor ligands to enrich the structural and functional diversities of coordination polymers because the N and O atoms in the electron-withdrawing group ($-NO_2$) can be not only used as coordination sites, but also as donors or acceptors of hydrogen-bond interactions. We and other authors have synthesized a large number of CPs with interesting structures and excellent properties based on 3-nitrobenzene-1,2-dicarboxylic acid ($H_2$3-Nbdc) [5–15]. However, the literature on the synthesis of CPs based on the mixed $H_2$3-Nbdc and 4,4′-bis(imidazolyl)biphenyl(bibp) ligands is relative rare [8].

X-ray crystallographic analysis reveals that the title complex crystallizes in monoclinic crystal system, space group $P2_1/c$ and features a two-dimensional grid layer. The asymmetric unit contains one Cu(II) ion, one 3-Nbdc dianion, one bibp molecule, one coordinated water and one guest water molecule, as shown in Figure (A: $x, 1+y, z$; B: $-1+x, 1.5-y, -0.5+z$). The Cu(II) ion is five-coordinated in a slightly distorted tetragonal-pyramidal geometry [CuO_3N_2] with the one carboxylate O(1) atom belonging to 3-Nbdc anion, one O(1W) atom from coordinated water molecule, and N(1) and N(4B) atoms from two symmetry-related bibp molecules, while another carboxylate O(4A) atom from symmetry-related 3-Nbdc dianion occupies the apical site. The Cu–O bond lengths are 1.974(3), 2.002(3) and 2.429(3) Å, and the Cu–N bond lengths are 2.013(5) and 2.037(5) Å, respectively.

Since the fivefold coordination geometry in the complex does not correspond to a perfect tetragonal pyramid, we used a convenient distortion parameter τ^5 for the quantitative characterisation of the copper coordination polyhedron [16]. The extreme values of distortion parameter (0 and 1) are associated with an ideal tetragonal pyramid and a regular trigonal bipyramid. The distortion parameter of the title compound is 0.23, the result reveals that the copper coordination polyhedron is the predominantly tetragonal pyramidal geometry (77%), additionally including a 23% contribution of the trigonal-bipyramid state.

The adjacent copper ions are linked by the carboxylate groups of 3-Nbdc dianions adopting monodentate coordination mode to form a metal-carboxylate chain with the Cu···Cu distance of 7.3474 Å. The metal-carboxylate chains are further connected by bibp molecules adopting exo-bidentate coordinated mode to produce a two-dimensional grid layer with the through-ligand Cu···Cu separation of 17.3226 Å. The discussed layers, stacking along the c direction adopting a -ABAB- mode, are cohered by interlayer hydrogen bonds forming a bilayer structure. There is a hydrogen bond between the coordinated water O(1W) and the carboxylate O(4) atom from 3-Nbdc anion (O(1W)–H(1WA)···O(4): d = 2.732(4) Å). Secondly, it there is a hydrogen bond between free water O(2W) and the carboxylate O(3) and O(2) atoms from 3-Nbdc anions (O(2W)–H(2WA)···O(3): d = 2.901(5) Å; O(2W)–H(2WB)···O(2): d = 2.989(5) Å). Bilayers further stack together to accomplish its entire three-dimensional structure by offset-stacking π–π interactions between imidazole ring and benzene ring of bibp molecules with the centroid distance of 4.1312 Å and the planar angle of 18.2°. It is obvious that H-bond interactions and π–π interactions play important roles in the self-assembly and enhanced the stability of resultant structure.

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Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Rigaku Oxford Diffraction. CrysAlis^{PRO} Software System; Rigaku Corporation: Oxford, UK, 2015.
2. Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, *42*, 339–341.
3. Sheldrick G. M. *SHELXTL* – integrated space-group and crystal-structure determination. *Acta Crystallogr.* 2015, *A71*, 3–8.
4. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
5. Wang X. L., Xiong Y., Sha X. T., Liu G. C., Lin H. Y. Various polycarboxylate-directed Cd(II) coordination polymers based on a semirigid bis-pyridyl-bis-amide ligand: construction and fluorescent and photocatalytic properties. *Cryst. Growth Des.* 2017, *17*, 483–496.
6. Liu G., Li Y., Lu Z., Li X., Chen X. Carboxylates directed versatile structures of ten 1D-3D Ni(II) coordination polymers: fluorescent behaviors and electrochemical activities. *CrystEngComm* 2019, *21*, 5344–5355.
7. Xu W., Hu K. K., Jin S., Zhang Y., Wang D. Constructions of seven noncovalent-bonded supramolecules from reactions of Cu(II)/Cd(II)/Zn(II) with isonicotinamide and carboxylates. *Inorg. Nano-Metal Chem.* 2021, *51*, 1842–1859.
8. Xiao Q. Q., Song Z. W., Li Y. H., Cui G. H. Two difunctional Co(II) coordination polymers for natural sunlight photocatalysis of methylene blue and selective fluorescence sensing of Cr(VI) ion in water media. *J. Solid State Chem.* 2019, *276*, 331–338.
9. Liu S., Li L. L., Wang W. Z., Jia X. G., Lin C. L. A carboxylate-bridged Co(II) layer complex: synthesis, structure and magnetic property. *Chin. J. Struct. Chem.* 2018, *37*, 973–980.
10. Huan D. H., Liu Y. G., Dong G. Y., Wang S. C. Three cobalt(II) coordination polymers constructed from flexible bis(thiabendazole) and dicarboxylate linkers: crystal structures, fluorescence, and photocatalytic properties. *Transition Met. Chem.* 2016, *41*, 447–457.
11. Li G. L., Liu G. Z., Xin L. Y., Li X. L., Ma L. F., Wang L. Y. Syntheses, structures and fluorescence properties of four Zn/Cd(II) coordination polymers with 3-nitrobenzene-1,2-dicarboxylate and dipyridyl-typed coligands. *J. Inorg. Organomet. Polym.* 2015, *25*, 694–701.
12. Li G. L., Yin W. D., Liu G. Z., Ma L. F., Huang L. L., Li L., Wang L. Y. Single-crystal to single-crystal photochemical structure transformation of a ladder-like coordination polymer with dinuclear Zn(II) platform. *Inorg. Chem. Commun.* 2014, *43*, 165–168.
13. Yin W. D., Li G. L., Liu G. Z., Xin L. Y., Li X. L., Ma L. F. Syntheses, structures and properties of two coordination polymers constructed by 3-nitrobenzene-1,2-dicarboxylate acid and Zn/Co. *Chin. J. Inorg. Chem.* 2015, *31*, 1439–1446.
14. Yin W. D., Liu Q. L., Li G. L. Crystal structure of *catena*-poly[triaqua-(1,3-di(1*H*-imidazol-1-yl)benzene- $\kappa^2N:N'$)- (3-nitrophthalato-κ^1O) cobalt(II)]-water (2/3), $C_{20}H_{22}N_5O_{10.5}Co$. *Z. Kristallogr. N. Cryst. Struct.* 2020, *235*, 125–128.
15. Yin W. D., Liu Q. L., Zhao Y. J., Gong X. R., Li G. L. Crystal structure of *catena*-poly[bis(μ_2-3,5-bis(1-imidazolyl) pyridine-$\kappa^2N:N'$)-(μ_2-3-nitrophthalato-$\kappa^3O,O':O''$)cadmium(II)] dihydrate, $C_{30}H_{25}N_{11}O_8Cd$. *Z. Kristallogr. N. Cryst. Struct.* 2021, *236*, 899–902.
16. Rodinaa T. A., Losevaa O. V., Smolentsevb A. I., Antzutkind O. N., Ivanova A. V. Crystal structure, solid-state ^{13}C and ^{15}N NMR characterisation, chemisorption activity and thermal behaviour of new mercury(II) dipropyldithiocarbamate: binuclear, pseudo-binuclear and heteronuclear complexes of $[Hg_2(PrDtc)_4]$, $[Hg(PrDtc)_2]_2$ and $[Au(PrDtc)_2]_2[Hg_2C_{l6}]$. *Inorg. Chim. Acta* 2020, *508*, 119630.