Xu Liu and Xiang-Ru Meng*

Crystal structure of [diaqua[2,2'-(1,2-phenylene)bis(1*H*-imidazole-4-carboxylato-5-carboxy)- $\kappa^4 N, N', O, O'$]nickel(II)] tetrahydrate, $C_{16}H_{12}N_4NiO_{10} \cdot 4H_2O$

Table 1: Data collection and handling.

Crystal:	Blue block
Size:	0.21 × 0.19 × 0.15 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	1.02 mm ⁻¹
Diffraction, scan mode:	Bruker D8 VENTURE PHOTON, φ and ω
$\theta_{\max}$, completeness:	27.5°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	19,289, 2457, 0.044
R_{int} :	
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 2071
$N(\text{param})_{\text{refined}}$:	173
Programs:	SHELX [1], BRUKER [2, 3]

<https://doi.org/10.1515/ncrs-2021-0463>

Received December 4, 2021; accepted January 15, 2022;

published online January 31, 2022

Abstract

$C_{16}H_{12}N_4NiO_{14}$, orthorhombic, $Pnma$ (No. 62), $a = 7.1945(2)$ Å, $b = 16.1805(4)$ Å, $c = 17.7912(5)$ Å, $V = 2071.08(10)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0353$, $wR_{\text{ref}}(F^2) = 0.0997$, $T = 293(2)$ K.

CCDC no.: 2142301

The title complex 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

The reagents used in this paper are purchased from commercial sources without further purification. An

aqueous solution (2 mL) of $NiCl_2 \cdot 4H_2O$ (0.02 mmol) was added dropwise to a methanol solution (2 mL) of 2,2'-(1,2-phenylene)bis(1*H*-imidazole-4,5-dicarboxylic acid) ($H_6Phbidc$, 0.02 mmol). A clear solution was obtained after filtration and placed in a closed container at room temperature. Light blue crystals can be obtained after four weeks (yield 51%, based $H_6Phbidc$).

Experimental details

Hydrogen atoms bound to C and N atoms were positioned geometrically and refined as riding atoms, with C–H = 0.93 Å and N–H = 0.86 Å. H atoms of the non-deprotonated carboxylic acid groups were refined as riding atoms, with O–H = 0.82 Å. H atoms on O5, O6, O7 were found according to the residual electron-density peaks around each 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 $U_{\text{iso}}(H) = 1.2 U_{\text{eq}}(C, N)$ and $1.5 U_{\text{eq}}(O)$. One guest water molecule (O8) is disordered and the hydrogen atoms of this water molecule could not be located in the difference Fourier map.

Comment

1*H*-Imidazole-4,5-dicarboxylic acid and its derivatives, such as 2-(hydroxymethyl)-1*H*-imidazole-4,5-dicarboxylic

*Corresponding author: Xiang-Ru Meng, College of Chemistry, Green Catalysis Center, Zhengzhou University, 450001, Henan, P. R. China, E-mail: mxr@zzu.edu.cn. <https://orcid.org/0000-0002-9055-9646>
Xu Liu, College of Chemistry, Green Catalysis Center, Zhengzhou University, 450001, Henan, P. R. China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	x	y	z	U_{iso}^*/U_{eq}
Ni1	0.85106 (6)	0.750000	−0.02377 (2)	0.02858 (14)
O1	0.8891 (3)	0.64733 (10)	−0.09459 (9)	0.0380 (4)
O2	0.8422 (3)	0.51153 (10)	−0.09723 (9)	0.0417 (4)
O3	0.7149 (3)	0.40744 (10)	−0.01041 (10)	0.0411 (4)
H3	0.761797	0.443422	−0.036739	0.062*
O4	0.5869 (3)	0.40029 (10)	0.10246 (10)	0.0462 (5)
O5	0.5726 (4)	0.750000	−0.05902 (15)	0.0439 (6)
H5	0.525959	0.789800	−0.083862	0.066*
O6	1.1317 (4)	0.750000	−0.00514 (17)	0.0472 (6)
H6	1.190801	0.795420	−0.007356	0.071*
O7	0.5062 (3)	0.49183 (12)	0.24964 (10)	0.0512 (5)
H7A	0.568851	0.484683	0.289612	0.077*
H7B	0.477481	0.441742	0.241101	0.077*
N1	0.7931 (3)	0.65986 (11)	0.05063 (10)	0.0276 (4)
N2	0.6759 (3)	0.56915 (11)	0.12886 (10)	0.0288 (4)
H2	0.629388	0.548025	0.169032	0.035*
C1	0.8400 (3)	0.58154 (14)	−0.06440 (13)	0.0316 (5)
C2	0.7783 (3)	0.58545 (13)	0.01493 (12)	0.0283 (4)
C3	0.7058 (3)	0.52823 (13)	0.06308 (12)	0.0286 (4)
C4	0.6643 (3)	0.43920 (14)	0.05327 (14)	0.0328 (5)
C5	0.7319 (3)	0.64909 (13)	0.12055 (12)	0.0272 (4)
C6	0.7391 (3)	0.70621 (13)	0.18527 (11)	0.0270 (4)
C7	0.7506 (3)	0.66589 (14)	0.25481 (12)	0.0350 (5)
H7	0.755439	0.608457	0.255346	0.042*
C8	0.7550 (4)	0.70717 (15)	0.32219 (12)	0.0381 (5)
H8	0.757917	0.678048	0.367237	0.046*
O8 ^a	0.451 (3)	0.3117 (7)	0.2578 (7)	0.252 (10)
O8 ^a	0.3126 (16)	0.3409 (5)	0.2470 (6)	0.129 (3)

^aOccupancy: 0.5.

acid, 2-(pyridin-4-yl)-1*H*-imidazole-4,5-dicarboxylic acid, 2,2'-(1,2-phenylene)bis(1*H*-imidazole-4,5-dicarboxylic acid), 2-phenyl-1*H*-imidazole-4,5-dicarboxylic acid, 2-(1*H*-tetrazol-1-yl)-1*H*-imidazole-4,5-dicarboxylic acid, 2,2'-(ethane-1,2-diyl)bis(1*H*-imidazole-4,5-dicarboxylic acid), are good linkers and have been widely used in the synthesis of new coordination complexes (CPs) since they contain not only N-donors but also O-donors, which have abundant coordination modes and can lead to CPs with various structures and interesting properties [4–12]. Among the reported ligands, 2,2'-(1,2-phenylene)bis(1*H*-imidazole-4,5-dicarboxylic acid) ($H_6Phbidc$), and corresponding deprotonated anions are excellent ligands as there are four potential N-donors and eight potential O-donors and can coordinate to almost all soft and hard metal ions with various coordination modes. Up to now, only a small number of CPs based on $H_6Phbidc$ have been reported [8, 13, 14]. In order to further enrich the categories and numbers of CPs based on this ligand, we synthesized the title compound.

The asymmetric unit of the title structure consists of one half of Ni(II) ion, one half of 2,2'-(1,2-phenylene)bis

(1*H*-imidazole-4,5-dicarboxylate anion ($H_4Phbidc^{2-}$), two halves of coordination water molecules and two uncoordinated water molecules. Each Ni1 ion is six-coordinated and located in a distorted octahedral NiN_2O_4 coordination environment formed by two N atoms (N1 and N1#1) and two O atoms (O1 and O1#1) from one $H_4Phbidc^{2-}$ anion and by two water molecules (O5 and O6). The Ni–N bond lengths is 2.0133(18) Å and the Ni–O bond lengths are 2.046(3), 2.099(3), 2.1028(16) and 2.1029(16) Å, respectively; these values are within the normal ranges and close to those reported in other Ni(II) complexes [15–17]. The bond angles of O6–Ni1–O5, N1–Ni1–O1#1 and N1#1–Ni1–O1 are 171.94(12)°, 173.30(7)° and 173.30(7)°, respectively. The other bond angles around the Ni1 ion are more or less deviated from the ideal values (81.29(7)°–95.63(8)°). There are O–H...O intramolecular hydrogen bonds between carboxyl and carboxylate groups, N–H...O intermolecular hydrogen bonds between imidazole units and solvent water molecules and O–H...O intermolecular hydrogen bonds involving coordination water molecules, solvent water molecules and carboxylate groups. Furthermore, there are π – π stacking interactions between C6/C7/C8/C6#1/C7#1/C8#1 benzene rings with a centroid-centroid distance of 3.6002(1) Å, which are in the range for common π – π interactions [9, 18, 19]. $[Ni(H_4Phbidc)(H_2O)_2]$ molecules are linked by the above hydrogen bonds and π – π interactions, resulting in a three-dimensional supramolecular architecture in the solid state.

Acknowledgements: This work was financially supported by the National Natural Science Foundation (no. 202010459001).

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: National Natural Science Foundation (no. 202010459001).

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

References

- Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
- Bruker. *SADABS*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2000.
- Bruker. *APEX3 and SAINT*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2016.
- Tahmasian A., Safarifar V., Morsali A., Joo S. W. Sonochemical syntheses of a new fibrous-like nano-scale strontium(II) 3D

- coordination polymer; precursor for the fabrication of a strontium carbonate nanostructure. *Polyhedron* 2014, 67, 81–88.
5. Huang X. Y., Sun S. X., Wang C. Q., Yao P. Crystal structure of *catena*-poly[μ_2 -(2-(hydroxymethyl)-1*H*-imidazole-4,5-dicarboxylato) cadmium(II)], $C_6H_8CdN_2O_7$. *Z. Kristallogr. N. Cryst. Struct.* 2020, 235, 1489–1491.
 6. Cheng D., Liu Y. J., Cheng F. R., Yang H. X., Meng X. R. Synthesis, structure and fluorescence properties of a Zn(II) coordination polymer based on 2-(hydroxymethyl)-1*H*-imidazole-4,5-dicarboxylate. *J. Chem. Res.* 2018, 42, 490–493.
 7. Li X., Wu B. L., Niu C. Y., Niu Y. Y., Zhang H. Y. Syntheses of metal-2-(pyridin-4-yl)-1*H*-imidazole-4,5-dicarboxylate networks with topological diversity: gas adsorption, thermal stability and fluorescent emission properties. *Cryst. Growth Des.* 2009, 9, 3423–3431.
 8. Liu Y. J., Cheng D., Li Y. X., Meng X. R., Yang H. X. A new two-dimensional manganese(II) coordination polymer constructed by 2,2'-(1,2-phenylene)bis(1*H*-imidazole-4,5-dicarboxylate). *Acta Crystallogr* 2018, C74, 599–603.
 9. Guo X. Y., Chen J. H., Meng X. R. Crystal structure of *catena*-poly[aqua[μ_2 -4,5-dicarboxylato-2-(2-carboxylatophenyl)imidazol-1-ido- $k^4N,O,O':N'$]] μ_2 -4,4'-bipyridine- $k^2N:N'$]dicopper(II)], $C_{22}H_{14}Cu_2N_4O_7$. *Z. Kristallogr. N. Cryst. Struct.* 2020, 235, 771–773.
 10. Wang W., Niu X., Gao Y., Zhu Y., Li G., Lu H., Tang M. One chiral and two achiral 3-D coordination polymers constructed by 2-phenyl imidazole dicarboxylate. *Cryst. Growth Des.* 2010, 10, 4050–4059.
 11. Xie W., Li R., Wang C. Q. Crystal structure of *catena*-poly[triqua-bis(μ_2 -2-(1*H*-tetrazol-1-methyl)-1*H*-imidazole-4,5-dicarboxylato) barium(II)] tetrahydrate, $C_{14}H_{14}BaN_{12}O_{15}$. *Z. Kristallogr. N. Cryst. Struct.* 2021, 236, 227–229.
 12. Li T., Xiu Y., Su X., Meng X. R. Syntheses, crystal structures, and fluorescent properties of two Cd(II) complexes based on 2,2'-(ethane-1,2-diyl)bis(1*H*-imidazole-4,5-dicarboxylic acid). *J. Coord. Chem.* 2012, 65, 3111–3121.
 13. Wang W. B., Shi X. C., Li Y. Y., Cheng F. R. Crystal structure of [aqua [2,2'-(1,2-phenylene)bis(1*H*-imidazole-4,5-dicarboxylato)- k^4N^3,N^3',O^4,O^4'] zinc(II)] monohydrate, $C_{16}H_{10}N_4O_9Zn \cdot H_2O$. *Z. Kristallogr. N. Cryst. Struct.* 2019, 234, 1133–1135.
 14. Liu Y. J., Cheng D., Li Y. X., Zhang J. D., Yang H. X. A new one-dimensional Cd^{II} coordination polymer incorporating 2,2'-(1,2-phenylene)bis(1*H*-imidazole-4,5-dicarboxylate). *Acta Crystallogr.* 2018, C74, 1128–1132.
 15. Huang Q. Y., Zhao Y., Meng X. R. Syntheses, structures and characterization of isomorphous Co^{II} and Ni^{II} coordination polymers based on 2-[(1*H*-imidazol-1-yl)methyl]-6-methyl-1*H*-benzimidazole and benzene-1,4-dicarboxylate. *Acta Crystallogr.* 2017, C73, 645–651.
 16. Li X. F., Yang Y. Q., Li Y. X., Yang H. X., Zhao W. F., Meng X. R. Synthesis, crystal structure, and BSA binding studies of new $Co(II)$ and $Ni(II)$ complexes of 2-(hydroxymethyl)-1*H*-imidazole-4,5-dicarboxylate. *Inorg. Chim. Acta* 2020, 505, 119469.
 17. Yang H. X., Liang Z., Hao B. L., Meng X. R. Syntheses, crystal structures, and characterization of three 1D, 2D and 3D complexes based on mixed multidentate N- and O-donor ligands. *J. Solid State Chem.* 2014, 218, 23–31.
 18. Cheng D., Zhang Y. P., Wang K., Meng X. R., Li X. F. Three-dimensional Zn(II) complex based on 2-[(1*H*-imidazol-1-yl)methyl]-6-methyl-1*H*-benzimidazole and aliphatic carboxylate. *J. Chem. Res.* 2018, 42, 575–578.
 19. Shao Z. C., Meng X. R., Hou H. W. Effect of pH on the construction of Cd^{II} coordination polymers involving the 1,1'-[1,4-phenylenebis-(methylene)]bis-(3,5-dicarboxylatopyridinium) ligand. *Acta Crystallogr.* 2019, C75, 1142–1149.