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Triaquabis(4-carboxy-1*H*-imidazole-5-carboxylato)cadmium(II) monohydrate: a three-dimensional hydrogen-bonded network

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Key indicators

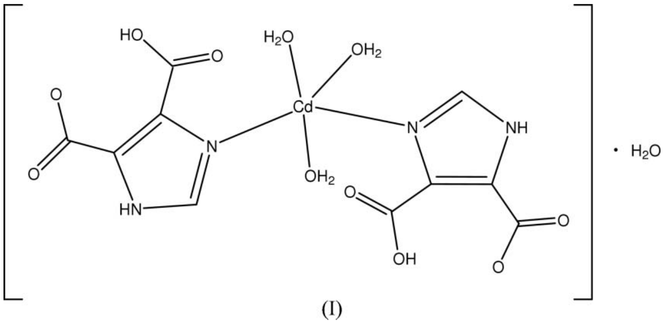
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.030
wR factor = 0.082
Data-to-parameter ratio = 11.5

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

In the title neutral mononuclear complex, $[Cd(H_2IDC)_2(H_2O)_3]\cdot H_2O$ (H_2IDC is the 4-carboxy-1*H*-imidazole-5-carboxylate anion, $C_5H_3N_2O_4$), the Cd^{II} atom is *trans*-coordinated by two H_2IDC ligands and three aqua molecules, displaying a distorted trigonal-bipyrimidal geometry. Interestingly, H_2IDC coordinates in an *N*-monodentate fashion to the central Cd^{II} atom, which is unprecedented. A three-dimensional supramolecular network is generated through N—H···O and O—H···O hydrogen bonds.

Comment

Assemblies of metal ions and organic ligands that may afford desirable covalent forces, hydrogen bonds or other cooperative interactions should lead to the formation of interesting supramolecular coordination complexes (Roesky & Andruh, 2003). Recently, an efficient N/O-donor ligand, 1*H*-imidazole-4,5-dicarboxylic acid (H_3IDC), which possesses diverse coordination modes and the potential ability for generating hydrogen bonds, has attracted considerable attention (Lu & Ge, 2005; Wang, Cao & Bi, 2004; Liu *et al.*, 2005). Notably, the sites and levels of deprotonation of H_3IDC when coordinating to the metal centers will result in a variety of structural motifs under appropriate conditions (Liu *et al.*, 2004; Maji *et al.*, 2005; Wang, Gao *et al.*, 2004). With respect to Cd^{II}—H_3IDC complexes, mononuclear (Zhang *et al.*, 2004) and one-dimensional zigzag coordination motifs have been reported (Sun *et al.*, 2004), in which H_3IDC is deprotonated to different levels and in varying positions. Here, we report the crystal structure of a new mononuclear Cd^{II} complex $[Cd(H_2IDC)_2(H_2O)_3](H_2O)$, (I), in which the H_2IDC anion acts as a monodentate ligand only, and rich hydrogen-bonded interactions extend the molecular structure into a three-dimensional supramolecular architecture.



(I)

In the neutral mononuclear molecule of (I), each H_3IDC ligand is mono-deprotonated at the 5-position carboxylate group, thus generating intramolecular O2—H2···O3 and

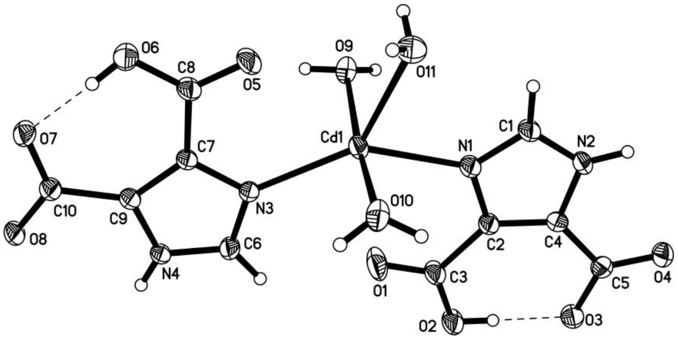


Figure 1
The structure of the title complex with atom labeling (anisotropic displacement ellipsoids are drawn at the 30% probability level). The uncoordinated water molecule has been omitted for clarity, and the intramolecular hydrogen bonds are indicated by dashed lines.

O6—H6*A*···O7 hydrogen bonds between the adjacent carboxyl and carboxylate groups (Fig. 1). The Cd^{II} center is coordinated by two N atoms of distinct H_2IDC anions and three water molecules (Table 1), with two carboxyl O atoms (O5 and O1) weakly bonded to Cd^{II} [Cd···O = 2.719 (1) and 2.722 (2) Å]. The coordination sphere of Cd^{II} could be described as a distorted trigonal bipyramid, with atoms N1, N3 and O11 in the basal plane and two aqua ligands (O9 and O10) in axial positions [O9—Cd1—O10 = 169.57 (9)°]. In all previously documented cases, the H_2IDC anion always served as an *N*,*O*-bidentate ligand. Of particular interest is the fact that H_2IDC in this structure uses only one N atom binding to the Cd^{II} atom, which is unprecedented in the coordination chemistry of H_3IDC and its complexes. Two related Cd^{II} complexes of H_3IDC have been reported recently. In the neutral mononuclear molecule $[Cd(H_2IDC)_2(H_2O)_2]$ (Zhang *et al.*, 2004), each H_3IDC ligand is also mono-deprotonated, however, at the 4-position carboxylate group, and coordinates to Cd^{II} in the common *N*,*O*-chelating fashion. Another case (Sun *et al.*, 2004) is a one-dimensional coordination chain, $[Cd(HIDC)(H_2O)_2]_n$, in which both the 5-position carboxyl and the imidazole group are deprotonated, and thus each HIDC dianion uses a pair of *N*,*O*-chelating coordination sites to bind two adjacent Cd^{II} centers. As expected, both structures are ultimately extended into three-dimensional hydrogen-bonded networks. In this structure, H_2IDC can provide both donor and acceptor components for hydrogen bonds. In addition both the ligand and the solvent water molecules can also participate in hydrogen-bonding interactions; as a result, rich hydrogen-bond networks are established, which link the mononuclear molecules to form a three-dimensional network (Table 2). Each mononuclear molecule is hydrogen-bonded to three adjacent subunits *via* two single N2—H2*A*···O5^{i} and a pair of N4—H4*A*···O8^{ii} interactions [synthon $R_2^2(10)$ (Bernstein *et al.*, 1995)] between the carboxylate and imidazole groups, affording a two-dimensional (6,3)-sheet (Fig. 2; symmetry codes as in Table 2). Furthermore, these sheets are linked *via* interlayer O9—H9*B*···O8^{iv}, O10—H10*A*···O7^{v} and O10—H10*B*···O4^{vi} bonds between the axial aqua ligands and carboxylate O atoms, resulting in a three-dimensional architecture. There also exist intermolecular O9—H9*A*···O12^{iii} and O11—H11*B*···O12^{vii} bonds between the coordinated and uncoordinated water molecules, and O12—H12*A*···O2^{viii} and O12—H12*B*···O3^{ix} interactions between the uncoordinated water and carboxyl/carboxylate O atoms, which may further stabilize the three-dimensional crystal packing. Examination of this structure with *PLATON* (Spek, 2003) reveals no solvent-accessible voids in the unit cell.

Experimental

A mixture of $Cd(OAc)_2\cdot2H_2O$ (30 mg, 0.1 mmol), 1*H*-imidazole-4,5-dicarboxylic acid (16 mg, 0.1 mmol), 2,5-bis(4-pyridyl)-1,3,4-oxadiazole (22 mg, 0.1 mmol) and triethylamine (0.2 ml) in water (10 ml) was sealed in a Teflon-lined stainless steel vessel (20 ml) and heated at 413 K for 5 d. Upon cooling to room temperature at a rate of 5 K h^{-1}, pale-yellow block-shaped crystals were produced in 61% yield (15 mg). IR (KBr pellet, cm^{-1}): 3229 (*b*), 1600 (*vs*), 1547 (*vs*), 1387 (*vs*), 1230 (*m*), 1059 (*w*), 1021(*w*), 829 (*w*), 772 (*s*), 694 (*s*), 522 (*w*).

Crystal data

$[Cd(C_5H_3N_2O_4)_2(H_2O)_3]\cdot H_2O$
M_r = 494.66
Monoclinic, $P2_1/c$
a = 6.8945 (9) Å
b = 17.432 (2) Å
c = 13.8726 (19) Å
β = 97.771 (2)°
V = 1652.0 (4) Å^3
Z = 4

D_x = 1.989 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4160 reflections
θ = 2.3–28.0°
μ = 1.40 mm^{-1}
T = 293 (2) K
Block, pale yellow
0.38 × 0.16 × 0.10 mm

Data collection

Bruker APEX-II CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.602, $T_{\max}$ = 0.870
9284 measured reflections

2913 independent reflections
2547 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.024
$\theta_{\max}$ = 25.0°
$h = -8 \rightarrow 8$
$k = -20 \rightarrow 20$
$l = -16 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.082
S = 1.05
2913 reflections
254 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.06P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.002
$\Delta\rho_{\max}$ = 1.08 e Å^{-3}
$\Delta\rho_{\min}$ = −0.63 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd1—N3	2.257 (2)	O3—C5	1.285 (3)
Cd1—N1	2.261 (2)	O4—C5	1.230 (4)
Cd1—O9	2.276 (2)	O5—C8	1.226 (4)
Cd1—O10	2.288 (3)	O6—C8	1.286 (4)
Cd1—O11	2.374 (2)	O7—C10	1.262 (3)
O1—C3	1.202 (4)	O8—C10	1.236 (3)
O2—C3	1.298 (4)		
N3—Cd1—N1	139.63 (8)	N1—Cd1—O11	84.45 (7)
N3—Cd1—O9	92.57 (8)	O9—Cd1—O11	87.41 (9)
N1—Cd1—O9	89.93 (8)	O10—Cd1—O11	82.35 (10)
N3—Cd1—O10	93.41 (8)	O1—C3—O2	123.1 (3)
N1—Cd1—O10	91.04 (8)	O4—C5—O3	125.5 (3)
O9—Cd1—O10	169.57 (9)	O5—C8—O6	122.5 (2)
N3—Cd1—O11	135.91 (7)	O8—C10—O7	125.1 (3)

Zhao *et al.* • $[Cd(C_5H_3N_2O_4)_2(H_2O)_3]\cdot H_2O$ **m1747**

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O3	0.82	1.64	2.458 (3)	179
O6—H6A···O7	0.82	1.63	2.450 (3)	178
N2—H2A···O5^{i}	0.86	2.16	2.998 (3)	164
N4—H4A···O8^{ii}	0.86	1.97	2.807 (3)	164
O9—H9A···O12^{iii}	0.85	1.85	2.703 (3)	178
O9—H9B···O8^{iv}	0.85	1.94	2.756 (3)	160
O10—H10A···O7^{v}	0.85	2.00	2.851 (3)	172
O10—H10B···O4^{vi}	0.85	1.91	2.727 (3)	160
O11—H11B···O12^{vii}	0.85	1.95	2.793 (3)	169
O12—H12A···O2^{viii}	0.85	2.09	2.929 (3)	170
O12—H12B···O3^{ix}	0.85	1.98	2.833 (3)	179

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

Although all H atoms were visible in difference maps, they were finally placed in geometrically calculated positions with C—H = 0.93 Å, N—H = 0.86 Å, and O—H = 0.82 Å for carboxyl groups and 0.85 Å for water molecules, and included in the final refinement in the riding model approximation, with displacement parameters derived from their parent atoms [$U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C,N,O_{water}})$ and $1.5U_{\rm eq}({\rm O_{COOH}})$]. The highest electron-density peak is located 0.97 Å from atom Cd1.

Data collection: *APEX-II* (Bruker, 2003); cell refinement: *APEX-II* and *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001) and *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *SHELXTL*.

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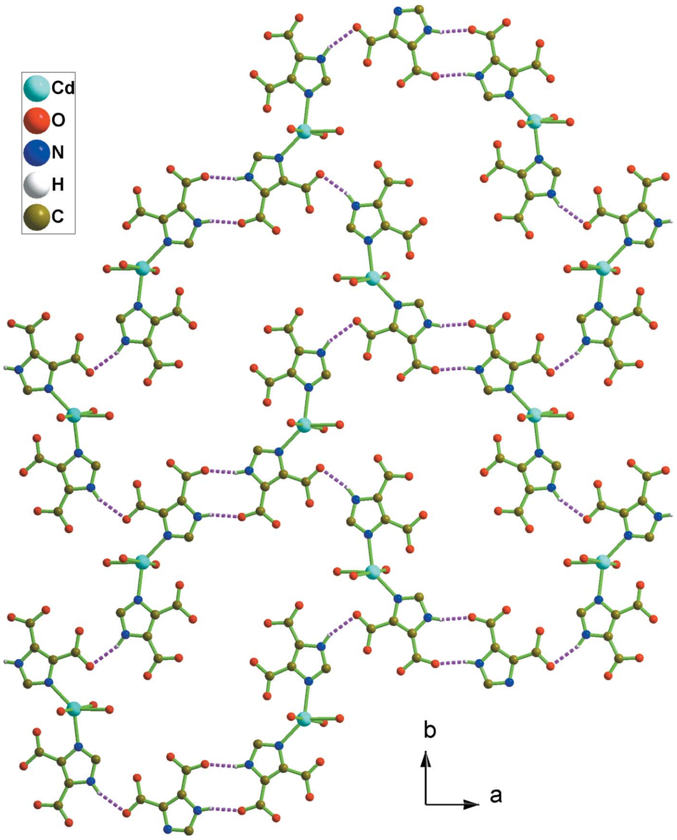

Figure 2
A perspective view of the two-dimensional hydrogen-bonded sheet extending along the (110) plane. Dashed lines indicate hydrogen bonds.

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