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Tetraaquabis(4-carboxy-1*H*-imidazole-5-carboxylato-κ^2*N,O*)calcium(II) monohydrate

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In the title complex, $[Ca(H_2IDC)_2(H_2O)_4]\cdot H_2O$, ($H_2IDC^-$ is 4-carboxy-1*H*-imidazole-5-carboxylate, $C_5H_3N_2O_4^-$), the Ca^{II} atom is located on a twofold rotation axis and is *trans*-coordinated by two *N,O* bidentate H_2IDC^- ligands and four water molecules, resulting in a distorted bicapped triangular prismatic configuration. The water molecule is also located on a twofold rotation axis. A three-dimensional network of N—H···O and O—H···O hydrogen bonds help to stabilize the crystal packing.

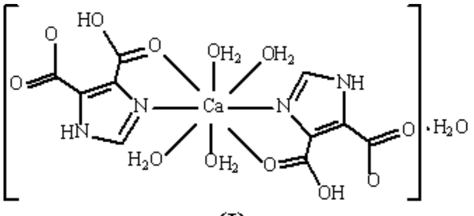
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.035
wR factor = 0.097
Data-to-parameter ratio = 13.3

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

Comment

The species 1*H*-imidazole-4,5-dicarboxylic acid (H_3IDC) has interesting possibilities as a multidentate or bridging ligand in coordination chemistry. It can be successively deprotonated to generate H_2IDC^-, $HIDC^{2-}$ and IDC^{3-} anions. To date, a few mononuclear (Zhang *et al.*, 2004; Xiao *et al.*, 2004; Ma *et al.*, 2003) and dinuclear (Rajendiran *et al.*, 2003) complexes have been reported. Recently, we have reported three six-coordinated complexes based on H_3IDC; one mononuclear complex $[Zn(H_2IDC)2(H_2O)_2]$ (Liu *et al.*, 2004), in which the dicarboxylic acid ligand exhibits a formal charge of −1, and two one-dimensional chain complexes, [Cd(HIDC)(1,10-phen)] and [Cd(HIDC)(2,2′-bipy)] (Gao, Gu *et al.*, 2004; Gao, Liu *et al.*, 2004), in which the carboxylic acid ligands exhibit a formal charge of −2. As part of our continuing studies in this field, we have isolated a new eight-coordinated calcium(II) complex, $[Ca(H_2IDC)_2(H_2O)_4]\cdot H_2O$, (I), by the reaction of H_3IDC and calcium nitrate tetrahydrate in an aqueous solution. We report here the crystal structure of this complex.



(I)

As shown in Fig. 1, the crystal structure of (I) consists of a neutral mononuclear $[Ca(H_2IDC)_2(H_2O)_4]$ complex and one uncoordinated water molecule. In the complex, the carboxylic acid (H_3IDC) ligand is singly deprotonated and bears a formal charge of −1, and the free carboxylate atoms O2 and O3 form an intramolecular hydrogen bond (Table 2). The Ca^{II} atom and O3*W* water molecule are located on different twofold rotation axes. The Ca^{II} atom is *trans*-coordinated by two *N,O*-bidentate H_2IDC^- ligands and four water molecules, and the

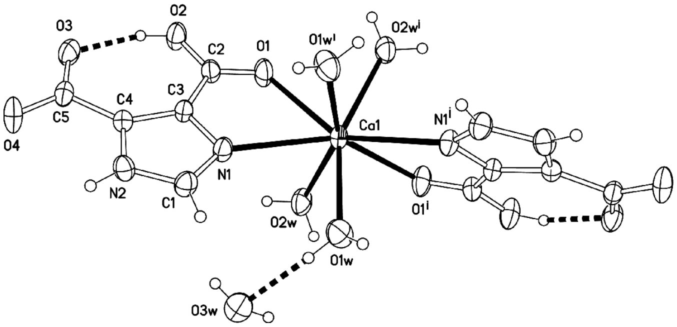


Figure 1
View of (I), with 50% probability displacement ellipsoids (H atoms are represented by arbitrary spheres). Hydrogen bonds are denoted by dashed lines. The symmetry code is as in Table 1.

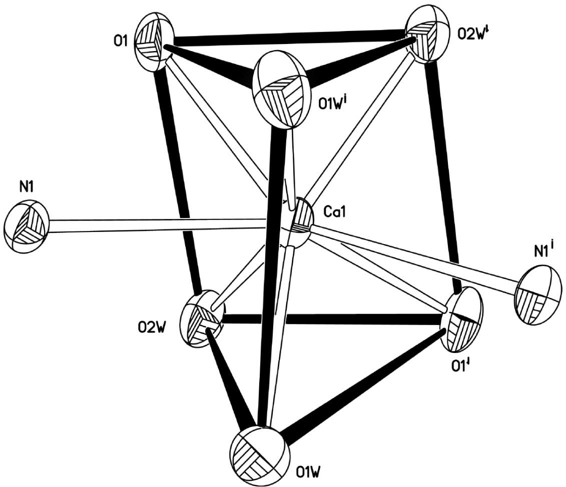


Figure 2
The polyhedral skeleton around the Ca^{II} atom in (I). The symmetry code is as in Table 1.

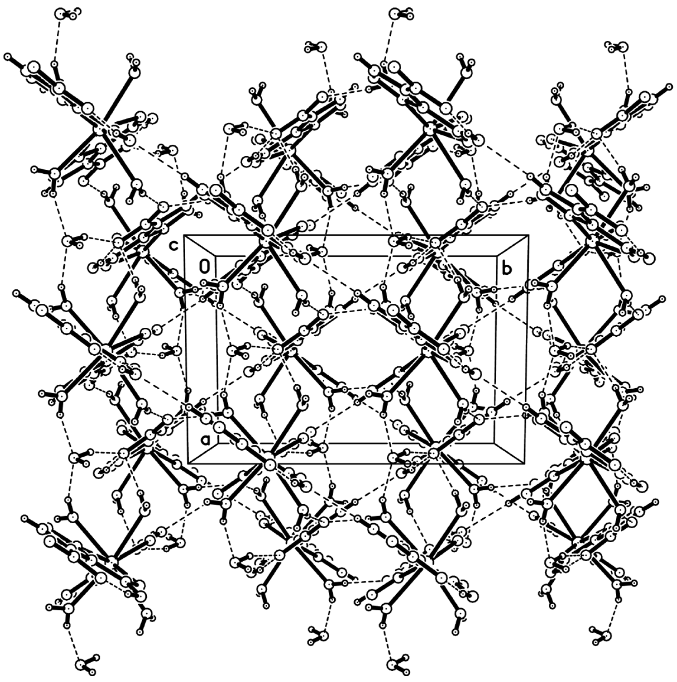


Figure 3
The unit-cell packing of (I), with the hydrogen bonds denoted by dashed lines. H atoms not involved in hydrogen bonding have been omited.

calcium geometry can best be described as distorted bicapped triangular prismatic (Fig. 2). The two basal planes of the triangular prism are formed by atoms O1/O2*W*^{i}/O1*W*^{i} and O2*W*/O1*W*/O1^i, respectively [symmetry code: (i) $1 - x$, y, $\frac{3}{2} - z$], and the two planes are nearly parallel with a dihedral angle of 8.95 (3)°. The capping N1 atom extends 1.935 (2) Å beyond the plane defined by O1/O2*W*/O1*W*/O1*W*^{i} [r.m.s. deviation = 0.15 (3) Å]. The capped Ca—N1 distance of 2.6434 (14) Å is significantly longer than the Ca—O distances (Table 1). It should be noted that the C2—O2 distance in the H$_2$IDC$^-$ ligand is longer than the C2—O1 distance, appropriate for the monodentate coordination mode of carboxyl group. The five-membered O1/C2/C3/N1/Ca1 chelate ring is approximately planar, with an r.m.s. deviation of 0.02 (3) Å. The H$_2$IDC$^-$ ligand is also essentially planar, with an r.m.s. deviation of 0.03 (3) Å.

A three-dimensional network is constructed *via* hydrogen-bonding interactions, involving the water molecules, the uncoordinated imidazole N atom, and carboxylate O atoms of the H$_2$IDC$^-$ ligands (Table 2 and Fig. 3).

Experimental

1*H*-Imidazole-4,5-dicarboxylic acid (4.60 g, 20 mmol) and calcium nitrate tetrahydrate (4.72 g, 20 mmol) were dissolved in water (15 ml). The mixture was sealed in a 25 ml Teflon-lined stainless steel bomb and held at 403 K for 3 d. The bomb was allowed to cool to room temperature and colorless prismatic crystals of (I) were obtained after several days. Analysis calculated for $C_{10}H_{16}CaN_4O_{13}$: C 27.28, H 3.66, N 12.72%; found: C 27.32, H 3.73, N 12.75%.

Crystal data

$[Ca(C_5H_3N_2O_4)_2(H_2O)_4]\cdot H_2O$
$M_r = 440.35$
Monoclinic, $C2/c$
$a = 8.2685\ (17)$ Å
$b = 11.949\ (2)$ Å
$c = 17.525\ (4)$ Å
$\beta = 103.64\ (3)^\circ$
$V = 1682.6\ (6)$ Å^3
$Z = 4$

$D_x = 1.738$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7559 reflections
$\theta = 3.1$–27.5°
$\mu = 0.46$ mm^{-1}
$T = 293\ (2)$ K
Prism, colorless
0.31 × 0.24 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.872$, $T_{max} = 0.922$
8019 measured reflections

1935 independent reflections
1712 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 27.5^\circ$
$h = -10 \rightarrow 10$
$k = -15 \rightarrow 14$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.097$
$S = 1.05$
1935 reflections
146 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.057P)^2 + 1.3396P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Ca1—O1*W*	2.3726 (14)	C2—O1	1.2194 (19)
Ca1—O1	2.5370 (13)	C2—O2	1.310 (2)
Ca1—N1	2.6434 (14)	C5—O3	1.268 (2)
Ca1—O2*W*	2.4015 (14)	C5—O4	1.240 (2)
N1^{i}—Ca1—N1	133.49 (6)	O1*W*^{i}—Ca1—O1*W*	98.54 (8)
O1^{i}—Ca1—N1	146.58 (4)	O1*W*^{i}—Ca1—O2*W*	152.84 (4)
O1—Ca1—N1	63.83 (4)	O1*W*—Ca1—O2*W*	79.27 (5)
O1^{i}—Ca1—O1	120.21 (6)	O2*W*—Ca1—O2*W*^{i}	114.75 (7)
O1*W*^{i}—Ca1—N1	73.85 (5)	O2*W*—Ca1—N1	79.38 (5)
O1*W*—Ca1—N1	76.28 (5)	O2*W*^{i}—Ca1—N1	127.59 (5)
O1*W*^{i}—Ca1—O1	85.20 (5)	O2*W*—Ca1—O1	78.85 (5)
O1*W*—Ca1—O1	137.22 (4)	O2*W*^{i}—Ca1—O1	69.88 (5)

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O2^{ii}	0.86	2.29	3.118 (2)	163
O2*W*—H2*W*1···O4^{iii}	0.84 (2)	1.91 (2)	2.742 (2)	169 (2)
O1*W*—H1*W*1···O3*W*	0.85 (2)	2.05 (2)	2.859 (2)	161 (2)
O1*W*—H1*W*2···O4^{iv}	0.85 (2)	1.92 (2)	2.750 (2)	167 (2)
O2*W*—H2*W*2···O3^{v}	0.84 (2)	2.13 (2)	2.972 (2)	171 (2)
O2—H3···O3	0.85 (2)	1.69 (2)	2.526 (2)	167 (3)
O3*W*—H3W1···O3^{iii}	0.86 (1)	2.09 (2)	2.921 (2)	162 (3)

Symmetry codes: (ii) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (iii) $\frac{3}{2} - x, \frac{3}{2} - y, 1 - z$; (iv) $x, 1 - y, \frac{1}{2} + z$; (v) $\frac{1}{2} + x, \frac{3}{2} - y, \frac{1}{2} + z$.

H atoms attached to C and N atoms were placed in calculated positions [C—H = 0.93 Å or N—H = 0.86 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N)] and refined using the riding-model approximation. The carboxy and water H atoms were located in difference Fourier maps and refined with O—H distance restraints of 0.85 (1) Å and the constraint $U_{\rm iso}$(H) = 1.5$U_{\rm eq}$(O).

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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