

2,3-Dihydroxy-*N*-methylbenzamide monohydrateJose Escalada, Danna Freedman  
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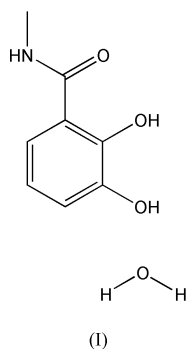
## Key indicators

Single-crystal X-ray study  
 $T = 126$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å  
 $R$  factor = 0.043  
 $wR$  factor = 0.052  
Data-to-parameter ratio = 7.6For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound,  $\text{C}_8\text{H}_9\text{NO}_3 \cdot \text{H}_2\text{O}$ , is a monohydrate. The molecules pack in pairs of planes, each pair of planes held together by a two-dimensional hydrogen-bonding network.

## Comment

Catechol and its derivatives complex a variety of metal ions once deprotonated. These ligands are found in iron-sequestering siderophores (Raymond *et al.*, 2003) and have been incorporated into supramolecular coordination clusters (Caulder *et al.*, 2001; Yeh *et al.*, 2001). 2,3-Dihydroxy-*N*-methylbenzamide (CAM-Me) is a model compound that has been synthesized to probe the electrochemical properties of larger supramolecular structures.



CAM-Me was crystallized from deuterated acetone, forming colorless blocks. The compound co-crystallized with water, (I), in space group  $P2_1/n$  (Fig. 1).

In addition to one intramolecular hydrogen bond, a two-dimensional hydrogen-bond network is apparent from the packing diagram (Fig. 2). The relevant hydrogen bonds are listed in Table 2. Hydrogen bonding connects CAM-Me and water to give repeating pairs of planes. Each pair of planes is parallel to (101), and is separated from the next pair by van der Waals contacts. Each individual hydrogen-bonded plane is defined by three distinct hydrogen bonds: donation of O2 to O4, donation of N1 to O4<sup>iii</sup>, and donation of O4 to O3<sup>ii</sup> (see Table 2 for symmetry codes). These planes are linked together into pairs by the hydrogen-bond donation of O4 to the hydroxyl O1<sup>i</sup>.

The hydrogen-bonding scheme in catechol has been extensively studied, both in the solid state and in molecular modeling investigations (Hay *et al.*, 2001; Zhang *et al.*, 2003). The orientation of the hydrogen bonds in CAM-Me differs from that of gas phase calculations and hydrogen-bonding schemes in similar molecules for which there is no coordinating solvent present (Eng-Wilmont & van der Helm, 1980; Tymiak *et al.*, 1985). These molecules exhibit an intramolecular hydrogen bond donated from the hydroxyl group *meta* to

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the amide, instead of the intermolecular hydrogen bond observed in the structure of CAM-Me. Taken as a set, these studies demonstrate that though the *meta*-hydroxyl group typically donates a hydrogen bond, there is no clear trend that predicts whether this hydrogen bond will be inter- or intramolecular in similar structures.

## Experimental

The starting material, a carboxylic acid of methyl-protected catechol (6.1 g, 33.5 mmol), was reacted with thionyl chloride to give the acid chloride. This intermediate was immediately reacted with methylamine to give the methyl-protected catecholamide (3.6 g, 55%). A portion of the intermediate (1.86 g, 10.2 mmol) was then deprotected with  $\text{BBr}_3$  to afford the title compound (1.36 g, 84%). X-Ray quality crystals were grown from deuterated acetone wet from atmospheric water.

### Crystal data

$\text{C}_8\text{H}_9\text{NO}_3 \cdot \text{H}_2\text{O}$   
 $M_r = 185.18$   
 Monoclinic,  $P2_1/n$   
 $a = 7.2905$  (8) Å  
 $b = 9.481$  (1) Å  
 $c = 11.886$  (1) Å  
 $\beta = 93.280$  (2)°  
 $V = 820.3$  (2) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.499$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 1569 reflections  
 $\theta = 2.8\text{--}24.5^\circ$   
 $\mu = 0.12$  mm<sup>-1</sup>  
 $T = 126.2$  K  
 Block, colorless  
 $0.40 \times 0.30 \times 0.15$  mm

### Data collection

Bruker SMART 1000 diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (Blessing, 1995)  
 $T_{\min} = 0.572$ ,  $T_{\max} = 0.982$   
 3625 measured reflections

1335 independent reflections  
 1016 reflections with  $F^2 > 3\sigma(F^2)$   
 $R_{\text{int}} = 0.031$   
 $\theta_{\text{max}} = 24.7^\circ$   
 $h = -8 \rightarrow 4$   
 $k = -10 \rightarrow 10$   
 $l = -13 \rightarrow 13$

### Refinement

Refinement on  $F$   
 $R = 0.044$   
 $wR = 0.052$   
 $S = 2.02$   
 1016 reflections  
 133 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o) + 0.00022|F_o|^2]$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.21$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.34$  e Å<sup>-3</sup>

**Table 1**

Selected bond distances (Å).

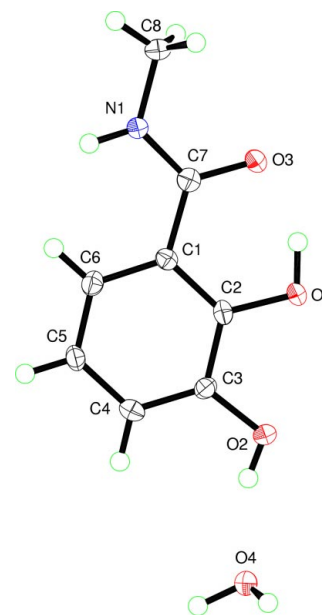
O1—C2	1.362 (3)	C1—C6	1.397 (3)
O2—C3	1.363 (3)	C1—C7	1.483 (3)
O3—C7	1.262 (3)	C2—C3	1.399 (3)
N1—C7	1.336 (3)	C3—C4	1.376 (3)
N1—C8	1.457 (3)	C4—C5	1.391 (3)
C1—C2	1.403 (3)	C5—C6	1.380 (3)

**Table 2**

Hydrogen-bonding geometry (Å, °).

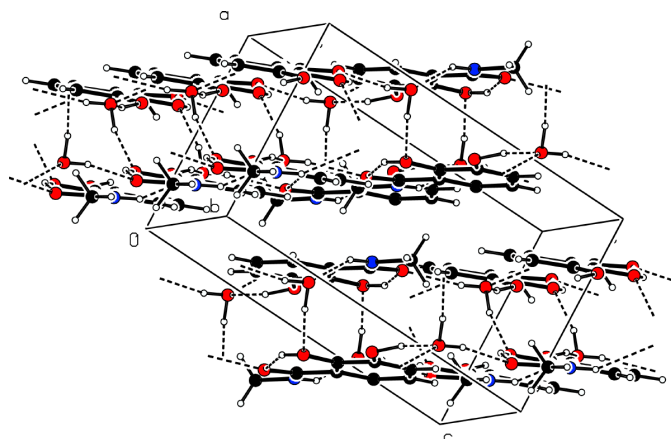
$D\text{—}H \cdots A$	$D\text{—}H$	$H \cdots A$	$D \cdots A$	$D\text{—}H \cdots A$
O4—H11 $\cdots$ O1 <sup>i</sup>	0.82 (2)	2.10 (3)	2.899 (2)	162 (2)
O4—H10 $\cdots$ O3 <sup>ii</sup>	0.95 (2)	1.86 (2)	2.792 (2)	167 (2)
O2—H2 $\cdots$ O4	0.84 (2)	1.89 (2)	2.697 (2)	160 (2)
O1—H1 $\cdots$ O3	0.94 (2)	1.64 (3)	2.506 (2)	151 (2)
N1—H3 $\cdots$ O4 <sup>iii</sup>	0.93 (2)	2.23 (2)	3.087 (3)	152 (2)

Symmetry codes: (i)  $1 - x, -1 - y, -z$ ; (ii)  $\frac{1}{2} + x, -\frac{1}{2} - y, \frac{1}{2} + z$ ; (iii)  $x, 1 + y, z$ .



**Figure 1**

The molecular structure and labeling of the title compound. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 2**

Packing diagram (Spek, 2004) of the title compound. O atoms are shown in red, N atoms in blue, and hydrogen bonds are indicated by dashed lines.

The hydroxyl, water and amide H atoms were located in a difference Fourier map and included with fixed displacement parameters. Their positional parameters were allowed to refine freely. All other H atoms were included in geometrically calculated positions, with C—H distances of 0.95 Å and  $U(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$ .

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *TEXSAN* (Molecular Structure Corporation and Rigaku, 1998); molecular graphics: *TEXSAN* and *PLATON* (Spek, 2004); software used to prepare material for publication: *TEXSAN*.

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