# Crystal structure of bis($\mu_3$-hydroxy)bis(isonicotinato-$\kappa O$:$O'$)(oxalato)-biscadmium(II)zinc(II), $Cd_2Zn(C_2O_4)(OH)_2(C_6NO_2H_4)_2$

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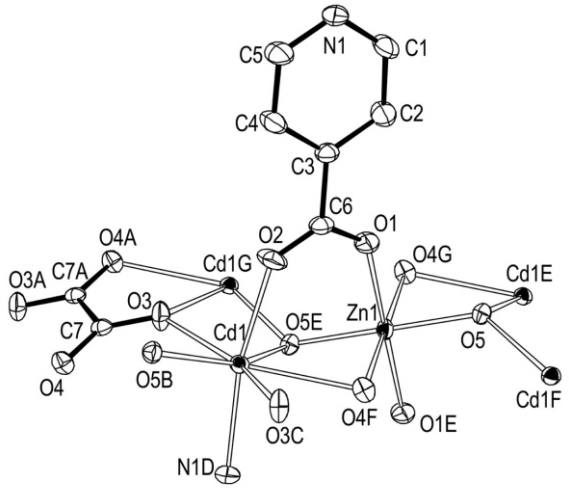


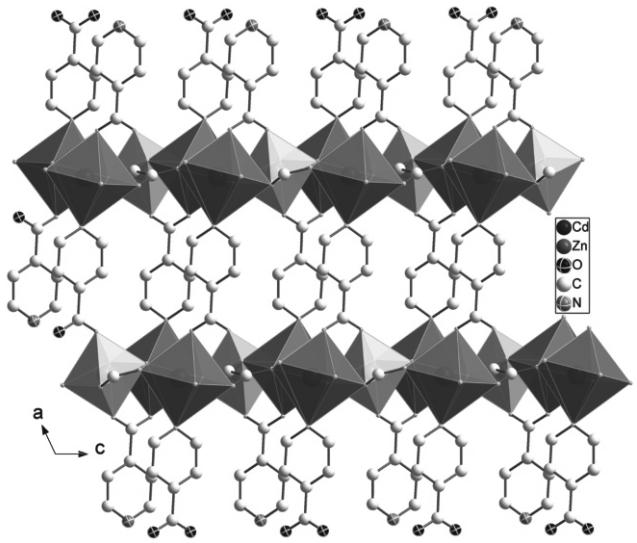


**Abstract**

$C_{14}H_{10}Cd_2N_2O_{10}Zn$, monoclinic, $P2_1/n$ (no. 14), $a$ = 10.292(5) Å, $b$ = 7.417(3) Å, $c$ = 12.303(5) Å, $\beta$ = 114.664(1)°, $V$ = 853.5 Å$^3$, $Z$ = 2, $R_{gt(F)}$ = 0.021, $wR_{ref(F^2)}$ = 0.053, $T$ = 293 K.

**Source of material**

In a typical synthesis, $Cd(NO_3)_2 \cdot 4H_2O$ (0.8 mmol, 247 mg), $Zn(ClO_4)_2 \cdot 6H_2O$ (0.4 mmol, 149 mg), isonicotinic acid (0.8 mmol, 98 mg), $Na_2C_2O_4$ (0.4 mmol, 54 mg), 3 mL ethanol, 6 mL water, and 4 drops of triethylamine were placed in a 25 mL Teflon-lined steel autoclave under autogenous pressure. The steel autoclave was placed in a programmable furnace and heated to 170 °C at a rate of 12.5 °C/h and kept there for 4 days, then cooled to 30 °C at a rate of 3.1 °C/h and the power was turned off. Brown block-shaped crystals were isolated manually and then washed with water, ethanol, ether and acetone. The crystals are stable in air (yield 52 % based on Cd). Elemental analysis — found: C, 25.25 %; H, 1.57 %; N, 4.32 %; calculated for $C_{14}H_{10}Cd_2N_2O_{10}Zn$: C, 25.62 %; H, 1.54 %; N, 4.27 %.

**Experimental details**

Except for the hydroxyl groups, which were yielded by difference Fourier maps, all hydrogen atoms were allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic displacement parameters.

**Discussion**

Recently, the design and construction of heterometallic complexes catch more and more attention due to their intriguing topologies and potential applications in, e.g., magnetism, gas storage, luminescent materials [1-5]. As known, the selection of metal centers and organic linkers is an extraordinary vital step in the construction of metal-organic frameworks (MOFs). Investigators have projected and constructed plenty of architectures by selecting ligands, metal centers and controlling formation of coordination bonds. Numerous examples of 1D, 2D and 3D structures have been rationally designed via various functional ligands. Isonicotinic acid (HIsn), a multi-functional chelating and/or bridging ligand, has shown its advantages in the construction of multi-dimensional MOFs, especially when auxiliary ligands participate in the building. In addition, the potential applications of isonicotinic acid complexes used in fluorescence probing have attracted a considerable amount of interest from researchers.

The symmetry independent unit of the title crystal structure contains one Isn ligand, half an ox ligand, a cadmium ion, half a zinc ion and a $\mu_3$-bridged hydroxyl group. The Zn2 atom has a slightly distorted octahedral environment, consisting of two O1 atoms from two In ligands, two O4 atoms from two different ox ligands and two O5 atoms from two $\mu_3$-bridged hydroxyl groups (figure, top). However, the arrangement of the ligand atoms around Cd1 leads to the formation of a pseudo-pentagonal bipyramid, consisting of two oxygen atoms (O3, O4) from one cheated ox ligand, one O3 atom from an ox ligand , two O5 atoms from two $\mu_3$-bridged hydroxyl groups, one N1 and one O2 atom from two different Isn ligands (figure, top). The Cd—O bond distances are in

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the range 2.259(2)-2.522(2) Å, the Zn—O bond distances vary from 2.019(2) to 2.172(2) Å, and *d*(Cd1—N1) = 2.323(2) Å, comparable with those found in the literature [6-7]. The ligand adopts the exo-tridentate bridging fashion (with a coordinating pyridyl group and a $\mu_2$, $\eta^2$-carboxylato bridge), affording a three-connecting mode. In the title crystal structure, all of the oxalate ligands exhibit only one coordination fashion, namely the bridging/bischelating fashion. The oxalate group acts as a bischelating ligand to connect two separated Cd1 centers (Cd—Cd separation: 6.313(2) Å).

Further, the four oxygen atoms of the oxalate ligand bridge two different Cd centers and two different Zn centers, respectively. This kind of coordination fashion of the ox ligand has been rarely found in the structures of the transitional metal complexes. In addition, two different Cd centers and one Zn center are linked together by a $\mu_3$-bridged hydroxyl group. As a result, the Cd1 and Zn2 centers are interconnected through $\mu_3$-In ligands, $\mu_3$-bridged hydroxyl groups, and bridging/bischelating ox ligands to generate a 3D architecture.

The detailed title crystal structure can be described stepwise. The $\mu_3$-bridged hydroxyl groups link Cd1 atoms to form a kind of [–Cd1–OH–Cd1–OH–Cd1–] zigzag chains extending along the *b* axis. The ox ligands join Zn2 atoms together through the N2 and N5 atoms to form the other kind of [–Zn1–ox–Zn1–ox–Zn1–] zigzag chains along (010). The two kinds of zigzag chains arrange in parallel in an interlaced way along a direction, joined together by Cd1—O3, Cd1—O4 and Zn2—O5 bonds to a layer. The layers are further interlinked through interlamellar In ligands into the 3D structure.

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

| | |
|---|---|
| Crystal: | brown block, size 0.10 × 0.20 × 0.40 mm |
| Wavelength: | Mo $K_\alpha$ radiation (0.71073 Å) |
| $\mu$: | 39.25 $cm^{-1}$ |
| Diffractometer, scan mode: | Rigaku Mercury CCD, $\omega$ |
| $2\theta_{max}$: | 54.96° |
| $N(hkl)_{measured}$, $N(hkl)_{unique}$: | 6432, 1926 |
| Criterion for $I_{obs}$, $N(hkl)_{gt}$: | $I_{obs} > 2\ \sigma(I_{obs})$, 1831 |
| $N(param)_{refined}$: | 136 |
| Program: | SHELXTL [8] |

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

| Atom | Site | *x* | *y* | *z* | $U_{iso}$ |
|---|---|---|---|---|---|
| H(5B) | 4*e* | 0.698(2) | 0.506(5) | 0.738(2) | 0.026 |
| H(1A) | 4*e* | 0.0915 | 0.4422 | 0.7955 | 0.044 |
| H(2A) | 4*e* | 0.2479 | 0.4558 | 0.7065 | 0.042 |
| H(4A) | 4*e* | –0.0348 | 0.1746 | 0.4318 | 0.037 |
| H(5A) | 4*e* | –0.1826 | 0.1690 | 0.5288 | 0.040 |

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

| Atom | Site | *x* | *y* | *z* | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| Cd(1) | 4*e* | 0.29487(2) | 0.21896(3) | 0.27323(2) | 0.0154(1) | 0.0162(1) | 0.0147(1) | –0.00085(6) | 0.00729(8) | –0.00069(6) |
| Zn(1) | 2*a* | ½ | ½ | ½ | 0.0144(2) | 0.0178(2) | 0.0131(2) | –0.0035(2) | 0.0037(2) | –0.0009(2) |
| O(1) | 4*e* | 0.3298(2) | 0.4267(3) | 0.5440(2) | 0.023(1) | 0.042(1) | 0.027(1) | –0.0105(9) | 0.0162(9) | –0.0069(9) |
| O(2) | 4*e* | 0.1904(3) | 0.2324(3) | 0.4040(2) | 0.034(1) | 0.043(1) | 0.033(1) | –0.014(1) | 0.026(1) | –0.015(1) |
| O(3) | 4*e* | 0.1177(2) | 0.4196(3) | 0.1387(2) | 0.028(1) | 0.022(1) | 0.0182(9) | 0.0038(8) | –0.0019(8) | –0.0004(8) |
| O(4) | 4*e* | 0.0233(2) | 0.2809(2) | –0.0381(2) | 0.025(1) | 0.0138(9) | 0.0190(9) | 0.0010(7) | 0.0079(8) | –0.0006(7) |
| O(5) | 4*e* | 0.6243(2) | 0.4889(2) | 0.6769(2) | 0.0143(9) | 0.0193(9) | 0.0150(9) | –0.0005(7) | 0.0028(7) | 0.0008(7) |
| N(1) | 4*e* | –0.0597(3) | 0.3034(3) | 0.6717(2) | 0.022(1) | 0.031(1) | 0.025(1) | –0.002(1) | 0.016(1) | 0.002(1) |
| C(1) | 4*e* | 0.0663(3) | 0.3870(5) | 0.7216(3) | 0.032(2) | 0.061(2) | 0.026(2) | –0.015(2) | 0.020(1) | –0.014(2) |
| C(2) | 4*e* | 0.1612(3) | 0.3957(5) | 0.6688(3) | 0.025(2) | 0.059(2) | 0.028(2) | –0.016(2) | 0.016(1) | –0.010(2) |
| C(3) | 4*e* | 0.1253(3) | 0.3139(4) | 0.5592(2) | 0.018(1) | 0.025(1) | 0.022(1) | –0.001(1) | 0.013(1) | 0.001(1) |
| C(4) | 4*e* | –0.0063(4) | 0.2292(4) | 0.5063(3) | 0.032(2) | 0.040(2) | 0.029(2) | –0.014(1) | 0.021(1) | –0.016(1) |
| C(5) | 4*e* | –0.0946(4) | 0.2268(5) | 0.5651(3) | 0.025(2) | 0.046(2) | 0.035(2) | –0.016(1) | 0.020(1) | –0.015(1) |
| C(6) | 4*e* | 0.2239(3) | 0.3252(4) | 0.4961(2) | 0.019(1) | 0.025(1) | 0.022(1) | –0.001(1) | 0.014(1) | 0.001(1) |
| C(7) | 4*e* | 0.0398(3) | 0.4131(3) | 0.0286(2) | 0.015(1) | 0.016(1) | 0.021(1) | –0.001(1) | 0.010(1) | –0.001(1) |

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