Crystal structure of diaquabis(aspirinato)cadmium(II), $Cd(H_2O)_2(C_9H_9O_5)_2$

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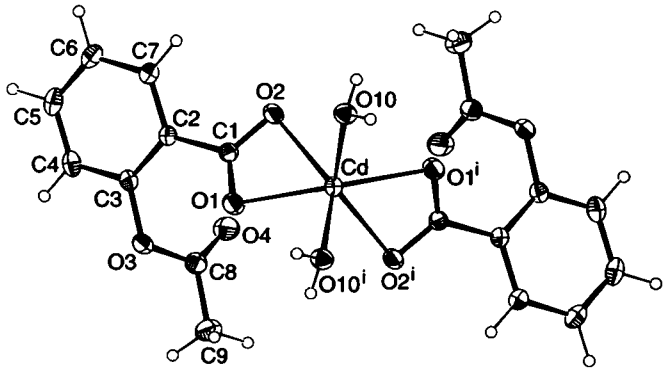

Abstract

$C_{18}H_{18}CdO_{10}$, monoclinic, $C12/c1$ (no. 15),
$a = 25.971(6)$ Å, $b = 7.369(2)$ Å, $c = 10.752(5)$ Å,
$\beta = 106.46(4)°$, $V = 1973.4$ Å^3, $Z = 4$,
$R_{gt}(F) = 0.026$, $wR_{ref}(F) = 0.035$, $T = 293$ K.

Source of material

In the synthesis of diaquabis(aspirinato)cadmium(II), a solution of sodium acetylsalicylate was prepared by neutralizing 1.6 g (0.01 mol) of acetylsalicylic acid in 15 mL of water at 273 K with a solution of 50 % NaOH. The final *p*H of the solution was in the range of 8.0 to 9.0. The $CdCl_2$ solution, prepared by dissolving 1.542 g (0.005 mol) of $Cd(NO_3)_2$ in 30 mL of water, was added to a stirred solution of sodium acetylsalicylate during a period of a few minutes. This solution was left upon standing for 24 hours. Colorless crystalline material precipitated slowly and was removed by filtration, washed with water, and left to dry at room temperature.

Discussion

Since zinc and cadmium belong to the same group 12 of the Periodic System of Elements, this study is an extension of an ongoing crystal structure investigation of non-steroidal zinc carboxylate complexes as anti-inflammatory and anticonvulsant drug agents [1].

The asymmetric unit of $[Cd(aspirinate)_2(H_2O)_2]$ contains one half of the formula unit. The Cd atom lies in the two-fold axis at ½,*y*,¾ (4*e* site), in a highly irregular octahedral geometry. In this bis(chelate)cadmium complex, the aspirinato ligand accounts for four basal oxygen donor atoms: O1, O2, $O1^i$, and $O2^i$ (symmetry code i: $1-x,y,\frac{3}{2}-z$) and bond lengths for Cd—O1, 2.276(2) Å, and Cd—O2, 2.411(2) Å, with their two-fold symmetrically related distances for Cd—$O1^i$ and Cd—$O2^i$. The remaining two sites are occupied by water oxygen atoms, Cd—Ow and Cd—Ow^i, with bond lengths of 2.259(2) Å. It is remarkable that these water oxygen atoms are the most tightly bonded of these oxygen atoms and the corresponding angle for Ow–Cd–Ow^i of 88.31(8)° leads to a distorted bicapped square pyramidal environment. Moreover, in the basal atomic donor set, there is a tetrahedral distortion of the four donor atoms: O1, O2, $O1^i$, and $O2^i$, with distances from their mean plane being 0.296 Å for O1 and –0.296 Å for O2, with Cd being 1.035 Å out of this plane. This hexacoordinated mononuclear form differs from that found in the dinuclear tetrakis(salicylato)tetraaquadicadmium complex $[Cd_2(salicylate)_4(H_2O)_4]$ [2] in which Cd is heptacoordinated and surrounded by seven oxygen atoms to form a distorted pentagonal bipyramid: five bonds formed with the aspirinato ligands, and two bonds formed with water molecules in a *trans* arrangement with respect to the plane through the other oxygen atoms.

Moreover, in this complex, the salicylate ligands are not equivalent since two of them bridge the Cd atoms giving rise to the dinuclear structure. In the mononuclear $[Cd(aspirinate)_2(H_2O)_2]$ complex, the Cd—O (carboxylato) distances lie in the range found for the dinuclear salicylate compound, 2.291(4) Å to 2.530(4) Å, as well as the Cd—Ow distance [2.259(2) Å] which lies in the range of the corresponding bonds in the dinuclear complex, 2.246(5) Å to 2.321(5) Å. The O1—C1 and O2—C1 bond lengths are equivalent and lie within the range found for the dimeric complex, 1.254(5) to 1.274(6) Å. Bond distances and angles for the aspirinato ligand are similar to those found in mononuclear $[Cu(aspirinate)_2(pyridine)_2]$ [3] or in dinuclear $[Cu_2(aspirinate)_4(dimethylformamide)_2]$ [4] except for the carboxylato ligand which exhibits a *syn-syn* bidentate bridging mode in this later compound. Packing is mainly determined by intermolecular O–H···O hydrogen bonds formed with each hydrogen atom of the water molecules bonding to the carbonyl oxygen of the acetyl group of one second supplementary aspirinate and to the carboxylato oxygen atom of an other aspirinato ligand.

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Table 1. Data collection and handling.

Crystal:	colorless, parallelepipedic, size 0.25 × 0.26 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	11.60 cm^{-1}
Diffractometer, scan mode:	Enraf-Nonius CAD4, ω-2θ
$2\theta_{max}$:	59.93°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3123, 2865
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 3\ \sigma(I_{obs})$, 2519
$N(param)_{refined}$:	132
Programs:	SIR92 [5], CRYSTALS [6], CAMERON [7], RC93 [8]

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

Atom	Site	x	y	z	U_{iso}
H(41)	8*f*	0.7464	0.4115	0.8935	0.047
H(51)	8*f*	0.7665	0.4126	0.6901	0.056
H(61)	8*f*	0.7050	0.2791	0.5032	0.052
H(71)	8*f*	0.6240	0.1405	0.5212	0.042
H(91)	8*f*	0.5828	0.3892	1.1045	0.060
H(92)	8*f*	0.6478	0.3683	1.1633	0.060
H(93)	8*f*	0.6110	0.1906	1.1068	0.060
H(101)	8*f*	0.4644	−0.3679	0.5978	0.050
H(102)	8*f*	0.4737	−0.2446	0.5231	0.050

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	4*e*	½	−0.07464(2)	¾	0.0237(1)	0.0301(1)	0.0312(1)	0	0.00690(6)	0
O(1)	8*f*	0.58600(7)	0.0256(3)	0.8284(2)	0.0357(7)	0.0511(8)	0.0343(7)	−0.0108(6)	0.0046(6)	0.0120(6)
O(2)	8*f*	0.54619(6)	0.1060(2)	0.6283(1)	0.0305(6)	0.0546(9)	0.0299(6)	−0.0117(6)	0.0026(5)	0.0066(6)
O(3)	8*f*	0.66577(6)	0.2724(2)	0.9483(1)	0.0324(6)	0.0435(8)	0.0291(6)	0.0013(6)	0.0031(5)	−0.0023(5)
O(4)	8*f*	0.59361(8)	0.4529(3)	0.8815(2)	0.053(1)	0.0501(9)	0.0431(8)	0.0185(8)	0.0150(7)	0.0011(7)
O(100)	8*f*	0.48533(6)	−0.2946(2)	0.5976(1)	0.0401(7)	0.0359(7)	0.0327(6)	−0.0055(6)	0.0085(5)	−0.0016(5)
C(1)	8*f*	0.58672(7)	0.1054(2)	0.7256(2)	0.0273(7)	0.0269(7)	0.0287(7)	−0.0028(6)	0.0073(6)	−0.0016(6)
C(2)	8*f*	0.63745(7)	0.1958(2)	0.7175(2)	0.0247(7)	0.0266(7)	0.0304(7)	−0.0005(6)	0.0074(6)	−0.0001(6)
C(3)	8*f*	0.67373(7)	0.2752(3)	0.8254(2)	0.0257(7)	0.0299(7)	0.0325(8)	0.0017(6)	0.0048(6)	−0.0010(6)
C(4)	8*f*	0.72088(8)	0.3548(3)	0.8156(2)	0.0261(8)	0.040(1)	0.050(1)	−0.0045(7)	0.0052(7)	−0.0033(9)
C(5)	8*f*	0.73238(9)	0.3557(4)	0.6974(3)	0.0288(9)	0.047(1)	0.063(1)	−0.0031(8)	0.0185(9)	0.003(1)
C(6)	8*f*	0.69678(9)	0.2775(3)	0.5888(2)	0.038(1)	0.046(1)	0.047(1)	0.0025(9)	0.0228(8)	0.0022(9)
C(7)	8*f*	0.64947(8)	0.1974(3)	0.5993(2)	0.0305(8)	0.0383(9)	0.0343(8)	0.0014(7)	0.0116(7)	−0.0006(7)
C(8)	8*f*	0.62179(8)	0.3590(3)	0.9646(2)	0.0358(9)	0.0335(8)	0.0347(9)	−0.0037(7)	0.0083(7)	−0.0062(7)
C(9)	8*f*	0.6154(1)	0.3234(4)	1.0954(2)	0.056(1)	0.051(1)	0.040(1)	−0.007(1)	0.020(1)	−0.0007(9)

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