Calcium Binding Capacity of Carboxylic Acids with an Ethereal Function. Crystal and Molecular Structure of Calcium Ethylenedioxydiacetate

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The influence of structural parameters on the calcium binding capacity of acyclic dicarboxylic ethers of general formula $HO_2C-(CH_2)_n-O-(CH_2)_m-O-(CH_2)_n-CO_2H$ (n = 1 or 2, m = 1—3 respectively) and $HO_2C-(CH_2)_n-O-(CH_2)_n-CO_2H$ (n= 1 or 2) has been investigated. A good building efficiency is displayed by oxydiacetic (oda) and ethylenedioxydiacetic (edoda) acids or their sodium salts: these are the only compounds examined capable of forming five-membered chelate rings. No increase of calcium sequestering capacity is observed going from the tridentate oda to the tetradentate edoda ligand. The crystal and molecular structure of $Ca(edoda)\cdot 3H_2O$ has been determined by three-dimensional *X*-ray analysis, using Patterson and Fourier methods and refined by block-diagonal least squares to *R* 0.030 for 1 792 independent observations. Crystals are triclinic, space group $P\bar{1}$, with Z = 1 in a unit cell of dimensions a = 8.560(2), b = 10.171(2), c = 7.851(2) Å, α = 101.5(1), β = 115.5(1), γ = 109.5(1)°. The crystal structure is built up of $\{Ca(edoda)\cdot 3H_2O\}_2$ dimers lying on centres of symmetry of the crystal lattice and linked together by hydrogen bonding involving the water molecules. The eight-fold co-ordination of the calcium atom is approximately dodecahedral. The Ca–O bond distances range from 2.378(2) to 2.645(2) Å. The values of the internal rotation angles of the seven single bonds of the edoda ligand are typical of *trans* and *gauche* conformations.

MANY organic sequestering agents have been claimed as potential phosphate substitutes in detergent formulations, for ecological reasons.[1] Although polycarboxylic acids with ethereal functions constitute a very important class for preparing such compounds,[2] little is known about their structure. The crystal structure of calcium oxydiacetate alone has been determined by *X*-ray methods.[3]

In contrast, there have been extensive structural studies of aminopolycarboxylic acids [4] and other ligands containing ethereal oxygens.[5]

In order to examine the effect of structural parameters on the calcium binding capacity, we initiated a research program on simple acyclic dicarboxylic ethers; here we report our results, including the crystal and molecular structure of calcium ethylenedioxydiacetate.

EXPERIMENTAL

Preparations.—Disodium ethylenedioxydipropionate, Na_2(edodp). The parent acid was prepared as described in the literature.[6,7] The sodium salt was obtained by neutralizing an aqueous solution of the acid with sodium hydroxide, and evaporating this to dryness and washing the product with dry acetone.

Disodium ethylenedioxydiacetate, Na_2(edoda). The sodium salt, obtained as described in the literature,[8] recrystallized from aqueous ethanol (*ca.* 10% w/w) as white, plate-like crystals, m.p. 133—135 °C.

Ethylenedioxydiacetic acid, H_2(edoda). This compound was obtained by cation-exchange resin treatment of an aqueous sodium-salt solution. The filtered solution, evaporated to dryness, gave a viscous oil, which crystallized to a white solid when set aside (Found: C, 40.35; H, 5.6. Calc. for $C_6H_{10}O_6$: C, 40.44; H, 5.81%); equiv. wt. Found, 90; Calc., 89.

Calcium ethylenedioxydiacetate—water (1/3), $Ca(edoda)\cdot 3H_2O$. This compound was prepared according to the procedure used for calcium oxydiacetate.[3] The crystalline material was filtered off, washed with water, and dried in air, m.p. 318—320 °C (Found: C, 26.4; H, 5.9; Ca, 15.25. Calc. for $C_6H_8CaO_6\cdot 3H_2O$: C, 26.66; H, 5.2; Ca, 14.8%).

Disodium trimethylenedioxydiacetate, Na_2(pdoda). The parent acid was prepared as described in the literature.[9,10] The sodium salt was precipitated from a concentrated neutralized acid solution by addition of a large amount of ethanol.

Disodium methylenedioxydiacetate, Na_2(mdoda). The parent acid obtained as described in the literature,[10,11] was used to prepare the disodium salt.

Disodium oxydipropionate, Na_2(odp). The parent acid obtained as described in the literature [6,12] was used to prepare the disodium salt.

Disodium oxydiacetate, Na_2(oda). This compound was prepared as previously described in the literature.[13]

Pentasodium tripolyphosphate, Na_5(tpp). A detergent-grade commercial product was used.

Calcium Sequestering Capacity.—Chelation of calcium

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[13] C.P. 853,647/1970.

ions by the various compounds investigated was determined as in the literature.[14]

Potentiometric Measurements.—Potentiometric titrations of ethylenedioxydiacetic acid for the determination of acidity and calcium chelate-formation constants employed a Metrohm Erisau E 500 digital pH meter with an EA 121 combination electrode. The pH meter was calibrated with standard buffers at pH values of 2, 4, 6, 7, 9, 10, and 11. The distilled water used to make up the solutions was de-aerated by evaporation under reduced pressure. The measurements, in the absence and in the presence of Ca^{2+} in 1 : 1 molar ratio, were carried out in 1 mol dm^{-3} KNO_3 at 25 °C.

All experiments were conducted under nitrogen. Acidity-constant measurements were made according to ref. 15, all computations being performed using a Siemens-306 digital computer and 68 data points. The calcium stability constant was calculated by a direct algebraic method.[16]

X-Ray Analysis.—Colourless, regular, prismatic crystals of $\{Ca(edoda)\cdot 3H_2O\}_2$ were sealed in thin-walled glass capillaries; no protection from air proved necessary.

Crystal Data.—$\{C_6H_8O_6Ca\cdot 3H_2O\}_2$, $M = 540.6$, Triclinic, $a = 8.560(2)$, $b = 10.171(2)$, $c = 7.851(2)$ Å, $\alpha = 101.5(1)$, $\beta = 115.5(1)$, $\gamma = 109.5(1)°$, $U = 532.1$ Å^3, $D_c = 1.686$ g cm^{-3}, $Z = 1$. Space group, $P\bar{1}$, Mo-K_α radiation, $\lambda = 0.710\ 69$ Å, μ(Mo-K_α) = 6.6 cm^{-1}.

TABLE 1

Atomic fractional co-ordinates ($\times 10^4$) and thermal parameters ($\times 10^2$ Å^2) for Ca(edoda)·$3H_2O$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ca	833(1)	1 944(1)	2 142(1)	O(1)	−1 045(2)	−827(1)	836(2)
O(2)	−3 013(2)	−2 837(2)	985(2)	O(3)	−945(2)	1 097(1)	3 764(2)
O(4)	−839(2)	3 587(2)	2 802(2)	O(5)	−2 176(2)	1 572(2)	−849(2)
O(6)	−3 210(2)	2 937(2)	−2 525(2)	O(7)	3 430(2)	1 286(2)	3 507(2)
O(8)	2 993(2)	3 704(2)	5 789(2)	O(9)	2 773(2)	4 209(2)	2 068(2)
C(1)	−2 123(3)	−1 441(2)	1 441(3)	C(2)	−2 458(3)	−429(2)	2 790(3)
C(3)	−1 374(3)	2 176(2)	4 724(3)	C(4)	−2 254(3)	2 847(2)	3 275(3)
C(5)	−1 648(3)	3 971(2)	1 101(3)	C(6)	−2 413(3)	2 716(2)	−929(3)

Atom	*x*	*y*	*z*	*B*	Atom	*x*	*y*	*z*	*B*
H′(C2)	−3 709(37)	−513(29)	1 917(39)	275(53)	H″(C2)	−2 532(42)	−790(34)	3 789(47)	406(64)
H′(C3)	−2 287(37)	1 634(29)	5 112(40)	256(51)	H″(C3)	−32(35)	2 982(28)	5 963(38)	240(49)
H′(C4)	−3 497(34)	2 034(27)	1 963(35)	180(43)	H″(C4)	−2 621(36)	3 575(29)	3 814(39)	260(51)
H′(C5)	−2 757(41)	4 117(32)	889(43)	357(60)	H″(C5)	−626(36)	4 889(29)	1 270(39)	247(50)
H′(O7)	3 261(47)	461(36)	2 885(49)	473(75)	H″(O7)	4 371(39)	1 673(31)	4 590(42)	306(56)
H′(O8)	3 136(41)	3 477(33)	6 740(45)	386(62)	H″(O8)	4 167(44)	4 383(35)	6 210(49)	438(67)
H′(O9)	2 829(51)	3 847(41)	998(54)	491(84)	H″(O9)	2 814(48)	5 076(39)	2 238(52)	494(78)

Weissenberg photographs showed triclinic symmetry; the $P\bar{1}$ space group was chosen and subsequently confirmed by the successful refinement of the crystal structure. Accurate cell dimensions were determined by a least-squares fit to the setting angles measured for 27 reflections on the diffractometer. Intensity data were collected from a crystal of approximate dimensions 0.12 × 0.24 × 0.42 mm, mounted with the *c* axis parallel to the spindle axis of an on-line Siemens AED diffractometer, using Zr-filtered Mo-K_α radiation. A total of 2 083 independent reflections (max. $\sin\theta/\lambda = 0.62$ Å^{-1}) were measured, following the θ—2θ scan method and 'five-points' technique;[17] 1 792 reflections with $I > 3.0\sigma(I)$, $\{\sigma^2(I) = [\text{total counts} + (0.005\ I)^2]\}$, were used for the structure determination. The variation of the intensity of a selected standard reflection, measured every 15 reflections, reached a maximum of 3% during the experiment; the scale factor was adjusted on the assumption that all the other intensities varied at the same rate.

A correction for Lorentz and polarization factors was applied but the absorption effect was neglected owing to the low value of μR (<0.2 for Mo-K_α).

Structure Determination and Refinement.—The structure was solved by standard Patterson and Fourier methods. Initial values of the atomic co-ordinates of the Ca atom were obtained from a three-dimensional Patterson synthesis. From the subsequent Fourier map the co-ordinates of all the non-hydrogen atoms were obtained. Isotropic block-diagonal least-squares refinement converged to $R = 0.079$.

A ΔF-map was then computed, which allowed the location of all the hydrogen atoms. A further four cycles with anisotropic thermal parameters and fixed contributions of the hydrogen atoms lowered R to 0.040. Two more cycles in which the hydrogen atoms were refined using isotropic thermal parameters led to a final R of 0.030. The function minimized was $\Sigma w(F_o - F_c)^2$, using Cruickshank's weighting scheme.[18] Atomic scattering factors were those of Cromer and Mann[19] for non-hydrogen atoms, and of Stewart[20] for the hydrogen atoms. The computer programs used were those of Immirzi.[21] The final values of positional and thermal parameters are reported in Table 1. Observed and calculated structure factors are deposited in SUP 22001 (13 pp., 1 microfiche).*

RESULTS

Calcium Sequestering Capacity.—Table 2 shows acid p*K* and log K_{CaA} values for H_2(oda) and H_2(edoda), while in Table 3 the building efficiency of the various compounds studied is reported.

As is evident from Table 3, only Na_2(edoda) and Na_2(oda) show a good sequestering capacity, although their efficiency remains significantly lower than that of

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* For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1976, Index issue.

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Na_5(tpp). The efficiency of the other compounds listed is almost negligible.

TABLE 2

Acid pK and log K_{CaA} at 25 °C

Compound	Formula	pK_1	pK_2	log K_{CaA}
H_2(oda) *	$HO_2C{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CO_2H$	2.90	4.03	3.4
H_2(edoda)	$HO_2C{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CO_2H$	3.03	3.94	3.24

* R. M. Tichane and W. E. Bennet, *J. Amer. Chem. Soc.*, 1957, **79**, 1293.

TABLE 3

Calcium sequestering capacity (g atom Ca mol^{-1}) at pH 10 and 25 and 60 °C

Compound	Formula	T/°C	
		25	60
Na_5(tpp)	$Na_5P_3O_{10}$	1	0.72
Na_2(edodp)	$NaO_2C{\cdot}(CH_2)_2{\cdot}O{\cdot}(CH_2)_2{\cdot}O{\cdot}(CH_2)_2{\cdot}CO_2Na$	1.5×10^{-2}	
Na_2(edoda)	$NaO_2C{\cdot}CH_2{\cdot}O{\cdot}(CH_2)_2{\cdot}O{\cdot}CH_2{\cdot}CO_2Na$	0.211	0.151
Na_2(pdoda)	$NaO_2C{\cdot}CH_2{\cdot}O{\cdot}(CH_2)_3{\cdot}O{\cdot}CH_2{\cdot}CO_2Na$	2.05×10^{-2}	
Na_2(mdoda)	$NaO_2C{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CO_2Na$	6.65×10^{-3}	
Na_2(odp)	$NaO_2C{\cdot}(CH_2)_2{\cdot}O{\cdot}(CH_2)_2{\cdot}CO_2Na$	6.57×10^{-3}	
Na_2(oda)	$NaO_2C{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CO_2Na$	0.242	0.203

Description and Discussion of the Structure.—The crystal structure of calcium ethylenedioxydiacetate–water (1/3), Ca(edoda)$\cdot$3H_2O, comprises {Ca(edoda)$\cdot$3H_2O}$_2$ dimers, which lie on the centres of symmetry of the crystal lattice. Both intra- and inter-molecular hydrogen bonds involving the water molecules are present in the crystals, with hydrogen bond lengths (Table 4) within the expected range of values. A projection of the crystal packing is shown in Figure 1. The primary co-ordination sphere of each Ca^{2+} ion contains eight oxygen atoms, three of which are from water molecules and five from the edoda ligands. A perspective view of the molecular structure of the {Ca(edoda)$\cdot$3H_2O}$_2$ dimer is shown in Figure 2.

TABLE 4

Hydrogen-bond distances (Å) and angles (°)

(*a*) Intramolecular			
O(2′) ··· O(9)	2.649	O(5′) ··· H′(07)	1.95
O(5′) ··· O(7)	2.744	O(2′) ··· H′(O9)–O(9)	168.7
O(2′) ··· H′(O9)	1.78	O(5′) ··· H′(O7)–O(7)	164.4
(*b*) Intermolecular			
O(2′) ··· O(8$^{\mathrm{I}}$)	2.838	O(6) ··· H″(O7$^{\mathrm{III}}$)	2.02
O(6′) ··· O(9$^{\mathrm{II}}$)	2.728	O(9′) ··· H″(O8$^{\mathrm{IV}}$)	2.10
O(6) ··· O(7$^{\mathrm{III}}$)	2.786	O(2′) ··· H′(O8)–O(8$^{\mathrm{I}}$)	169.9
O(9′) ··· O(8$^{\mathrm{IV}}$)	2.943	O(6′) ··· H″(O9)–O(9$^{\mathrm{II}}$)	171.2
O(2′) ··· H′(O8$^{\mathrm{I}}$)	2.05	O(6) ··· H″(O7)–O(7$^{\mathrm{III}}$)	172.4
O(6′) ··· H″(O9$^{\mathrm{II}}$)	1.88	O(9′) ··· H″(O8)–O(8$^{\mathrm{IV}}$)	162.9

Roman numerals as superscripts refer to the equivalent positions:

I	$x, y, z - 1$	III	$x - 1, y, z - 1$
II	$x, y - 1, z$	IV	$x - 1, y - 1, z - 1$

Each edoda ligand is co-ordinated to a cation through two ether oxygens, O(3) and O(4), and two carboxylate oxygens O(5) and O(1). Since the O(1) atom is bonded to two Ca^{2+} ions, it leads, with its centrosymmetric O(1′), to the planar four-membered ring Ca_2O_2. The O(1)–Ca–O(1′) and Ca–O(1)–Ca′ bond angles are 72.9(1) and 107.0(1)° respectively. A similar four-membered ring has been observed in calcium dipicolinate–water (1/3).[22] The oxygen atoms O(3), O(1), O(1′) and the water oxygen O(9), lie in a plane which is nearly perpendicular to another plane formed by O(4), O(5) and the water oxygens O(7) and O(8); both planes contain the calcium atom. The maximum deviations of the atoms from their mean planes are within 0.07 Å (see Table 5). In the crystal structure of calcium oxydiacetate–water (1/6), Ca(oda)$\cdot$6H_2O, a similar arrangement is seen where one ether, one water, and 2 carboxylate oxygens form a plane perpendicular to another plane containing four water-oxygen atoms (see Table 5); the eightfold co-ordination of the cation was defined as irregular in this complex.[3]

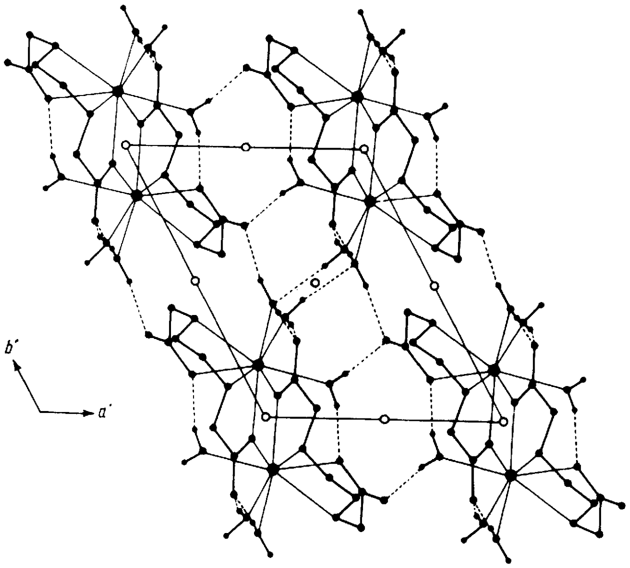

FIGURE 1 Molecular packing of Ca(edoda)$\cdot$3H_2O projected down the *c* axis. The dashed lines represent the hydrogen bonds and the open circles the crystallographic centres of symmetry

In order to define the co-ordination geometry around the calcium atom, a test proposed by Muetterties and Guggenberger,[23] based on the evaluation of appropriate dihedral angles, was applied to both the structure of

[22] G. Strahs and R. E. Dickerson, *Acta Cryst.*, 1968, **B24**, 571.

[23] E. L. Muetterties and L. J. Guggenberger, *J. Amer. Chem. Soc.*, 1974, **96**, 1748.

$Ca(edoda)\cdot 3H_2O$ and that of $Ca(oda)\cdot 6H_2O$. On the basis of this test (Table 5), one can conclude that in both complexes the co-ordination around the calcium atom is approximately dodecahedral.

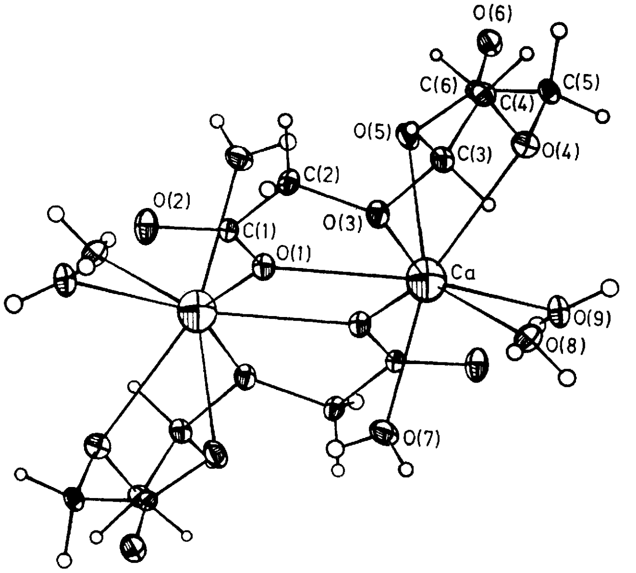

FIGURE 2 A perspective view of the molecular structure of the $\{Ca(edoda)\cdot 3H_2O\}_2$ dimer

TABLE 5

Comparison between least-squares planes of $Ca(edoda)\cdot 3H_2O$ and $Ca(oda)\cdot 6H_2O$. Equations of planes are in the form $AX + BY + CZ - D = 0$, where $X = ax$, $Y = by$, and $Z = cz$ (x, y, z are the crystallographic fractional co-ordinates and a, b, c the unit-cell parameters). Distances of atoms from planes (in Å) are in square parentheses

$Ca(edoda)\cdot 3H_2O$

(*a*) Plane Ca, O(1), O(1'), O(3), O(9)

$$0.685\,1X - 0.514\,2Y + 0.361\,6Z - 0.006\,6 = 0$$

[Ca 0.073, O(1) 0.050, O(1') −0.064, O(3) −0.066, O(9) 0.006]

(*b*) Plane Ca, O(4), O(5), O(7), O(8)

$$-0.509\,7X - 0.619\,4Y + 0.687\,7Z + 0.447\,9 = 0$$

[Ca 0.016, O(4) 0.067, O(5) −0.051, O(7) 0.034, O(8) −0.066]

$Ca(oda)\cdot 6H_2O$ [a]

(*a*) Plane Ca, O(2), O(5), O(1), O(7)

$$0.526\,6X + 0.086\,2Y + 0.499\,1Z - 3.115\,2 = 0$$

[Ca −0.082, O(2) 0.006, O(5) −0.033, O(1) 0.054, O(7) 0.056]

(*b*) Plane Ca, O(8), O(9), O(10), O(11)

$$-0.433\,3X - 0.834\,8Y + 0.503\,5Z + 6.770\,3 = 0$$

[Ca 0.064, O(8) −0.090, O(9) 0.043, O(10) 0.105, O(11) −0.123]

Observed δ' and ϕ angles (°) [b]

δ'	ϕ	δ'	ϕ
37.0	3.5	31.1	2.5
35.0	3.2	33.6	6.2
20.8		45.7	
20.9		35.1	

[a] Labelling of the atoms and their fractional co-ordinates according to ref. 3. [b] According to ref. 23. Note that for an ideal dodecahedron δ' and ϕ values are 29.5, 29.5, 29.5, 29.5, and 0° respectively.

TABLE 6

Geometrical parameters for $Ca(edoda)\cdot 3H_2O$, with Ca–O distances for $Ca(oda)\cdot 6H_2O$ in square parentheses [a]

(*a*) Bond distances

Ca–O(1)(c) [b]	2.448(2)	[Ca–O(2)(c)	2.446(3)]
Ca–O(1')(c)	2.497(2)	[Ca–O(5)(c)	2.472(3)]
Ca–O(3)(e)	2.432(2)	[Ca–O(1)(e)	2.431(3)]
Ca–O(9)(w)	2.378(2)	[Ca–O(7)(w)	2·375(2)]
Ca–O(4)(e)	2.645(2)	[Ca–O(8)(w)	2.497(3)]
Ca–O(5)(c)	2.465(2)	[Ca–O(9)(w)	2.549(3)]
Ca–O(7)(w)	2.400(2)	[Ca–O(10)(w)	2.422(3)]
Ca–O(8)(w)	2.453(2)	[Ca–O(11)(w)	2.455(3)]
O(1)–C(1)	1.257(3)	O(2)–C(1)	1.252(3)
O(3)–C(2)	1.416(3)	O(3)–C(3)	1.444(3)
O(4)–C(4)	1.436(3)	O(4)–C(5)	1.416(4)
O(5)–C(6)	1.255(3)	O(6)–C(6)	1.250(3)
C(1)–C(2)	1.513(3)	C(3)–C(4)	1.497(4)
C(5)–C(6)	1.527(3)		

(*b*) Bond angles (°)

O(1)–C(1)–O(2)	126.2(1)	O(5)–C(6)–O(6)	126.0(1)
O(1)–C(1)–C(2)	118.1(1)	O(2)–C(1)–C(2)	115.7(1)
O(3)–C(2)–C(1)	110.8(1)	O(3)–C(3)–C(4)	110.0(1)
O(4)–C(4)–C(3)	107.1(1)	O(4)–C(5)–C(6)	111.9(1)
O(5)–C(6)–C(5)	117.6(1)	O(6)–C(6)–C(5)	116.3(1)
C(2)–O(3)–C(3)	113.7(1)	C(4)–O(4)–C(5)	112.6(1)

(*c*) Internal rotation angles (°)

O(2)–C(1)–C(2)–O(3)	160.5	C(3)–C(4)–O(4)–C(5)	166.6
C(1)–C(2)–O(3)–C(3)	167.8	C(4)–O(4)–C(5)–C(6)	267.7
C(2)–O(3)–C(3)–C(4)	265.3	O(4)–C(5)–C(6)–O(6)	177.3
O(3)–C(3)–C(4)–O(4)	300.3		

[a] Labelling of the atoms from ref. 3. [b] Labelling of oxygen atoms: c, carboxylate; e, ether; w, water.

The Ca–O bond distances range from 2.378(2) to 2.645(2) Å; as is evident from Table 6, these values are very similar to the corresponding ones in $Ca(oda)\cdot 6H_2O$. The three calcium–carboxylate-oxygen bond distances differ only slightly from each other [2.448(2)—2.497(2) Å]; on the other hand, there is a significant difference between the two calcium–ether-oxygen separations Ca–O(3) and Ca–O(4) [2.432(2) and 2.645(2) Å respectively]. The large value of the latter distance is probably due to conformational hindrances to the close approach of the O(4) atom to the cation; the reduction of the C(3)–C(4)–O(4) bond angle from the typical tetrahedral value to 107.1(1)°, which certainly reduces the distance between the calcium atom and the O(4) atom, is consistent with the above explanation. The 'coiled' conformation of the edoda ligand is characterized by the geometric parameters reported in Table 6; the bond distances and angles are similar to those observed for the planar oda ligand in the crystal structure of $Ca(oda)\cdot 6H_2O$,[3] and are in any case within the expected range of values. The edoda group, even though it is made up of two chemically equivalent $O_2C{-}CH_2{-}O{-}CH_2$ groups, displays an asymmetric geometry, as shown by the values of the internal rotation angles of the seven single bonds of the ligand (the bond distances and angles practically satisfy the above equivalence); these values, however, are close to those typical of the *trans* (T) and *gauche* (G_+ or G_-) conformations.* Therefore the conformation of the edoda ligand can be schematically indicated, starting from the C(1)–C(2) bond, by the sequence $TTG_-G_-TG_-T$. It

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* In this report the convention was adopted in which the T, G_+, and G_- conformations are characterized by internal rotation angles of 180, 60, and 300° respectively.

may be pointed out that the significant deviations of 35° from the regular G_- conformation occurring for the C(3)–O(3) and C(5)–O(4) bonds, have also been found for crystalline poly(1,3-dioxolan),[24] whose chain contains CH_2–O–CH_2–CH_2–O–CH_2 sequences identical to the C(2)–O(3)–C(3)–C(4)–O(4)–C(5) of the edoda ligand.

DISCUSSION

In the choice of the compounds to be investigated, the following structural parameters were considered: (1) the number of methylene groups, n, connecting an ether oxygen with the carboxylic group, O–$(CH_2)_n$–CO_2; (2) the number of methylene groups, m, connecting two ether oxygens, O–$(CH_2)_m$–O; and (3) the increase in the number of ligating oxygens.

The results in Table 3 show that the sequestering capacity is strongly dependent on parameters (1) and (2). In particular, only when $n = 1$ [Na_2(oda)] and $n = 1$, $m = 2$ [Na_2(edoda)], is a good building efficiency displayed; in both cases only five-membered chelate rings involving carboxylate linkages are formed, as observed in the crystal structure of the corresponding calcium complexes, Ca(oda)·$6H_2O$ and Ca(edoda)·$3H_2O$. A larger chelate ring ($n = 2$) results in a breakdown of the sequestering capacity; this effect is consistent with the results reported for aminopolycarboxylic ligands.[4]

Similarly, only for $m = 2$ can five-membered chelate rings form with the two ether oxygens; so the sequestering capacity is good only in this case. An increased complexation ability has been seen also for macrocyclic polyethers when O–$(CH_2)_2$–O fragments are present.[25] The requirement of five-membered chelate-ring formation in calcium complexation is related to the fact that only then is the distance between the two chelating donor atoms (ether or carboxylate oxygens) near to that expected for two adjacent co-ordination sites of the cation (in the range 2.6—3.0 Å). In the crystal structure of Ca(edoda)·$3H_2O$, these distances are in fact 2.77 Å (ether oxygen to ether oxygen) and 2.66 Å (ether oxygen to carboxylate oxygen); a distance of 2.60 Å (ether oxygen to carboxylate oxygen) has been observed in the crystal structure of Ca(oda)·$6H_2O$. In contrast the distance between the two ether oxygens should be lower (2.4 Å) when $m = 1$ (four-membered ring) and larger (for minimum energy conformations) when $m = 3$ (six-membered ring); in this last case the minimum value predictable is 3.5 Å, corresponding to a sequence of *gauche* conformations (G_+G_+ or G_-G_-) of the two C–C bonds. Similarly, when $n = 2$ (six-membered ring), the distance between the ether oxygen and the carboxylate oxygen is expected to be very large (*ca.* 4 Å), since only the *trans* conformation of the CH_2–CH_2 single bond is favourable on the basis of steric considerations.

The close similarity between the calcium sequestering capacity of Na_2(oda) and Na_2(edoda) (Table 3) is the reverse of the trend of increasing capacity that would be expected in going from a tridentate (oda) to a tetradentate ligand (edoda).[4] Considerations of the solid state of the related calcium complexes, Ca(oda)·$6H_2O$ and Ca(edoda)·$3H_2O$, seem inadequate to explain the above result. In any case, in the crystal structure of the two complexes, the oda and edoda ligands behave effectively as tridentate and tetradentate ligands respectively, in spite of the weaker interaction between the calcium atom and one of the ether oxygens [Ca–O(4) 2.645(2) Å] observed in Ca(edoda)·$3H_2O$. However, the situation is complicated by the lack of knowledge of the detailed structure of Ca(edoda) in solution. For Ca(oda), on the other hand, by means of Raman spectroscopy, it was concluded that the oda ligand has the same planar conformation both in aqueous solution and in the solid state.[3] In the case of Ca(edoda), the application of Raman spectroscopy led to ambiguous results that established only that the conformation of the edoda ligand in aqueous solution is different from that in the solid state.[26]

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