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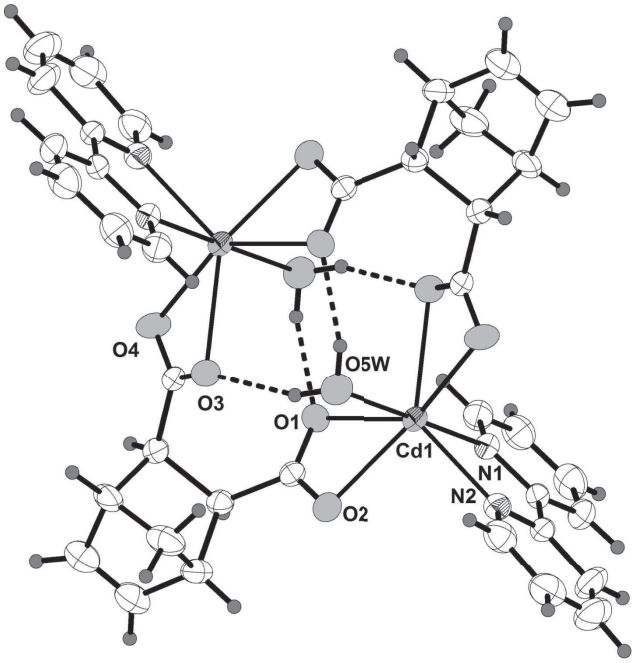
Crystal structure of diaquabis(bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate-κ^4O, O′:/O″,O‴)bis-(2,2′-bipyridine-κ^2N, N′)dicadmium(II) hydrate



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Abstract

The complex: $C_{19}H_{18}CdN_2O_5$, Triclinic, P-1, $a = 9.6654(11)$ Å, $b = 10.5458(12)$ Å, $c = 10.7081(12)$ Å, $\alpha = 108.5220(10)°$, $\beta = 92.0640(10)°$, $\gamma = 111.4760(10)°$, $V = 948.62(19)$ Å^3, $R_{gt}(F) = 0.0200$, $wR_{ref}(F^2) = 0.0535$, $Z = 2$, $T = 293(2)$ K.

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Table 1: Data collection and handling.

Crystal:	Colourless, Block, size 0.13×0.28×0.36 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	11.83 cm^{-1}
Diffractometer, scan mode:	CCD area detector, φ and ω scans
$2\theta_{max}$:	51°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	7197, 3493
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3342
$N(param)_{refined}$:	244
Programs:	SHELXS-97 (SHELDRICK, 1990)

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

Atom	Site	x	y	z	U_{iso}
H(1W)	2*i*	0.1838	0.5004	0.0843	0.081
H(2W)	2*i*	0.0662	0.4376	0.1399	0.081
H(2)	2*i*	0.3527	0.831	−0.138	0.045
H(3)	2*i*	0.3006	0.6237	−0.3046	0.061
H(4)	2*i*	0.4678	0.489	−0.2512	0.119
H(5)	2*i*	0.614	0.6896	−0.333	0.117
H(6)	2*i*	0.6754	0.9178	−0.1668	0.089
H(7)	2*i*	0.5747	0.8854	0.0351	0.06
H(8A)	2*i*	0.4649	0.6169	−0.0005	0.078
H(8B)	2*i*	0.6342	0.6668	−0.0283	0.078
H(10)	2*i*	0.3172	0.7895	0.482	0.07
H(11)	2*i*	0.4448	0.9713	0.6847	0.084
H(12)	2*i*	0.4175	1.19	0.7428	0.091
H(13)	2*i*	0.2586	1.2207	0.5986	0.078
H(16)	2*i*	0.1097	1.2406	0.4598	0.067
H(17)	2*i*	−0.037	1.2537	0.2915	0.077
H(18)	2*i*	−0.1365	1.06	0.0922	0.072
H(19)	2*i*	−0.0891	0.8555	0.0645	0.062

Source of material

The mixtures of 5-norbornene-2,3-dicarboxylic acid (0.1 mmol, 18.2 mg), 2,2′-bipyridine (0.1 mmol, 15.6 mg), $Cd(OAC)_2{\cdot}2H_2O$ (0.1 mmol, 26.7 mg), NaOH (0.1 mmol), and H_2O (6.0 ml) were placed in a 23 ml Teflon liner stainless steel reactor. The vessel was heated to 393 K for 4 days, and then slowly cooled to room temperature. Colorless crystals

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Table 3: Atomic displacement parameters (Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd(1)	2*i*	0.09327(2)	0.72129(1)	0.20513(1)	0.0396(1)	0.03015(9)	0.0378(1)	0.01035(7)	0.00811(6)	0.00505(6)
O(1)	2*i*	0.1250(2)	0.7184(2)	−0.0224(2)	0.0396(8)	0.0429(8)	0.0525(9)	0.0179(6)	0.0108(7)	0.0139(7)
O(2)	2*i*	0.3261(2)	0.7904(2)	0.1260(2)	0.0497(9)	0.057(1)	0.0370(8)	0.0125(7)	0.0051(7)	0.0076(7)
O(3)	2*i*	0.1802(2)	0.4418(2)	−0.1136(2)	0.0485(9)	0.0397(8)	0.0524(9)	0.0084(7)	0.0129(7)	0.0110(7)
O(4)	2*i*	0.0786(2)	0.4148(2)	−0.3108(2)	0.051(1)	0.055(1)	0.051(1)	−0.0040(8)	0.0008(8)	0.0071(8)
O(5W)	2*i*	0.1485(2)	0.5119(2)	0.1567(2)	0.058(1)	0.0479(9)	0.056(1)	0.0220(8)	0.0072(8)	0.0162(8)
N(1)	2*i*	0.0392(2)	0.9253(2)	0.2391(2)	0.0377(9)	0.0369(9)	0.0377(9)	0.0138(7)	0.0069(7)	0.0061(7)
N(2)	2*i*	0.2163(2)	0.8953(2)	0.4187(2)	0.0384(9)	0.047(1)	0.0371(9)	0.0114(8)	0.0064(7)	0.0122(8)
C(1)	2*i*	0.2651(2)	0.7546(2)	0.0083(2)	0.040(1)	0.0245(9)	0.042(1)	0.0111(8)	0.0078(8)	0.0082(8)
C(2)	2*i*	0.3615(2)	0.7599(2)	−0.1010(2)	0.037(1)	0.032(1)	0.041(1)	0.0098(8)	0.0068(8)	0.0137(8)
C(3)	2*i*	0.3185(3)	0.6108(2)	−0.2196(2)	0.046(1)	0.043(1)	0.040(1)	0.002(1)	0.0145(9)	0.0034(9)
C(4)	2*i*	0.4733(3)	0.5881(3)	−0.2075(4)	0.051(2)	0.041(1)	0.152(3)	0.002(1)	0.055(2)	−0.019(2)
C(5)	2*i*	0.5790(4)	0.7059(4)	−0.2520(4)	0.063(2)	0.091(3)	0.092(2)	−0.004(2)	0.038(2)	0.012(2)
C(6)	2*i*	0.6123(3)	0.8284(3)	−0.1633(3)	0.054(2)	0.067(2)	0.090(2)	0.011(1)	0.030(2)	0.028(2)
C(7)	2*i*	0.5322(2)	0.8049(2)	−0.0510(3)	0.035(1)	0.041(1)	0.060(1)	0.0055(9)	0.005(1)	0.012(1)
C(8)	2*i*	0.5339(3)	0.6610(3)	−0.0529(3)	0.038(1)	0.060(2)	0.103(2)	0.021(1)	0.013(1)	0.035(2)
C(9)	2*i*	0.1846(2)	0.4814(2)	−0.2117(2)	0.041(1)	0.034(1)	0.044(1)	0.0073(9)	0.0148(9)	−0.0012(9)
C(10)	2*i*	0.3061(3)	0.8776(3)	0.5050(3)	0.051(1)	0.074(2)	0.054(1)	0.023(1)	0.012(1)	0.031(1)
C(11)	2*i*	0.3829(3)	0.9863(4)	0.6273(3)	0.051(1)	0.105(2)	0.044(1)	0.015(2)	0.002(1)	0.033(2)
C(12)	2*i*	0.3663(4)	1.1155(4)	0.6619(3)	0.076(2)	0.076(2)	0.041(1)	0.005(2)	−0.007(1)	0.008(1)
C(13)	2*i*	0.2726(3)	1.1340(3)	0.5756(2)	0.076(2)	0.049(1)	0.039(1)	0.007(1)	0.002(1)	−0.001(1)
C(14)	2*i*	0.1988(2)	1.0220(2)	0.4534(2)	0.039(1)	0.038(1)	0.034(1)	0.0037(8)	0.0108(8)	0.0057(8)
C(15)	2*i*	0.0999(2)	1.0382(2)	0.3556(2)	0.038(1)	0.034(1)	0.039(1)	0.0092(8)	0.0150(8)	0.0075(8)
C(16)	2*i*	0.0705(3)	1.1633(3)	0.3785(3)	0.058(1)	0.036(1)	0.060(2)	0.016(1)	0.019(1)	0.004(1)
C(17)	2*i*	−0.0181(3)	1.1704(3)	0.2781(3)	0.063(2)	0.057(2)	0.088(2)	0.036(1)	0.025(2)	0.030(2)
C(18)	2*i*	−0.0774(3)	1.0561(3)	0.1602(3)	0.053(1)	0.070(2)	0.070(2)	0.034(1)	0.015(1)	0.030(1)
C(19)	2*i*	−0.0475(3)	0.9346(3)	0.1443(2)	0.046(1)	0.057(1)	0.048(1)	0.023(1)	0.005(1)	0.013(1)

were obtained, and further crystals were filtered off, washed with mother liquid, and dried under ambient conditions. Yield 38%.

Experimental details

One equivalent of solvent water was removed from the data using the squeeze option of the platon program [10]. The details of the data collection and handling are summarized in Table 1, the fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters are shown in Table 2, and the atomic displacement parameters for this complex are shown in Table 3.

Discussion

Recently in material science and chemical research, much attention has been paid to the rational design and construction of novel coordination networks, not only for their structural diversity and intriguing topology architecture [1, 2], but also for potential applications in the fields of gas adsorption [3], ion-exchange [4], optics [5], magnetism [6] and catalysis [7]. Usually, the assembly of metal complexes can be realized by the judicious chose of metal ions (joints) and multifunctional organic ligands (struts). Among various organic ligands, benzene multi-carboxylate ligands play crucial roles in the design and construction of desirable frameworks, owing to their fascinating characteristics including strong coordination ability, diverse coordination modes, different organic skeletons of carboxylate linkers, and abundant hydrogen-bonding interactions. The doubly deprotonated anion of the 5-norbornene-2,3-dicarboxylic acid (H2ndca) is a desired, steric, non-coplanar dicarboxylate for the formation of coordinated polymers, which has received little attention in the literature. On the other hand, the addition of a N-containing coligand [8, 9] can provide much more complicated and fascinating structures in view of its cooperative coordination. On the condition that one spacer (main ligand) and the metal center are fixed, the other spacer (secondary ligand) can be used as a structure-directing agent in the formation of various dimensional architectures, to some extent. The asymmetric unit of the title structure contains one Cd atom, one 5-norbornene-2,3-dicarboxylato(bicyclo[2.1.1]hept-5-ene-2,3dicarboxylate) ligand (ndca), one 2,2′-bipyridine coligand and one ligated water. The Cd atom displays a highly distorted pentagonal bipyramidal coordination with four oxygen atoms from two chelating carboxylate group belonging to two ndca

ligands (Cd—O: 2.3493(18) Å – 2.5135(16) Å), two nitrogen atoms from one chelating 2,2′-bipyridine coligand (Cd—N: 2.3180(17) Å and 2.3559(17) Å), and one ligated water molecule (Cd—O: 2.3631(16) Å). The symmetry-related two cadmium atoms are connected by two ndca ligands in $\kappa^4O,O':O'',O'''$ coordination mode to form a binuclear complex with the Cd$\cdots$Cd distance of 4.9573(4) Å. Notably, the presence of coordinated water molecules lead to the formation of intramolecular hydrogen bonds.

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References

1. Liu, G. Z.; Xin, L. Y.; Wang, L. Y.: Ancillary Ligand-Mediated Syntheses and Fluorescence Properties of Zinc(II) Complexes Based on Flexible Benzene Dicarboxylic Acid. CrystEngComm. **13** (2011) 3013–3020.
2. Zhang, Y. B.; Zhang, W. X.; Feng, F. Y.; Zhang, J. P.; Chen, X. M.: A Highly Connected Porous Coordination Polymer with Unusual Channel Structure and Sorption Properties. Angew. Chem., Int. Ed. **48** (2009) 5287–5290.
3. Pan, L. K.; Adams, M.; Hernandez, H. E.; Wang, X. T.; Zheng, C.; Hattori, Y.; Kaneko, K.: Porous Lanthanide-Organic Frameworks: Synthesis, Characterization, and Unprecedented Gas Adsorption Properties. J. Am. Chem. Soc. **125** (2003) 3062–3067.
4. Zhu, H. F.; Fan, J.; Okamura, T.; Zhang, Z. H.; Liu, G. X.; Yu, K. B.; Sun, W. Y.; Ueyama, N.: Metal-Organic Architectures of Silver(I), Cadmium(II), and Copper(II) with a Flexible Tricarboxylate Ligand. Inorg. Chem. **45** (2006) 3941–3948.
5. Lu, W. G.; Jiang, L.; Feng, X. L.; Lu, T. B.: Three-Dimensional Lanthanide Anionic Metal-Organic Frameworks with Tunable Luminescent Properties Induced by Cation Exchange. Inorg. Chem. **48** (2009) 6997–6999.
6. Xin, L. Y.; Liu, G. Z.; Ma, L. F.; Wang, L. Y.: Coligand-regulated Assembly, Fluorescence, and Magnetic Properties of Co(II) and Cd(II) Complexes with a Non-coplanar Dicarboxylate. J. Solid State Chem. **206** (2013) 233–241.
7. Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K.: A Homochiral Metal-Organic Porous Material for Enantioselective Separation and Catalysis. Nature. **404** (2000) 982–986.
8. Ma, L. F.; Wang, L. Y.; Wang, Y. Y.; Batten, S. R.; Wang, J. G.: Self-Assembly of a Series of Cobalt(II) Coordination Polymers Constructed from H2tbip and Dipyridyl-Based Ligands. Inorg. Chem. **48** (2009) 915–924.
9. Xin, L. Y.; Liu, G. Z.; Wang, L. Y.: New Coordination Polymers from 1D Chain, 2D Layer to 3D Framework Constructed from 1,2-Phenylenediacetic Acid and 1,3-Bis(4-pyridyl)propane Flexible Ligands. J. Solid State Chem. **184** (2011) 1387–1392.
10. Spek, A. L.: Structure Validation in Chemical Crystallography. Acta Cryst. D **65** (2009) 148–155.