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A capped trigonal prismatic cadmium complex with tetra- and tridentate ligands: bis(triethanolamine)-$\kappa^3N,O,O';\kappa^4N,O,O',O''$-cadmium(II) squarate monohydrate

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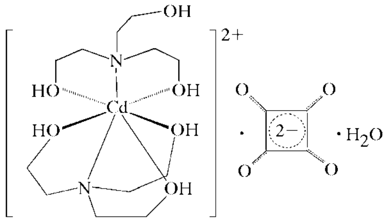
In the crystal structure of the title compound, $[Cd(C_6H_{15}NO_3)_2](C_4O_4)\cdot H_2O$, a supramolecular structure is observed. The asymmetric unit consists of one unit of the cationic Cd complex, one water molecule and two half-squarate anions, each sitting on a crystallographic inversion center. The different coordinations of the two triethanolamine (TEA) ligands results in an unusual example of coordination number seven for the Cd^{II} ion. Both TEA ligands coordinate to the Cd^{II} ion, forming a distorted monocapped trigonal prismatic geometry with approximate C_{2v} symmetry. One of the TEA ligands acts as an N,O,O'-tridentate ligand, whereas the other behaves as an N,O,O',O''-tetradentate donor. The anions and cations are linked to one another by hydrogen bonds between hydroxy H atoms of the TEA ligands and squarate O atoms. The crystal structure is stabilized by O—H···O hydrogen bonds between the unligated water molecule and a squarate O atom, together with a weak π–ring interaction between the ethylene group of a TEA ligand and a squarate anion.

Comment

Supramolecular structures containing metal ions have attracted much interest from a variety of scientific disciplines for different kinds of applications, such as zeolite-like materials (Venkataraman *et al.*, 1995), catalysts (Fujita *et al.*, 1994) and magnetic materials (Kahn, 1993). In order to understand the properties of supramolecular architectures, detailed structural information is required. In this context, we have synthesized bis(triethanolamine)cadmium(II) squarate monohydrate, (I). Squaric acid was selected because of its utility in building cocrystals (Bouma *et al.*, 1999; Bertolasi *et al.*, 2001; Bulut *et al.*, 2003), and the triethanolamine (TEA) molecule was used as a ligand because it contains four donor atoms, *viz.* three hydroxy O atoms and one amine N atom. The TEA ligand usually acts as an N,O,O'-tridentate ligand in transition metal complexes (Sen & Dotson, 1970; İçbudak *et al.*, 1995; Ucar *et al.*, 2004). However, TEA may also act as an N,O,O',O''-tetradentate ligand when geometric demands enforce high coordination numbers or the metal ions have large ionic radii (Naiini & Verkade, 1995, 1996; Topcu *et al.*, 2002; Starynowicz & Gatner, 2003), although such behavior is not common. Coordination number seven is rare because of increased ligand–ligand repulsion, weaker bonds and, usually, reduced crystal field stabilization in comparison with octahedral complexes. Seven-coordination is most commonly found in discrete complexes of second- and third-row transition metals, such as lanthanides and actinides (Arndt *et al.*, 2002; Han *et al.*, 1999). The three known coordination geometries for seven-coordination are (i) pentagonal bipyramidal, (ii) capped octahedral with a seventh ligand added to a rectangular face and (iii) capped trigonal prismatic with a seventh ligand added to a rectangular face. These geometries are considered to have approximately equal *a priori* probabilities (Park *et al.*, 1970). The third coordination geometry, *viz.* (iii), is observed in (I).



(I)

An *ORTEP*III (Burnett & Johnson, 1996) view of (I) and the atom-labeling scheme are shown in Fig. 1. The crystal structure contains a $[Cd(TEA)_2]^{2+}$ complex cation and an uncoordinated squarate dianion, $C_4O_4^{2-}$. The structure of the complex cation reveals a heptacoordinated Cd^{II} ion with a coordination polyhedron best described as a distorted monocapped trigonal prism with approximate C_{2v} symmetry. In the complex cation, in which the Cd^{II} ion is coordinated by

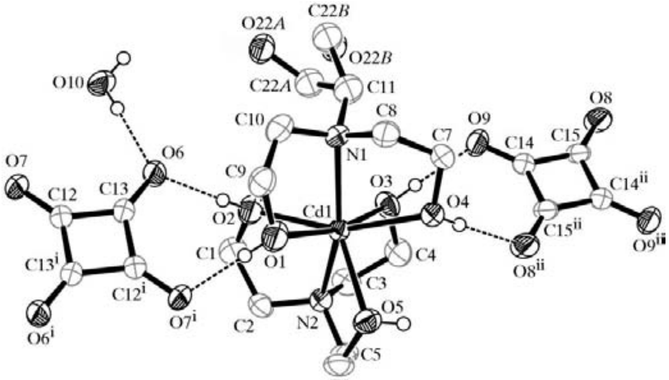


Figure 1
A view of (I), showing the atom-numbering scheme. H atoms of hydroxy groups and of the water molecule are shown as small circles, and hydrogen bonds are indicated by dashed lines. Methylene H atoms have been omitted. [Symmetry codes: (i) $x, y, 1 + z$; (ii) $1 + x, 1 + y, 2 + z$.]

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two TEA ligands and is seven-coordinate, both tri- and tetradentate TEA molecules are present. The coordination modes of the two TEA molecules are different. One molecule coordinates to the Cd^{II} ion through all donor atoms, behaving as an *N*,*O*,*O*′,*O*″-tetradentate ligand, while the other coordinates through two hydroxy O atoms and the amine group, acting as an *N*,*O*,*O*′-tridentate ligand and leaving the other hydroxy group free. The C and O atoms of the free hydroxy group, C22 and O22, are disordered over two positions, with occupancies of 0.7 for O22*A*/C22*A* and 0.3 for O22*B*/C22*B*.

In the monocapped trigonal prism, the O1/O4/O5 and O2/O3/N2 triangular planes form the bases; these planes are nearly parallel to one another, with a dihedral angle of 6.08 (3)°. The rectangular faces [O3/O4/N2/O5 (plane 1), O1/O2/O3/O4 (plane 2) and O1/O2/N2/O5 (plane 3)] are almost planar, with r.m.s. deviations of 0.0679, 0.0884 and 0.1223 Å, and the maximum deviations from these planes are 0.071 (2) Å for atom N2, 0.092 (2) Å for atom O3 and 0.131 (2) Å for atom N2, respectively. The dihedral angles between these least-squares planes are 77.07 (11)° between planes 1 and 3, 51.14 (9)° between planes 2 and 3, and 51.86 (11)° between planes 1 and 2. The dihedral angles between plane 1 and the nearly parallel triangular bases are 86.03 (12) and 82.51 (13)°. In the monocapped trigonal prism, atom N1 is located at the axial position, while atoms N2 and O5 are in pseudo-axial positions. When the capping atom N1 (additional ligand) is added on top of a face of the trigonal prism, a slight distortion occurs. The Cd—O bond distances are in the range 2.310 (4)–2.457 (4) Å (Table 1), while the Cd—N bond distances are 2.390 (4) and 2.404 (4) Å. The Cd—O and Cd—N bond distances are different in the tetra- and tridentate TEA ligands, so the two TEA ligands are not equivalent. All the O—Cd—O angles deviate significantly from 90 and 180°. The central Cd^{II} ion is located 0.2498 (16) Å below plane 2. These values are comparable to those observed for another Cd^{II}–TEA complex (Andac *et al.*, 2001; Naiini & Verkade, 1995). The values also indicate that the coordination geometry around the Cd^{II} ion is irregular, presumably as a result of the steric constraints arising from the shape of the polydentate ligands.

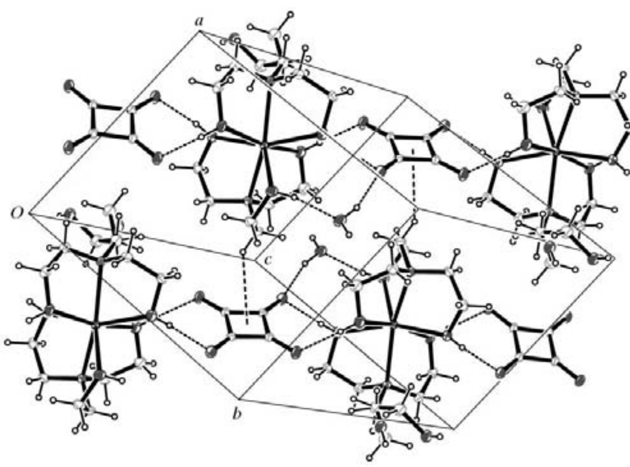

Figure 2
The three-dimensional structure of (I). Dashed lines illustrate the hydrogen bonds and π–ring interactions.

The uncoordinated squarate anions are almost coplanar and play an important role in the supramolecular architecture. The O—C bond distances are in the range 1.246 (6)–1.256 (6) Å in the squarate anion, while the unique C—C bond distances are 1.451 (6) and 1.458 (7) Å. These bond lengths agree with the fact that the squarate anion, which possesses a pronounced degree of delocalization, is considered to be aromatic. Each squarate anion is surrounded by four [Cd(TEA)$_2$]$^{2+}$ cations. As shown in Fig. 2, the squarate O atoms participate in hydrogen bonds with the hydroxy H atoms (O atoms lie on the equatorial plane) of the TEA ligands. The uncoordinated water molecules link the complex cation to the squarate ion through hydrogen-bonding interactions (see Table 2 for details). In the extended structure (Fig. 2), there is also a weak C—H···π interaction between atoms C5 and H5*B* of the tetradentate TEA ligand and a squarate anion. For the C—H···*Cg* contact (*Cg* is the center of the squarate ion containing atoms C14 and C15), the distance between the squarate centroid and the nearest methylene H atom is 2.99 Å. The perpendicular distance between atom H5*B* and the center of the squarate ion is 2.86 Å and the C—H···*Cg* angle is 144°. An extensive network of hydrogen bonds and C—H···π intermolecular interactions embeds the complex in an infinite three-dimensional lattice.

Experimental

Squaric acid (0.57 g, 5 mmol), dissolved in water (25 ml), was neutralized with NaOH (0.40 g, 10 mmol) and was added to a hot solution of CdCl$_2$·H$_2$O (0.201 g, 5 mmol) in water (50 ml). The mixture was stirred at 333 K for 12 h and then cooled to room temperature. The resulting yellow crystals were filtered off, washed with water and alcohol, and dried in a vacuum. A solution of triethanolamine (0.298 g, 2 mmol) in methanol (50 ml) was added dropwise with stirring to a suspension of cadmium squarate dihydrate (0.26 g, 1 mmol) in water (50 ml). The mixture was heated to 323 K, maintained at this temperature for 12 h and then left to cool to room temperature. A few days later, well formed crystals were selected for X-ray studies.

Crystal data

[Cd(C$_6$H$_{15}$NO$_3$)$_2$](C$_4$O$_4$)·H$_2$O
M_r = 539.83
Triclinic, $P\bar{1}$
a = 9.135 (5) Å
b = 10.972 (5) Å
c = 11.968 (5) Å
α = 71.537 (5)°
β = 70.118 (5)°
γ = 86.582 (5)°
V = 1068.4 (9) Å^3
Z = 2
D_x = 1.678 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 16 158 reflections
θ = 1.9–25.9°
μ = 1.08 mm^{-1}
T = 293 (2) K
Prism, colorless
0.4 × 0.3 × 0.2 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: by integration (*X-RED*32; Stoe & Cie, 2002)
$T_{\min}$ = 0.480, $T_{\max}$ = 0.819
4123 measured reflections
4123 independent reflections
3368 reflections with $I > 2\sigma(I)$
$\theta_{\max}$ = 25.9°
$h = -10 \rightarrow 11$
$k = -12 \rightarrow 13$
$l = 0 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.118$
$S = 0.97$
4123 reflections
277 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0878P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.17$ e Å^{-3}
$\Delta\rho_{\min} = -2.53$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.023 (2)

Table 1
Selected geometric parameters (Å, °).

Cd1—O1	2.310 (4)	O6—C13	1.256 (6)
Cd1—O3	2.363 (4)	O7—C12	1.246 (6)
Cd1—O4	2.379 (4)	O8—C15	1.248 (6)
Cd1—N1	2.390 (4)	O9—C14	1.253 (6)
Cd1—O5	2.399 (4)	C12—C13	1.458 (7)
Cd1—N2	2.404 (4)	C14—C15	1.451 (6)
Cd1—O2	2.457 (4)		
O1—Cd1—O3	166.28 (14)	O3—Cd1—N2	72.78 (13)
O1—Cd1—O4	104.74 (14)	O4—Cd1—N2	123.19 (13)
O3—Cd1—O4	81.38 (13)	N1—Cd1—N2	157.68 (14)
O1—Cd1—N1	73.67 (15)	O5—Cd1—N2	73.42 (13)
O3—Cd1—N1	96.99 (13)	O1—Cd1—O2	80.65 (15)
O4—Cd1—N1	72.97 (13)	O3—Cd1—O2	89.51 (14)
O1—Cd1—O5	78.40 (14)	O4—Cd1—O2	159.51 (14)
O3—Cd1—O5	115.27 (13)	N1—Cd1—O2	90.13 (15)
O4—Cd1—O5	73.66 (13)	O5—Cd1—O2	126.77 (14)
N1—Cd1—O5	128.56 (13)	N2—Cd1—O2	70.41 (14)
O1—Cd1—N2	112.22 (15)		
O7—C12—C13—O6	−0.2 (12)	O9—C14—C15—O8	0.0 (11)

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

D—H···A	D—H	H···A	D···A	D—H···A
O10—H7···O8$^{\rm iii}$	0.83 (8)	2.03 (6)	2.770 (5)	148 (10)
O10—H6···O6	0.83 (3)	1.92 (3)	2.749 (6)	171 (7)
O3—H3···O9	0.81 (3)	1.88 (3)	2.685 (5)	179 (6)
O4—H4···O8$^{\rm iv}$	0.82 (3)	1.86 (3)	2.662 (5)	168 (7)
O5—H5···O10$^{\rm v}$	0.86 (9)	1.85 (4)	2.690 (6)	164 (9)
O1—H1···O7$^{\rm vi}$	0.78 (3)	1.83 (7)	2.614 (6)	177 (8)
O2—H2···O6	0.77 (3)	1.89 (3)	2.658 (6)	176 (6)

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

The hydroxy and water H atoms were located from a difference map and then restrained to an O—H distance of 0.84 (3) Å. Other H atoms were placed at calculated positions (C—H = 0.97 Å) and were allowed to ride on their parent atoms [$U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$]. The disordered hydroxymethyl moiety [site-occupancy factors of 0.694 (6) for O22*A*/C22*A* and 0.306 (6) for O22*B*/C22*B*] was refined anisotropically, with constraints and restraints imposed on the C—C and O—C distances, the N—C—C and C—C—O angles, and the anisotropic displacement parameters of the O and C atoms. The highest peak and deepest hole are located 0.05 and 0.11 Å from atoms O2 and O22*B*, respectively, and are thus related to disorder in the O atoms.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe & Cie, 2002); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1064). Services for accessing these data are described at the back of the journal.

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