

## The Structure of Monoaquabis(2-ethoxybenzoato)calcium(II)

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(Received 29 October 1980; accepted 17 February 1981)

### Abstract

$C_{18}H_{20}CaO_7$  is orthorhombic, space group  $P2_12_12_1$ , with  $a = 6.61$  (5),  $b = 10.76$  (5),  $c = 26.62$  (5) Å,  $U = 1893.31$  Å<sup>3</sup>,  $Z = 4$ ,  $d_m = 1.38$  (2),  $d_c = 1.36$  Mg m<sup>-3</sup>,  $F(000) = 806.57$ ,  $\mu(\text{Cu } K\alpha) = 3.068$  mm<sup>-1</sup>. The structure was solved by direct methods, using visually estimated integrated Weissenberg data, to give a final  $R = 0.104$  for 1236 independent reflections. The Ca atom is eight-coordinate with a distorted bicapped trigonal-prismatic geometry, and the molecular structure develops as a linear polymer, through the formation of four-membered Ca–O–Ca–O rings, to feature a tight packing of the metal ions along the chain axes. No hydrogen-bond interactions are present between adjacent chains and cohesion in this direction is limited to packing interactions.

### Introduction

The use of 2-ethoxybenzoic acid (hereafter referred to as *o*-eba) as a fortifying agent in the ZnO/eugenol dental cement (Brauer, 1965, 1967, 1972) has stimulated interest in the structure of the parent acid (Gopalakrishna & Cartz, 1972) and the  $[\text{Zn}(\text{o-eba})_2(\text{H}_2\text{O})]$  reaction product (Natarajan, Gowda & Cartz, 1974). The coordination potential of the *o*-eba ligand also raises the possibility of adhesion to tooth enamel  $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ , through coordination to  $\text{Ca}^{2+}$ , with the attendant advantage of increased marginal integrity and pulp isolation. The present complex resulted from attempts to prepare such a Ca/*o*-eba system, and its structure was determined for comparison with that of  $[\text{Zn}(\text{o-eba})_2(\text{H}_2\text{O})]$ .

### Experimental

$[\text{Ca}(\text{o-eba})_2(\text{H}_2\text{O})]$  was prepared as follows: 1 g *o*-ethoxybenzoic acid ( $6 \times 10^{-3}$  M) dissolved in 15 ml MeOH was added to a suspension of 0.22 g  $\text{Ca}(\text{OH})_2$

( $3 \times 10^{-3}$  M) in 15 ml H<sub>2</sub>O. The resultant mixture was stirred for 4 h and the volume increased to 35 ml (H<sub>2</sub>O), after which the solution was filtered and allowed to evaporate at room temperature. Crystals suitable for X-ray analysis were obtained after 10 days. Composition: found: C = 56.15, H = 5.28, Ca = 10.05%;  $C_{18}H_{20}CaO_7$  requires C = 55.66, H = 5.19, Ca = 10.32%.

Crystal and refinement data are summarized in the *Abstract* and in Table 1. Cell parameters were obtained from precession photographs and the space group uniquely determined as  $P2_12_12_1$  from absences:  $h00$  for  $h$  odd;  $0k0$  for  $k$  odd;  $00l$  for  $l$  odd. The intensities were collected photographically by multifilm equi-inclination Weissenberg techniques, with two-dimensional integration of the spot shape. Intensities were measured by visual comparison with a calibrated scale. The main collection yielded 1354 measurable intensities for levels  $0kl-5kl$  and the cross-reference 243 intensities for  $h0l-h2l$ . All reflections were retained in data reduction in which Lorentz and polarization corrections were applied; no correction was made for absorption.

As a Patterson synthesis did not yield a clear indication of the metal position, structure determination was attempted with the manual non-centrosymmetric direct-methods technique as incorporated in *SHELX* 76 (Sheldrick, 1976). Origin, enantiomorph, and multisolution phases were hand-selected from reflections whose  $E$  values were  $> 1.2$ , in accordance with the restrictions for  $P2_12_12_1$ . A set of Fourier maps were calculated with these  $E$  values which suggested the position of the metal. Subsequent

Table 1. Refinement data

Data used	$0kl-5kl$ and $h0l-h2l$
Number of unique reflections	1236
Number of parameters varied	147
$R (= \sum \Delta / \sum  F_o )$	0.1045
$R_w (= \sum \Delta w^{1/2} / \sum  F_o  w^{1/2})$	0.1034
Maximum final shift/e.s.d.	0.003
Residual electron density (e Å <sup>-3</sup> )	0.74
Number of atoms anisotropic	7

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Fourier calculations were phased by an increasing number of atom positions and ultimately yielded the positions of all the non-hydrogen atoms. Complex neutral-atom scattering factors (Cromer & Waber, 1965; Cromer & Liberman, 1970) were used, and anisotropic temperature factors introduced for the metal and coordination sphere. The structure was refined by full-matrix least squares (minimizing  $\sum w|F_o - F_c|^2$ ) until the shift in any parameter was  $<0.005\sigma$ . H atom positions were calculated with C-H = 1.08 Å and floated, during refinement, on the associated C atom; this calculation was not extended to the water molecule. Three reflections, for which  $|F_o - F_c| > 5\sigma$ , were omitted for the final cycles. The final  $R = 0.014$ . Table 2 lists the atomic coordinates;\* bond lengths and angles are presented in Table 3; Table 4 gives some mean planes; and Table 5 some non-bonding interactions.

### Description of structure and discussion

The structure consists of a linear (one-dimensional) polymer in which both *o*-eba groups (I and II, Fig. 1)

\* Lists of structure factors, H-atom positions and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35948 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Fractional coordinates ( $\times 10^4$ ) for non-hydrogen atoms and isotropic temperature factors ( $\text{Å}^2 \times 10^3$ )

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Ca	181 (6)	6832 (4)	289 (2)	35 (3)†
O(1)	-6525 (21)	6119 (12)	252 (6)	43 (11)†
O(2)	-3261 (17)	6457 (12)	141 (5)	27 (9)†
O(3)	-966 (18)	5067 (13)	800 (5)	43 (10)†
O(4)	1890 (20)	7941 (15)	1027 (5)	48 (13)†
O(5)	-1374 (24)	8183 (17)	923 (6)	62 (13)†
O(6)	-2561 (27)	8934 (19)	1883 (7)	80 (6)
O(7)	112 (26)	5995 (12)	-540 (5)	55 (10)†
C(1)	-4163 (28)	4503 (19)	472 (7)	33 (6)
C(2)	-2482 (27)	4177 (19)	714 (7)	28 (5)
C(3)	-2110 (33)	2907 (22)	834 (8)	52 (7)
C(4)	-3597 (36)	1993 (25)	734 (8)	64 (7)
C(5)	-5288 (40)	2372 (22)	507 (8)	63 (7)
C(6)	-5704 (28)	3572 (18)	370 (7)	42 (6)
C(7)	-4656 (37)	5758 (19)	276 (8)	45 (5)
C(8)	-119 (51)	5048 (28)	1307 (9)	97 (9)
C(9)	-1796 (56)	5329 (35)	1669 (12)	139 (14)
C(10)	292 (34)	9619 (18)	1463 (7)	42 (5)
C(11)	-1134 (38)	9874 (25)	1834 (9)	64 (7)
C(12)	-1029 (36)	10882 (25)	2146 (9)	59 (7)
C(13)	504 (34)	11716 (27)	2059 (8)	66 (7)
C(14)	1960 (41)	11539 (27)	1716 (9)	76 (8)
C(15)	1866 (37)	10438 (23)	1413 (9)	56 (7)
C(16)	311 (39)	8544 (18)	1118 (7)	41 (5)
C(17)	-4135 (45)	9164 (33)	2233 (12)	105 (11)
C(18)	-5477 (38)	8084 (26)	2231 (9)	79 (8)

$$\dagger U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

and the water molecule are coordinated to the metal [O(2)–O(5), O(7)]. Three additional donor sites are provided by symmetry-related *o*-eba systems (I<sup>I</sup> and II<sup>II</sup>, Fig. 1)\* to complete an eight-coordinate stereochemistry featuring a distorted bicapped trigonal-prismatic geometry. The carboxylate group of both *o*-eba systems is bidentate to define the uncapped face [O(1<sup>I</sup>), O(2<sup>I</sup>), O(4), O(5), Table 4, plane 8], but, in addition, that of I<sup>I</sup> forms a bridging interaction with both adjacent metal ions to generate the polymeric linkage of four-membered rings [Ca–O(1<sup>II</sup>)–Ca<sup>I</sup>–O(2<sup>I</sup>)]. These rings are essentially planar (Table 4, plane 7). The two capped faces are defined by O(1<sup>I</sup>), O(5), O(3), O(7) and O(2<sup>I</sup>), O(4), O(3) and O(7), respectively (Table 4, planes 9 and 10). A second

\* For key to symmetry operations, see Table 3.

Table 3. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

O(1 <sup>I</sup> )–Ca	2.87 (3)	C(2)–C(1)	1.33 (3)
O(1 <sup>II</sup> )–Ca	2.31 (2)	C(6)–C(1)	1.45 (3)
O(2)–Ca	2.34 (1)	C(7)–C(1)	1.48 (3)
O(2 <sup>I</sup> )–Ca	2.40 (2)	C(3)–C(2)	1.43 (3)
O(3)–Ca	2.46 (2)	C(4)–C(3)	1.42 (3)
O(4)–Ca	2.56 (3)	C(5)–C(4)	1.33 (3)
O(5)–Ca	2.45 (2)	C(6)–C(5)	1.37 (3)
O(7)–Ca	2.38 (2)	C(9)–C(8)	1.50 (4)
C(7)–O(1)	1.30 (3)	C(11)–C(10)	1.39 (3)
C(7)–O(2)	1.24 (2)	C(15)–C(10)	1.37 (3)
C(2)–O(3)	1.41 (2)	C(16)–C(10)	1.48 (3)
C(8)–O(3)	1.46 (3)	C(12)–C(11)	1.37 (3)
C(16)–O(4)	1.25 (3)	C(13)–C(12)	1.37 (3)
C(16)–O(5)	1.29 (3)	C(14)–C(13)	1.34 (3)
C(11)–O(6)	1.39 (3)	C(15)–C(14)	1.44 (3)
C(17)–O(6)	1.42 (3)	C(18)–C(17)	1.46 (4)
O(1 <sup>I</sup> )–Ca–O(4)	101.6 (3)	C(7)–C(1)–C(2)	126.4 (20)
O(1 <sup>I</sup> )–Ca–O(5)	74.0 (6)	C(7)–C(1)–C(6)	114.0 (18)
O(1 <sup>I</sup> )–Ca–O(7)	79.5 (7)	C(1)–C(2)–O(3)	119.6 (20)
O(1 <sup>II</sup> )–Ca–O(2)	148.3 (6)	C(3)–C(2)–O(3)	119.6 (18)
O(1 <sup>II</sup> )–Ca–O(2 <sup>I</sup> )	80.2 (4)	C(3)–C(2)–C(1)	120.4 (20)
O(1 <sup>II</sup> )–Ca–O(3)	93.3 (2)	C(4)–C(3)–C(2)	120.3 (22)
O(1 <sup>II</sup> )–Ca–O(4)	76.8 (4)	C(5)–C(4)–C(3)	117.0 (27)
O(1 <sup>II</sup> )–Ca–O(7)	81.6 (7)	C(6)–C(5)–C(4)	125.2 (27)
O(2)–Ca–O(1 <sup>I</sup> )	70.5 (7)	C(5)–C(6)–C(1)	117.3 (21)
O(2)–Ca–O(3)	70.1 (5)	O(2)–C(7)–O(1)	120.8 (21)
O(2)–Ca–O(5)	79.1 (6)	C(1)–C(7)–O(1)	120.0 (19)
O(2)–Ca–O(7)	76.2 (6)	C(1)–C(7)–O(2)	119.3 (23)
O(2 <sup>I</sup> )–Ca–O(4)	79.6 (3)	C(9)–C(8)–O(3)	107.9 (27)
O(2 <sup>I</sup> )–Ca–O(5)	93.1 (3)	C(15)–C(10)–C(11)	117.1 (21)
O(2 <sup>I</sup> )–Ca–O(7)	81.8 (6)	C(16)–C(10)–C(11)	127.0 (23)
O(3)–Ca–O(4)	94.1 (6)	C(16)–C(10)–C(15)	115.9 (21)
O(3)–Ca–O(5)	87.0 (5)	C(10)–C(11)–O(6)	112.5 (23)
O(3)–Ca–O(7)	102.4 (6)	C(12)–C(11)–O(6)	123.7 (24)
C(7)–O(1)–Ca <sup>II</sup>	174.4 (14)	C(12)–C(11)–C(10)	123.5 (25)
C(7)–O(2)–Ca	140.9 (14)	C(13)–C(12)–C(11)	117.0 (25)
C(2)–O(3)–Ca	131.1 (11)	C(14)–C(13)–C(12)	123.5 (28)
C(8)–O(3)–Ca	113.8 (15)	C(15)–C(14)–C(13)	118.0 (27)
C(8)–O(3)–C(2)	114.5 (18)	C(14)–C(15)–C(10)	120.6 (23)
C(16)–O(5)–Ca	95.4 (14)	O(5)–C(16)–O(4)	119.1 (19)
C(17)–O(6)–C(11)	115.6 (23)	C(10)–C(16)–O(4)	122.2 (23)
C(6)–C(1)–C(2)	119.6 (20)	C(10)–C(16)–O(5)	118.6 (21)
		C(18)–C(17)–O(6)	107.7 (25)

Symmetry code

- (i) 0.5 + *x*, 1.5 – *y*, –*z* (iii) –1.0 + *x*, *y*, *z*  
 (ii) 1.0 + *x*, *y*, *z*

Table 4. Equations of least-squares planes of the form  $lX + mY + nZ = p$ , where  $X$ ,  $Y$  and  $Z$  are orthogonal axes, with deviations ( $\text{\AA}$ ) of relevant atoms in square brackets

	$l$	$m$	$n$	$p$
Plane (1): C(1)–C(6)				
	–0.423 (1)	0.163 (1)	0.891 (1)	3.096 (4)
[r.m.s.d. = 0.015 (1) $\text{\AA}$ ]				
[C(1) –0.021, C(2) 0.026, C(3) –0.016, C(4) 0.002, C(5) 0.003, C(6) 0.005]				
Plane (2): O(1), O(2), C(7)				
	0.066 (2)	0.363 (14)	0.929 (6)	3.166 (107)
Plane (3): O(3), C(8), C(9)				
	0.205 (4)	0.976 (1)	–0.070 (12)	5.042 (10)
Plane (4): C(10)–C(15)				
	0.549 (1)	–0.506 (5)	0.666 (3)	–2.520 (67)
[r.m.s.d. = 0.020 (4) $\text{\AA}$ ]				
[C(10) –0.014, C(11) –0.013, C(12) 0.030, C(13) –0.022, C(14) –0.005, C(15) 0.023]				
Plane (5): O(4), O(5), C(16)				
	–0.172 (1)	–0.575 (14)	0.800 (10)	–2.944 (150)
Plane (6): O(6), C(17), C(18)				
	0.547 (3)	–0.421 (6)	0.723 (6)	–1.351 (80)
Plane (7): Ca, Ca', O(1 <sup>h</sup> ), O(2 <sup>h</sup> )				
	0.213 (2)	0.444 (2)	0.870 (1)	3.981 (31)
[r.m.s.d. = 0.019 (9) $\text{\AA}$ ]				
[Ca –0.020, Ca' –0.017, O(1 <sup>h</sup> ) 0.017, O(2 <sup>h</sup> ) 0.021]				
Plane (8): O(1 <sup>h</sup> ), O(2 <sup>h</sup> ), O(4), O(5)				
	0.112 (1)	0.970 (1)	0.214 (1)	8.992 (20)
[r.m.s.d. = 0.024 (1) $\text{\AA}$ ]				
[O(1 <sup>h</sup> ) 0.024, O(2 <sup>h</sup> ) –0.024, O(4) 0.024, O(5) –0.024]				
Plane (9): O(1 <sup>h</sup> ), O(5), O(3), O(7)				
	0.973 (1)	0.180 (1)	0.145 (1)	0.846 (16)
[r.m.s.d. = 0.193 (2) $\text{\AA}$ ]				
[O(1 <sup>h</sup> ) –0.207, O(5) 0.209, O(3) –0.178, O(7) 0.176]				
Plane (10): O(2 <sup>h</sup> ), O(4), O(3), O(7)				
	0.891 (1)	–0.454 (1)	–0.023 (1)	–2.972 (9)
[r.m.s.d. = 0.145 (1) $\text{\AA}$ ]				
[O(2 <sup>h</sup> ) –0.168, O(4) 0.144, O(3) –0.120, O(7) 0.143]				

Angles ( $^\circ$ ) between normals to mean planes

Planes 1 and 2	30.7 (3)	Planes 4 and 5	43.2 (2)
1 and 3	89.4 (6)	4 and 6	5.9 (3)
1 and 4	73.8 (3)		

Table 5. Some selected non-bonded distances ( $\text{\AA}$ )

For key to symmetry operations, see Table 3.

Ca–Ca	3.92 (2)
C(4)–O(7 <sup>h</sup> )	3.37 (3)
C(15)–O(7 <sup>h</sup> )	3.52 (3)

bridging interaction occurs *via* fused four-membered metal–carboxylato rings [Ca–O(1<sup>h</sup>)–C(7<sup>h</sup>)–O(2<sup>h</sup>)] and six-membered rings [Ca<sup>i</sup>–O(3<sup>h</sup>)–C(2<sup>h</sup>)–C(1<sup>h</sup>)–C(7<sup>h</sup>)–O(2<sup>h</sup>)], the latter formed by way of the *o*-ethoxy group in I<sup>h</sup>. The axes of the ring-linked metal chains develop parallel to **a** through the operation of screw symmetry. Projections of the chain packing are

presented in Fig. 2. No unusual bond lengths or angles occur in the ligands (Gopalakrishna & Cartz, 1972). The main features of the coordination stereochemistry are comparable with diaquamalonatocalcium(II) (Karipides, Ault & Reed, 1977) and diaquasuccinatocalcium(II) monohydrate (Karipides & Reed, 1980), and the four-membered Ca–O ring linkage is also observed in calcium terephthalate trihydrate (Matsuzaki & Iitaka, 1972) and dicalcium dihydrogen mellitate nonahydrate (Uchtman & Jandacek, 1980). In the present structure, however, the rings involve one somewhat longer bond length [Ca–O(1<sup>h</sup>), 2.87 (3)  $\text{\AA}$ ], to give a less regular trapezoidal system, but a tight packing of the metal ions parallel to the chain direction is again observed (Ca–Ca, 3.92  $\text{\AA}$ ).

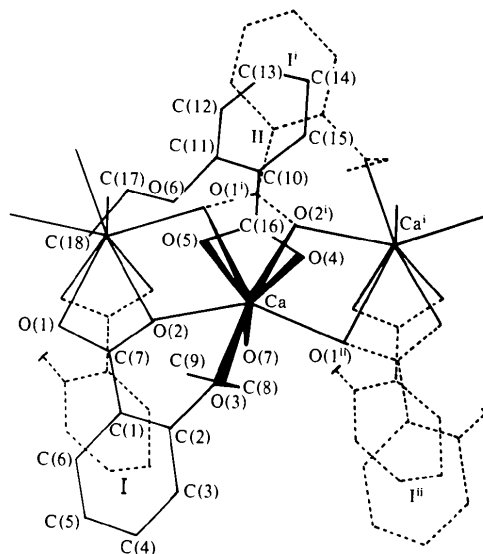


Fig. 1. Portion of the polymeric bridged structure showing the atom labelling and coordination to the metal. H atoms have been omitted for clarity. The key to symmetry-related atoms is: (i)  $0.5 + x, 1.5 - y, -z$ ; (ii)  $1 + x, y, z$ .

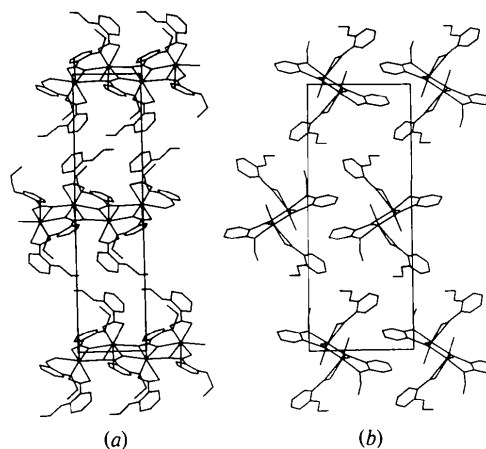


Fig. 2. Projections of chain packing in the unit cell. (a) Axes: **b** out of paper, **c** and **a** →. (b) Axes: **a** out of paper, **c** and **b** →.

It is of interest to compare the present structure with that of  $[\text{Zn}(o\text{-eba})_2(\text{H}_2\text{O})]$  (Natarajan, Gowda & Cartz, 1974),\* the latter involving coordination by both carboxylate groups, one *o*-ethoxy group and the water molecule to give a *cis*-distorted octahedral stereochemistry.† The bonding mode of one *o*-eba molecule is comparable to that of the non-bridging system (II) in the present structure, but the absence of a chelate function in the bridging carboxylate of the second *o*-eba system results in the formation of  $\text{Zn}-\text{O}-\text{C}-\text{O}-\text{Zn}$  chains (rather than four-membered rings), which are less effective in packing the metal ions ( $\text{Zn}-\text{Zn}$ , 4.861 Å). The restriction of the polymeric nature of  $[\text{M}(o\text{-eba})_2(\text{H}_2\text{O})]$  ( $M = \text{Ca}, \text{Zn}$ ) to a linear function can probably be explained in terms of steric constraints which limit the bridging potential of the ligand, due to the *ortho* configuration of the substituents. Previously mentioned systems, which involve sterically unhindered or polyfunctional ligands such as succinic acid (Karipides & Reed, 1980), malonic acid (Karipides, Ault & Reed, 1977), and benzenehexacarboxylic acid (Uchtman & Jandacek, 1980), result in a three-dimensional polymeric network with Ca. In addition, the utilization of nearly all the polar sites in coordination, in both the Ca and Zn *o*-eba complexes, results in the absence of hydrogen-bond contacts between adjacent chains so that cohesion is limited to weak packing forces. In the present complex, the packing of chains parallel to *a* is quite inefficient (Fig. 2) and gives rise to minimized interactions in the (004) plane, resulting in the observed perfect cleavage of the crystals parallel to (001). No cleavage data have, however, been reported for  $[\text{Zn}(o\text{-eba})_2(\text{H}_2\text{O})]$ . On the other hand, an extensive network of hydrogen-bond contacts is observed in calcium terephthalate trihydrate (Matsuzaki & Iitaka, 1972) and dicalcium dihydrogen mellitate nonahydrate (Uchtman & Jandacek, 1980).

The conformations of the *o*-eba groups in the present structure are similar to those in  $[\text{Zn}(o\text{-eba})_2(\text{H}_2\text{O})]$  (Natarajan, Gowda & Cartz, 1974) but differ in decreased internal coplanarity from the parent acid (Gopalakrishna & Cartz, 1972). While the O(6)–C(17)–C(18) linkage of the uncoordinated *o*-ethoxy group (II) is still reasonably coplanar with its associated benzene ring (planes 4 and 6, Table 4), that of

the coordinated system [O(3), C(8), C(9)] of (I) is almost perpendicular (planes 1 and 3, Table 4). In addition, each carboxylate group is substantially rotated from the plane of the benzene ring (planes 1 and 2, 4 and 5, Table 4), both of which effects are probably due to the restricted bite of the ligand system and packing factors.

While the present structure suggests the possibility of hydroxyapatite–*o*-eba interactions in tooth enamel, the structure of  $[\text{Ca}(o\text{-eba})_2(\text{H}_2\text{O})]$  is seriously deficient in cohesion through a limited polymeric network and the absence of hydrogen-bond interactions. A similar conclusion applies to  $[\text{Zn}(o\text{-eba})_2(\text{H}_2\text{O})]$  (Natarajan, Gowda & Cartz, 1974). Thus, no obvious structural rationale is apparent in the use of *o*-eba as a fortifying agent in the ZnO/eugenol cement and other, more extensively bridging, carboxylate ligands may be more efficient.

The authors thank Professor W. T. MacCulloch (Department of Dental Prosthetics, UCC) for helpful discussions, Drs G. Sheldrick, S. Motherwell and R. Taylor (Cambridge University) for the use of their programs, the Computer Bureau and Microanalysis Division (UCC), and Mr D. Hathaway for assistance with the plotting routines.

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\* Attention is drawn to an error in Table 2 of this reference; *y* for O(4) should read 8724 (to give a fractional coordinate of 0.08724).

† Not tetrahedral, as reported in this reference.