Complexes with Substituted 2,5-Dihydroxy-*p*-benzoquinones. Hydrogen Bonding of Ca[C₆(C₂H₅)₂O₄] · 3H₂O: A Neutron Diffraction Study

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Orthorhombic crystals of $Ca[C_6(C_2H_5)_2O_4] \cdot 3H_2O$ were grown in an aqueous silica gel. Lattice constants were $a = 503.1(1)$ pm, $b = 1561.9(4)$ pm, $c = 1613.6(4)$ pm, $Z = 4$, space group $P2_12_12_1$. Anisotropic refinement on single-crystal neutron diffraction data led to $R_w = 0.038$. Infinite, corrugated chains formed by Ca^{2+} and the *bis*-chelating $[C_6(C_2H_5)_2O_4]^{2-}$ ions are the main feature of the crystal structure. These chains extend along [010] and are linked to each other by asymmetric hydrogen bonds. Ca^{2+} is coordinated by three water molecules and four oxygen atoms of the $[C_6(C_2H_5)_2O_4]^{2-}$ ions. Six Ca–O distances are within the range from 237.7 to 243.0 pm. The seventh oxygen atom of the coordination sphere is more remote from Ca^{2+} (Ca–O(1) 254.9(5) pm). Although the oxygen atoms of the dianion are not equally bound to Ca^{2+} C–O and C–C bond lengths do not indicate a severe perturbation of the π electron delocalization. In one-half of the dianion the C–O bond lengths are nearly identical (C(2)–O(2) 126.1(4) and C(4)–O(4) 125.5(4) pm) and the C–C bonds differ by only 1.6 pm (C(2)–C(3) 141.2(4) and C(3)–C(4) 139.6(4) pm). In the other half containing O(1) which is more weakly bound to Ca^{2+} than the other oxygen atoms of the dianion there is a very slight tendency toward a system of alternating double bonds (C(1)–O(1) 128.4(4), C(1)–C(6) 138.2(4), C(6)–C(5) 142.3(4), and C(5)–O(5) 124.7(4) pm). Obviously hydrogen bonding prevents a greater perturbation of resonance stabilization of the dianion by compensating for deficient coordination by Ca^{2+} ions of the partially negatively charged oxygen atoms, since O(1) is involved in three hydrogen bonds, whereas each of the three other oxygen atoms of the dianion which are more tightly bound to Ca^{2+} occurs as proton acceptor only in one hydrogen bond. © 1989 Academic Press, Inc.

Introduction

Polydentate ligands, such as, for example, the dianion of 2,5-dihydroxy-*p*-benzoquinone, can form complex compounds with polymeric structures which often pro-

vide interesting applications in solid state chemistry. Some of these compounds which can possess zeolite or clathrate-like structures may undergo intercalation reactions or exhibit ion-exchange properties *(1–5)*.

Although the number of suitable ligands is enormous, it has been difficult so far to

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predict the properties of these compounds with desirable accuracy. This is mainly due to a lack of knowledge concerning the influences determining the crystal structures of these compounds. Therefore systematic structural studies have been carried out in order to elaborate relations between the structural features and the type of cation and anion employed. 2,5-Dihydroxy-*p*-benzoquinones are suitable compounds for this purpose since substituents of various nature may easily be introduced into the 3,6 position. This should have an important influence on the complexing properties of the resulting dianions.

The studies proved that in addition to the type of cations and anions employed a third component of equal importance has to be considered: the water of crystallization. Water molecules do not merely complete the coordination sphere of the cations, but play an important role in stabilizing these compounds by extensive systems of hydrogen bonds. Therefore the understanding of the hydrogen bonding systems of these coordination polymers is crucial for the design of novel solid state structures with taylor-made properties.

Experimental

Dark-violet single crystals of Ca[C$_6$(C$_2$H$_5$)$_2$O$_4$] · 3H$_2$O were grown in an aqueous silica gel as described in Ref. (*6*). A crystal with approximate dimensions 1.6 × 1.0 × 1.0 mm was chosen for data collection on the D9B four-circle diffractometer at the Institut Laue Langevin, Grenoble, France, under the following experimental conditions: orthorhombic cell with a = 503.1(1) pm, b = 1561.9(4) pm, c = 1613.6(4) pm, V = 1268.0 × 10^6 pm^3 (calculated from single-crystal X-ray data, 293 K, λ = 71.07 pm), space group $P2_12_12_1$ (No. 19), Z = 4, M_r = 288.31, D_x = 1.51 g/cm^3.

Neutron data collection was carried out at 296 K, λ = 84.62 pm, Cu(220) monochromator in transmission, λ/2 contamination filtered by 0.62 mm erbium foil, μ = 1.71 cm^{-1} (calculated). Numerical absorption correction and anisotropic extinction correction according to the model of Becker and Coppens (*7*) were applied. One octant of reciprocal space and Friedel equivalents were collected in ω-2θ scan mode up to θ_{max} = 35°. In addition to these, 212 strong reflections and their Friedel equivalents selected by means of the structure model refined with the lower angle data were collected as well, yielding a total number of 2678 reflections. Fifteen reflections obviously affected by multiple diffraction were not used for structure refinement. Since anomalous dispersion effects are negligible the reflections were merged according to Laue-class *mmm* to 2150 unique reflections (merging R = 0.046). Reflections with I < $2\sigma_I$ were considered unobserved (1397 observed).

Scattering lengths were taken from Ref. (*8*). Refinement on $|F|$ was carried out using the program system Prometheus (*9*), minimizing $\Sigma w(|F_o| - |F_c|)^2$ and assigning weights $1/\sigma_{|F|}^2$ from counting statistics. Starting parameters were obtained from the results of the X-ray structure determination (*6*). Full-matrix least-squares refinement with harmonically anisotropic thermal parameters converged at R = 0.053 and R_w = 0.038, GOF = 1.03 (307 parameters). Final atomic parameters are given in Table I. Supplementary material has been deposited.[1]

Results and Discussion

Bond lengths and angles of the Ca^{2+} coordination sphere are collected in Table II.

TABLE I

PARAMETERS FOR $Ca[C_6(C_2H_5)_2O_4] \cdot 3H_2O$

Atom	X	Y	Z	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca	.9913(9)	.3211(2)	.3650(2)	.0395(26)	.0182(17)	.0190(18)	.0029(19)	.0025(18)	.0007(13)
O(w1)	.9279(11)	.8151(3)	.9874(2)	.0404(26)	.0318(18)	.0193(19)	−.0050(22)	.0007(21)	.0015(14)
O(w2)	.6863(9)	.8079(4)	.2419(3)	.0297(24)	.0436(26)	.0401(24)	−.0090(24)	.0049(21)	.0027(21)
O(w3)	.4151(10)	.8723(3)	.0718(3)	.0473(29)	.0509(26)	.0299(21)	−.0218(25)	.0104(22)	−.0154(19)
O(1)	.8926(9)	.6653(2)	.1050(2)	.0497(25)	.0204(16)	.0250(17)	−.0074(18)	−.0151(19)	.0104(13)
O(2)	.2570(8)	.7147(2)	.2071(2)	.0304(20)	.0188(15)	.0355(18)	−.0073(16)	−.0040(18)	.0065(14)
O(4)	.8307(8)	.9632(2)	.1377(2)	.0318(21)	.0186(15)	.0296(16)	.0036(16)	−.0098(17)	−.0071(13)
O(5)	.2077(8)	.9135(2)	.2390(2)	.0348(21)	.0223(16)	.0279(17)	.0027(17)	−.0064(17)	−.0102(14)
C(1)	.0600(6)	.1130(2)	.3353(2)	.0277(16)	.0141(11)	.0157(11)	.0030(12)	−.0008(12)	−.0055(10)
C(2)	.8453(6)	.1432(2)	.2759(2)	.0204(15)	.0156(12)	.0231(13)	.0007(12)	.0000(12)	−.0026(10)
C(3)	.7630(6)	.0938(2)	.2072(2)	.0255(16)	.0152(12)	.0209(12)	.0004(12)	−.0042(13)	−.0017(10)
C(4)	.8863(7)	.0148(2)	.1947(2)	.0234(15)	.0152(11)	.0222(13)	−.0008(12)	−.0047(13)	−.0022(10)
C(5)	.1063(6)	.9845(2)	.2548(2)	.0230(14)	.0137(11)	.0185(12)	.0013(12)	−.0041(13)	−.0034(10)
C(6)	.1834(6)	.0349(2)	.3242(2)	.0245(16)	.0159(12)	.0221(14)	.0037(12)	−.0060(13)	−.0049(10)
C(7)	.5553(8)	.1261(2)	.1492(2)	.0338(20)	.0253(15)	.0325(17)	.0080(16)	−.0103(16)	−.0034(13)
C(8)	.3847(9)	.9985(2)	.3836(2)	.0503(25)	.0247(16)	.0338(17)	.0121(18)	−.0218(18)	−.0072(13)
C(9)	.6566(13)	.1940(4)	.0904(3)	.0676(36)	.0655(31)	.0515(30)	.0049(33)	−.0014(30)	.0305(25)
C(10)	.2578(18)	.9401(4)	.4461(4)	.1290(61)	.0653(37)	.0450(30)	.0192(42)	−.0047(40)	.0236(27)
H(11)	.0750(17)	.8234(5)	.9491(4)	.0485(43)	.0556(42)	.0291(34)	.0011(40)	.0041(37)	.0017(30)
H(12)	.7714(20)	.8211(7)	.9578(6)	.0641(59)	.0710(58)	.0674(64)	−.0202(56)	−.0239(56)	.0110(48)
H(21)	.5511(15)	.7650(5)	.2382(5)	.0408(42)	.0415(41)	.0673(51)	−.0065(37)	.0163(43)	.0036(35)
H(22)	.5895(21)	.8558(6)	.2548(6)	.0687(62)	.0556(51)	.0862(62)	−.0168(54)	.0253(61)	−.0141(49)
H(31)	.5236(17)	.9188(5)	.0933(5)	.0412(45)	.0473(40)	.0674(48)	−.0036(37)	.0000(42)	−.0158(37)
H(32)	.4224(18)	.8730(6)	.0139(5)	.0671(55)	.0863(57)	.0400(40)	−.0376(52)	.0145(44)	−.0013(41)
H(71)	.5287(19)	.5733(5)	.3856(5)	.0765(65)	.0440(38)	.0687(48)	.0077(42)	−.0486(49)	.0127(36)
H(72)	.6112(16)	.6538(6)	.3164(5)	.0392(43)	.0736(52)	.0678(50)	−.0191(43)	−.0038(43)	.0044(41)
H(81)	.4622(18)	.4636(6)	.1507(5)	.0539(50)	.0767(55)	.0602(50)	−.0298(49)	−.0106(43)	.0066(43)
H(82)	.5143(24)	.5494(5)	.0826(6)	.1224(94)	.0482(44)	.0883(65)	−.0262(55)	−.0772(67)	.0216(42)
H(91)	.5150(32)	.2171(8)	.0510(8)	.1357(116)	.1063(91)	.1130(92)	.0137(86)	−.0400(90)	.0631(77)
H(92)	.8125(37)	.1682(12)	.0500(9)	.1562(129)	.1751(161)	.1118(103)	.0568(128)	.0876(107)	.0664(108)
H(93)	.7405(34)	.2457(8)	.1249(8)	.1549(132)	.0771(70)	.1055(92)	−.0366(91)	−.0096(107)	.0319(68)
H(101)	.3901(45)	.9143(12)	.4903(9)	.2150(191)	.1964(154)	.0899(83)	.0528(153)	−.0238(119)	.0851(103)
H(102)	.1739(39)	.8836(8)	.4149(10)	.1831(163)	.0585(64)	.1460(117)	−.0229(92)	.0245(122)	.0372(76)
H(103)	.1002(44)	.9674(11)	.4757(8)	.2105(192)	.1404(126)	.0788(91)	.0610(137)	.0654(111)	.0480(82)

Note. w = water oxygen atom. Anisotropic temperature factors in the form: $\exp(-2\pi^2(U^{11}h^2a^{*2} + \ldots + 2U^{12}hka^*b^* + \ldots))$.

Ca^{2+} has CN 7 (Fig. 1). It is surrounded by three water molecules and four oxygen atoms stemming from the $[C_6(C_2H_5)_2O_4]^{2-}$ anions. A further Ca–water contact is by far too long to be of influence in the coordination sphere (Ca–O(w3)′ 325.5(7) pm; w = water oxygen atom).

Six Ca–O distances are within the range from 237.7 to 243.0 pm, thereby water molecules and oxygen atoms of $[C_6(C_2H_5)_2O_4]^{2-}$ behave similarly. The seventh coordination partner (O(1)), however, is markedly more remote from Ca^{2+} (254.9 pm). The connection of Ca^{2+} with the *bis*-chelating dianions leads to corrugated, infinite chains extending along [010] (Fig. 2). The corrugation of
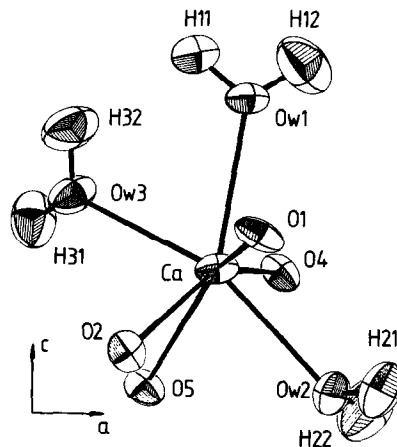

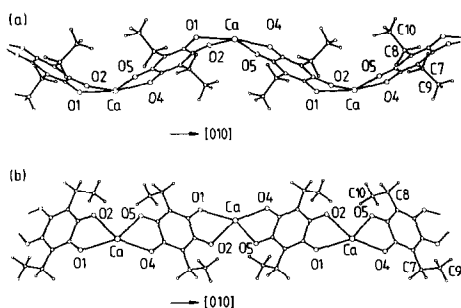FIG. 1. The coordination sphere of Ca^{2+} viewed from [010] direction (50% probability ellipsoids).

FIG. 2. Different views of the corrugated chains formed by Ca^{2+} and [C$_6$(C$_2$H$_5$)$_2$O$_4$]$^{2-}$ and extending along [010].

Application of a riding model bond length correction yielded O–H distances between 96.0 and 99.1 pm (Table III). O(w1) and its bonding partners. (Ca, H(11) and H(12)) lie approximately in a common plane (max. deviation 7.9 pm), but for O(w3) and particularly O(w2) the Ca–Ow bond vector is considerably inclined against the HOH plane.

Deviations from a least-squares plane fitted to the nonhydrogen atoms of the [C$_6$(C$_2$H$_5$)$_2$O$_4$]$^{2-}$ ion except methyl groups

the chains provides a better space filling than could be achieved by an arrangement of straight chains. Adjacent chains are interlinked by asymmetric hydrogen bonds which involve only oxygen atoms of the dianions as proton acceptors, in particular O(1) which is more weakly bound to Ca^{2+} than the other coordination partners (Table III).

The hydrogen bonds via H(21), H(22), and H(31) interlinked chains which the equivalent due to translational symmetry. The hydrogen bonds with H(11), H(12), and H(32) involve chains related by a 2$_1$ screw axis.

O(1) occurs three times as proton acceptor, whereas the other oxygen atoms of the dianion participate in only one hydrogen bond each. The shortest H$_2$O–O contact appears between O(w2) and O(2) (266.5 pm). The other distances between hydrogen bonded oxygen atoms reach from 274.1 (O(w3)–O(4)) to 309.4 pm (O(w1)′–O(1)). Only the O(w1)′–H(12)–O(1) bond is nearly straight (176.74°). The other OHO angles are markedly bent, in particular the one with H(22) (142.60°). The HOH angles vary as well. The angles at O(w1) and O(w3) are close to tetrahedral, but H(21)–O(w2)–H(22) is contracted to 102.03° which is smaller than the HOH angle in free water molecules.

TABLE II

THE COORDINATION OF Ca^{2+}

Ca–O(w2)	237.7(6)
–O(2)	238.2(5)
–O(4)	239.4(5)
–O(w1)	241.8(6)
–O(w3)	242.1(7)
–O(5)	243.0(5)
–O(1)	254.9(5)

Angles A–Ca–B A/B		A–B (pm)
O(w2)/O(2)	86.73(20)	326.8
O(w2)/O(4)	79.15(21)	304.0
O(w2)/O(w1)	126.66(26)	428.5
O(w2)/O(w3)	155.57(25)	468.9
O(w2)/O(5)	80.26(19)	309.9
O(w2)/O(1)	84.19(21)	330.5
O(2)/O(4)	146.50(22)	457.3
O(2)/O(w1)	122.85(22)	421.5
O(2)/O(w3)	89.61(21)	338.5
O(2)/O(5)	81.98(18)	315.7
O(2)/O(1)	63.06(16)	258.3
O(4)/O(w1)	89.48(19)	338.7
O(4)/O(w3)	90.97(20)	343.3
O(4)/O(5)	65.85(16)	262.2
O(4)/O(1)	143.42(24)	469.4
O(w1)/O(w3)	74.94(20)	294.4
O(w1)/O(5)	140.61(22)	456.5
O(w1)/O(1)	74.80(17)	301.9
O(w3)/O(5)	75.30(19)	296.3
O(w3)/O(1)	115.44(22)	420.2
O(5)/O(1)	142.42(21)	471.4

Note. Distances in picometers; angles in degrees; w = water oxygen atom.

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TABLE III

WATER AND HYDROGEN BONDS

	Uncorrected	Riding model correction		
O(w1)–H(11)	97.3(9)	99.1	H(11)–O(w1)–H(12)	107.77(84)
O(w1)–H(12)	92.6(1.1)	98.0		
H(11)–O(1)	182.9(9)		O(w1)–H(11)–O(1)	168.62(75)
H(12)–O(1)	216.9(1.1)		O(w1)′–H(12)–O(1)	176.74(89)
O(w1)–O(1)	278.9(7)			
O(w1)′–O(1)	309.4(7)			
O(w2)–H(21)	95.7(9)	97.1	H(21)–O(w2)–H(22)	102.03(91)
O(w2)–H(22)	91.7(1.2)	96.0		
H(21)–O(2)	174.9(9)		O(w2)–H(21)–O(2)	159.11(76)
H(22)–O(5)	213.7(1.1)		O(w2)–H(22)–O(5)	142.60(93)
O(w2)–O(2)	266.5(6)			
O(w2)–O(5)	291.8(6)			
O(w3)–H(31)	97.2(9)	98.0	H(31)–O(w3)–H(32)	109.06(86)
O(w3)–H(32)	93.6(9)	96.6		
H(31)–O(4)	183.8(9)		O(w3)–H(31)–O(4)	153.18(78)
H(32)–O(1)	201.4(9)		O(w3)–H(32)–O(1)	160.96(83)
O(w3)–O(4)	274.1(6)			
O(w3)–O(1)	291.5(6)			

Note. Distances in picometers; angles in degrees; w = water oxygen atom.

are negligible (max. deviation 5.8 pm). The planes of the C_2H_5 groups are in rough approximation perpendicular to the quinone ring plane (76.7° (C(7), C(9)), and 84.2° (C(8), C(10)) with CH_3 groups pointing in opposite directions with respect to each other.

A rigid body motion analysis (TLS (*10*)) showed little librational movement yielding librational bond length corrections smaller than the e.s.d.'s. The translational movement is small as well and almost isotropic with a mean displacement of approx 0.1 Å. The atoms of the CH_3 groups show rather high displacement factors. Therefore the bond lengths are foreshortened artificially. In the case of vigorously moving atoms harmonically anisotropic temperature factors cannot describe properly the probability density function. A more appropriate treatment could be achieved by use of anhar-

monic temperature factors. This would lead to bond lengths free of inaccuracies caused by librational motion and stretch anharmonicity as shown in previous studies (compare for example Refs. (*11–13*)). This procedure, however, would have demanded considerably more high-angle data which in the present case were not accessible under feasible conditions.

Dianions of 3,6-disubstituted 2,5-dihydroxy-p-benzoquinones may be regarded as built up by two 1-oxopropen-3-olate fragments with delocalized π electrons interlinked by two C–C single bonds. This point of view in principle is confirmed by the bonding geometry of $[C_6(C_2H_5)_2O_4]^{2-}$ (Table IV), although the different bonding of its oxygen atoms to Ca^{2+} should cause a considerable perturbation of the π electron delocalization.

In the system O(2)–C(2)–C(3)–C(4)–O(4)

TABLE IV

THE [C$_6$(C$_2$H$_5$)$_2$O$_4$]$^{2-}$ ION

C(1)–O(1)	128.4(4)	C(4)–C(5)	154.5(4)	C(8)–H(81)	109.4(1.0)
C(1)–C(2)	152.0(4)	C(5)–O(5)	124.7(4)	C(8)–H(82)	108.9(1.0)
C(1)–C(6)	138.2(4)	C(5)–C(6)	142.3(4)	C(9)–H(91)	102.0(1.6)
C(2)–O(2)	126.1(4)	C(6)–C(8)	150.6(5)	C(9)–H(92)	109.7(1.8)
C(2)–C(3)	141.2(4)	C(7)–C(9)	151.2(7)	C(9)–H(93)	106.7(1.5)
C(3)–C(4)	139.6(4)	C(7)–H(71)	108.4(9)	C(10)–H(101)	105.5(2.0)
C(3)–C(7)	149.1(5)	C(7)–H(72)	109.4(9)	C(10)–H(102)	110.0(1.6)
C(4)–O(4)	125.5(4)	C(8)–C(10)	150.2(8)	C(10)–H(103)	101.9(2.1)

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O(1)–C(1)–C(2)	114.13(27)	C(9)–C(7)–H(71)	109.90(53)
O(1)–C(1)–C(6)	125.15(31)	C(9)–C(7)–H(72)	107.40(57)
C(2)–C(1)–C(6)	120.72(23)	H(71)–C(7)–H(72)	105.44(74)
O(2)–C(2)–C(3)	122.41(30)	C(6)–C(8)–C(10)	111.75(44)
O(2)–C(2)–C(1)	115.25(27)	C(6)–C(8)–H(81)	109.79(53)
C(1)–C(2)–C(3)	122.33(23)	C(6)–C(8)–H(82)	110.94(58)
C(2)–C(3)–C(4)	117.76(26)	C(10)–C(8)–H(81)	109.64(61)
C(7)–C(3)–C(2)	120.89(25)	C(10)–C(8)–H(82)	107.84(61)
C(7)–C(3)–C(4)	121.34(25)	H(81)–C(8)–H(82)	106.72(86)
O(4)–C(4)–C(3)	125.06(31)	C(7)–C(9)–H(91)	113.76(96)
O(4)–C(4)–C(5)	115.00(28)	C(7)–C(9)–H(92)	110.82(1.02)
C(3)–C(4)–C(5)	119.93(24)	C(7)–C(9)–H(93)	109.64(85)
O(5)–C(5)–C(4)	115.98(26)	H(91)–C(9)–H(92)	105.09(1.23)
O(5)–C(5)–C(6)	122.73(29)	H(91)–C(9)–H(93)	109.52(1.20)
C(4)–C(5)–C(6)	121.28(23)	H(92)–C(9)–H(93)	107.78(1.38)
C(1)–C(6)–C(5)	117.97(26)	C(8)–C(10)–H(101)	114.65(1.33)
C(1)–C(6)–C(8)	123.51(26)	C(8)–C(10)–H(102)	110.11(94)
C(5)–C(6)–C(8)	118.45(25)	C(8)–C(10)–H(103)	113.00(1.09)
C(3)–C(7)–C(9)	113.27(36)	H(101)–C(10)–H(102)	104.20(1.44)
C(4)–C(7)–H(71)	109.94(52)	H(101)–C(10)–H(103)	109.49(1.41)
C(3)–C(7)–H(72)	110.58(51)	H(102)–C(10)–H(103)	104.55(1.64)

Note. Distances in picometers; angles in degrees.
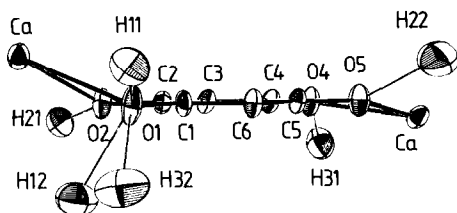
FIG. 3. Surrounding of the oxygen atoms of [C$_6$(C$_2$H$_5$)$_2$O$_4$]$^{2-}$ by Ca^{2+} and protons stemming from hydrogen bonds. These coordination partners are not in plane with the dianion. The plane described by Ca, O(1), and O(2) is inclined by 26.9° against the plane of the dianion, the one with Ca, O(4), and O(5) by 10.4°. (C$_2$H$_5$ groups have been omitted for sake of clarity.)

the C–O bond lengths are equal within the limits of experimental error. The C(2)–C(3) and C(3)–C(4) bonds differ by only 1.6 pm. Somewhat greater differences appear in the system O(1)–C(1)–C(6)–C(5)–O(5). C(1)–O(1) is the longest C–O bond of [C$_6$(C$_2$H$_5$)$_2$ O$_4$]$^{2-}$, whereas C(5)–O(5) is the shortest, pointing to a higher contribution of double bonding. The same is true for C(5)–C(6) and C(1)–C(6).

Altogether these differences are surprisingly small. Obviously this is made possible by hydrogen bonding which compensates for the deficient surrounding of O(1) by positively charged calcium ions (Fig. 3). Thus

hydrogen bonding prohibits the perturbation of the resonance stabilization of the dianion and contributes crucially to the stabilization of the crystal structure. Similar relations have been observed in barium polyporate tetrahydrate $(Ba[C_6(C_6H_5)_2O_4] \cdot 4H_2O)$ (*14*).

Acknowledgments

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