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Poly[[diaqua(μ_3-3-nitrophthalato)-calcium(II)] monohydrate]

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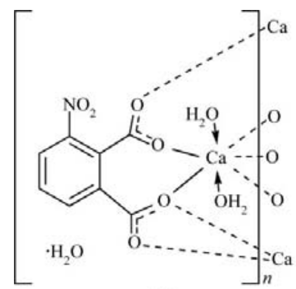
The title 3-nitrophthalate–calcium coordination polymer, $\{[Ca(C_8H_3NO_6)(H_2O)_2]\cdot H_2O\}_n$, crystallizes as a one-dimensional framework. The Ca^{II} centre has a distorted pentagonal–bipyramidal geometry, being seven-coordinated by five O atoms from three different 3-nitrophthalate groups and by two water molecules, resulting in a one-dimensional zigzag chain along the *a*-axis direction by the interconnection of the four O atoms from the two carboxylate groups. There is a *D*3 water cluster composed of the coordinated and the solvent water molecules within such chains. Adjacent chains are aggregated into two-dimensional layers *via* hydrogen bonds in the *c*-axis direction. The whole three-dimensional structure is further stabilized by weak O—H···O hydrogen bonds between the O atoms of the nitro group and the water molecules.

Comment

The vast majority of current work in crystal engineering centres on the controlled assembly of donor and acceptor building blocks in order to tune the properties of metal–organic frameworks (Guilera & Steed, 1999; Burrows *et al.*, 2000; Guo & Guo, 2009). Aromatic multidentate carboxylic acids are often ligands of choice for the design of metal–organic frameworks or molecular assemblies (Volkringer *et al.*, 2007). Several Ca^{II} complexes are known with the ligands benzene-1,2-dicarboxylic acid (Schuckmann *et al.*, 1978), benzene-1,3-dicarboxylic acid (Dale & Elsegood, 2003*a*), benzene-1,4-dicarboxylic acid (Dale & Elsegood, 2003*b*), benzene-1,2,4-tricarboxylic acid (Volkringer *et al.*, 2007), benzene-1,3,5-tricarboxylic acid (Yang *et al.*, 2004), benzene-1,3,5-triacetic acid (Zhu *et al.*, 2005), naphthalene-2,6-dicarboxylic acid and biphenyl-4,4′-dicarboxylic acid (Volkringer *et al.*, 2008). 3-Nitrophthalic acid, which has two carboxylate groups and a nitro group, can act as a good building block in constructing metal–organic frameworks. Some lanthanide complexes containing one bidentate 1,3-chelating carboxylate group and two 1,6-chelating carboxylate groups have been reported, *e.g.* bis(μ-3-nitrobenzene-1,2-dicarboxylato)-$\kappa^8O^1,O^2:O^2,O^3;O^3,O^2:O^2,O^1$-bis[triaqua(2-carboxy-3-nitrobenzoato-κ^2O,O')lanthanum(III)] dihydrate (Xiong & Qi, 2007) and its isotypic complexes with Dy^{III}, Tb^{III}, Pr^{III} and Eu^{III} (Huang *et al.*, 2007). An example in which the nitro group of the 3-nitrophthalate dianion coordinated to the metal ion has also been reported in poly[[di-μ-aqua-tetraaquadi-μ-hydroxido-bis(μ_3-3-nitrophthalato)tricopper(II)] dihydrate] (Wang *et al.*, 2009). We report here the crystal structure of a novel one-dimensional calcium(II) polymer, poly[[diaqua(μ_3-3-nitrophthalato)calcium(II)] monohydrate], (I), constructed from the 3-nitrophthalate dianionic ligand.



(I)

The asymmetric unit in the structure of (I) comprises one Ca^{II} centre, one complete 3-nitrophthalate dianion, two coordinated water molecules and one solvent water molecule, and is shown in Fig. 1 in a symmetry-expanded view which displays the full coordination of the Ca^{II} centre. Selected geometric parameters are given in Table 1.

The Ca^{II} centre in (I) is surrounded by an O_7 donor set in a distorted pentagonal–bipyramidal geometry. The five equatorial sites are occupied by one O atom of a water molecule (O8), two 1,6-chelating O atoms (O2 and O3) and two 1,3-bidentate chelating O atoms ($O3^{ii}$ and $O4^{ii}$; see Fig. 1 for symmetry codes). Atom O7 from the other coordinated water molecule and bridging atom $O1^{i}$ occupy the two opposing apical sites of the pentagonal bipyramid. The *cis* O—Ca—O angles range from 71.65 (6) to 107.92 (6)°, except for $O3^{ii}$—Ca1—$O4^{ii}$, which is 58.58 (5)°; the *trans* $O1^{i}$—Ca—O7 angle is 158.98 (6)°. The Ca—O_{water} distances in (I) are slightly shorter than those [2.387 (2) and 2.4694 (16) Å, respectively] in both seven-coordinate calcium phthalate monohydrate (Schuckmann *et al.*, 1978) and eight-coordinate *catena*-[(μ_5-hydrogen 1,2,4-benzenetricarboxylato-*O,O,O′,O″,O″,O‴,O‴*)aquacalcium] (Volkringer *et al.*, 2007), while the Ca—O(3-nitrophthalate) distances are comparable to the values [range = 2.303 (2)–2.595 (2) Å and average = 2.406 (2) Å] reported for calcium phthalate monohydrate (Schuckmann *et al.*, 1978).

As is observed in a related 3-nitrophthalate–Cd^{II} framework, the two carboxylate groups are noncoplanar (Guo *et al.*, 2007). The O1/C1/O2 carboxylate group is rotated by 76.7 (2)° out of the benzene ring plane, while the other carboxylate group, O3/C8/O4, forms an angle with the same benzene ring plane of 40.9 (2)°. The nitro group is rotated from the benzene ring plane by 13.6 (3)°. These deviations contribute to the coordination modes and the conformation of the supramolecular structure. In the present structure, the versatility of the dianionic 3-nitrophthalate ligands can be clearly seen. Bidentate 1,3-chelating, bidentate 1,3-bridging, 1,6-chelating and 1,6-bridging modes *via* the benzene ring are present (Figs. 1 and 2). Atoms O2 and O3 adopt a 1,6-chelating mode *via* the benzene ring to connect with Ca1 and atom O3 also acts as a bridging atom *via* a bidentate 1,3-chelating mode to atom Ca1^{ii}. Atom O1 coordinates to Ca1^{i} (see Fig. 1 for symmetry codes) *via* a 1,3-bridging mode. In this way, each dianionic 3-nitrophthalate ligand binds to three Ca atoms. Each Ca^{II} centre is therefore coordinated by five O atoms from four different carboxylate groups. Two Ca^{II} centres are linked into a centrosymmetric binuclear unit by two bridging atoms (O3 and O3^{ii}) from two different dianionic 3-nitrophthalate ligands. All the binuclear units are connected by two carboxylate O atoms (O1 and O1^{i}), giving rise to one-dimensional Ca—O—Ca—O—C—O—Ca chains along the *a*-axis direction. In the chain, atoms O1 and O4 adopt a 1,6-bridging mode. The 3-nitrophthalate dianion interconnects Ca^{II} centres to form different rings, namely a seven-membered ring, two four-membered rings and an eight-membered ring, and these are arranged alternately along the one-dimensional chains (see Fig. 2). These result in Ca$\cdots$Ca^{ii} and Ca$\cdots$Ca^{i} separations within the chains of 3.897 (1) and 4.949 (1) Å, respectively, and a Ca1$^{i}\cdots$Ca1$\cdots$Ca1^{ii} angle of 88.42 (1)°.

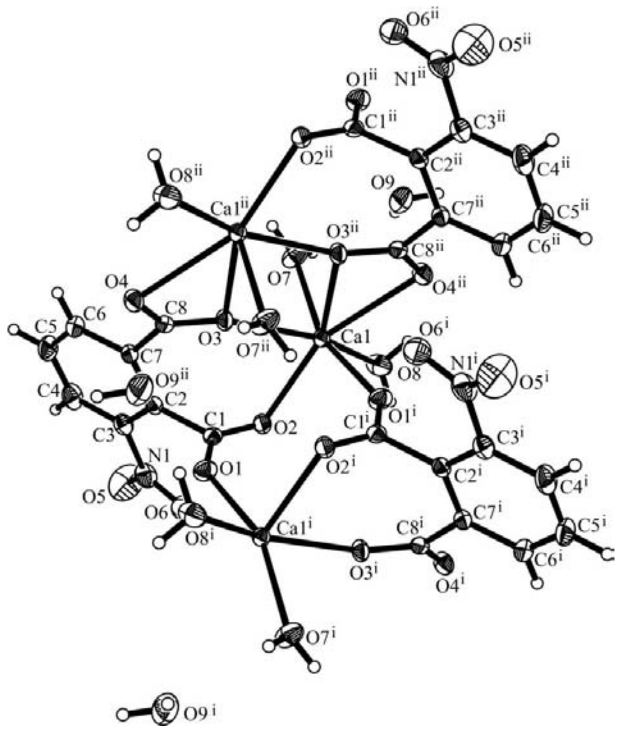


Figure 1
A view of the structure of (I), showing the atom-numbering scheme and the coordination environment for the Ca^{II} centre. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x, -y + 1, -z + 1$.]

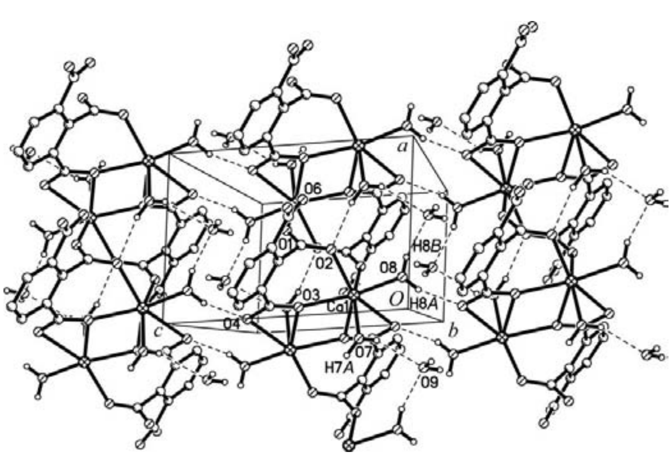


Figure 2
A partial packing diagram for (I), viewed down the *b* axis, showing a two-dimensional layer in the *ac* plane formed *via* hydrogen bonds.

A comparison with the previously reported structure of calcium phthalate monohydrate (Schuckmann *et al.*, 1978) reveals that the two structures contain different numbers of water molecules. In the present structure, the two water molecules within the coordination environment of the Ca^{II} centre and the solvent water molecule engage in distinct hydrogen-bonding interactions (see Table 2). Along the *a*-axis direction, the three water molecules are connected to one another through hydrogen bonds and produce a *D*3 water cluster (Infantes & Motherwell, 2002); this plays an important role in the propagation of the one-dimensional chain structure, owing to its contribution to an eight-membered hydrogen-bonded ring [graph set $R_3^2(8)$; Bernstein *et al.*, 1995] formed *via* an intermolecular O7—H7*A*$\cdots$O2^{iii} hydrogen bond. These *D*3 water clusters and an intermolecular O8—H8*A*$\cdots$O4^{v} hydrogen bond are also involved in forming a 16-membered hydrogen-bonded ring [graph set $R_6^4(16)$] and an eight-membered hydrogen-bonded ring [graph set $R_2^2(8)$] in the *ac* plane (Fig. 2). In this way, a complete two-dimensional layer is formed. The O atoms of the nitro group as a hydrogen-bond acceptor take part in the formation of the polymeric networks. In the *bc* plane, neighboring chains are linked together *via* weak O9—H9*B*$\cdots$O5^{iv} hydrogen-bond interactions. This also results in the aryl rings of the 3-nitrophthalate ligands stacking in an offset fashion along the *b*-axis direction. Thus, the three-dimensional connectivity of the structure is achieved.

Experimental

The title complex was prepared with successive addition of 3-nitrophthalic acid (0.42 g, 2 mmol) and $CaCO_3$ (0.25 g, 2.5 mmol) to distilled water (15 ml) at room temperature with continuous stirring. After filtration, slow evaporation over a period of one week at room temperature provided colorless prismatic crystals of (I).

Crystal data

$[Ca(C_8H_3NO_6)(H_2O)_2]\cdot H_2O$
$M_r = 303.24$
Monoclinic, $P2_1/c$
$a = 6.2142$ (12) Å
$b = 20.959$ (4) Å
$c = 8.9443$ (18) Å
$\beta = 95.24$ (3)°
$V = 1160.1$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.59$ mm^{-1}
$T = 133$ K
0.14 × 0.08 × 0.06 mm

Data collection

Rigaku Saturn CCD area-detector diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
$T_{min} = 0.940$, $T_{max} = 0.972$
8389 measured reflections
2052 independent reflections
1938 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.087$
$S = 1.07$
2052 reflections
172 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.24$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ca1—O1^{i}	2.3402 (15)	Ca1—O8	2.3402 (16)
Ca1—O2	2.3679 (14)	Ca1···Ca1^{ii}	3.8966 (12)
Ca1—O3	2.3470 (14)	O1—C1	1.250 (2)
Ca1—O3^{ii}	2.4581 (14)	O2—C1	1.252 (2)
Ca1—O4^{ii}	2.5915 (16)	O3—C8	1.263 (2)
Ca1—O7	2.3587 (16)	O4—C8	1.253 (2)
O1^{i}—Ca1—O3	103.64 (6)	O1^{i}—Ca1—O3^{ii}	81.96 (5)
O1^{i}—Ca1—O7	158.98 (6)	O3—Ca1—O3^{ii}	71.65 (6)
O1^{i}—Ca1—O8	95.49 (6)	O7—Ca1—O3^{ii}	83.43 (6)
O8—Ca1—O7	82.72 (6)	O8—Ca1—O4^{ii}	80.18 (6)
O3—Ca1—O7	85.89 (6)	O1^{i}—Ca1—O4^{ii}	74.21 (6)
O8—Ca1—O2	82.81 (6)	O7—Ca1—O4^{ii}	84.88 (6)
O1^{i}—Ca1—O2	92.55 (5)	O3^{ii}—Ca1—O4^{ii}	51.58 (5)
O3—Ca1—O2	77.51 (5)	O1—C1—O2	126.86 (18)
O7—Ca1—O2	107.92 (6)	O4—C8—O3	121.91 (19)

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, -y+1, -z+1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O7—H7A···O2^{iii}	0.85	2.09	2.920 (2)	164
O7—H7A···O6^{iii}	0.85	2.53	3.039 (3)	119
O7—H7B···O9	0.85	2.34	2.885 (3)	122
O7—H7B···O5^{iv}	0.85	2.38	3.120 (3)	147
O8—H8A···O4^{v}	0.85	1.93	2.747 (2)	160
O8—H8B···O9^{vi}	0.85	1.94	2.738 (2)	156
O9—H9A···O1^{vii}	0.85	2.44	3.053 (3)	130
O9—H9B···O5^{iv}	0.85	2.37	2.949 (3)	126

Symmetry codes: (iii) $x-1, y, z$; (iv) $x-1, -y+\frac{1}{2}, z-\frac{1}{2}$; (v) $x, y, z-1$; (vi) $x+1, y, z$; (vii) $x-1, y, z-1$.

H atoms of the water molecules were found in difference Fourier maps. However, during refinement, they were restrained at O—H distances of 0.85 (1) Å and their U_{iso}(H) values were set at $1.2U_{eq}$(O). H atoms of CH groups were treated as riding [C—H = 0.93 Å and U_{iso}(H) = $1.2U_{eq}$(C)].

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3344). Services for accessing these data are described at the back of the journal.

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