Crystal structure of bis(2,2′-bipyridine-*N*,*N*′)bis(4-chlorobenzoato)cadmium(II) trihydrate, $[Cd(C_7H_4O_2Cl)_2(C_{10}H_8N_2)_2] \cdot 3H_2O$

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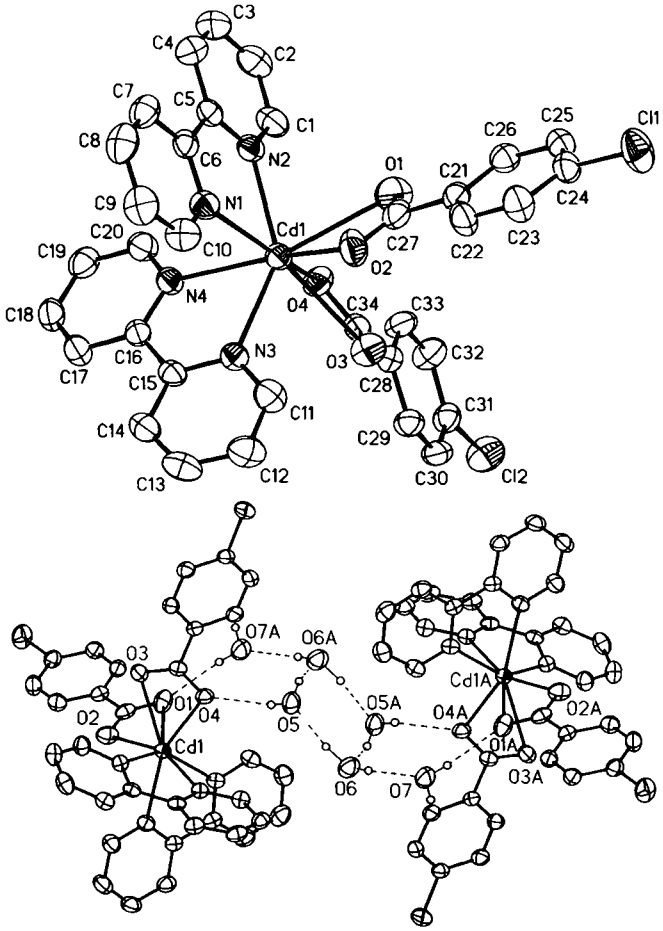

Abstract

$C_{34}H_{30}CdCl_2N_4O_7$, monoclinic, $P12_1/c1$ (no. 14), $a = 13.7555(2)$ Å, $b = 20.4059(3)$ Å, $c = 12.3696(2)$ Å, $\beta = 106.568(1)°$, $V = 3327.9$ Å^3, $Z = 4$, $R_{gt}(F) = 0.030$, $wR_{ref}(F^2) = 0.068$, $T = 293$ K.

Source of material

Freshly prepared $CdCO_3$ (0.17 g, 0.99 mmol), 2,2′-bipyridine (0.08 g, 0.51 mmol), 4-chlorobenzoic acid (0.12 g, 0.77 mmol), 12 mL CH_3OH/H_2O (1:2 *v*/*v*) were mixed and stirred for ca. 4.5 h. Subsequently, the resulting suspension was heated in a 23 ml Teflon-lined stainless steel autoclave at 393 K for 6 day. After the autoclave was cooled to room temperature, the solid was filtered off. The resulting colorless filtrate was allowed to stand at room temperature and slow evaporation for two months afforded red block-shaped crystals.

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Experimental details

While H atoms bonded to C atoms were treated under using riding rigid-body approximations and restrained U_{iso} values, all water H atoms were found from Fourier difference maps and refined freely.

Discussion

The title crystal structure is similar to the structures of bipyridine-cadmium(II) salicylate, $C_{27}H_{25}CdN_3O_7$ [1], and bipyridine-cadmium(II) fluorobenzoate, $[Cd(H_2O)(C_7H_4O_2F)_2(C_{10}H_8N_2)]$ [2]. The title complex molecules $[Cd(C_7H_4O_2Cl)_2(C_{10}H_8N_2)_2]$ (figure, top) and water molecules build up the crystal structure. The polyhdron of the Cd atom is a distorted bicapped dodecahedron formed by four N atoms from two bidentately chelating 2,2-bipyridine ligands and four O atoms from two 4-chlorobenzoic acid anions ligands with Cd—N distances varying between 2.368(2) Å and 2.506(2) Å and Cd—O distances of 2.309(1) Å and 2.756(2) Å. Along the [010] direction, the crystal water molecules show hydrogen-bonding to the coordinated carboxylate O atom of 4-chlorobenzoic acid anions. The carboxylate O4 atoms of the 4-chlorobenzoic acid anions and crystal water molecules are linked to each other with d(O–H···O) between 2.807 Å and 3.013 Å (∠O–H···O = 165.5° – 177.6°) to complete 1D supramolecular chains. Moreover, there are hydrogen bonds between the water molecules themselves and a weak hydrogen interaction with d(C14–H14···O5^i) = 3.344 Å and, ∠C14–H14···O5^i = 143.6° (i: $1-x,1-y,2-z$). Through the hydrogen bond interactions the complex molecules are interlinked to form corrugated layers parallel (100). The large displacement parameters of 0.21(2) Å^2 and 0.26(3) Å^2 for H5A and H6A, respectively, represent the delocalization of these atoms in the O5-O6-O5A-O6A square which is formed by four hydrogen bonds being pairwise equivalent (figure, bottom). Interplanar distances of 3.398 Å and 3.488 Å indicate π-π interactions between neighboring bipyridine ligands. A weak hydrogen interaction was observed for C23–H23···Cl2^{ii} (d(C23···Cl2^{ii}) = 3.625 Å and ∠C23–H23···Cl2^{ii} = 139.8°, ii: $-1+x,y,z$).

Table 1. Data collection and handling.

Crystal:	red block, size 0.19 x 0.23 x 0.28 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.72 cm^{-1}
Diffractometer, scan mode:	Bruker SMART APEX CCD II, ω/φ
$2\theta_{max}$:	56.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	34964, 7990
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 5686
$N(param)_{refined}$:	458
Programs:	SHELXS-97 [3], SHELXL-97 [4]

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

Atom	Site	x	y	z	U_{iso}
H(5A)	4e	0.508(3)	0.568(2)	0.553(5)	0.21(2)
H(5B)	4e	0.502(2)	0.552(1)	0.674(2)	0.034(8)
H(6A)	4e	0.481(4)	0.954(3)	0.890(5)	0.26(3)
H(6B)	4e	0.447(2)	0.887(1)	0.928(2)	0.052(9)
H(7A)	4e	0.280(2)	0.823(2)	0.951(3)	0.10(1)
H(7B)	4e	0.320(2)	0.788(2)	0.890(3)	0.10(1)
H(1)	4e	0.3077	0.5501	0.5182	0.066
H(2)	4e	0.2857	0.4772	0.3730	0.078
H(3)	4e	0.1599	0.3983	0.3482	0.085
H(4)	4e	0.0627	0.3940	0.4715	0.073
H(7)	4e	−0.0213	0.3928	0.5900	0.068
H(8)	4e	−0.1010	0.3905	0.7305	0.081
H(9)	4e	−0.0530	0.4639	0.8779	0.081
H(10)	4e	0.0728	0.5385	0.8793	0.072
H(11)	4e	0.2223	0.6797	0.9428	0.069

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(12)	4e	0.2375	0.6859	1.1325	0.079
H(13)	4e	0.2929	0.5937	1.2434	0.077
H(14)	4e	0.3421	0.5020	1.1629	0.063
H(17)	4e	0.4161	0.4297	1.0902	0.065
H(18)	4e	0.4935	0.3551	1.0016	0.069
H(19)	4e	0.4772	0.3660	0.8124	0.064
H(20)	4e	0.3778	0.4497	0.7138	0.062
H(22)	4e	−0.0325	0.7440	0.6742	0.069
H(23)	4e	−0.1452	0.8250	0.5885	0.074
H(25)	4e	−0.0193	0.8314	0.3343	0.062
H(26)	4e	0.0872	0.7470	0.4161	0.059
H(29)	4e	0.5154	0.7621	0.9121	0.058
H(30)	4e	0.6691	0.8121	0.9285	0.060
H(32)	4e	0.6838	0.7225	0.6454	0.069
H(33)	4e	0.5315	0.6711	0.6324	0.063

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

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd(1)	4e	0.24248(1)	0.586939(7)	0.74170(1)	0.03943(9)	0.0423(1)	0.0380(1)	−0.00217(7)	0.00866(6)	0.00314(7)
N(1)	4e	0.1033(1)	0.50959(8)	0.7417(2)	0.0421(9)	0.052(1)	0.046(1)	−0.0035(8)	0.0102(8)	0.0018(9)
N(2)	4e	0.2047(1)	0.51513(8)	0.5842(1)	0.0425(9)	0.047(1)	0.039(1)	−0.0048(8)	0.0044(8)	0.0054(8)
N(3)	4e	0.2748(1)	0.59088(8)	0.9401(1)	0.0428(9)	0.046(1)	0.042(1)	0.0027(8)	0.0096(8)	0.0025(8)
N(4)	4e	0.3435(1)	0.49108(8)	0.8405(1)	0.0419(9)	0.043(1)	0.040(1)	−0.0008(8)	0.0072(8)	0.0043(8)
O(1)	4e	0.1810(1)	0.66751(8)	0.5642(2)	0.062(1)	0.069(1)	0.077(1)	0.0214(9)	0.0086(9)	−0.0059(9)
O(2)	4e	0.1104(1)	0.66262(8)	0.7035(2)	0.059(1)	0.056(1)	0.074(1)	0.0043(8)	0.0065(9)	0.0216(9)
O(3)	4e	0.3491(1)	0.70111(8)	0.8107(1)	0.0560(9)	0.064(1)	0.064(1)	−0.0093(8)	0.0275(8)	−0.0077(8)
O(4)	4e	0.3958(1)	0.61976(7)	0.7181(1)	0.0481(8)	0.0440(9)	0.061(1)	−0.0099(7)	0.0125(7)	−0.0048(7)
O(5)	4e	0.5339(2)	0.5371(1)	0.6533(2)	0.076(1)	0.070(1)	0.071(1)	0.021(1)	0.026(1)	0.007(1)
O(6)	4e	0.4923(2)	0.9098(1)	0.9355(2)	0.107(2)	0.060(1)	0.078(2)	−0.009(1)	0.030(1)	−0.009(1)
O(7)	4e	0.3174(2)	0.8237(1)	0.9125(2)	0.144(2)	0.059(1)	0.107(2)	−0.016(1)	0.075(2)	−0.011(1)
Cl(1)	4e	−0.17384(6)	0.89927(3)	0.39326(6)	0.0962(5)	0.0776(5)	0.0837(5)	0.0415(4)	0.0310(4)	0.0275(4)
Cl(2)	4e	0.80290(5)	0.81295(3)	0.79597(6)	0.0504(3)	0.0745(4)	0.0861(5)	−0.0180(3)	0.0231(3)	−0.0071(3)
C(1)	4e	0.2587(2)	0.5175(1)	0.5097(2)	0.052(1)	0.068(2)	0.042(1)	−0.006(1)	0.009(1)	0.008(1)
C(2)	4e	0.2455(2)	0.4747(1)	0.4218(2)	0.072(2)	0.079(2)	0.044(2)	0.005(2)	0.019(1)	0.005(1)
C(3)	4e	0.1712(2)	0.4279(1)	0.4077(2)	0.098(2)	0.064(2)	0.047(2)	0.001(2)	0.015(1)	−0.010(1)
C(4)	4e	0.1140(2)	0.4250(1)	0.4814(2)	0.069(2)	0.054(2)	0.054(2)	−0.011(1)	0.010(1)	−0.007(1)
C(5)	4e	0.1326(2)	0.4687(1)	0.5712(2)	0.042(1)	0.041(1)	0.041(1)	0.0040(9)	−0.0005(9)	0.0061(9)
C(6)	4e	0.0758(1)	0.4665(1)	0.6567(2)	0.035(1)	0.040(1)	0.047(1)	0.0023(9)	0.0021(9)	0.0077(9)
C(7)	4e	−0.0019(2)	0.4218(1)	0.6503(2)	0.045(1)	0.047(1)	0.073(2)	−0.003(1)	0.010(1)	−0.001(1)
C(8)	4e	−0.0497(2)	0.4207(1)	0.7335(3)	0.049(1)	0.059(2)	0.098(2)	−0.009(1)	0.026(1)	0.008(2)
C(9)	4e	−0.0217(2)	0.4640(1)	0.8204(2)	0.054(1)	0.076(2)	0.080(2)	−0.002(1)	0.031(1)	0.010(2)
C(10)	4e	0.0545(2)	0.5082(1)	0.8209(2)	0.053(1)	0.069(2)	0.061(2)	−0.004(1)	0.019(1)	−0.004(1)
C(11)	4e	0.2476(2)	0.6437(1)	0.9882(2)	0.056(1)	0.061(2)	0.056(2)	0.012(1)	0.018(1)	0.003(1)
C(12)	4e	0.2551(2)	0.6477(1)	1.1015(2)	0.065(2)	0.077(2)	0.057(2)	0.012(1)	0.022(1)	−0.011(1)
C(13)	4e	0.2895(2)	0.5935(1)	1.1672(2)	0.055(1)	0.096(2)	0.040(1)	0.002(1)	0.014(1)	−0.004(1)
C(14)	4e	0.3187(2)	0.5389(1)	1.1192(2)	0.050(1)	0.063(2)	0.042(1)	−0.003(1)	0.009(1)	0.006(1)
C(15)	4e	0.3131(1)	0.5391(1)	1.0060(2)	0.034(1)	0.050(1)	0.037(1)	−0.0093(9)	0.0048(9)	0.0042(9)
C(16)	4e	0.3551(1)	0.4853(1)	0.9518(2)	0.035(1)	0.041(1)	0.043(1)	−0.0072(9)	0.0028(9)	0.0050(9)
C(17)	4e	0.4102(2)	0.4339(1)	1.0138(2)	0.060(1)	0.052(1)	0.047(1)	0.001(1)	0.007(1)	0.011(1)
C(18)	4e	0.4557(2)	0.3894(1)	0.9608(2)	0.059(1)	0.044(1)	0.061(2)	0.002(1)	0.002(1)	0.012(1)
C(19)	4e	0.4457(2)	0.3953(1)	0.8491(2)	0.045(1)	0.046(1)	0.066(2)	−0.003(1)	0.009(1)	−0.004(1)
C(20)	4e	0.3871(2)	0.4464(1)	0.7911(2)	0.051(1)	0.054(1)	0.046(1)	0.000(1)	0.010(1)	0.001(1)
C(21)	4e	0.0410(2)	0.7375(1)	0.5550(2)	0.045(1)	0.038(1)	0.050(1)	−0.0025(9)	0.006(1)	−0.001(1)
C(22)	4e	−0.0300(2)	0.7612(1)	0.6055(2)	0.071(2)	0.054(1)	0.050(1)	0.006(1)	0.023(1)	0.014(1)
C(23)	4e	−0.0969(2)	0.8100(1)	0.5549(2)	0.073(2)	0.060(2)	0.061(2)	0.019(1)	0.032(1)	0.008(1)
C(24)	4e	−0.0914(2)	0.8361(1)	0.4545(2)	0.058(1)	0.045(1)	0.051(1)	0.009(1)	0.013(1)	0.006(1)
C(25)	4e	−0.0224(2)	0.8134(1)	0.4023(2)	0.059(1)	0.050(1)	0.045(1)	0.002(1)	0.015(1)	0.006(1)
C(26)	4e	0.0418(2)	0.7636(1)	0.4524(2)	0.048(1)	0.048(1)	0.051(1)	0.001(1)	0.014(1)	−0.003(1)
C(27)	4e	0.1167(2)	0.6853(1)	0.6119(2)	0.049(1)	0.038(1)	0.063(2)	−0.006(1)	−0.003(1)	−0.001(1)
C(28)	4e	0.5080(2)	0.71027(9)	0.7721(2)	0.047(1)	0.036(1)	0.041(1)	−0.0042(9)	0.0105(9)	0.0013(9)
C(29)	4e	0.5498(2)	0.7535(1)	0.8589(2)	0.056(1)	0.049(1)	0.041(1)	−0.009(1)	0.018(1)	−0.006(1)
C(30)	4e	0.6412(2)	0.7839(1)	0.8687(2)	0.057(1)	0.049(1)	0.043(1)	−0.012(1)	0.011(1)	−0.008(1)
C(31)	4e	0.6905(2)	0.7720(1)	0.7882(2)	0.042(1)	0.041(1)	0.054(1)	−0.0062(9)	0.012(1)	0.002(1)
C(32)	4e	0.6501(2)	0.7301(1)	0.6996(2)	0.064(2)	0.054(1)	0.063(2)	−0.011(1)	0.033(1)	−0.012(1)
C(33)	4e	0.5591(2)	0.6994(1)	0.6921(2)	0.065(2)	0.049(1)	0.047(1)	−0.017(1)	0.020(1)	−0.016(1)
C(34)	4e	0.4100(2)	0.6756(1)	0.7664(2)	0.044(1)	0.047(1)	0.040(1)	−0.003(1)	0.008(1)	0.007(1)

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