# Crystal structure of bis[(hydrogen 5-methylisophthalato)-(2,5-bis(4-pyridyl)-1,3,4-thiadiazole)]zinc(II) dihydrate, $Zn(C_9H_7O_4)_2(C_{12}H_8N_4S)_2 \cdot 2H_2O$

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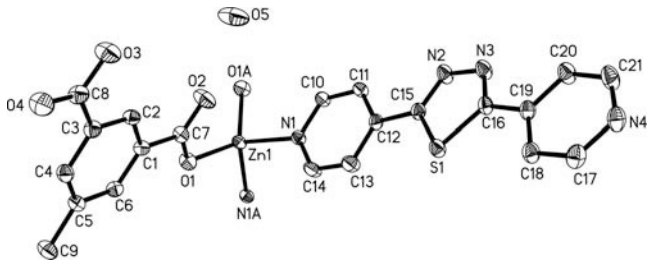


**Abstract**

$C_{42}H_{34}N_8O_{10}S_2Zn$, monoclinic, *C*12/*c*1 (no. 15), $a = 35.004(4)$ Å, $b = 8.1439(9)$ Å, $c = 15.779(2)$ Å, $\beta = 112.011(1)°$, $V = 4170.2$ Å$^3$, $Z = 4$, $R_{gt}(F) = 0.033$, $wR_{ref}(F^2) = 0.086$, $T = 296$ K.

**Source of material**

Direct mixing of the starting materials in solution leads to immediate fine precipitate formation. In order to obtain crystals, suitable for X-ray diffraction analysis, the hydrothermal methods were applied. A mixture of 5-methylisophthalic acid ($CH_3H_2ip$, 0.1 mmol), 2,5-bis(4-pyridyl)-1,3,4-thiadiazole (bpt, 0.1 mmol), $Zn(OAc)_2 \cdot 4H_2O$ (0.1 mmol), KOH (0.10 mmol) and $H_2O$ (15 mL) was placed in a Teflon-lined stainless steel vessel, heated to 140 °C for 4 days, and then cooled to room temperature over 24 h. Colorless block-shaped crystals of the title compound were obtained.

**Discussion**

The rational design and assembly of inorganic coordination polymers or metal-organic frameworks have received remarkable attention and have been developed rapidly in recent years. Being easily and efficiently synthesized from relatively simple subunits, these complexes exhibit fascinating structural topologies and potential applications as functional materials [1-8]. To build these molecular architectures, researchers often employ bridging poly-carboxylate and bipyridyl ligands to construct coordination polymers because of their versatile coordination modes and high structural stability. Exo-bidentate rod-like *N*,*N*′-donor ligands, such as 4,4-bipyridine, can have significant influence on the assembly systems of multicarboxylate ligands and metal centers. Its derivatives dpe (1,2-bi(4-pyridyl)ethene), bpa (1,2-bi(4-pyridyl) ethane) and bpp (1,3-di(4-pyridyl)propane) with certain spacers between the two 4-pyridyl rings may also lead to fascinating architectures with interesting properties. Unlike the more commonly used 4,4-bipyridine-like ligands, 2,5-bis(4-pyridyl)-1,3,4-thiadiazole possesses an angular disposition of its terminal pyridyl spacers. Its central thiadiazole ring and two more potential N-donor atoms inducing flexible coordination modes, which favours the construction of unexpected, unpredictable and interesting frameworks.

The asymmetric unit contains one Zn(II) cation, two bpt ligands, two $CH_3Hip$ anions and two lattice water molecules. The $Zn^{II}$ ion is four-coordinated with a distorted tetrahedral environment, provided by two pyridyl N atoms from two different bpt molecules, two carboxylate O atoms from two $CH_3Hip$ molecules. The Zn—N bond length is 2.046(2) Å and the Zn—O distances is 1.950(2) Å. 5-Methylisophthalate acts as a monodentate ligand in an mono-anion mode. 2,5-Bis(4-pyridyl)-1,3,4-thiadiazole acts as a mono-dentate ligand. Several kinds of hydrogen bonding are observed in the crystal structure: (a) hydrogen bonding between water oxygen atoms and uncoordinated oxygen atoms of carboxylate group O5–H1W···O2 with the bond distance of 3.082(3) Å and bond angle of 135.6°; (b) hydrogen bonding between water oxygen atoms and coordinated oxygen atoms of carboxylate unit (O5–H2W···O1, 2.784(3) Å, 163.3°); (c) hydrogen bonding between uncoordinated oxygen atoms of carboxylate group and uncoordinated nitrogen atoms of pyridyl group (O3–H3···N4, 2.677(2) Å, 174.2°). These weak hydrogen bonds form a 2D supramolecular network.

**Table 1.** Data collection and handling.

| | |
|---|---|
| Crystal: | colorless block, size 0.09 × 0.22 × 0.32 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 7.59 cm$^{-1}$ |
| Diffractometer, scan mode: | Bruker SMART CCD, $\varphi/\omega$ |
| $2\theta_{max}$: | 51° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 15358, 3880 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\,\sigma(I_{obs})$, 3150 |
| $N(param)_{refined}$: | 287 |
| Programs: | SHELXS-97 [9], SHELXL-97 [10], SHELXTL [11] |

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

| Atom | Site | *x* | *y* | *z* | $U_{iso}$ |
|---|---|---|---|---|---|
| H(3) | 8*f* | 0.2913 | 0.0916 | 0.5140 | 0.089 |
| H(2) | 8*f* | 0.3708 | 0.3120 | 0.6254 | 0.040 |
| H(4) | 8*f* | 0.3143 | 0.2166 | 0.7982 | 0.045 |
| H(6) | 8*f* | 0.4183 | 0.4799 | 0.8832 | 0.040 |
| H(9A) | 8*f* | 0.3423 | 0.4537 | 0.9447 | 0.078 |
| H(9B) | 8*f* | 0.3886 | 0.4027 | 0.9929 | 0.078 |
| H(9C) | 8*f* | 0.3540 | 0.2684 | 0.9662 | 0.078 |

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**Table 2.** Continued.

| Atom | Site | *x* | *y* | *z* | $U_{iso}$ |
|---|---|---|---|---|---|
| H(10) | 8*f* | 0.5013 | 0.7503 | 0.5668 | 0.040 |
| H(11) | 8*f* | 0.4628 | 0.8815 | 0.4340 | 0.039 |
| H(13) | 8*f* | 0.3960 | 1.0822 | 0.5647 | 0.056 |
| H(14) | 8*f* | 0.4363 | 0.9456 | 0.6941 | 0.053 |
| H(17) | 8*f* | 0.2309 | 1.5034 | 0.1799 | 0.055 |

**Table 2.** Continued.

| Atom | Site | *x* | *y* | *z* | $U_{iso}$ |
|---|---|---|---|---|---|
| H(18) | 8*f* | 0.2821 | 1.3556 | 0.2875 | 0.049 |
| H(20) | 8*f* | 0.3318 | 1.2794 | 0.0998 | 0.056 |
| H(21) | 8*f* | 0.2786 | 1.4264 | –0.0024 | 0.062 |
| H(1W) | 8*f* | 0.4620 | 0.3877 | 0.5743 | 0.149 |
| H(2W) | 8*f* | 0.5016 | 0.3897 | 0.5784 | 0.149 |

**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* | ½ | 0.67678(4) | ¾ | 0.0263(2) | 0.0367(2) | 0.0210(2) | 0 | 0.0056(1) | 0 |
| S(1) | 8*f* | 0.35354(2) | 1.17790(8) | 0.38426(4) | 0.0353(3) | 0.0474(4) | 0.0337(3) | 0.0128(3) | 0.0135(3) | 0.0110(3) |
| O(1) | 8*f* | 0.46129(5) | 0.5670(2) | 0.7935(1) | 0.0324(8) | 0.050(1) | 0.0343(9) | –0.0118(7) | 0.0079(7) | –0.0039(7) |
| O(2) | 8*f* | 0.43408(6) | 0.4767(3) | 0.6520(1) | 0.056(1) | 0.086(1) | 0.042(1) | –0.025(1) | 0.0274(9) | –0.015(1) |
| O(3) | 8*f* | 0.31009(6) | 0.1450(3) | 0.5509(1) | 0.048(1) | 0.084(2) | 0.044(1) | –0.032(1) | 0.0151(9) | –0.027(1) |
| O(4) | 8*f* | 0.27611(6) | 0.0897(3) | 0.6421(1) | 0.049(1) | 0.076(1) | 0.063(1) | –0.032(1) | 0.024(1) | –0.022(1) |
| N(1) | 8*f* | 0.47180(5) | 0.8317(2) | 0.6426(1) | 0.0296(9) | 0.036(1) | 0.0255(9) | 0.0028(8) | 0.0088(8) | 0.0022(8) |
| N(2) | 8*f* | 0.40711(6) | 1.0723(3) | 0.3242(1) | 0.037(1) | 0.056(1) | 0.034(1) | 0.016(1) | 0.0119(9) | 0.015(1) |
| N(3) | 8*f* | 0.37769(6) | 1.1499(3) | 0.2517(1) | 0.038(1) | 0.056(1) | 0.033(1) | 0.0150(9) | 0.0114(9) | 0.0144(9) |
| N(4) | 8*f* | 0.24957(6) | 1.4792(3) | 0.0787(1) | 0.034(1) | 0.052(1) | 0.045(1) | 0.0070(9) | 0.0067(9) | 0.015(1) |
| C(1) | 8*f* | 0.40021(6) | 0.4080(3) | 0.7517(1) | 0.025(1) | 0.034(1) | 0.029(1) | –0.0003(9) | 0.0075(9) | –0.0031(9) |
| C(2) | 8*f* | 0.36971(6) | 0.3210(3) | 0.6831(2) | 0.032(1) | 0.037(1) | 0.031(1) | –0.002(1) | 0.0112(9) | –0.006(1) |
| C(3) | 8*f* | 0.33771(6) | 0.2480(3) | 0.7009(2) | 0.031(1) | 0.035(1) | 0.035(1) | –0.005(1) | 0.010(1) | –0.005(1) |
| C(4) | 8*f* | 0.33596(7) | 0.2648(3) | 0.7867(2) | 0.034(1) | 0.041(1) | 0.042(1) | –0.005(1) | 0.018(1) | –0.000(1) |
| C(5) | 8*f* | 0.36565(7) | 0.3517(3) | 0.8560(2) | 0.035(1) | 0.041(1) | 0.031(1) | 0.001(1) | 0.014(1) | 0.000(1) |
| C(6) | 8*f* | 0.39791(6) | 0.4222(3) | 0.8374(1) | 0.029(1) | 0.036(1) | 0.029(1) | –0.0005(9) | 0.0049(9) | –0.004(1) |
| C(7) | 8*f* | 0.43393(6) | 0.4874(3) | 0.7296(2) | 0.029(1) | 0.039(1) | 0.032(1) | –0.001(1) | 0.011(1) | –0.000(1) |
| C(8) | 8*f* | 0.30461(7) | 0.1536(3) | 0.6289(2) | 0.035(1) | 0.046(1) | 0.046(2) | –0.009(1) | 0.013(1) | –0.011(1) |
| C(9) | 8*f* | 0.36233(8) | 0.3709(3) | 0.9484(2) | 0.058(2) | 0.066(2) | 0.038(1) | –0.005(1) | 0.025(1) | –0.003(1) |
| C(10) | 8*f* | 0.47951(7) | 0.8169(3) | 0.5658(1) | 0.031(1) | 0.041(1) | 0.030(1) | 0.007(1) | 0.0120(9) | 0.004(1) |
| C(11) | 8*f* | 0.45672(6) | 0.8957(3) | 0.4860(1) | 0.031(1) | 0.041(1) | 0.026(1) | 0.004(1) | 0.0114(9) | 0.002(1) |
| C(12) | 8*f* | 0.42456(6) | 0.9966(3) | 0.4838(1) | 0.029(1) | 0.031(1) | 0.030(1) | 0.0035(9) | 0.0089(9) | 0.0054(9) |
| C(13) | 8*f* | 0.41715(8) | 1.0145(3) | 0.5634(2) | 0.048(1) | 0.055(2) | 0.038(1) | 0.025(1) | 0.019(1) | 0.009(1) |
| C(14) | 8*f* | 0.44138(7) | 0.9315(3) | 0.6407(2) | 0.049(1) | 0.057(2) | 0.030(1) | 0.015(1) | 0.020(1) | 0.004(1) |
| C(15) | 8*f* | 0.39874(6) | 1.0762(3) | 0.3977(2) | 0.032(1) | 0.034(1) | 0.034(1) | 0.0050(9) | 0.012(1) | 0.007(1) |
| C(16) | 8*f* | 0.34797(7) | 1.2105(3) | 0.2724(2) | 0.031(1) | 0.037(1) | 0.032(1) | 0.004(1) | 0.010(1) | 0.009(1) |
| C(17) | 8*f* | 0.25144(7) | 1.4571(3) | 0.1637(2) | 0.029(1) | 0.049(2) | 0.059(2) | 0.009(1) | 0.015(1) | 0.012(1) |
| C(18) | 8*f* | 0.28228(7) | 1.3693(3) | 0.2291(2) | 0.035(1) | 0.047(1) | 0.040(1) | 0.005(1) | 0.013(1) | 0.010(1) |
| C(19) | 8*f* | 0.31335(7) | 1.3021(3) | 0.2061(2) | 0.030(1) | 0.036(1) | 0.035(1) | 0.002(1) | 0.008(1) | 0.008(1) |
| C(20) | 8*f* | 0.31160(8) | 1.3239(3) | 0.1178(2) | 0.039(1) | 0.060(2) | 0.041(1) | 0.016(1) | 0.016(1) | 0.014(1) |
| C(21) | 8*f* | 0.27947(8) | 1.4125(3) | 0.0568(2) | 0.045(2) | 0.068(2) | 0.039(1) | 0.013(1) | 0.011(1) | 0.019(1) |
| O(5) | 8*f* | 0.47696(8) | 0.3773(3) | 0.5436(2) | 0.100(2) | 0.130(2) | 0.088(2) | –0.007(2) | 0.057(2) | –0.042(2) |

## References


1. Du, M.; Li, C. P.; You, Y. P.; Jiang, X. J.; Cai, H.; Wang, Q.; Guo, J. H.: New supramolecular complexes generated from $Mn^{II}$, $Fe^{II}$, $Co^{II}$, $Zn^{II}$, $Fe^{III}$ with a bent dipyridyl ligand: Metal- and anion-directed assembly. Inorg. Chim. Acta **360** (2007) 2169-2174.
2. Cai, J. W.; Chen, C. H.; Feng, X. L.; Liao, C. Z.; Chen, X. M.: A novel supramolecular synthon for H-bonded coordination networks: syntheses and structures of extended two-dimensional cadmium(II) arenedisulfonates. J. Chem. Soc. Dalton (2001) 2370-2375.
3. Du, M.; Zou, R. Q.; Zhong, R. Q.; Xu, Q.: Metal-regulated assemblies of $Cu^{II}$, $Ni^{II}$, and $Zn^{II}$ complexes with isoquinoline-3-carboxylate displaying diverse supramolecular networks. Inorg. Chim. Acta **360** (2007) 3442-3447.
4. Liu, C. S.; Shi, X. S.; Li, J, R.; Wang, J. J.; Bu, X, H.: Cd(II) coordination architectures with mixed ligands of 3-(2-pyridyl)pyrazole and pendant carboxylate ligands bearing different aromatic skeletons: syntheses, crystal structures, and emission properties. Cryst. Growth Des. **6** (2006) 656-663.
5. Shi, Q.; Cao, R.; Sun, D. F.; Hong, M. C.; Liang, Y. C.: Solvothermal syntheses and crystal structures of two metal coordination polymers with double-chain structures. Polyhedron **20** (2001) 3287-3293.
6. Shi, X.; Zhu, G. S.; Fang, Q. R.; Wu, G.; Tian, G.; Wang, R. W.; Zhang, D.: Novel Supramolecular Frameworks Self-Assembled from One-Dimensional Polymeric Coordination Chains. Eur. J. Inorg. Chem. (2004) 185-191.
7. Cao, R.; Sun, D. F.; Liang, Y. C.; Hong, M. C.; Tatsumi, K.; Shi, Q.: Syntheses and Characterizations of Three-Dimensional Channel-like Polymeric Lanthanide Complexes Constructed by 1,2,4,5-Benzenetetracarboxylic Acid. Inorg. Chem. **41** (2002) 2087-2094.
8. Luo, F.; Hu, D. X.; Che, Y. X.; Zheng, J. M.: Pillared 3d-4f Frameworks with Rare 3D Architecture Showing the Coexistence of Ferromagnetic and Antiferromagnetic Interactions between Gadolinium Ions. Cryst. Growth Des. **7** (2007) 851 -853.
9. Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
10. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.
11. Sheldrick, G. M.: SHELXTL. Structure Determination Software Suite. Version 6.14. Bruker AXS, Madison, Wisconsin, USA 2000.