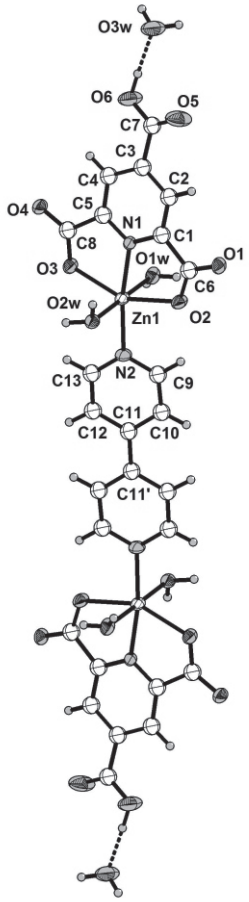
Crystal structure of tetraaquabis(4-carboxypyridine-2,6-dicarboxylato-κ^3N,O,O')(μ_2-4,4'-bipyridine-$\kappa^2N:N'$)dizinc(II)dihydrate, $[Zn_2(C_8H_3NO_6)_2(C_{10}H_8N_2)(H_2O)_4]\cdot 2H_2O$, $C_{26}H_{26}N_4O_{18}Zn_2$

Youngjin Jeon[*, I], Myunghan Lee[I], Hyunuk Kim[II] and Ki-Min Park[*, III]

[I] Department of Applied Chemistry, Konkuk University, 322 Danwol-dong, Chungju 380-701, Republic of Korea
[II] Energy Materials and Convergence Research Department, Korea Institute of Energy Research, Daejeon 305-343, Republic of Korea
[III] Research Institute of Natural Science, Gyeongsang National University, Jinju 660-701, Republic of Korea

Received December 16, 2014, accepted June 01, 2015, available online June 03, 2015, CCDC no. 1267/4320



Abstract

$C_{26}H_{26}N_4O_{18}Zn_2$, monoclinic, $P2_1/c$ (no. 14), a = 11.4727(7) Å, b = 20.281(1) Å, c = 7.0745(4) Å, β = 103.328(1)°, V = 1601.8 Å^3, Z = 2, $R_{gt}(F)$ = 0.0436, $wR_{ref}(F^2)$ = 0.1314, T = 203 K.

Source of material

Pyridine-2,4,6-tricarboxylic acid (H_3**L**) was synthesized by oxidation of 2,4,6-trimethylpyridine with potassium permanganate according to literature procedure [1]. The title compound was prepared by slow evaporation method. A mixture of zinc nitrate hexahydrate (45.6 mg, 0.153 mmol), pyridine-2,4,6-tricarboxylic acid (21.1 mg, 0.100 mmol), 4,4'-bipyridine (15.6 mg, 0.100 mmol) in water (6 mL) were placed in a vial. After heated to boiling point for 1 hr, the solution was naturally cooled to room temperature. After 1 day, slow evaporation of aqueous solution afforded colourless crystalline product of the title compound.

* Correspondence author
(e-mail: jeonyj@kku.ac.kr and kmpark@gnu.ac.kr)

Table 1. Data collection and handling.

Crystal:	colourless hexagonal plates, size 0.10×0.40×0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	15.86 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8601, 3140
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2959
$N(param)_{refined}$:	226
Programs:	SADABS, SMART, SHELX [8–10]

Experimental details

Hydrogen atoms attached to oxygen atoms of carboxylic acid group and water molecules located in difference electron density maps, and treated as riding atoms. The U_{iso} values of the hydrogen atoms of carboxylic acid group and water molecules were set to $1.5U_{eq}$(O) and the U_{iso} values of all other hydrogen atoms were set to $1.2U_{eq}$(C).

Discussion

For over two decades, metal-organic frameworks have attracted considerable attention because of their potential applications such as gas storage, catalysis, chiral resolution, etc [2–3]. Pyridine-2,4,6-tricarbolylic acid (H_3**L**) has been used as a versatile building block to construct various coordination polymers or metal-organic frameworks [4–6]. 4.4'-Bipyridine (4,4'-bpy) has also been used as a good bridging ligand to form a metal complexes and metal-organic frameworks [7]. Herein we report the crystal structure of the title compound prepared by the reaction of zinc nitrate with the H_3**L** and 4,4'-bpy ligands. The structure of the title compound is isostructural with that of the cobalt(II) complex preported by Bharadwaj *et al.* [4]. Slow evaporation of the aqueous solution with **L** and zinc nitrate in the presence of 4,4'-bpy coligand afforded colourless crystals of the title structure suitable for X-ray analysis. The crystallographic analysis reveals that the product is a discrete dinuclear complex of formula $[Zn_2(H\mathbf{L})_2(4,4'\text{-bpy})(H_2O)_4]\cdot 2H_2O$, in which two [Zn(H**L**)] units are bridged by 4,4'-bpy coligand. In the title structure each Zn atom is six-coordinated, being bound to the two monodentate carboxylate oxygen atoms and one nitrogen atom of H$\mathbf{L}^{2-}$ and one nitrogen atom of the 4,4'-bpy. The remaining sites are occupied by two oxygen atoms from two water molecules. The Zn–O (carboxylate) distances [Zn1–O2 2.259(2), Zn1–O3 2.158(2) Å]

are slightly longer than those of Zn–O(water) [Zn1–O1W 2.145(2), Zn1–O2W 2.129(2) Å], suggesting that the water molecules are bonded more strongly to the Zn centre. The coordination geometry of Zn(II) atom can best be described as a distorted octahedron, in which the equatorial plane consists of the O_2N_2 donors from H**L**$^{2-}$ and 4,4'-bpy and the apical positions are occupied by two oxygen atoms of water molecules [O1W–Zn1–O2W 179.32(8)°]. The pyridine ring of H**L**$^{2-}$ ligand in the complex is tilted by 21.92(14)° with respect to the mean plane of the 4,4'-bpy coligand. In the H**L**$^{2-}$ ligand, the uncoordinated carboxylic acid moiety interacts with lattice water molecule (O6···O3W 2.544(4) Å). Furthermore, the carboxylate oxygen atoms are hydrogen-bonded with the coordinated water molecules as well as the lattice water molecules, resulting in the formation of a three-dimensional supramolecular network.

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(6)	4*e*	–0.0429	0.7370	0.2243	0.082
H(2)	4*e*	0.3274	0.7976	0.2177	0.026
H(4)	4*e*	0.1748	0.6230	0.3004	0.027
H(9)	4*e*	0.7742	0.6414	–0.0090	0.036
H(10)	4*e*	0.9453	0.6043	–0.0899	0.036
H(12)	4*e*	0.9060	0.4327	0.1735	0.047
H(13)	4*e*	0.7375	0.4749	0.2500	0.045
H(1WA)	4*e*	0.5049	0.5612	–0.1628	0.039
H(1WB)	4*e*	0.5041	0.6273	–0.1603	0.039
H(2WA)	4*e*	0.6761	0.5690	0.5455	0.036
H(2WB)	4*e*	0.6421	0.6330	0.5489	0.036
H(3WA)	4*e*	–0.2332	0.7590	0.1727	0.083
H(3WB)	4*e*	–0.1753	0.8131	0.1119	0.083

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn(1)	4*e*	0.58664(3)	0.60093(2)	0.19429(5)	0.0206(2)	0.0179(2)	0.0313(3)	0.0030(1)	0.0137(2)	–0.0007(1)
O(1)	4*e*	0.5486(2)	0.8093(1)	0.1659(3)	0.030(1)	0.016(1)	0.033(1)	–0.0007(9)	0.012(1)	0.0005(9)
O(2)	4*e*	0.6261(2)	0.7085(1)	0.1547(3)	0.023(1)	0.020(1)	0.038(1)	–0.0004(9)	0.015(1)	–0.0016(9)
O(3)	4*e*	0.4712(2)	0.5245(1)	0.2599(3)	0.027(1)	0.017(1)	0.034(1)	0.0009(9)	0.015(1)	0.0003(9)
O(4)	4*e*	0.2960(2)	0.5093(1)	0.3460(4)	0.025(1)	0.020(1)	0.045(1)	–0.0006(9)	0.015(1)	0.005(1)
O(5)	4*e*	0.1166(2)	0.8128(1)	0.2595(6)	0.030(1)	0.030(2)	0.112(3)	0.007(1)	0.018(2)	–0.008(2)
O(6)	4*e*	0.0259(2)	0.7155(1)	0.2421(5)	0.025(1)	0.035(2)	0.109(3)	0.002(1)	0.025(2)	–0.002(2)
N(1)	4*e*	0.4393(2)	0.6520(1)	0.2373(3)	0.020(1)	0.015(1)	0.022(1)	0.0009(9)	0.009(1)	–0.0003(9)
N(2)	4*e*	0.7395(2)	0.5623(1)	0.1303(4)	0.021(1)	0.025(1)	0.037(2)	0.006(1)	0.014(1)	–0.000(1)
C(1)	4*e*	0.4331(3)	0.7170(1)	0.2174(4)	0.022(2)	0.020(2)	0.017(1)	0.001(1)	0.006(1)	–0.002(1)
C(2)	4*e*	0.3304(3)	0.7514(2)	0.2282(4)	0.024(2)	0.018(1)	0.022(2)	0.004(1)	0.004(1)	–0.001(1)
C(3)	4*e*	0.2324(3)	0.7159(2)	0.2547(4)	0.021(2)	0.023(2)	0.023(2)	0.002(1)	0.004(1)	–0.003(1)
C(4)	4*e*	0.2401(3)	0.6476(2)	0.2792(5)	0.019(2)	0.022(2)	0.030(2)	–0.002(1)	0.011(1)	–0.002(1)
C(5)	4*e*	0.3475(3)	0.6173(2)	0.2711(4)	0.023(2)	0.020(2)	0.023(2)	–0.001(1)	0.007(1)	–0.001(1)
C(6)	4*e*	0.5449(3)	0.7480(2)	0.1774(4)	0.022(2)	0.019(2)	0.020(1)	–0.001(1)	0.007(1)	0.000(1)
C(7)	4*e*	0.1188(3)	0.7533(2)	0.2537(5)	0.021(2)	0.029(2)	0.040(2)	0.003(1)	0.008(1)	–0.006(1)
C(8)	4*e*	0.3727(3)	0.5438(2)	0.2953(4)	0.028(2)	0.016(2)	0.025(2)	–0.001(1)	0.008(1)	0.001(1)
C(9)	4*e*	0.8017(3)	0.5987(2)	0.0292(6)	0.029(2)	0.022(2)	0.043(2)	0.006(1)	0.017(2)	0.004(1)
C(10)	4*e*	0.9039(3)	0.5765(2)	–0.0214(5)	0.031(2)	0.025(2)	0.040(2)	0.002(1)	0.021(2)	0.003(1)
C(11)	4*e*	0.9459(3)	0.5132(2)	0.0284(5)	0.020(2)	0.024(2)	0.031(2)	0.002(1)	0.011(1)	–0.004(1)
C(12)	4*e*	0.8809(3)	0.4757(2)	0.1339(6)	0.038(2)	0.029(2)	0.059(2)	0.014(2)	0.029(2)	0.014(2)
C(13)	4*e*	0.7800(3)	0.5014(2)	0.1800(6)	0.037(2)	0.032(2)	0.054(2)	0.008(2)	0.030(2)	0.013(2)
O(1W)	4*e*	0.4941(2)	0.5934(1)	–0.1052(3)	0.034(1)	0.018(1)	0.031(1)	0.0001(9)	0.015(1)	–0.0010(9)
O(2W)	4*e*	0.6798(2)	0.6093(1)	0.4907(3)	0.024(1)	0.020(1)	0.032(1)	0.0031(8)	0.013(1)	0.0013(9)
O(3W)	4*e*	–0.1677(2)	0.7810(1)	0.1968(5)	0.024(1)	0.039(2)	0.104(3)	0.001(1)	0.018(2)	0.002(2)

Acknowledgments. This work was supported by Konkuk University in 2012.

References

1. Syper, L.; Kloc, K.; Mochowski, J.: Synthesis of ubiquinone and menaquinone analogues by oxidative demethylation of alkenylhydroquinone ethers with argentic oxide or ceric ammonium nitrate. Tetrahedron **36** (1980) 123–129.
2. Zhou, H.-C.; Kitagawa, S.: Metal-Organic Framework (MOFs). Chem. Soc. Rev. **43** (2014) 5415–5418.
3. Zhou, H.-C.; Long, J. R.; Yaghi, O. M.: Introduction to Metal-Organic Frameworks. Chem. Rev. **112** (2012) 673–674.
4. Ghosh, S. K.; Bharadwaj, P. K.: Self-assembly of a Co(II) dimer through H-bonding of water molecules to a 3D open-framework structure. J. Chem. Sci. **117** (2005) 23–26.
5. Ghosh, S. K.; Savitha, G.; Bharadwaj, P. K.: Reactivity of Pyridine-2,4,6-tricarboxylic acid toward Zn(II) Salts under Different Reaction Conditions. Inorg. Chem. **43** (2004) 5495–5497.
6. Fu, D.-W.; Xu, H.-J.: *catena*-Poly[[diaquamanganese(II)]-μ-pyridine-2,4,6-tricarboxylato-k^5*N*,*O*^{2},*O*^{6}:*O*^{4},*O*^{4}]. Acta Crystallogr. **E64** (2008) m35.
7. Irwin, M.; Krämer, T.; McGrady, J. E.; Goicoechea, J. M.: On the structural and Electronic Properties of $[Zn_2(4,4'\text{-bipyridine})(mes)_4]^{n-}$ (n = 0–2), a Homologous Series of Bimetallic Complexes Bridged by Neutral, Anionic, and Dianionic 4,4'-Bipyridine. Inorg. Chem. **50** (2011) 5006–5014.
8. Bruker (1999). SADABS, Empirical absorption and correction software, Version 2.03. Bruker AXS Inc., Madison, Wisconsin, USA.
9. Bruker (2000). SMART (Version 5.625) and SAINT-plus (Version. 6.22), Area Detector Control and Integration Software, Bruker AXS Inc., Madison, Wisconsin, USA.
10. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.