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## Structure of Diaquasuccinatocadmium(II) Hemihydrate

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**Abstract.**  $C_4H_8CdO_6 \cdot \frac{1}{2}H_2O$ ,  $M_r = 273.5$ , monoclinic,  $P2_1/a$ ,  $Z = 8$ ,  $a = 8.405(2)$ ,  $b = 12.719(4)$ ,  $c = 15.295(7)$  Å,  $\beta = 96.20(1)^\circ$ ,  $V = 1625$  Å<sup>3</sup>,  $D_x = 2.23$ ,  $D_m = 2.17(2)$  Mg m<sup>-3</sup>,  $\mu = 2.66$  mm<sup>-1</sup>,  $\lambda = 0.71073$  Å; final  $R = 0.040$  with 3966 observations. The structure consists of two crystallographically independent seven-coordinate Cd atoms in an approximately pentagonal-bipyramidal arrangement. These are then bridged by succinate ions to form a three-dimensional polymer.

**Introduction.** <sup>113</sup>Cd NMR spectroscopy with a chemical-shift range of ~850 p.p.m. has been shown in recent years to offer potential as a sensitive probe of metal-ion sites in a variety of compounds (Rodesiler, Griffith, Ellis & Amma, 1980, and references therein). However, there is a lack of single-crystal X-ray structure data to correlate with NMR data deemed necessary to place the <sup>113</sup>Cd NMR on a solid base as a probe of metal sites. As part of a comprehensive program involved in the synthesis, crystal structure

analysis and <sup>113</sup>Cd NMR measurement, we synthesized the title compound and determined its crystal structure.

The title compound was prepared by mixing 30 ml of a 0.1 M aqueous solution of Cd(NO<sub>3</sub>)<sub>2</sub> and 60 ml of 0.1 M succinic acid and adjusting to a pH of 6.5 with NaOH. Crystals grew by slow evaporation of the resulting solution over a period of days. The crystalline compound was not soluble in the solvents we have used on other Cd complexes and we were not able to obtain a solution <sup>113</sup>Cd Fourier transform (FT) NMR. However, efforts are underway to make <sup>113</sup>Cd FT NMR measurements on solids in the near future. Hence, although the data presented herein are not immediately useful for the crystal structure/<sup>113</sup>Cd NMR correlations, they will be useful in the future. In addition, the coordination polyhedron presented here is similar to that of bis(*o*-hydroxybenzoato)cadmium(II) dihydrate and bis(*p*-aminobenzoato)cadmium(II) monohydrate for which we have <sup>113</sup>Cd NMR solution data.

A single crystal ~0.2 × 0.3 × 0.3 mm was mounted on a CAD-4 diffractometer interfaced to a PDP-11/40 computer and the crystal was aligned and intensity data collected by standard techniques (Enraf–Nonius, 1980). Details are found in Table 1.

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Table 1. Cell data, data collection and refinement parameters

Wavelength,  $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$   
 Graphite monochromator,  $2\theta = 6.1^\circ$   
 Space group  $P2_1/a$   
 $h0l: h = 2n + 1; 0k0: k = 2n + 1$  absent  
 $\mu = 2.66 \text{ mm}^{-1}$   
 Faces of the form  $\{100\}\{110\}\{011\}$   
 Absorption corrections were made and the maximum and minimum transmission factors were 0.524–0.466 (Frenz, 1980)  
 $P$  factor = 0.030 in  $\sigma(F_o^2) = \{\sigma(I_{\text{raw}})^2 + (PI_{\text{raw}})^2\}^{1/2}/Lp$  and  $w = 1/\sigma(F_o)^2$   
 Data considered non-zero if  $F^2 > 4\sigma(F^2)$   
 4726 independent  $hkl$ 's measured in the  $\omega$ - $2\theta$  mode  
 3966 reflections used to solve and refine the structure  
 Variable scan speed with preliminary scan speed of  $4^\circ (2\theta) \text{ min}^{-1}$   
 25 reflections used in orientation matrix (checked every 24 h)  
 3 standard reflections monitored every 100 reflections; decay less than 2% I  
 Room temperature  $\sim 291 \text{ K}$   
 Structure refined by full-matrix least squares, including anisotropic temperature factors and anomalous-dispersion corrections with weights based on intensity statistics (Frenz, 1980)  
 Secondary-extinction coefficient =  $1.25 \times 10^{-7}$   
 Largest shift at end of refinement =  $0.17\sigma$   
 Final least-squares refinement performed on Amdahl V6 (Stewart, 1979)  
 Number of variables = 208  
 Final  $R = 0.040$ ; weighted  $R = 0.068$   
 Error on an observation of unit weight = 1.41

Table 2. Positional parameters and equivalent isotropic thermal parameters, with e.s.d.'s in parentheses

$$B_{\text{eq}} = \frac{2}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$B_{\text{eq}} (\text{\AA}^2)$
Cd(1)	0.09075 (2)	0.06915 (1)	-0.15948 (1)	1.73 (1)
Cd(2)	0.08259 (2)	0.11117 (1)	0.34454 (1)	1.74 (1)
O(1)	0.4665 (3)	0.4402 (2)	0.6974 (2)	2.5 (1)
O(10)	0.3507 (3)	0.3932 (2)	0.8951 (2)	2.26 (7)
O(5)	0.0182 (3)	0.1017 (2)	0.1833 (2)	2.8 (1)
O(3)	0.1882 (3)	0.2294 (2)	0.4475 (2)	2.43 (7)
O(12)	0.3465 (3)	0.0849 (2)	0.3258 (2)	3.0 (1)
C(1)	0.4447 (4)	0.3431 (3)	0.6856 (2)	1.8 (1)
C(3)	0.3289 (4)	0.1935 (3)	0.5903 (2)	2.7 (1)
O(7)	0.2507 (3)	0.1896 (2)	0.9306 (2)	2.7 (1)
C(2)	0.3474 (4)	0.3098 (3)	0.6010 (2)	2.3 (1)
O(2)	0.5020 (4)	0.2804 (2)	0.7424 (2)	3.4 (1)
C(4)	0.2251 (4)	0.1635 (3)	0.5062 (2)	2.0 (1)
O(4)	0.1753 (3)	0.0692 (2)	0.4976 (2)	2.5 (1)
O(6)	0.9809 (4)	0.2490 (2)	0.2476 (2)	3.2 (1)
C(5)	0.4645 (4)	0.3050 (3)	0.1799 (2)	2.1 (1)
C(8)	0.2720 (4)	0.1252 (3)	-0.0078 (2)	2.1 (1)
C(7)	0.3621 (5)	0.1531 (3)	0.0813 (2)	2.9 (1)
C(6)	0.3856 (6)	0.2691 (3)	0.0933 (3)	3.2 (2)
O(9)	0.3013 (3)	0.9886 (2)	0.7860 (2)	3.1 (1)
O(8)	0.2118 (4)	0.0349 (2)	0.9834 (2)	3.0 (1)
O(11)	0.3187 (3)	0.4107 (2)	0.3816 (2)	2.11 (7)
O(13)	0.0873 (3)	0.4153 (2)	0.7720 (2)	3.2 (1)

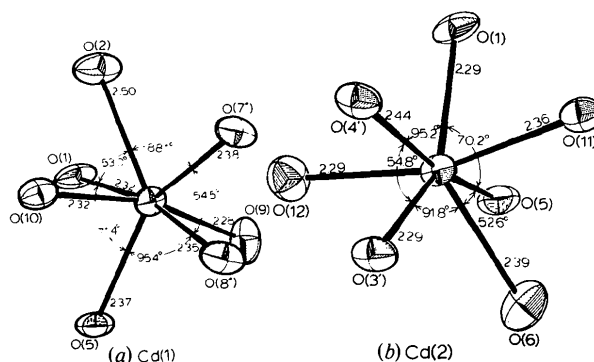


Fig. 1. (a) An ORTEP (Johnson, 1970) drawing of the environment about Cd(1) showing the interatomic distances (Å) and the angles ( $^\circ$ ) defining the approximate pentagonal planes. This view and the notation are consistent with the text and Fig. 2, if Fig. 2 is viewed from under the paper toward the reader. Atoms here and in Fig. 2 are related to the atomic positions shown in Table 2 by the following transformations: Cd(1) ( $x, y, 1+z$ ); O(1) ( $\frac{1}{2} + x - 1, \frac{1}{2} - y, z$ ); O(2) as O(1); O(5) ( $-x, -y, 1-z$ ); O(7''), O(8'') as in Table 2; O(9) ( $x, y - 1, z$ ); O(10) ( $\frac{1}{2} + x - 1, \frac{1}{2} - y, z$ ). The axial O–Cd–O angle is O(9)–Cd–O(10) =  $165.05 (8)^\circ$ . The e.s.d.'s of the Cd–O distances are  $\pm 0.003 \text{ \AA}$  or less, and the O–Cd–O angular e.s.d.'s are  $\pm 0.1^\circ$ , or less. (b) An ORTEP (Johnson, 1970) drawing of the environment about Cd(2) as for Cd(1) above. The view and notation are consistent with the text with Fig. 2 viewed normally. Atoms here and in Fig. 2 are related to the atomic positions in Table 2 by the following transformations: O(1) ( $\frac{1}{2} - x, \frac{1}{2} + y - 1, 1 - z$ ); O(3'), O(4'), O(5), O(12) as in list; O(6) ( $1 - x, y, z$ ); O(11) ( $\frac{1}{2} + x - 1, \frac{1}{2} - y, z$ ). The axial O–Cd–O angle is O(11)–Cd–O(12) =  $163.4 (1)^\circ$ . E.s.d.'s are the same as in (a).

The structure was solved by standard heavy-atom methods and refined as indicated in Table 1.\* The atomic coordinate parameters and errors are listed in Table 2. Selected interatomic distances and angles and errors are in Fig. 1(a,b) (ORTEP, Johnson, 1970) and detailed distances and angles have been deposited.\* Drawings of the immediate environment of Cd(1) and Cd(2) are shown in Fig. 1(a,b) and a view of the polymer is shown in Fig. 2.

**Discussion.** The structure may be described as an infinite three-dimensional polymer, accounting for its insolubility. The succinato ligand chelates the Cd atoms, and one chelating O of the carboxyl group at one end of the ligand bridges Cd(1) and Cd(2) together, whereas the other end of the ligand is used to form the three-dimensional polymer, Fig. 2. Of particular interest for the coordination chemist and the  $^{113}\text{Cd}$  NMR spectroscopist is the local environment about the Cd atoms. Both Cd(1) and Cd(2) are seven-coordinate Cd atoms. The simplest description of the Cd coordination polyhedron is as a pentagonal bipyramid of O atoms (see Fig. 1a,b). The pentagonal plane for Cd(1) (Fig. 1a) is composed of O(7''), O(8''), O(5), O(1), O(2), with O(9) and O(10) defining the axial ligands. The analogous atoms for Cd(2) (Fig. 1b) are O(3'), O(4'),

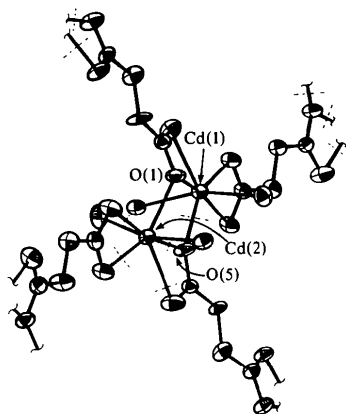


Fig. 2. An ORTEP (Johnson, 1970) drawing of the structure showing the interconnected nature of the polymer. The asymmetric unit is composed of two succinato groups, four waters bound to Cd, and two Cd atoms. These are separated from the other atoms in the figure by dashed lines (the upper right-hand corner to center). The curled lines are continuation bonds to other Cd atoms. For simplicity only Cd(1), Cd(2), O(1) and O(5) are labeled; O(1) and O(5) are referred to in text. Cd(1) and Cd(2) are reference atoms for Fig. 1(a,b).

O(1), O(5), O(6), O(11) and O(12). It is clear from the deviations from least-squares planes ( $\sim 0.1\text{--}0.3$  Å) and the O(10)—Cd(1)—O(9) and O(12)—Cd(2)—O(11) angles of  $165.05(8)$  and  $163.4(1)^\circ$ , respectively, that the pentagonal-bipyramid description is not ideal. However, a description of the coordination polyhedron of Cd in this structure in terms of the other most common seven-coordinate geometry, that of the monocapped trigonal antiprism, is less satisfactory. The Cd—O distances within the equatorial plane for Cd(1) vary from  $2.325(3)$  to  $2.496(3)$  Å with axial distances of  $2.279(3)$  and  $2.315(3)$  Å. The analogous distances for Cd(2) are:  $2.291(3)$  to  $2.471(3)$  Å and  $2.292(3)$ ,  $2.364(3)$  Å. One might expect, at least on steric grounds, some systematic elongation of the axial

\* Lists of structure factors, anisotropic thermal parameters, all distances and angles, and details of the least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36269 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Cd—O distances compared to the in-plane distances. No such elongation occurs. The relatively sharp bite angle (O—Cd—O) of  $52.56(9)$  to  $54.84(9)^\circ$  contributes to the availability of coordination sites for higher coordination numbers.

This is not a unique example of seven coordination for Cd. We have found a similar coordination geometry for Cd in bis(*p*-aminobenzoato)aquacadmium(II) and diaquabis(*o*-hydroxybenzoato)cadmium(II) (Rodesiler, Griffith, Turner & Amma, 1981). Seven-coordinate Cd has also been observed by Harrison & Trotter (1972) in cadmium diacetate dihydrate, but the coordination polyhedron in this case is much more irregular.

The bonding of both O(5) and O(1) is interesting, as they are bound to two metal atoms as well as the carbon of the carboxyl group. The chelating metal—oxygen distances to O(5), O(1) are  $2.471(3)$ ,  $2.325(3)$  Å, respectively, whereas the bridging metal—oxygen distances are  $2.371(3)$ ,  $2.291(3)$  Å. The bridging O—Cd distances are shorter than the chelating Cd—O distance of these atoms. The remaining distances and angles are normal and have the expected values.

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