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Bis(triethanolamine)calcium 3,5-Dinitrobenzoate

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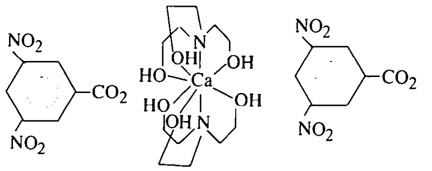
Abstract

In the title complex, $[Ca(C_6H_{15}NO_3)_2](C_7H_3N_2O_6)_2$, the Ca^{2+} ion is sandwiched between two triethanolamine ligands (IUPAC nomenclature: 2,2′,2″-nitrilotriethanol), each of them coordinating through all four potential donor sites. The coordination polyhedron is distorted cubic. The 3,5-dinitrobenzoate counteranions do not interact directly with the cation but are hydrogen bonded to the hydroxy groups of the triethanolamine ligands.

Comment

In the complexes of *s*-block metal ions having a general formula *M*(anion)(ligand)(solvent), where the ligand is a neutral molecule having O or N as donor atom, the structure depends on whether or not the ligand has a polar or polarizable H atom (Poonia & Bajaj, 1979; Fenton, 1987). Important ligands in the latter category are 1,10-phenanthroline, 2,2′-bipyridine, *etc.* These ligands only interact with the cation and do not interact with the counteranion through hydrogen bonding. The neutral ligands possessing polar or polarizable H atoms include hydroxy compounds and amines. Important examples include glycols, ethylenediamine, triethanolamine, *etc.* These ligands usually interact with the cation and are hydrogen bonded with the counteranion through polar H atoms. In the complexes of such ligands with *s*-block metals, the counteranion can interact with the complexed cation or can be excluded from the coordination sphere around the cation to give complexes where the counteranion is not directly interacting with the cation. The counteranion of the title compound is 3,5-dinitrobenzoate (DNB), which exhibits a wide range of coordination modes. In Ca^{2+} complexes, DNB has been found to act as a bridging bidentate, chelating bidentate and bridging tridentate ligand (Hundal, Martinez-Ripoll, Hundal & Poonia, 1995; Cradwick & Poonia, 1977; Kanters, Harder & Poonia, 1987). The structure of the title compound, (I), has been solved to determine the behaviour of the neutral ligand triethanolamine (TEA) and to determine the nature of the interaction of the counteranion 3,5-dinitrobenzoate with the cation and to compare the behaviour of the counteranion with that of 2,4-dinitrophenolate (DNP). Thermogravimetric analysis of the compound revealed that the solvent was not present in the final crystalline phase.



(I)

The crystal structure is shown in Fig. 1. The Ca atom is eightfold coordinated by two triethanolamine ligands. The TEA ligands use all four potential donor atoms, *i.e.* three O and one N atom. The coordination around Ca can be classified as distorted cubic, as can be seen from Fig. 2. The Ca—O distances are in the range 2.393 (7)–2.454 (8) Å and the Ca—N distances are 2.708 (5) and 2.730 (5) Å. The Ca—N bond distances are slightly longer than that observed in $Ca(TEA)(DNP)_2$ [2.600 (7) Å; Hundal *et al.*, 1995]. In the other complexes of TEA with NaI (Voegele, Fischer & Weiss, 1974*a*), $Sr(nitrate)_2$ (Voegele, Fischer & Weiss, 1974*b*), $Ba(acetate)_2$ (Voegele, Thierry & Weiss, 1974), $Ba(DNP)_2$ (Kanters, Smeets, Venkatasubramanian & Poonia, 1984), and $Ca(DNP)_2$ (Hundal *et al.*, 1995), the TEA ligand normally has an extended conformation, due to the presence of at least three almost planar C—N—C—C fragments, and a *gauche* conformation of the terminal OH group with respect to the

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C—N bonds. In the present complex, one TEA ligand [referred to as TEA(*C*) in the text] fulfills the above conditions (torsion angles are in the range given in the literature) and is considered to have an extended conformation, but the second [with all atoms having letters *D* in the label, referred to as TEA(*D*)] deviates significantly from this. The two ligands also differ from each other with respect to their bond distances. Bond distances in TEA(*D*) are in general shorter than those found in TEA(*C*). Mean C—O and C—N distances are 1.438 (9) and 1.476 (12) Å, respectively, in TEA(*C*) and 1.396 (10) and 1.416 (17) Å, respectively, in TEA(*D*).

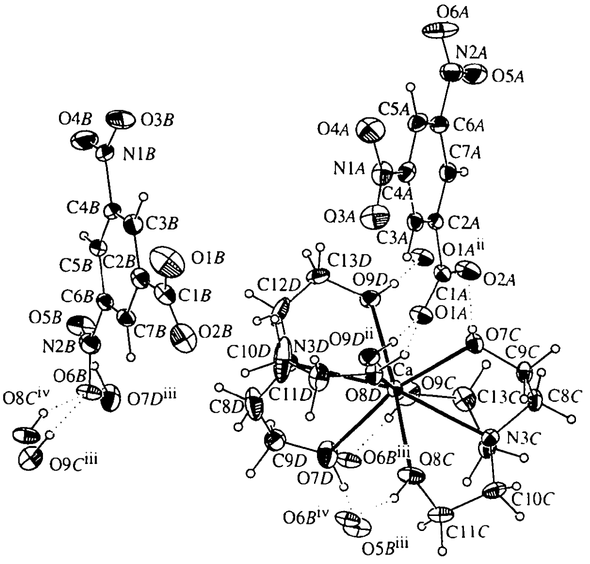

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the final model showing the atomic labelling and hydrogen-bonding scheme. Non-H atoms are shown with displacement ellipsoids drawn at the 30% probability level. H-atom labels have been omitted for clarity.

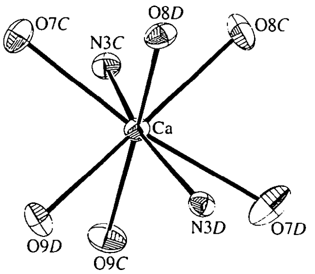

Fig. 2. The distorted cubic coordination around the Ca^{2+} ion.

Bond lengths and bond angles of the DNB counterannions are normal and comparable except for the carboxylate and O5—N2—O6 groups in both. Bond distances of the carboxylate group in DNB(*B*) are smaller than in DNB(*A*) and the reverse is true for the O5—N2—O6 group. This might be due to the fact that the —COO group of DNB(*A*) and O5—N2—O6 of DNB(*B*) are involved in hydrogen bonding, thus giving relatively longer bond lengths. Substitution does not influence the planarity of the phenyl rings, the average deviations being 0.009 (8) and 0.005 (8) Å for DNB(*A*) and DNB(*B*), respectively. In DNB(*A*) the carboxylate and the nitro groups attached at positions 3 and 5 form dihedral angles of 12.8 (6), 174.3 (4) and 5.2 (8)°, respectively, with the phenyl ring, while these angles are 16.9 (4), 176.0 (9) and 11.4 (6)° in DNB(*B*). All the hydroxy H atoms of TEA are involved in extensive inter- and intramolecular hydrogen bonding (Table 3) with the DNB anions. O7*C* and O8*D* act as hydrogen-bond donors towards O2*A* and O1*A* of the carboxylate group of DNB(*A*) giving rise to two intramolecular hydrogen bonds. O1*A* also accepts an H atom from O9*D*. Both O8*C* and O9*C* donate H atoms to O6*B*. O7*D* forms another hydrogen bond with O5*B*. The hydrogen bonding decreases the nucleophilic character of the anion and, as a result, the tendency of the anion to interact with Ca^{2+} is decreased and the anion is not involved in metal coordination. On the other hand, as was observed in our previous studies on Ca(TEA)(2,4-dinitrophenolate)$_2$, an ion-paired complex is formed (Hundal *et al.*, 1995) because the interaction between the highly nucleophilic chelating anion and the Ca^{2+} cation is very strong and hydrogen bonding is not strong enough to separate the cation from the anion. On the basis of this trend, we expect that in the Ca(picrate)$_2$(TEA)$_2$ system the cation would not coordinate with the anion because the picrate anion is more resonance stabilized and less nucleophilic than 2,4-dinitrophenolate and 3,5-dinitrobenzoate.

Experimental

The title compound was prepared by adding triethanolamine to a solution of Ca(3,5-dinitrobenzoate) in 1:1 ratio, and crystallizing by slow evaporation. The density D_m was measured by flotation.

Crystal data

$[Ca(C_6H_{15}NO_3)_2]$-
$(C_7H_3N_2O_6)_2$
$M_r = 760.68$
Triclinic
$P\bar{1}$
$a = 7.2894 (9)$ Å
$b = 14.221 (4)$ Å
$c = 17.324 (5)$ Å
$\alpha = 106.49 (3)^\circ$
$\beta = 99.47 (2)^\circ$
$\gamma = 93.37 (1)^\circ$
$V = 1687.9 (8)$ Å^3
$Z = 2$
$D_x = 1.497$ Mg m^{-3}
$D_m = 1.487$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 41 reflections
$\theta = 8$–20°
$\mu = 0.263$ mm^{-1}
$T = 293$ K
Prism
0.30 × 0.25 × 0.20 mm
Light yellow

Data collection

Philips PW1100 diffractometer
ω scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.945$, $T_{\max} = 1.000$
6052 measured reflections
5964 independent reflections
3828 observed reflections [$F > 2\sigma(F)$]
$R_{\rm int} = 0.0269$
$\theta_{\max} = 25.03°$
$h = -8 \rightarrow 8$
$k = -16 \rightarrow 16$
$l = 0 \rightarrow 20$
2 standard reflections
frequency: 90 min
intensity decay: 1%

Refinement

Refinement on F
$R = 0.062$
$wR = 0.08$
$S = 1.115$
3828 reflections
460 parameters
H-atom parameters not refined
Weighting scheme: *PESOS* (Martinez-Ripoll & Cano, 1975)
$(\Delta/\sigma)_{\max} = 0.074$
$\Delta\rho_{\max} = 1.301$ e Å^{-3}
$\Delta\rho_{\min} = -0.915$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ca	0.1461 (2)	−0.0345 (1)	0.22833 (9)	0.0321 (7)
O1*A*	0.6693 (7)	0.1269 (4)	0.1743 (4)	0.056 (3)
O2*A*	0.4075 (8)	0.1481 (4)	0.0996 (4)	0.066 (3)
O3*A*	1.2102 (10)	0.3777 (6)	0.2248 (5)	0.090 (4)
O4*A*	1.1626 (11)	0.5220 (6)	0.2193 (5)	0.105 (5)
O5*A*	0.3234 (14)	0.4696 (6)	0.0640 (5)	0.098 (5)
O6*A*	0.5466 (12)	0.5864 (6)	0.1064 (6)	0.111 (6)
N1*A*	1.1086 (12)	0.4368 (7)	0.2084 (5)	0.067 (4)
N2*A*	0.4845 (16)	0.5021 (7)	0.0954 (6)	0.075 (5)
C1*A*	0.5697 (11)	0.1750 (6)	0.1367 (5)	0.042 (4)
C2*A*	0.6526 (10)	0.2772 (5)	0.1396 (4)	0.039 (3)
C3*A*	0.8406 (11)	0.3073 (6)	0.1683 (5)	0.045 (4)
C4*A*	0.9058 (12)	0.4034 (6)	0.1732 (5)	0.050 (4)
C5*A*	0.7943 (14)	0.4693 (6)	0.1511 (5)	0.057 (5)
C6*A*	0.6097 (12)	0.4344 (6)	0.1208 (5)	0.049 (4)
C7*A*	0.5357 (11)	0.3402 (6)	0.1143 (5)	0.049 (4)
O1*B*	0.9144 (12)	0.4041 (8)	0.5464 (7)	0.131 (6)
O2*B*	0.8372 (10)	0.2551 (8)	0.5333 (5)	0.093 (5)
O3*B*	0.4479 (15)	0.6292 (6)	0.6000 (6)	0.121 (6)
O4*B*	0.2284 (18)	0.5952 (6)	0.6596 (6)	0.126 (7)
O5*B*	0.1224 (9)	0.2712 (5)	0.6931 (4)	0.073 (4)
O6*B*	0.3557 (8)	0.1748 (4)	0.6871 (4)	0.060 (3)
N1*B*	0.3656 (18)	0.5755 (6)	0.6294 (5)	0.087 (6)
N2*B*	0.2803 (13)	0.2507 (6)	0.6811 (5)	0.073 (5)
C1*B*	0.8122 (12)	0.3397 (9)	0.5549 (6)	0.056 (5)
C2*B*	0.6489 (12)	0.3655 (7)	0.5911 (5)	0.055 (4)
C3*B*	0.5926 (14)	0.4573 (7)	0.5949 (6)	0.061 (5)
C4*B*	0.4354 (15)	0.4783 (6)	0.6253 (5)	0.060 (5)
C5*B*	0.3304 (13)	0.4144 (6)	0.6540 (5)	0.054 (4)
C6*B*	0.3948 (11)	0.3233 (6)	0.6502 (5)	0.044 (4)
C7*B*	0.5551 (11)	0.2980 (6)	0.6195 (5)	0.045 (4)
O7*C*	0.1821 (8)	−0.0050 (4)	0.1016 (3)	0.055 (3)
O8*C*	0.3200 (8)	−0.1741 (5)	0.2140 (4)	0.068 (3)
O9*C*	−0.1851 (8)	−0.0841 (5)	0.2125 (4)	0.069 (3)
N3*C*	0.0144 (8)	−0.1909 (4)	0.0922 (4)	0.043 (3)
C8*C*	0.0098 (12)	−0.1555 (6)	0.0201 (5)	0.054 (4)
C9*C*	0.1792 (11)	−0.0864 (6)	0.0300 (5)	0.048 (4)
C10*C*	0.1356 (14)	−0.2705 (6)	0.0919 (6)	0.065 (5)
C11*C*	0.2188 (13)	−0.2690 (7)	0.1755 (7)	0.065 (5)
C12*C*	−0.1776 (12)	−0.2231 (7)	0.0994 (5)	0.059 (4)
C13*C*	−0.2836 (11)	−0.1375 (8)	0.1297 (6)	0.065 (5)
O7*D*	0.1123 (11)	−0.1066 (5)	0.3389 (4)	0.088 (4)
O8*D*	0.4665 (7)	0.0372 (4)	0.2554 (3)	0.051 (3)
O9*D*	0.0180 (7)	0.1226 (4)	0.2548 (4)	0.056 (3)
N3*D*	0.2670 (8)	0.0890 (4)	0.3819 (4)	0.039 (3)
C8*D*	0.241 (2)	0.0392 (10)	0.4411 (7)	0.117 (8)
C9*D*	0.1127 (16)	−0.0486 (7)	0.4155 (6)	0.072 (6)
C10*D*	0.4580 (16)	0.1169 (11)	0.3911 (7)	0.139 (9)
C11*D*	0.5671 (12)	0.0757 (8)	0.3375 (6)	0.070 (5)
C12*D*	0.166 (3)	0.1726 (12)	0.3908 (8)	0.189 (11)
C13*D*	0.0718 (13)	0.2001 (6)	0.3291 (6)	0.068 (5)

Table 2. *Selected geometric parameters (Å, °)*

Ca—O8*C*	2.393 (7)	O6*B*—N2*B*	1.263 (11)
Ca—O7*C*	2.400 (6)	N1*B*—C4*B*	1.487 (14)
Ca—O8*D*	2.409 (5)	N2*B*—C6*B*	1.551 (13)
Ca—O9*C*	2.424 (6)	C1*B*—C2*B*	1.454 (13)
Ca—O9*D*	2.424 (6)	C2*B*—C3*B*	1.378 (14)
Ca—O7*D*	2.454 (8)	C2*B* C7*B*	1.390 (14)
Ca—N3*C*	2.730 (5)	C3*B*—C4*B*	1.352 (15)
Ca—N3*D*	2.708 (5)	C4*B*—C5*B*	1.401 (14)
O1*A*—C1*A*	1.255 (11)	C5*B*—C6*B*	1.391 (12)
O2*A*—C1*A*	1.231 (9)	C6*B*—C7*B*	1.387 (12)
O3*A*—N1*A*	1.214 (13)	O7*C*—C9*C*	1.433 (9)
O4*A*—N1*A*	1.203 (13)	O8*C*—C11*C*	1.421 (10)
O5*A*—N2*A*	1.213 (14)	O9*C*—C13*C*	1.459 (11)
O6*A*—N2*A*	1.206 (13)	N3*C*—C8*C*	1.470 (12)
N1*A*—C4*A*	1.496 (11)	N3*C*—C10*C*	1.476 (12)
N2*A*—C6*A*	1.472 (14)	N3*C*—C12*C*	1.482 (11)
C1*A*—C2*A*	1.526 (12)	C8*C*—C9*C*	1.486 (12)
C2*A*—C3*A*	1.376 (10)	C10*C*—C11*C*	1.468 (16)
C2*A*—C7*A*	1.381 (12)	C12*C*—C13*C*	1.495 (14)
C3*A*—C4*A*	1.394 (12)	O7*D*—C9*D*	1.349 (12)
C4*A*—C5*A*	1.371 (13)	O8*D*—C11*D*	1.423 (10)
C5*A*—C6*A*	1.369 (12)	O9*D*—C13*D*	1.416 (10)
C6*A*—C7*A*	1.382 (12)	N3*D*—C10*D*	1.396 (14)
O1*B*—C1*B*	1.203 (16)	N3*D*—C12*D*	1.42 (2)
O2*B*—C1*B*	1.189 (16)	N3*D*—C8*D*	1.431 (16)
O3*B*—N1*B*	1.211 (16)	C8*D*—C9*D*	1.429 (17)
O4*B*—N1*B*	1.214 (18)	C10*D*—C11*D*	1.352 (16)
O5*B*—N2*B*	1.239 (12)	C12*D*—C13*D*	1.34 (2)
O8*C*—Ca—O7*C*	97.0 (2)	C7*A*—C6*A*—N2*A*	118.9 (8)
O8*C*—Ca—O8*D*	76.5 (2)	C2*A*—C7*A*—C6*A*	118.9 (7)
O8*C*—Ca—O9*C*	110.9 (2)	O3*B*—N1*B*—O4*B*	124 (1)
O8*C*—Ca—O9*D*	170.7 (2)	O3*B*—N1*B*—C4*B*	117 (1)
O8*C*—Ca—O7*D*	71.2 (3)	O4*B*—N1*B*—C4*B*	119 (1)
O7*C*—Ca—O8*D*	76.6 (2)	O5*B*—N2*B*—O6*B*	127.5 (9)
O7*C*—Ca—O9*C*	105.2 (2)	O5*B*—N2*B*—C6*B*	116.7 (8)
O7*C*—Ca—O9*D*	83.5 (2)	O6*B*—N2*B*—C6*B*	115.8 (8)
O7*C*—Ca—O7*D*	166.0 (2)	O2*B*—C1*B*—O1*B*	123 (1)
O8*D*—Ca—O9*C*	171.9 (2)	O2*B*—C1*B*—C2*B*	118 (1)
O8*D*—Ca—O9*D*	94.6 (2)	O1*B*—C1*B*—C2*B*	119 (1)
O8*D*—Ca—O7*D*	106.7 (2)	C3*B*—C2*B*—C7*B*	122.7 (9)
O9*C*—Ca—O9*D*	77.9 (2)	C3*B*—C2*B*—C1*B*	118 (1)
O9*C*—Ca—O7*D*	73.5 (3)	C7*B*—C2*B*—C1*B*	119.8 (9)
O9*D*—Ca—O7*D*	109.4 (2)	C4*B*—C3*B*—C2*B*	117 (1)
O9*D*—Ca—N3*D*	65.5 (2)	C3*B*—C4*B*—C5*B*	124.5 (9)
O8*D*—Ca—N3*D*	65.5 (2)	C3*B*—C4*B*—N1*B*	119 (1)
O7*D*—Ca—N3*D*	65.0 (2)	C5*B*—C4*B*—N1*B*	116 (1)
N3*C*—Ca—N3*D*	166.6 (2)	C6*B*—C5*B*—C4*B*	116.6 (9)
N3*C*—Ca—O9*D*	123.5 (2)	C7*B*—C6*B*—C5*B*	121.3 (8)
N3*C*—Ca—O8*D*	120.1 (2)	C7*B*—C6*B*—N2*B*	121.1 (8)
N3*C*—Ca—O7*D*	101.7 (2)	C5*B*—C6*B*—N2*B*	117.6 (8)
O9*C*—Ca—N3*D*	108.1 (2)	C6*B*—C7*B*—C2*B*	118.2 (8)
O9*C*—Ca—N3*C*	67.3 (2)	C9*C*—O7*C*—Ca	120.0 (5)
O8*C*—Ca—N3*D*	107.5 (2)	C11*C*—O8*C*—Ca	117.3 (5)
O8*C*—Ca—N3*C*	64.6 (2)	C13*C*—O9*C*—Ca	116.5 (5)
O7*C*—Ca—N3*D*	127.3 (2)	C8*C*—N3*C*—C12*C*	110.6 (6)
O7*C*—Ca—N3*C*	65.7 (2)	C10*C*—N3*C*—C12*C*	110.5 (7)
O4*A*—N1*A*—O3*A*	123.2 (9)	N3*C*—C8*C*—C9*C*	111.0 (6)
O4*A*—N1*A*—C4*A*	117.7 (9)	O7*C*—C9*C*—C8*C*	107.4 (7)
O3*A*—N1*A*—C4*A*	119.1 (8)	C11*C*—C10*C*—N3*C*	111.6 (8)
O6*A*—N2*A*—O5*A*	124 (1)	O8*C*—C11*C*—C10*C*	106.5 (9)
O6*A*—N2*A*—C6*A*	118.7 (9)	N3*C*—C12*C*—C13*C*	112.0 (7)
O5*A*—N2*A*—C6*A*	117.7 (9)	O9*C*—C13*C*—C12*C*	106.4 (7)

O2*A*—C1*A*—O1*A*	125.6 (8)	C9*D*—O7*D*—Ca	120.9 (7)
O2*A*—C1*A*—C2*A*	116.7 (8)	C11*D*—O8*D*—Ca	120.3 (5)
O1*A*—C1*A*—C2*A*	117.7 (6)	C13*D*—O9*D*—Ca	123.7 (5)
C3*A*—C2*A*—C7*A*	120.2 (8)	C10*D*—N3*D*—C12*D*	111 (1)
C3*A*—C2*A*—C1*A*	120.7 (7)	C10*D*—N3*D*—C8*D*	109 (1)
C7*A*—C2*A*—C1*A*	119.1 (7)	C12*D*—N3*D*—C8*D*	112 (1)
C2*A*—C3*A*—C4*A*	117.8 (8)	C9*D*—C8*D*—N3*D*	118.3 (9)
C5*A*—C4*A*—C3*A*	124.0 (8)	O7*D*—C9*D*—C8*D*	114 (1)
C5*A*—C4*A*—N1*A*	118.7 (8)	C11*D*—C10*D*—N3*D*	125 (1)
C3*A*—C4*A*—N1*A*	117.3 (8)	C10*D*—C11*D*—O8*D*	113.0 (8)
C6*A*—C5*A*—C4*A*	115.6 (8)	C13*D*—C12*D*—N3*D*	125 (1)
C5*A*—C6*A*—C7*A*	123.4 (8)	C12*D*—C13*D*—O9*D*	114.1 (9)
C5*A*—C6*A*—N2*A*	117.7 (8)		

C10*C*—N3*C*—C12*C*—C13*C*	159.5 (7)
C8*C*—N3*C*—C12*C*—C13*C*	−74.9 (9)
C8*C*—N3*C*—C10*C*—C11*C*	149.5 (8)
C10*C*—N3*C*—C8*C*—C9*C*	−79.4 (9)
C12*C*—N3*C*—C8*C*—C9*C*	156.3 (7)
C12*C*—N3*C*—C10*C*—C11*C*	−86.1 (9)
N3*C*—C8*C*—C9*C*—O7*C*	−59.7 (8)
N3*C*—C10*C*—C11*C*—O8*C*	−57.7 (10)
N3*C*—C12*C*—C13*C*—O9*C*	−63.8 (9)
C10*D*—N3*D*—C12*D*—C13*D*	99.6 (17)
C8*D*—N3*D*—C12*D*—C13*D*	−139.5 (15)
C8*D*—N3*D*—C10*D*—C11*D*	109.0 (14)
C10*D*—N3*D*—C8*D*—C9*D*	−136.7 (12)
C12*D*—N3*D*—C8*D*—C9*D*	101.3 (13)
C12*D*—N3*D*—C10*D*—C11*D*	−128.4 (14)
N3*D*—C8*D*—C9*D*—O7*D*	37.1 (15)
N3*D*—C10*D*—C11*D*—O8*D*	28.7 (17)
N3*D*—C12*D*—C13*D*—O9*D*	23 (2)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
O7*C*—H7*C*···O2*A*	1.89	2.661 (9)	155
O8*D*—H8*D*···O1*A*	1.66	2.695 (9)	151
O9*D*—H9*D*···O1*A*^{i}	1.78	2.704 (8)	163
O7*D*—H7*D*···O5*B*^{ii}	1.60	2.68 (1)	166
O9*C*—H9*C*···O6*B*^{ii}	1.72	2.83 (1)	164
O8*C*—H8*C*···O6*B*^{iii}	1.73	2.684 (8)	159

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

All H atoms were fixed geometrically except for the hydroxy H atoms which were located from a difference Fourier map. Weights were applied empirically so as to give no trends in $<w\Delta^2F>$ *versus* $<F_o>$ or $<\sin\theta/\lambda>$, using *PESOS* (Martinez-Ripoll & Cano, 1975).

Data collection: Philips PW1100 software. Cell refinement: *LSUCRE* (Appleman, 1995). Data reduction: *Xtal*3.2 (Hall, Flack & Stewart, 1994). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *Xtal*3.2. Molecular graphics: *Xtal*3.2. Software used to prepare material for publication: *Xtal*3.2.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: NA1201). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$\{Ca(OH_2)_3[Ca(DOTA)].7.7H_2O\}_n$

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Abstract

The octadentate ligand H_4DOTA (H_4DOTA = 1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid) forms the most stable calcium complexes known. The overall solid-state structure of the title complex {poly[triaqua-μ-(1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetato)-dicalcium 7.7-hydrate], $[Ca_2(C_{16}H_{24}N_4O_8)(H_2O)_3].7.7H_2O$} contains two independent eight-coordinate Ca^{2+} ions on a twofold crystallographic axis with the Ca^{2+} ions bound to four of the eight O atoms [mean Ca—O = 2.45 (3) Å] and the four N atoms [mean Ca—N = 2.59 (2) Å] of the DOTA ligand. The coordination geometry of the Ca atom encapsulated by the DOTA ligand is distorted square antiprismatic. Carboxylate bridges link $[Ca(DOTA)]^{2-}$

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