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The crystal structure of poly[bis(μ_4 -2,3-pyridinedicarboxylato)-(μ_2 -oxalyl dihydrazide)-dicadmium(II) dihydrate], $C_{16}H_{16}O_{12}N_6Cd_2$

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Abstract

$C_{16}H_{16}O_{12}N_6Cd_2$, monoclinic, $P2_1/n$ (no. 14), $a = 9.9709(2)$ Å, $b = 7.1597(2)$ Å, $c = 15.4572(4)$ Å, $\beta = 108.401(1)^\circ$, $V = 1047.05(5)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0168$, $wR_{ref}(F^2) = 0.0401$, $T = 297(2)$ K.

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Table 1: Data collection and handling.

Crystal:	Colorless cubic
Size:	$0.35 \times 0.33 \times 0.32$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	2.11 mm^{-1}
Diffractometer, scan mode:	Bruker Smart Apex, ω
$\theta_{\max}$, completeness:	28.3° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	10466, 2602, 0.019
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2425
$N(\text{param})_{\text{refined}}$:	172
Programs:	Bruker [1], SHELX [2, 3], Diamond [4]

A part of 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.

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

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd1	0.34499(2)	0.33271(2)	0.34110(2)	0.01856(5)
O1	0.87783(14)	0.20557(19)	0.70165(9)	0.0235(3)
O2	0.72062(15)	−0.01774(19)	0.68764(9)	0.0260(3)
O3	0.57370(14)	0.35372(18)	0.62792(8)	0.0221(3)
O4	0.39136(14)	0.3240(2)	0.50042(9)	0.0249(3)
O5	−0.10751(17)	0.5614(3)	0.39011(11)	0.0429(4)
O6	0.6068(2)	0.6544(3)	0.26489(13)	0.0521(5)
H6A	0.6907(18)	0.645(5)	0.294(2)	0.078*
H6B	0.555(3)	0.639(5)	0.299(2)	0.078*
N1	0.57286(16)	0.2178(2)	0.41000(10)	0.0211(3)
H11	0.179(3)	0.393(3)	0.4777(16)	0.025*
N2	0.12079(17)	0.4092(2)	0.34702(10)	0.0223(3)
H21	0.0961	0.5190	0.3197	0.027*
H22	0.0598	0.3246	0.3149	0.027*
N3	0.10636(18)	0.4198(3)	0.43536(11)	0.0244(3)
C1	0.6554(2)	0.1442(3)	0.36565(13)	0.0278(4)
H1A	0.6272	0.1531	0.3024	0.033*
C2	0.7819(2)	0.0549(3)	0.41056(13)	0.0302(5)
H2	0.8375	0.0045	0.3781	0.036*
C3	0.8235(2)	0.0425(3)	0.50436(13)	0.0247(4)
H3A	0.9075	−0.0172	0.5358	0.030*
C4	0.73951(18)	0.1195(2)	0.55162(11)	0.0167(3)
C5	0.61425(18)	0.2071(2)	0.50176(11)	0.0166(3)
C6	0.51767(19)	0.3016(2)	0.54692(12)	0.0170(3)
C7	0.78129(18)	0.1009(3)	0.65391(11)	0.0173(3)
C8	−0.0055(2)	0.4987(3)	0.44935(13)	0.0247(4)

Source of material

Chemical materials were purchased from commercial source and used without further purification. The solvent is deionized water. IR spectra were measured on a Nicolet 170SX spectrometer in the 4000–400 cm^{−1} region.

The synthesis was carried out in a 20 mL high pressure resistant glass bottle under autogenous pressure. The reactor with a mixture of 2,3-pyridinedicarboxylic acid (0.5 mmol, 83.5 mg), NaOH (1 mmol, 40 mg) and H₂O (6 mL) was sealed and heated at 353 K for 30 min. And then a solution of oxalyl dihydrazide (0.5 mmol, 59 mg), Cd(CH₃COO)₂ · H₂O (1 mmol, 266 mg) and H₂O (6 mL) was added and continuously heated at 393 K for 24 h before cooling to room temperature. The colorless crystals were collected by filtration, washed with water and ethanol and dried in air. The product yield was 48% based on Cd(II). IR (cm^{−1}, KBr): 3592(m), 3403(m), 3304(s), 3194(m), 2978(w), 1573(vs), 1467(w), 1383(vs), 1187(w), 1112(m), 832(m), 707(m), 673(m), 524(m), 504(w).

Experimental details

H atoms were positioned geometrically and treated as riding, with C—H = 0.93 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Comment

Coordination polymers have received considerable attention because of their magnetic behaviors, optical activities as well as catalytic and luminescent properties. Acting as polyfunctional ligand 2,3-pyridinedicarboxylates were widely studied owing to their rich coordination modes [5–10]. Most of them are six-coordinated Cd-complexes.

The structure of the complex is as shown in the Figure (symmetry operations A: $-1/2 + x, 1/2 - y, -1/2 + z$; B: $1 - x, -y, 1 - z$; C: $1 - x, 1 - y, 1 - z$ and D: $-x, 1 - y, 1 - z$). The Cd(II) is seven coordinated by five oxygen atoms and one nitrogen atom from four deprotonated 2,3-pyridinedicarboxylato ligands (pda^{2−})(O1A, O2A, O2B, O3C, O4, and N1), and one nitrogen atom (N2) from oxaloyl dihydrazide. The two carboxyl groups from the same pda^{2−} show two different types of coordination and connect Cd(II) centers forming a three-dimensional network. The Cd—O and Cd—N bond distances range from 2.2965(13) Å to 2.3836(13) Å and from 2.3313(16) Å to 2.3338(16) Å, respectively. The data are different from those of reported [10] Cd—O (pda^{2−}) (2.2652 Å to 2.6319 Å) and Cd—N (pda^{2−}) (2.2912 Å) distances, with the former obviously shorter and the latter a little longer. These phenomena can be attributed to the different coordination modes.

There are intermolecular hydrogen-bonding interactions between crystal water molecules and pda^{2−}, oxaloyl dihydrazide and pda^{2−} as well as crystal water molecules and oxaloyl dihydrazide. The D—A distances range from 2.784(2) Å to 2.999(3) Å.

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