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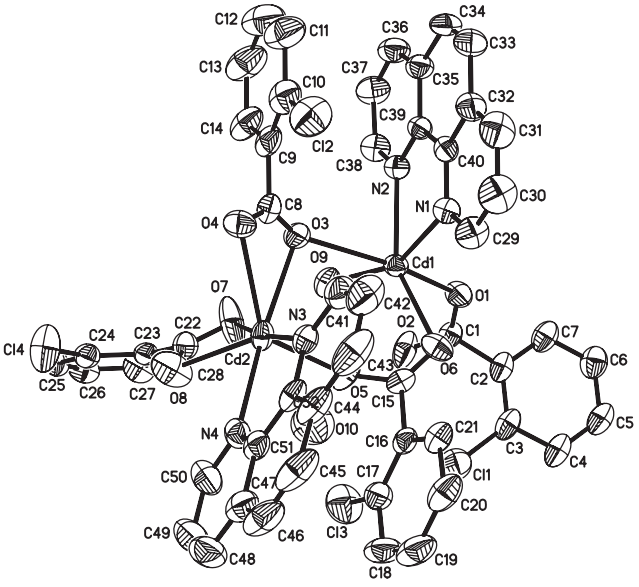
Chao Liu*

Crystal structure of bis(μ_2-2-chlorobenzoato-κ^3*O*,*O*′:*O*′)-(2-chlorobenzoato-κ*O*)-(2-chlorobenzoato-κ*O*,*O*′)-bis(1,10-phenanthroline-κ^2*N*,*N*′)-dicadmium(II) monohydrate, $C_{52}H_{36}Cd_2Cl_4N_4O_{10}$



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Abstract

$C_{52}H_{36}Cd_2Cl_4N_4O_{10}$, triclinic, $P\bar{1}$ (no. 2), $a = 11.3651(8)$ Å, $b = 12.9707(10)$ Å, $c = 18.7281(14)$ Å, $\alpha = 79.327(1)°$, $\beta = 74.543(1)°$, $\gamma = 70.703(1)°$, $V = 2497.1(3)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0393$, $wR_{ref}(F^2) = 0.0933$, $T = 293$ K.

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The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Chao Liu,** Changsha Enviromental Protection College, 410004, Changsha, Hunan, People's Republic of China, e-mail: chaoliu2017@126.com

Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.25 × 0.20 × 0.18 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	11.3 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$2\theta_{max}$, completeness:	50.2°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	13176, 8786, 0.050
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 6947
$N(param)_{refined}$:	782
Programs:	SHELX [1], Bruker programs [2]

Source of materials

A mixture of $Cd(CH_3COO)_2{\cdot}2H_2O$ (0.1 mmol), 2-chlorobenzoic acid (0.2 mmol), 1,10-phenanthroline (0.2 mmol), triethylamine (0.1 mL) and 15 mL CH_3OH/H_2O (1:2, v/v) was sealed in a 25 mL teflon-lined stainless-steel reactor and heated to 393 K for 72 h. The colorless block crystals suitable for X-ray diffraction analysis were obtained after the autoclave was cooled to room temperature.

Experimental details

Aromatic hydrogen atoms were placed in calculated positions (C—H = 0.93 Å) and refined as riding atoms with $U_{iso}(H) = 1.2U_{eq}(C)$. Water H atoms were permitted to ride at the positions located in difference maps with $U_{iso}(H) = 1.5U_{eq}(O)$, giving the O—H distances 0.85 Å. Some oxygen atoms of the carboxylate groups are disordered over two positions in this structure (ratio: 1/1). The two aromatic rings of the two 2-chlorobenzoic acids were disordered over opposite direction and overlapped each other with site occupation factors of 0.662 and 0.338. The disorder is omitted in the figure for clarity.

Comment

In the last two decades, the design and synthesis of metal-organic frameworks is one of the most active areas in coordination chemistry not only because of their intriguing variety

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

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cd1	0.21644(3)	0.17774(2)	0.337088(15)	0.05170(10)
Cd2	0.15039(3)	0.41437(2)	0.180239(16)	0.05440(10)
Cl1[a]	0.6810(2)	0.02429(19)	0.19125(12)	0.1009(8)
C2[a]	0.5952(8)	−0.0585(5)	0.3312(5)	0.0598(19)
C3[a]	0.6808(8)	−0.0774(4)	0.2630(4)	0.0721(19)
C4[a]	0.7653(6)	−0.1816(5)	0.2520(3)	0.088(2)
H4A[a]	0.8225	−0.1942	0.2063	0.106*
C5[a]	0.7642(6)	−0.2669(4)	0.3091(4)	0.085(2)
H5A[a]	0.8207	−0.3366	0.3017	0.102*
C6[a]	0.6786(6)	−0.2480(5)	0.3772(3)	0.087(2)
H6A[a]	0.6779	−0.3051	0.4154	0.104*
C7[a]	0.5942(7)	−0.1438(6)	0.3883(4)	0.079(2)
H7A[a]	0.5369	−0.1312	0.4339	0.095*
Cl1B[b]	0.5643(4)	−0.1497(4)	0.4607(3)	0.124(2)
C2B[b]	0.5947(16)	−0.0565(12)	0.3213(11)	0.070(4)
C3B[b]	0.6269(14)	−0.1531(13)	0.3680(8)	0.076(3)
C4B[b]	0.7281(12)	−0.2421(9)	0.3415(7)	0.076(3)
H4B[b]	0.7497	−0.3067	0.3728	0.092*
C5B[b]	0.7969(10)	−0.2346(9)	0.2683(7)	0.082(3)
H5B[b]	0.8646	−0.2942	0.2506	0.099*
C6B[b]	0.7647(13)	−0.1380(11)	0.2215(7)	0.089(3)
H6B[b]	0.8107	−0.1329	0.1725	0.107*
C7B[b]	0.6635(17)	−0.0489(9)	0.2480(10)	0.082(3)
H7B[b]	0.6420	0.0157	0.2167	0.098*
Cl2	−0.28452(15)	0.36103(15)	0.32795(10)	0.1148(5)
Cl4	0.15106(17)	0.81331(12)	0.16508(12)	0.1258(6)
O1	0.3842(2)	0.0457(2)	0.36781(17)	0.0729(9)
O2	0.5292(3)	0.1337(3)	0.3355(2)	0.1020(13)
O3[c]	0.0663(11)	0.3670(9)	0.3171(6)	0.076(3)
O4[c]	−0.0826(9)	0.4691(9)	0.2574(6)	0.071(2)
O5[c]	0.3212(8)	0.2561(8)	0.1914(5)	0.068(2)
O6[c]	0.2806(10)	0.0978(9)	0.2181(7)	0.076(3)
O7[c]	0.2555(12)	0.4756(11)	0.2581(8)	0.132(5)
O8[c]	0.2204(11)	0.5755(8)	0.1575(5)	0.113(3)
O3B[c]	0.0581(11)	0.3317(8)	0.2952(6)	0.055(2)
O4B[c]	−0.0363(8)	0.5010(7)	0.2553(5)	0.067(2)
O5B[c]	0.2660(7)	0.2367(7)	0.2142(5)	0.0509(18)
O6B[c]	0.3368(10)	0.0575(8)	0.2195(7)	0.070(3)
O7B[c]	0.3091(10)	0.4598(10)	0.2170(6)	0.073(3)
O8B[c]	0.1381(7)	0.5924(5)	0.1995(5)	0.0719(18)
O9	0.3100(3)	0.3001(2)	0.35879(16)	0.0715(8)
H9A	0.3147	0.3557	0.3273	0.107*
H9B	0.3854	0.2564	0.3554	0.107*
N1	0.0519(3)	0.1025(3)	0.34581(18)	0.0562(8)
N2	0.0881(3)	0.1883(3)	0.45823(17)	0.0526(8)
N3	0.0452(3)	0.3390(2)	0.11973(18)	0.0544(8)
N4	0.2251(3)	0.4427(3)	0.0502(2)	0.0632(9)
C1	0.4947(4)	0.0503(3)	0.3457(2)	0.0577(10)
C8	−0.0386(4)	0.4211(3)	0.3102(3)	0.0599(10)
C9	−0.1336(5)	0.4324(4)	0.3837(3)	0.0725(13)
C10	−0.2453(5)	0.4081(4)	0.3961(3)	0.0873(15)
C11	−0.3359(6)	0.4182(6)	0.4650(4)	0.116(2)
H11A	−0.4102	0.3981	0.4736	0.139*
C12	−0.3068(7)	0.4596(7)	0.5181(4)	0.130(3)
H12A	−0.3646	0.4694	0.5638	0.156*
C13	−0.1979(8)	0.4870(6)	0.5069(3)	0.125(3)
H13A	−0.1850	0.5143	0.5459	0.150*

Table 2 (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C14	−0.1040(5)	0.4772(4)	0.4418(3)	0.0927(17)
H14A	−0.0299	0.4968	0.4352	0.111*
C15	0.3198(4)	0.1581(4)	0.1781(2)	0.0567(10)
Cl3[a]	0.5485(2)	0.2392(2)	0.06877(17)	0.1194(10)
C16[a]	0.3561(7)	0.1466(6)	0.0939(2)	0.055(2)
C17[a]	0.4513(6)	0.1844(5)	0.0438(3)	0.070(2)
C18[a]	0.4765(6)	0.1723(6)	−0.0315(3)	0.095(3)
H18A[a]	0.5402	0.1976	−0.0650	0.114*
C19[a]	0.4064(7)	0.1222(6)	−0.0567(2)	0.102(3)
H19A[a]	0.4232	0.1140	−0.1070	0.122*
C20[a]	0.3112(6)	0.0844(5)	−0.0065(3)	0.086(2)
H20A[a]	0.2643	0.0509	−0.0234	0.103*
C21[a]	0.2861(6)	0.0965(6)	0.0687(3)	0.067(2)
H21A[a]	0.2224	0.0712	0.1023	0.080*
Cl3B[b]	0.2167(5)	0.0574(4)	0.0808(3)	0.0967(15)
C16B[b]	0.3703(14)	0.1649(13)	0.0995(5)	0.054(4)
C17B[b]	0.3284(12)	0.1236(11)	0.0506(7)	0.071(4)
C18B[b]	0.3798(13)	0.1359(12)	−0.0255(6)	0.096(5)
H18B[b]	0.3518	0.1083	−0.0582	0.116*
C19B[b]	0.4730(13)	0.1895(13)	−0.0528(5)	0.104(5)
H19B[b]	0.5073	0.1977	−0.1037	0.125*
C20B[b]	0.5149(11)	0.2307(10)	−0.0039(7)	0.099(5)
H20B[b]	0.5772	0.2666	−0.0222	0.119*
C21B[b]	0.4635(13)	0.2184(12)	0.0722(6)	0.084(5)
H21B[b]	0.4916	0.2461	0.1049	0.101*
C22	0.2515(5)	0.5581(4)	0.2149(3)	0.0653(11)
C23	0.3118(4)	0.6368(3)	0.2305(2)	0.0555(10)
C24	0.2748(4)	0.7477(3)	0.2107(2)	0.0642(11)
C25	0.3357(5)	0.8158(4)	0.2268(3)	0.0760(14)
H25A	0.3087	0.8912	0.2135	0.091*
C26	0.4345(5)	0.7710(5)	0.2621(3)	0.0817(15)
H26A	0.4760	0.8155	0.2727	0.098*
C27	0.4717(5)	0.6614(5)	0.2817(3)	0.0887(15)
H27A	0.5390	0.6307	0.3058	0.106*
C28	0.4117(5)	0.5950(4)	0.2666(3)	0.0740(13)
H28A	0.4389	0.5199	0.2809	0.089*
C29	0.0326(5)	0.0626(4)	0.2915(3)	0.0789(13)
H29A	0.0947	0.0544	0.2474	0.095*
C30	−0.0754(6)	0.0323(5)	0.2972(3)	0.0970(17)
H30A	−0.0867	0.0064	0.2572	0.116*
C31	−0.1641(5)	0.0408(5)	0.3616(4)	0.0916(16)
H31A	−0.2369	0.0200	0.3663	0.110*
C32	−0.1477(4)	0.0804(4)	0.4211(3)	0.0687(12)
C33	−0.2354(4)	0.0894(4)	0.4912(3)	0.0850(15)
H33A	−0.3074	0.0662	0.4986	0.102*
C34	−0.2184(4)	0.1292(4)	0.5461(3)	0.0808(15)
H34A	−0.2787	0.1342	0.5911	0.097*
C35	−0.1092(4)	0.1647(4)	0.5378(2)	0.0658(12)
C36	−0.0878(5)	0.2104(4)	0.5933(3)	0.0826(14)
H36A	−0.1473	0.2196	0.6384	0.099*
C37	0.0192(5)	0.2414(5)	0.5819(3)	0.0859(15)
H37A	0.0345	0.2707	0.6190	0.103*
C38	0.1060(4)	0.2284(4)	0.5129(3)	0.0709(12)
H38A	0.1798	0.2490	0.5054	0.085*
C39	−0.0175(3)	0.1560(3)	0.4701(2)	0.0506(9)
C40	−0.0379(3)	0.1120(3)	0.4109(2)	0.0523(10)
C41	−0.0411(5)	0.2885(4)	0.1530(3)	0.0784(13)
H41A	−0.0610	0.2780	0.2048	0.094*

Table 2 (continued)

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C42	−0.1037(5)	0.2503(5)	0.1145(4)	0.104(2)
H42A	−0.1649	0.2154	0.1398	0.125*
C43	−0.0741(5)	0.2648(5)	0.0388(4)	0.104(2)
H43A	−0.1152	0.2394	0.0121	0.125*
C44	0.0179(5)	0.3177(4)	0.0004(3)	0.0764(14)
C45	0.0528(6)	0.3382(5)	−0.0792(3)	0.100(2)
H45A	0.0107	0.3182	−0.1082	0.120*
C46	0.1427(7)	0.3844(5)	−0.1119(3)	0.107(2)
H46A	0.1661	0.3926	−0.1637	0.129*
C47	0.2053(5)	0.4222(4)	−0.0709(3)	0.0837(16)
C48	0.2993(7)	0.4739(6)	−0.1032(4)	0.116(2)
H48A	0.3241	0.4856	−0.1548	0.139*
C49	0.3544(7)	0.5069(6)	−0.0602(4)	0.124(3)
H49A	0.4189	0.5398	−0.0816	0.149*
C50	0.3142(5)	0.4916(4)	0.0165(3)	0.0917(16)
H50A	0.3513	0.5167	0.0457	0.110*
C51	0.1710(4)	0.4069(3)	0.0075(2)	0.0593(11)
C52	0.0762(4)	0.3532(3)	0.0437(2)	0.0565(10)
O10	0.5701(5)	0.3055(5)	0.2163(3)	0.184(2)
H10A	0.4947	0.3122	0.2129	0.277*
H10B	0.5754	0.3652	0.2257	0.277*

[a]Occupancy: 0.662(3); [b]Occupancy: 0.338(3); [c]Occupancy: 0.5.

of structures but also due to their potential applications in gas storage and separation, magnetism, catalysis, sensor, luminescence, and so forth [3–12].

2-Chlorobenzoic acid and the deprotonated corresponding carboxylate anion is an excellent ligand and widely used in construction of coordination polymers because it posseses rich coordination modes, such as monodentate, chelating, and various modes of bridging coordination of two, three, or even more metal centers. It can also act as hydrogen-bond acceptor and donor in assembling supramolecular complexes [13, 14]. 1,10-Phenanthroline (phen) is a typical *N*-donor ligand and also widely used in coordination polymers, due to its rigidity, planarity, aromaticity, basicity and chelating capability [15, 16].

The asymmetric unit of the title complex consists of two Cd(II), four chlorobenzoato ligands, two phen ligands, one coordinated water molecule, and one free water molecule. Both Cd1 and Cd2 exhibit distorted pentagonal-bipyramidal coordination geometries. Cd1 is coordinated by two nitrogen atoms from one phen ligand, four oxygen atoms from three carboxylate ligands, and one oxygen atom from one water molecule. Cd2 is coordinated by two nitrogen atoms from one phen ligand and five oxygen atoms from three carboxylate ligands. The two Cd atoms are bridged by O3 and O5 to form a dinuclear complex. Each dinuclear unit is connected to adjacent ones through O—H···O hydrogen bonds.

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