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Bis(acetylsalicylato-κ^2O,O')diaquacadmium(II)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.020
wR factor = 0.055
Data-to-parameter ratio = 20.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

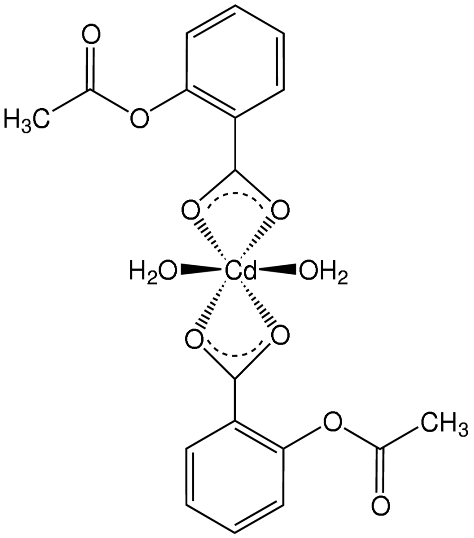
In the title compound {systematic name: bis[2-(acetyloxy)benzoato-κ^2O,O']diaquacadmium(II)}, $[Cd(C_9H_7O_4)_2(H_2O)_2]$, the Cd^{II} ion is located on a twofold rotation axis and is coordinated by two water molecules and two aspirinate ligands. The complex is almost isostructural with the corresponding zinc(II) complex. However, for the title compound, the aspirinate should be considered as an asymmetric chelating ligand, with Cd—O(carboxylate) bond lengths of 2.2777 (12) and 2.4121 (12) Å.

Comment

The coordination chemistry of non-steroidal anti-inflammatory drugs (NSAIDs) has been studied by several groups worldwide. Some complexes have increased pharmaceutical or biological activity with respect to the drug, or are interesting from a purely chemical point of view (Abuhijleh & Woods, 2001; Bucci *et al.*, 2000; Fini *et al.*, 2001; Kovala-Demertzi *et al.*, 1998; Méndez-Rojas *et al.*, 1999). However, there is still little information on the interactions of heavy and other pollutant metals with these drugs. In the case of Cd^{II}, anthropogenic activities have increased the amounts of this heavy metal ion released in the environment (air, water and soil), especially those related to fuel burning, mining, metal processing, plastic production, and degradation of old batteries, among others. However, it has been established that 80–90% of the cadmium(II) that enters into organisms is ingested from water or foods contaminated by contact with pipes or containers containing this metal ion (Harte *et al.*, 1991). Human exposure during working time and cadmium(II)-contaminated drinking water have been shown to be related to severe illnesses (Friberg *et al.*, 1974; Kobayashi, 1978). Tobacco smokers also increase the risk as they have twice the levels of cadmium(II) in their organisms than the non-smoking population (Yue, 2001). As some of the symptoms of cadmium(II) intoxication (extreme restlessness, headache, chest pain and abdominal pain, among others) may not be traced to metal intoxication, analgesics such as aspirin (acetylsalicylic acid) may be prescribed or even acquired over-the-counter, without a medical prescription.

Most of the NSAIDs, including aspirin, possess a carboxylate group, which is able to coordinate metal ions. It is thus important to characterize discrete metal complexes formed by the interaction of pollutant metals with NSAIDs, in order to better understand the possible synergistic or toxic effects that this interaction may produce (Méndez-Rojas *et al.*, 1999). We report here the crystal structure of a cadmium(II) complex including acetylsalicylate as a ligand, (I).

The asymmetric unit of (I) contains one-half molecule, with the Cd atom located on a twofold rotation axis and the other atoms placed in general positions. The metal center is then coordinated by two carboxylate groups of two symmetry-related acetylsalicylate ligands and two symmetry-related water molecules (Fig. 1). The angles around Cd1 span a large range [55.52 (4)–142.08 (7)°; Table 1], the bite angle arising from the carboxylate group. Such a distorted [CdO_6] coordination sphere including twofold symmetry was previously observed with *p*-nitrobenzoate or *p*-chlorobenzoate in place of aspirinate (Rodesiler *et al.*, 1985). Another common feature with these previously reported structures is the marked asymmetry of the carboxylate coordination, with Cd—O bond lengths of 2.2777 (12) and 2.4121 (12) Å. With *p*-nitrobenzoate as ligand, corresponding bond lengths are 2.258 and 2.509 Å.



(I)

The coordination geometry can alternatively be described as a distorted tetrahedron, by considering each carboxylate group as a monodentate ligand. This description is supported by a comparison of (I) with the corresponding Zn-containing complex, characterized at 100.0 (1) K (Spasojević-de Biré *et al.*, 2002); this compound crystallizes in the same space group, *C*2/*c*, with very similar cell parameters [a previous room-temperature study included a refinement of the zinc(II) complex in the space group *Cc* (Hartmann & Vahrenkamp, 1994), but a recent reinterpretation confirmed the correct space group to be *C*2/*c* (Marsh, 2004)]. The zinc(II) complex may be considered as tetrahedral, with one O atom of the carboxylate group coordinating the metal center [Zn—O = 1.9957 (5) Å], while the non-coordinating O atom involves a Zn···O separation of 2.5200 (5) Å (Spasojević-de Biré *et al.*, 2002). When substituting Zn by Cd, the increase of 0.19 Å for the van der Waals radius of the metal (Bondi, 1964) allows the coordination of the two O atoms of the carboxylate group, although in an asymmetric manner. In both Zn and Cd complexes, the acetyl group remains uncoordinated and the conformation of the aspirinate moiety is almost unaffected by the metal substitution. For instance, a fit between the aspirinate ligands in (I) and the room-temperature refinement of the zinc(II) complex (Marsh, 2004), excluding H atoms, gives an r.m.s. deviation of 0.020 Å. In contrast, significantly different conformations are observed for this ligand in copper(II) complexes, mainly because the carboxylate group then acts as a bidentate bridging group, forming binuclear (Viossat *et al.*, 2003) or polymeric (Manojlović-Muir, 1973; Garcia *et al.*, 2003) species.

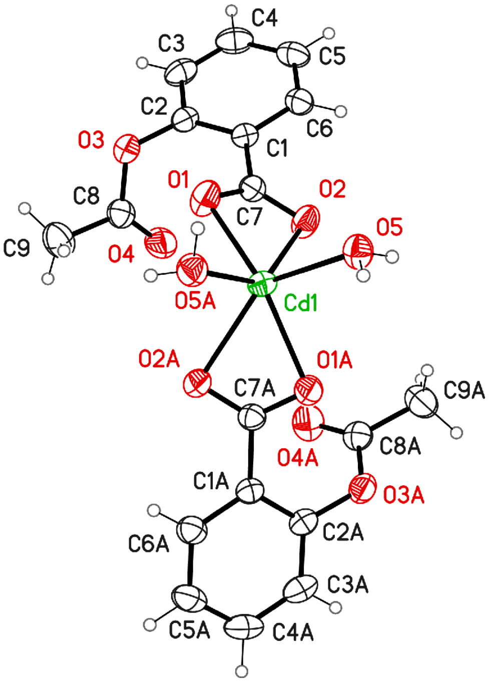


Figure 1
The structure of (I) with displacement ellipsoids at the 50% probability level. Atoms labelled with the suffix A are related by the symmetry code ($1 - x, y, \frac{1}{2} - z$).

Experimental

All manipulations were carried out in air. Methanol (reagent grade), $CdCl_2 \cdot 2.5H_2O$ and acetylsalicylic acid were purchased from Aldrich and used as received. Into a 100 ml round-bottomed flask containing acetylsalicylic acid (1.00 g, 11.1 mmol) in a mixture of methanol (20 ml) and water (15 ml) was added slowly a 0.5 *M* NaOH solution (11.1 ml) with stirring at 298 K. After addition was complete, $CdCl_2 \cdot 2.5H_2O$ (0.634 g, 5.55 mmol) was added with stirring and a cloudy solution formed. Stirring was continued for 2 h and, after this time, most of the solvent was removed under vacuum and the remaining solution left for slow evaporation. The crystalline product was isolated by filtration and dried (yield: 92%).

Crystal data

$[Cd(C_9H_7O_4)_2(H_2O)_2]$	$D_x = 1.702$ Mg m^{-3}
$M_r = 506.72$	Mo *Kα* radiation
Monoclinic, *C*2/*c*	Cell parameters from 56 reflections
$a = 26.006$ (3) Å	$\theta = 4.5–13.1°$
$b = 7.3714$ (6) Å	$\mu = 1.16$ mm^{-1}
$c = 10.7541$ (12) Å	$T = 293$ (2) K
$\beta = 106.416$ (8)°	Irregular fragment, colorless
$V = 1977.6$ (3) Å^3	0.6 × 0.4 × 0.2 mm
$Z = 4$	

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Data collection

Bruker *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: ψ scan (Siemens, 1996)
$T_{\rm min} = 0.607$, $T_{\rm max} = 0.794$
6264 measured reflections
2881 independent reflections
2763 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.017$
$\theta_{\rm max} = 30.0^\circ$
$h = -36 \rightarrow 16$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.055$
$S = 1.11$
2881 reflections
139 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0309P)^2 + 0.8564P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.007$
$\Delta\rho_{\rm max} = 0.33$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.58$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—O5	2.2574 (11)	C8—O3	1.3590 (19)
Cd1—O1	2.2777 (12)	C8—C9	1.489 (2)
Cd1—O2	2.4121 (12)	O5—H51	0.81 (3)
C8—O4	1.202 (2)	O5—H52	0.86 (4)
O5—Cd1—O5$^{\rm i}$	88.01 (6)	O1$^{\rm i}$—Cd1—O2	101.95 (5)
O5—Cd1—O1	116.79 (5)	O2—Cd1—O2$^{\rm i}$	112.91 (7)
O5$^{\rm i}$—Cd1—O1	90.96 (4)	O4—C8—O3	122.24 (15)
O1—Cd1—O1$^{\rm i}$	142.08 (7)	O4—C8—C9	126.47 (17)
O5—Cd1—O2	90.86 (4)	O3—C8—C9	111.29 (14)
O5$^{\rm i}$—Cd1—O2	141.26 (4)	H51—O5—H52	111 (3)
O1—Cd1—O2	55.52 (4)		

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Aqua H atoms were found in a difference map and the remaining H atoms were placed in idealized positions. Aqua H atoms were refined with free coordinates and a fixed isotropic displacement parameter [$U_{\rm iso}$(H) = 0.08 Å^2]. Other H atoms were treated as riding atoms, with C—H distances constrained to 0.96 (methyl groups) and 0.93 Å (aromatic C—H). Isotropic displacement parameters were fixed at $U_{\rm iso}({\rm H}) = xU_{\rm eq}$(parent C), with $x = 1.5$ for the methyl group and $x = 1.2$ for aromatic C—H groups.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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