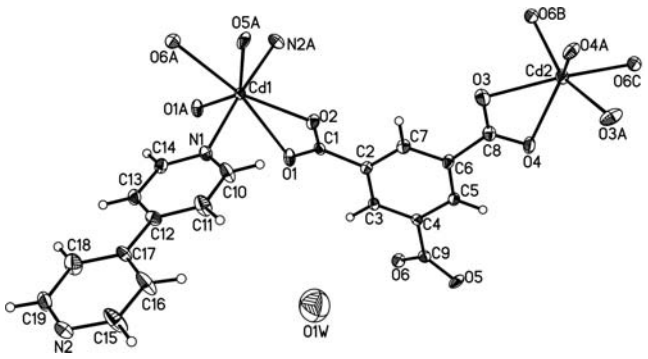
Crystal structure of bis(bipyridine)bis(1,3,5-benzenetricarboxylato)-tricadmium(II) monohydrate, $Cd_3(C_{10}H_8N_2)_2(C_9H_3O_6)_2 \cdot H_2O$

Jing Zhang[I], Di-Ping He[*,I] and Seik Weng Ng[II]

[I] Shaanxi Normal University, School of Chemistry and Materials Science, Xi'an 710062, P. R. China
[II] University of Malaya, Department of Chemistry, 50603 Kuala Lumpur, Malaysia

Received December 24, 2010, accepted and available on-line April 9, 2011; CCDC no. 1267/3345



Abstract

$C_{38}H_{24}Cd_3N_4O_{13}$, monoclinic, *C*12/*c*1 (no. 15), a = 23.700(5) Å, b = 11.688(1) Å, c = 20.563(5) Å, β = 135.16(4)°, V = 4016.5 Å^3, Z = 4, $R_{gf}(F)$ = 0.044, $wR_{ref}(F^2)$ = 0.145, T = 293 K.

Source of material

The title compound was synthesized hydrothermally in a 40 ml Teflon-lined autoclave by heating a mixture of 1,3,5-benzenetricarboxylic acid (H_3btc, 0.1 mmol), 4,4′-bipyridine (4,4′-bipy, 0.1 mmol), $Cd(NO_3)_2 \cdot 4H_2O$ (0.2 mmol), and NaOH (0.3 mmol) in 8 ml of water and 2 ml of ethanol at 120 °C for 2 days, then cooled to room temperature. The resulting colorless crystals were collected and dried in air at ambient temperature. Elemental analysis — found: C, 42.09 %; H, 2.16 %; N, 4.83 %; calculated for $C_{38}H_{24}Cd_3N_4O_{13}$: C, 42.19 %; H, 2.24 %; N, 5.18 %. A powder XRD pattern and the simulated patterns on the basis of single-crystal structure corresponded well in peak positions. Differences in reflection intensities were due to preferred particle orientation in the powder samples. The TG analysis shows that the title compound has one step of mass loss between 100 °C and 580 °C, which corresponds to the loss of two 1,3,5-benzenetricarboxylic, one 4,4′-bipy molecule and one lattice water molecule (found: 65.09 %; calculated: 64.39 %). In the DTA curve, the endothermic peak at 500 °C is related to the one-step decomposition.

Experimental details

The O1W atom of the water molecule is located on a split-position close to a two-fold symmetry axis. The split positions are alternatively occupied (occ. = 0.5). Due to the disorder of the oxygen atom the hydrogen atoms could not be located in the difference fourier map.

Discussion

The investigation of porous metal-organic frameworks (MOFs) has attracted much interest due to their structural diversity and promising applications for ion exchange, gas storage, separation, and catalysis. One of the most effective approaches to synthesize novel porous MOFs with unique structures and properties is the hydrothermal/solvothermal method by coordinating appropriate metal ions with carboxylic acid ligands. So far, many metal coordination polymers assembled from 1,3,5-benzenetricarboxylic acid (H_3btc) and bipyridine (bipy) ligands were reported [1-4].

The symmetry independent part of the crystal structure of the title compound contains three Cd(II) cations which have two different coordination modes, two btc^{3-} ligands, two 4,4′-bipy ligands and one lattice water molecule. The Cd1 is seven-coordinated by two nitrogen atoms (N1, N2A) from two different 4,4′-bipy ligands in the monodentate mode, four carboxyl oxygen atoms (O1A, O2, O5A, O6A) from two different btc^{3-} ligands in the chelate mode, and one oxygen atom (O1) from btc^{3-} ligand in the monodentate mode. The Cd2 is six-coordinated by four oxygen atoms (O3, O4, O3A, O4A) from two different btc^{3-} ligands in the chelate mode, and two oxygen atoms (O6B, O6C) from two different btc^{3-} ligand in the monodentate mode, forming a distorted octahedron. The Cd—O bond lengths are in the range from 2.285(5) Å to 2.550(5) Å, and Cd—N bond lengths range from 2.296(6) Å to 2.325(6) Å. Each completely deprotonated btc^{3-} serves as a 3-connected node to coordinate three Cd(II) atoms through its carboxylate groups, and each Cd1 atoms are further connected by 4,4′-bipy ligands to give rise to the complex 3D framework.

The luminescent property of this complex in the solid state at room temperature was investigated. Upon excitation of the solid sample at 355 nm, it exhibited a strong fluorescent emission band at 450 nm, while at the same excitation wavelength, there is no obvious ligand emission spectra. The fluorescence emission of this complex may arise from the charge transfer of ligand to metal (LMCT) [5].

Table 1. Data collection and handling.

Crystal:	colorless column, size 0.02 × 0.03 × 0.06 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	16.42 cm^{-1}
Diffractometer, scan mode:	Xcalibur Eos Gemini, ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	6953, 3445
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2922
$N(param)_{refined}$:	267
Programs:	SHELXS-97, SHELXL-97 [6]

* Correspondence author (e-mail: hediping@snnu.edu.cn)

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(3)	8*f*	0.0848	0.4961	0.3816	0.024
H(5)	8*f*	0.2811	0.6181	0.4535	0.028
H(7)	8*f*	0.2748	0.5868	0.6425	0.031
H(10)	8*f*	0.1844	0.2698	0.6716	0.046
H(11)	8*f*	0.1906	0.0725	0.6805	0.051
H(13)	8*f*	–0.0321	0.0713	0.5685	0.035
H(14)	8*f*	–0.0333	0.2660	0.5615	0.032
H(15)	8*f*	0.1839	–0.3009	0.6768	0.065
H(16)	8*f*	0.1884	–0.1068	0.6755	0.061
H(18)	8*f*	–0.0244	–0.1010	0.5913	0.066
H(19)	8*f*	–0.0223	–0.2964	0.5949	0.063

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

Atom	Site	Occ.	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd(1)	8*f*		0.07866(3)	0.48249(4)	0.63198(3)	0.0191(3)	0.0176(3)	0.0165(3)	–0.0002(2)	0.0126(2)	0.0018(2)
Cd(2)	4*e*		½	0.80087(7)	¾	0.0168(4)	0.0309(4)	0.0228(4)	0	0.0117(3)	0
O(1)	8*f*		0.0573(3)	0.4994(4)	0.4853(4)	0.017(3)	0.038(3)	0.031(3)	–0.001(2)	0.015(2)	0.007(2)
O(2)	8*f*		0.1742(3)	0.4925(5)	0.6293(3)	0.027(3)	0.042(3)	0.017(3)	–0.004(2)	0.016(2)	0.002(2)
O(3)	8*f*		0.3977(3)	0.6879(6)	0.7078(3)	0.039(3)	0.067(4)	0.020(3)	–0.024(3)	0.020(3)	–0.011(3)
O(4)	8*f*		0.4016(3)	0.7143(5)	0.6054(4)	0.028(3)	0.053(4)	0.030(3)	–0.011(3)	0.023(2)	–0.004(3)
O(5)	8*f*		0.1802(3)	0.5231(5)	0.2917(3)	0.027(3)	0.058(4)	0.018(3)	0.004(2)	0.017(2)	–0.004(2)
O(6)	8*f*		0.0625(3)	0.5558(5)	0.2401(3)	0.019(2)	0.040(3)	0.017(2)	0.000(2)	0.010(2)	0.000(2)
O(1W)	8*f*	0.50	0.016(3)	0.298(2)	0.264(4)	0.18(2)	0.18(2)	0.16(2)	–0.02(1)	0.13(1)	–0.00(1)
N(1)	8*f*		0.0747(3)	0.2875(5)	0.6159(4)	0.028(3)	0.020(3)	0.029(3)	–0.001(3)	0.020(3)	0.003(3)
N(2)	8*f*		0.0807(4)	–0.3187(6)	0.6371(4)	0.032(4)	0.021(3)	0.033(4)	–0.002(3)	0.019(3)	–0.002(3)
C(1)	8*f*		0.1319(4)	0.5060(6)	0.5446(5)	0.021(4)	0.016(3)	0.027(4)	–0.002(3)	0.017(3)	–0.002(3)
C(2)	8*f*		0.1740(4)	0.5349(6)	0.5170(5)	0.019(3)	0.025(4)	0.019(3)	0.002(3)	0.013(3)	0.002(3)
C(3)	8*f*		0.1369(4)	0.5238(6)	0.4266(5)	0.017(3)	0.021(3)	0.021(3)	0.000(3)	0.013(3)	0.001(3)
C(4)	8*f*		0.1773(4)	0.5539(6)	0.4031(5)	0.019(3)	0.023(3)	0.022(3)	–0.004(3)	0.014(3)	–0.005(3)
C(5)	8*f*		0.2540(4)	0.5982(6)	0.4692(5)	0.021(3)	0.027(4)	0.022(3)	–0.002(3)	0.016(3)	0.000(3)
C(6)	8*f*		0.2905(4)	0.6128(6)	0.5591(4)	0.017(3)	0.036(4)	0.018(3)	–0.001(3)	0.012(3)	0.001(3)
C(7)	8*f*		0.2499(4)	0.5791(6)	0.5820(5)	0.025(4)	0.034(4)	0.017(3)	–0.001(3)	0.014(3)	0.004(3)
C(8)	8*f*		0.3689(4)	0.6742(7)	0.6293(5)	0.023(4)	0.029(4)	0.025(4)	0.001(3)	0.016(3)	0.003(3)
C(9)	8*f*		0.1377(4)	0.5437(6)	0.3055(5)	0.023(4)	0.025(4)	0.018(3)	–0.002(3)	0.013(3)	0.000(3)
C(10)	8*f*		0.1404(5)	0.2291(7)	0.6508(6)	0.026(4)	0.021(4)	0.057(5)	–0.002(3)	0.026(4)	0.001(4)
C(11)	8*f*		0.1447(5)	0.1101(7)	0.6569(6)	0.032(4)	0.022(4)	0.062(6)	0.005(3)	0.030(4)	0.006(4)
C(12)	8*f*		0.0794(4)	0.0477(6)	0.6273(5)	0.034(4)	0.018(4)	0.029(4)	0.001(3)	0.021(4)	0.002(3)
C(13)	8*f*		0.0132(5)	0.1095(6)	0.5907(5)	0.035(4)	0.023(4)	0.037(4)	–0.002(3)	0.029(4)	0.003(3)
C(14)	8*f*		0.0126(4)	0.2271(6)	0.5863(5)	0.029(4)	0.025(4)	0.033(4)	0.002(3)	0.024(3)	0.004(3)
C(15)	8*f*		0.1415(5)	–0.2595(7)	0.6597(7)	0.025(4)	0.021(4)	0.069(6)	0.002(4)	0.017(4)	0.002(4)
C(16)	8*f*		0.1448(5)	–0.1429(7)	0.6591(7)	0.033(4)	0.023(4)	0.067(6)	–0.008(4)	0.026(5)	–0.003(4)
C(17)	8*f*		0.0815(4)	–0.0777(6)	0.6334(5)	0.031(4)	0.016(4)	0.034(4)	–0.003(3)	0.021(4)	–0.002(3)
C(18)	8*f*		0.0193(6)	–0.1395(7)	0.6094(8)	0.066(6)	0.022(4)	0.107(9)	0.007(4)	0.071(7)	0.004(5)
C(19)	8*f*		0.0208(6)	–0.2579(7)	0.6118(8)	0.071(6)	0.025(4)	0.102(8)	–0.013(4)	0.076(7)	–0.011(5)

References

1. Yang, X. J.; Wu, B.; Sun, W. H.; Janiak, C.: Second-sphere coordination of 5,5′-diamino-2,2′-bipyridine metal complexes with oxygen ligands through N–H···O hydrogen bonding. Inorg. Chim. Acta **343** (2003) 366-372.
2. He, H. Y.; Dai, F. G.; Xie, A. P.; Tong, X.; Sun, D. F.: Three novel 3D metal-organic frameworks with a 1D ladder, tube or chain as assembly units. CrystEngComm **10** (2008) 1429-1435.
3. Li, X. J.; Sun, D. F.; Cao, R.; Sun, Y. Q.; Wang, Y. Q.; Bi, W. H.; Gao, S. Y.; Hong, M. C.: $[Zn_2(H_2O)_3(2,2'\text{-bipy})_2(btc)][Zn(H_2O)(2,2'\text{-bipy})(btc)] \cdot 8H_2O$: a novel zinc-carboxylate complex consisting of independently cationic and anionic chains. Inorg. Chem. Commun. **6** (2003) 908-911.
4. Li, X. J.; Cao, R.; Sun, D. F.; Yuan, D. Q.; Bi, W. H.; Li, X.; Wang, Y. Q.: A three-dimensional zinc(II) complex consisting of single metal centers and pentanuclear clusters bridged by 1,3,5-benzenetricarboxylate. J. Mol. Struct. **694** (2004) 205-210.
5. Chen, W.; Wang, J. Y.; Chen, C.; Yue, Q.; Yuan, H. M.; Chen, J. S.; Wang, S. N.: Photoluminescent Metal-Organic Polymer Constructed from Trimetallic Clusters and Mixed Carboxylates. Inorg. Chem. **42** (2002) 944.
6. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.