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Crystal structure of tetraaqua-bis(1*H*-indazole-6-carboxylate- κN)cadmium (II), $C_{16}H_{18}CdN_4O_8$

<https://doi.org/10.1515/ncrs-2020-0581>

Received November 5, 2020; accepted November 29, 2020;

published online December 14, 2020

Abstract

$C_{16}H_{18}CdN_4O_8$, monoclinic, $P2_1/c$ (no. 14), $a = 6.2751(4)$ Å, $b = 21.7902(13)$ Å, $c = 13.3401(8)$ Å, $\beta = 90.793(1)^\circ$, $V = 1823.89(19)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0252$, $wR_{ref}(F^2) = 0.0603$, $T = 296(2)$ K.

CCDC no.: 2047037

The molecular structure 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 title compound was synthesized by a hydrothermal method under autogenous pressure. A mixture of $CdCl_2 \cdot H_2O$

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	$0.16 \times 0.14 \times 0.12$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	1.25 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	25.5° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13,899, 3398, 0.021
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3074
$N(\text{param})_{\text{refined}}$:	303
Programs:	Bruker [1], SHELX [2, 3], Diamond [4]

(0.029 g, 0.1 mmol), 1*H*-indazole-5-carboxylic acid (HIA) (0.0324 g, 0.2 mmol), NaOH (0.2 mL, 0.1 mol/L) and distilled water (15 mL) was sealed in a teflon-lined stainless reactor (25 mL) and heated at 120 °C for 72 h, and then cooled to room temperature. The colorless block crystals were filtered and washed with water and ethanol. Yield 60% (based on HIA). **Analysis calculated** for $C_{16}H_{18}CdN_4O_8$: C, 37.92; H, 3.58; N, 11.06%; found: C, 37.26; H, 3.71; N, 10.86%.

Experimental details

All H atoms were included in calculated positions and refined as riding atoms, with C–H = 0.93 Å with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ for methyl H atoms and $1.2 U_{\text{eq}}(\text{C})$ for all other H atoms.

Comment

In recent years, the design and synthesis of metal-organic frameworks (MOFs) with *N*-heterocyclic carboxylato ligands

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{iso} */ <i>U</i> _{eq}
Cd1	0.73109 (3)	0.24657 (2)	0.12363 (2)	0.02646 (8)
N1	0.8087 (4)	0.35180 (10)	0.12669 (17)	0.0338 (5)
N2	0.6853 (4)	0.39968 (10)	0.09396 (18)	0.0333 (5)
N3	0.6574 (4)	0.14095 (10)	0.13023 (18)	0.0336 (5)
N4	0.7913 (4)	0.09632 (10)	0.09807 (18)	0.0297 (5)
O1	0.9209 (3)	0.66753 (8)	0.12391 (15)	0.0399 (5)
O2	0.6622 (3)	0.63481 (8)	0.02220 (17)	0.0472 (6)
O3	0.9044 (3)	−0.13461 (8)	0.03350 (18)	0.0492 (6)
O4	0.6169 (4)	−0.17608 (9)	0.09721 (17)	0.0498 (6)
O5	0.8819 (3)	0.23963 (10)	−0.03148 (16)	0.0346 (4)
O6	1.0618 (4)	0.22785 (13)	0.1927 (2)	0.0492 (6)
O7	0.6059 (5)	0.24982 (13)	0.28438 (19)	0.0544 (7)
O8	0.3944 (3)	0.25607 (10)	0.05675 (16)	0.0301 (4)
C1	0.9888 (4)	0.37567 (12)	0.1608 (2)	0.0342 (6)
H1	1.1003	0.3529	0.1886	0.041*
C2	0.9906 (4)	0.43998 (11)	0.14981 (18)	0.0268 (5)
C3	0.7909 (4)	0.45379 (11)	0.10648 (18)	0.0269 (5)
C4	0.7283 (4)	0.51408 (11)	0.0851 (2)	0.0297 (6)
H4A	0.5951	0.5226	0.0570	0.036*
C5	0.8707 (4)	0.56011 (11)	0.10696 (18)	0.0276 (5)
C6	1.0736 (4)	0.54699 (12)	0.14965 (19)	0.0296 (6)
H6	1.1670	0.5791	0.1638	0.036*
C7	1.1351 (4)	0.48783 (12)	0.17056 (19)	0.0294 (6)
H7	1.2692	0.4796	0.1978	0.035*
C8	0.8135 (4)	0.62551 (11)	0.0834 (2)	0.0314 (6)
C9	0.4838 (4)	0.11286 (12)	0.1622 (2)	0.0343 (6)
H9	0.3671	0.1327	0.1896	0.041*
C10	0.4997 (4)	0.04887 (11)	0.14921 (18)	0.0257 (5)
C11	0.7010 (4)	0.04017 (11)	0.10771 (18)	0.0237 (5)
C12	0.7794 (4)	−0.01819 (11)	0.08512 (19)	0.0263 (5)
H12	0.9152	−0.0234	0.0594	0.032*
C13	0.6492 (4)	−0.06750 (11)	0.10217 (18)	0.0253 (5)
C14	0.4427 (4)	−0.05936 (12)	0.14292 (19)	0.0285 (6)
H14	0.3570	−0.0935	0.1535	0.034*
C15	0.3679 (4)	−0.00250 (12)	0.16674 (19)	0.0286 (5)
H15	0.2333	0.0024	0.1939	0.034*
C16	0.7292 (4)	−0.13051 (12)	0.0763 (2)	0.0323 (6)
H1W	0.953 (5)	0.2664 (15)	−0.049 (2)	0.032 (9)*
H2W	0.956 (6)	0.208 (2)	−0.035 (3)	0.081 (15)*
H3W	1.154 (7)	0.2324 (19)	0.167 (3)	0.063 (15)*
H4W	1.073 (5)	0.2108 (15)	0.242 (3)	0.038 (10)*
H5W	0.676 (9)	0.244 (2)	0.328 (5)	0.12 (2)*
H6W	0.525 (7)	0.2713 (19)	0.306 (3)	0.066 (14)*
H7W	0.374 (5)	0.2880 (18)	0.034 (3)	0.054 (11)*
H8W	0.387 (5)	0.2320 (16)	0.009 (3)	0.045 (10)*
H2	0.567 (4)	0.3903 (13)	0.063 (2)	0.032 (8)*
H4	0.899 (5)	0.1054 (13)	0.067 (2)	0.032 (8)*

have attracted much attention because of their potential applications as microporous, magnetic, nonlinear optical, and fluorescent materials [5, 6]. Over the past few years, extensive investigation has focused on the construction of coordination polymers using 4,5-imidazoledicarboxylic acid and derivatives

as bridging ligands [7–14]. Recently, our group also reported five coordination polymer with the 2-methyl-1*H*-imidazole-4,5-dicarboxylate ligand (MIA). The reported coordination polymer with MIA not only shows beautiful and interesting topological structures, for instance 0D, 1D, 2D and 3D but also exhibits very flexible coordination modes [10–14]. Therefore, we have been engaged in new MOFs with *N*-heterocyclic carboxylate ligands. We have synthesised 1*H*-indazole-6-carboxylic acid (HIA) and not long ago we obtained a cadmium complex with the anionic IA ligand via a hydrothermal reaction.

The title complex consists of [Cd(IA)₂(H₂O)₄], one cadmium(II) ion, two deprotonated 1*H*-indazole-6-carboxylate (IA[−]) anions and four coordinated water molecules. Each six-coordinated Cd(II) adopts a distorted octahedral geometry where the basal plane is occupied by two indazole ring nitrogen atoms (N(1), N(3)) from two equivalent IA[−] ligands and two oxygen atoms from coordinated water (O(5), O(7)); the axial positions are occupied by two oxygen atoms from coordinated water (O(6), O(8)). The Cd–N bond distances are 2.341(3) and 2.345(3) Å, the Cd–O bond distances are in the range of 2.294(3), 2.299(3), 2.293(4) and 2.291(3) Å, respectively. The N–Cd–N bond angle is 176.81(11)°, the N–Cd–O bond angles vary from 85.59(11) to 96.14(11)° and the O–Cd–O bond angles vary from 87.10(16) to 175.12(14)°, which are similar to those in Cu(II) complexes with 1*H*-indazole derivatives [15, 16]. Intermolecular O–H⋯O hydrogen bonds between the two coordinated water O atoms [O(5) and O(7), O(6) and O(8)] link the complexes into a two-dimensional hydrogen bonded network. The 2D networks are further linked into a three-dimensional framework through O–H⋯O hydrogen bonding interactions between the four coordinated water O atom [O(5), O(6), O(7) and O(8)] and carboxylate O atoms [O(1), O(2), O(3) and O(4)].

Acknowledgements: X-ray data were collected at Instrumental Analysis Center Nanchang Hangkong University, Nanchang, 330063, People's Republic of China.

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

Research funding: The Jiangxi key R & D project (20192ACB60011 and 20202BABL205003), the Key Research Foundation of Educational Department of Jiangxi Province of China (GJJ180205, GJJ160382).

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

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