Alkaline–Earth Squarates

V. Hydrogen Bonding in BaC₄O₄·3H₂O: A Neutron Diffraction Study*

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Triclinic crystals of BaC₄O₄·3H₂O were grown in an aqueous silica gel. Lattice constants were a = 660.38(9) pm, b = 859.83(8) pm, c = 878.26(9) pm, α = 61.281(8)°, β = 63.827(9)°, γ = 70.53(1)°; Z = 2, space group $P\bar{1}$. Anisotropic refinement of neutron diffraction data led to R_w = 0.0234 including anharmonic thermal parameters for H atoms. Ba²⁺ has CN 8 + 1. It is surrounded by five water molecules and four O$_{squarate}$ atoms (Ba–O 271.3–323.1 pm). The squarate dianion is almost planar and shows C–C and C–O bond lengths indicating the existence of undisturbed resonance stabilization, although one O$_{squarate}$ atom is not connected to Ba²⁺ (C–O 124.4–125.5 pm, C–C 145.6–147.7 pm). Asymmetric hydrogen bonds between H₂O and O$_{squarate}$ play an important part in this structure. Obviously the bonding between O$_{squarate}$ and its noncarbon neighbors is dominated by electrostatic and ionic interactions. © 1988 Academic Press, Inc.

Introduction

Squaric acid (3,4-dihydroxycyclobut-3-ene-1,2-dione) is one of the so-called oxocarbon acids. Its dianion is strongly stabilized by resonance effects (2). Therefore its four oxygen atoms are to be regarded as equivalent and the dianion can act in principle as a fourfold monodentate ligand providing interesting applications in structural and coordination chemistry.

Many different types of inorganic squarates have already been studied, particularly by describing their crystal structures which often are of special interest (3, 4). Mostly polymeric complex compounds are formed, the most important of which show clathrate-, zeolite-like, or intercalation properties (5–7).

C₄O₄²⁻ was often found to be coordinated by less than its four oxygen atoms to the metal cations (8–12). This, however, did not result in C–O bond lengths differing sufficiently to allow discernment between the differently coordinated O$_{squarate}$ atoms. Instead, the C–O and C–C distances were typical of completely delocalized π-elec-

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* For part IV, see Ref. (*1*). Dedicated with best wishes to Prof. Dr. Dr.h.c. Armin Weiss on the occasion of his 60th birthday.

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trons indicating that the resonance effects remained essentially undisturbed. This surprising fact can be explained by taking the water of crystallization into consideration. Close distances between H$_2$O and particularly those O$_{squarate}$ atoms not bound to metal cations appear pointing to the existence of strong hydrogen bonds.

The crystal structure of BaC$_4$O$_4$·3H$_2$O is a good example. One O$_{squarate}$ atom is bound to two Ba^{2+}, two are coordinated by one Ba^{2+} each, and the fourth has no bonding contact with Ba^{2+}. In order to shed light on the effects of hydrogen bonding in this compound we carried out a neutron diffraction study, the results of which are presented here.

Experimental Details and Structure Refinement

Neutron diffraction data were recorded with a single crystal of BaC$_4$O$_4$·3H$_2$O. The compound was obtained as colorless platelets from an aqueous silica gel according to Ref. (11).

Crystallographic and measuring details include the following: triclinic, a = 660.38(9) pm, b = 859.83(8) pm, c = 878.26(9) pm, α = 61.281(8)°, β = 63.827(9)°, γ = 70.53(1)°, V = 387.81 × 10^6 pm^3 (calculated from single-crystal X-ray data, 293 K, λ = 71.07 pm). The space group $P\bar{1}$ (No. 2) was confirmed by structure refinement and E statistics. Z = 2, M_r = 303.43, D_x = 2.60 Mg m^{-3}.

Neutron data collection was carried out using the following: D9B four circle diffractometer at the ILL, 296 K, λ = 84.36 pm (H3 beam tube), Cu(220) monochromator in transmission, $\lambda/2$ contamination filtered by Erbium foil, μ = 1.04 cm^{-1}, crystal dimensions 3 × 5 × 1 mm, numerical absorption correction, anisotropic extinction correction, $\omega - 2\theta$ scan, θ limit 42°, 3580 reflections recorded, 3225 unique, merging R =

TABLE I
RESIDUALS AFTER REFINEMENT

Type of refinement	Number of parameters	R (All reflections: 3225)	R_w	R (Observed reflections only: 2661)	R_w	GOF
Harmonically anisotropic	163	0.0302	0.0263	0.0207	0.0240	1.21
H anharmonic significant C^{ijk} only	190	0.0296	0.0257	0.0201	0.0234	1.18
H anharmonic all C^{ijk}	223	0.0296	0.0256	0.0200	0.0233	1.18

0.0057, refinement on $|F|$, quantity minimized $\Sigma w(|F_o| - |F_c|)^2$, weights $1/\sigma_{|F|}^2$ from counting statistics, scattering lengths from Ref. (13), reflections with $I < 3\sigma_I$ considered as unobserved (2661 reflections observed).

Starting parameters for the refinements were obtained from the results of the X-ray structure determination (11). H positions were found in difference Fourier maps. For H atoms anharmonic thermal parameters were refined as well. The resulting probability density function was calculated by the Gram–Charlier expansion using third order moments (program system PROMETHEUS (14)). C^{ijk} not differing distinctly from their e.s.d.'s in preliminary refinements were set to zero during the final cycles. According to Hamilton (15) the refinement of third order moments leads to a reduction of R_w which is better than the 0.5% significance level. The further improvement by introduction of all C^{ijk} is not significant even at the 50% level (see Table I). Atom parameters are listed in Tables II–IV. Additional material has been deposited with the NAPS.[1]

TABLE II

PARAMETERS FOR $BaC_4O_4\cdot 3H_2O$

Atom	X	Y	Z	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ba	.14749(7)	.18532(5)	.07304(5)	.0159(2)	.0125(2)	.0120(2)	−.0012(1)	−.0034(1)	−.0035(1)
W(1)	.76796(7)	.46701(6)	.01501(6)	.0190(2)	.0278(2)	.0193(2)	−.0029(1)	−.0053(1)	−.0102(2)
W(2)	.36522(8)	.10281(6)	.32402(6)	.0279(2)	.0210(2)	.0227(2)	−.0058(2)	−.0071(2)	−.0092(2)
W(3)	.82434(9)	.97024(8)	.20656(9)	.0244(2)	.0256(2)	.0514(3)	−.0072(2)	−.0026(2)	−.0169(2)
O(1)	.83804(9)	.19958(6)	.40884(6)	.0344(2)	.0210(2)	.0173(2)	−.0060(2)	−.0009(2)	−.0115(1)
O(2)	.15518(8)	.37914(6)	.71967(5)	.0315(2)	.0180(2)	.0119(1)	−.0076(1)	−.0042(1)	−.0004(1)
O(3)	.35422(8)	.42957(6)	.29493(6)	.0298(2)	.0182(2)	.0178(2)	−.0050(1)	−.0034(1)	−.0098(1)
O(4)	.38775(7)	.84092(5)	.16234(5)	.0249(2)	.0138(2)	.0130(1)	−.0031(1)	−.0016(1)	−.0015(1)
C(1)	.21533(5)	.69916(4)	.51056(4)	.0175(1)	.0137(1)	.0115(1)	−.0023(1)	−.0021(1)	−.0051(1)
C(2)	.20932(5)	.50854(4)	.56910(4)	.0162(1)	.0135(1)	.0102(1)	−.0031(1)	−.0027(1)	−.0028(1)
C(3)	.30195(5)	.53084(4)	.37669(4)	.0164(1)	.0128(1)	.0110(1)	−.0024(1)	−.0028(1)	−.0043(1)
C(4)	.31533(5)	.71828(4)	.31632(4)	.0157(1)	.0116(1)	.0105(1)	−.0016(1)	−.0021(1)	−.0032(1)
H(11)	.25851(28)	.51888(15)	.09194(14)	.0419(4)	.0421(5)	.0291(4)	−.0064(4)	−.0128(3)	−.0166(3)
H(12)	.62297(17)	.44683(19)	.11712(14)	.0289(4)	.0414(4)	.0295(4)	−.0078(3)	−.0024(3)	−.0161(3)
H(21)	.34535(23)	.20346(26)	.35345(18)	.0444(4)	.0335(4)	.0401(4)	−.0046(3)	−.0140(4)	−.0206(4)
H(22)	.28736(28)	.00907(20)	.43472(15)	.0416(4)	.0345(4)	.0309(4)	−.0114(3)	−.0095(3)	−.0071(3)
H(31)	.66284(33)	.01856(14)	.24828(27)	.0314(4)	.0396(5)	.0549(6)	−.0049(3)	−.0068(4)	−.0231(4)
H(32)	.83322(21)	.84218(23)	.26664(16)	.0455(5)	.0319(4)	.0357(4)	−.0075(3)	−.0128(4)	−.0109(3)

Note. $W = H_2O$. Harmonically anisotropic temperature factors according to $\exp(-2\pi^2(U^{11}h^2a^{*2} + \cdots + 2U^{12}hka^*b^* + \ldots))$.

Results and Discussion

The results of the previous X-ray structure determination are confirmed. Ba^{2+} is coordinated by four $O_{squarate}$ atoms and five water molecules. One of the latter is much more remote than the others; therefore, CN is 8 + 1 (see Tables V and VI). Bond lengths and angles of the squarate dianion are shown in Table VII. They are in good agreement with the X-ray results. The asymmetric environment of $C_4O_4^{2-}$ in this type structure leads to C–C and C–O bond lengths differing outside the limits of experimental error. However, there are no hints to any considerable disturbation of the π-electron delocalization. Furthermore the squarate dianion exhibits only slight deviations from planarity. The oxygen atoms are particularly bent out of plane in a bisphenoidal fashion which was observed in other squarate-type structures as well (*5, 8, 10,*

TABLE III

$BaC_4O_4\cdot 3H_2O$: ANHARMONIC TEMPERATURE FACTOR COEFFICIENTS (GRAM–CHARLIER EXPANSION)

Atom	C^{111}	C^{222}	C^{333}	C^{112}	C^{122}	C^{113}	C^{133}	C^{223}	C^{233}	C^{123}
H(11)	−.40(12)	0	0	0	.14(5)	0	.14(4)	0	0	−.08(3)
H(12)	0	−.06(6)	0	0	.03(4)	.05(4)	0	0	0	0
H(21)	0	−.14(7)	0	−.13(6)	−.06(5)	0	.15(4)	.18(5)	−.16(4)	0
H(22)	.37(15)	.24(6)	0	0	−.21(5)	−.16(6)	0	0	0	.13(3)
H(31)	−.32(15)	0	−.13(9)	0	0	0	.12(8)	.14(7)	0	0
H(32)	0	.11(6)	0	.26(7)	0	−.12(7)	.14(5)	0	0	−.11(3)

Note. Multiplied by 10^5; coefficients not significantly greater than e.s.d.'s were set to zero for final refinements.

TABLE IV

MEAN POSITIONS OF H ALONG THE
COVALENT O–H BOND

Atom	X	Y	Z
H(11)	.25869	.51866	.09234
H(12)	.62223	.44723	.11699
H(21)	.34510	.20535	.35245
H(22)	.28723	.00685	.43525
H(31)	.66212	.01895	.24837
H(32)	.83222	.84142	.26650

TABLE VI

BOND ANGLES AROUND Ba^{2+}

A/B	Angles A–Ba–B (°)	Distance A–B (pm)
O(2)/O(4)	118.42(2)	470.4
O(2)/W(3)[a]	100.74(3)	422.5
O(2)/O(1)	132.92(3)	504.0
O(2)/W(2)	144.45(4)	528.4
O(2)/O(4)′	72.47(2)	329.1
O(2)/W(1)	63.08(2)	293.0
O(2)/W(1)′	75.89(2)	344.8
O(2)/W(3)′	53.61(2)	272.0
O(4)/W(3)	75.99(3)	340.8
O(4)/O(1)	105.10(2)	440.4
O(4)/W(2)	67.86(2)	312.6
O(4)/O(4)′	65.73(2)	304.8
O(4)/W(1)	157.96(4)	554.0
O(4)/W(1)′	135.16(4)	522.7
O(4)/W(3)′	71.89(2)	353.9
W(3)/O(1)	72.04(3)	326.8
W(3)/W(2)	114.36(3)	471.3
W(3)/O(4)′	129.64(3)	509.0
W(3)/W(1)	82.12(3)	371.5
W(3)/W(1)′	146.82(4)	542.8
W(3)/W(3)′	64.41(3)	322.3
O(1)/W(2)	67.47(3)	312.2
O(1)/O(4)′	147.58(4)	541.2
O(1)/W(1)	69.84(2)	324.4
O(1)/W(1)′	86.11(2)	387.5
O(1)/W(3)′	135.82(4)	557.7
W(2)/O(4)′	80.60(3)	367.9
W(2)/W(1)	125.22(3)	507.6
W(2)/W(1)′	77.60(3)	358.9
W(2)/W(3)′	138.26(3)	567.1
O(4)′/W(1)	129.93(2)	519.5
O(4)′/W(1)′	81.54(3)	375.0
O(4)′/W(3)′	73.17(3)	363.9
W(1)/W(1)′	66.76(3)	317.6
W(1)/W(3)′	96.44(3)	456.4
W(1)′/W(3)′	128.05(2)	550.6

[a] W = H$_2$O.

12). Obviously this is due to repulsive interactions between the negatively charged oxygen atoms. A thermal motion analysis in terms of a rigid body model (TLS (*16*)) gave isotropic translational and librational components with almost insignificant helical motions; the coordinates of the origin which symmetrizes the S tensor are 0.3138, 0.6204, and 0.3637 (compared to the center of gravity at 0.2629, 0.6132, and 0.4425 this position is shifted toward C(3) and C(4)).

Interesting insights are provided by inspecting the system of hydrogen bonds. Each of the three crystallographically independent water molecules is involved in hydrogen bonding leading to six unique asymmetric hydrogen bonds. Thereof, five occur between O$_{squarate}$ atoms and H$_2$O, but only one between water molecules (compare Fig. 1). *W*(1) (*W* = H$_2$O) connects two centrosymmetrically related C$_4$O$_4^{2-}$ by hydrogen bonding to O(3). Two C$_4$O$_4^{2-}$ which are

TABLE V

Ba–O DISTANCES
IN pm

Ba–O(2)	271.3(1)
Ba–O(4)	276.3(1)
Ba–W(3)	277.3(1)
Ba–O(1)	278.4(1)
Ba–W(2)	283.6(1)
Ba–O(4)′	285.2(1)
Ba–W(1)	288.1(1)
Ba–W(1)′	289.1(1)
Ba–W(3)′	323.1(1)

equivalent due to translational symmetry are connected via O(3) and O(1) by *W*(2). *W*(3) is proton donator to O(2) and *W*(2). A rather complicated network results, if the connections between Ba^{2+} and the O$_{squarate}$ atoms are taken into consideration (*11*).

It should be emphasized that O(4) which is bound to 2 Ba^{2+} does not participate in hydrogen bonding. O(1) and O(2) have one

TABLE VII

The Geometry of the $C_4O_4^{2-}$ Dianion

C(1)–C(2)	147.2(1)	C(1)–O(1)	124.5(1)
C(2)–C(3)	145.7(1)	C(2)–O(2)	124.4(1)
C(3)–C(4)	145.6(1)	C(3)–O(3)	125.5(1)
C(4)–C(1)	147.7(1)	C(4)–O(4)	125.1(1)
O(1)–C(1)–C(2)	135.27(4)	O(2)–C(2)–C(1)	135.51(4)
O(1)–C(1)–C(4)	135.46(4)	O(2)–C(2)–C(3)	134.38(5)
C(2)–C(1)–C(4)	89.26(3)	C(1)–C(2)–C(3)	90.07(3)
O(3)–C(3)–C(2)	134.98(4)	O(4)–C(4)–C(1)	136.01(5)
O(3)–C(3)–C(4)	134.28(4)	O(4)–C(4)–C(3)	134.06(4)
C(2)–C(3)–C(4)	90.73(3)	C(1)–C(4)–C(3)	89.91(3)

Equation of least-squares plane:

$$6.3813x + 0.7102y + 3.2540z = 3.5517$$

Deviations from plane (pm)	C(1)	−1.97	O(1)	−2.61
	C(2)	−0.30	O(2)	4.96
	C(3)	−2.21	O(3)	−2.65
	C(4)	−0.01	O(4)	4.81

Note. Bond lengths are given in picometers, angles in degrees.

proton neighbor each. O(3) which is not coordinated by Ba^{2+} is involved in three hydrogen bonds.

Using the anharmonic thermal parameters the mean positions along the O–H bond were calculated for each H atom. These coordinates were employed in the calculation of bond lengths and angles involving H atoms. In this way, it was possible to compensate for systematic errors in the bond geometry as obtained in the usual
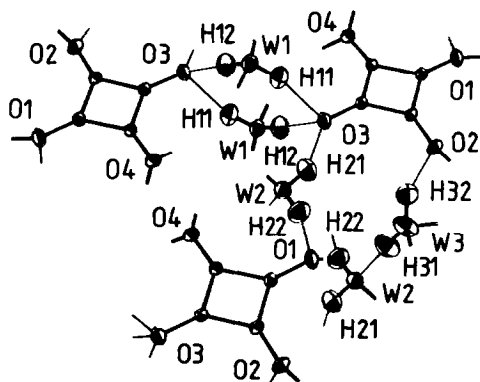

FIG. 1. System of hydrogen bonds in BaC_4O_4 · $3H_2O$. (Hydrogen bonds are denoted by thin lines; thick lines lend to the Ba^{2+}, which is not shown; W, water oxygen.)

harmonic treatment as a result of librations and stretch anharmonicity of the H atoms. In Table VIII the O–H bond lengths calculated by this method are compared with those obtained from the refined atomic coordinates of the anharmonic and the conventional harmonic treatment. The mean coordinates lead to bond distances in a range which is well known from the literature. O–H distances calculated with the harmonically refined coordinates are some-

TABLE VIII

Water and Hydrogen Bonds

	Anharmonic refinement		
	With refined atomic coordinates	With mean positions of H along O–H	With harmonically refined atomic coordinates
H(11)–W(1)	97.4(2)	97.7	97.5
H(12)–W(1)	97.7(2)	98.0	97.7
H(11)–O(3)′	187.7(2)	187.3	187.8
H(12)–O(3)	176.6(2)	176.3	176.6
H(21)–W(2)	97.1(3)	98.1	97.4
H(22)–W(2)	97.0(2)	98.2	97.3
H(21)–O(3)″	177.1(3)	175.8	176.7
H(22)–O(1)	184.7(2)	183.1	184.3
H(31)–W(3)	97.5(3)	98.0	97.4
H(32)–W(3)	95.9(2)	96.5	96.4
H(31)–W(2)	178.6(3)	178.2	178.7
H(32)–O(2)	182.6(3)	181.7	182.1

All further distances and angles involving H have been calculated using the mean positions of H along O–H.

H(11)–W(1)–H(12)	106.06(20)	W(1)–H(11)–O(3)′	164.03(16)
H(11)–W(1)–Ba	109.27(13)	W(1)–H(12)–O(3)	175.63(18)
H(11)–W(1)–Ba′	104.88(11)		
H(12)–W(1)–Ba	115.59(11)	W(1)–O(3)	274.1(1)
H(12)–W(1)–Ba′	107.05(13)	W(1)–O(3)′	282.6(1)
Ba–W(1)–Ba′	113.24(4)		
	$\bar{\theta}$ = 109.35		
H(21)–W(2)–H(22)	109.97(15)	W(2)–H(21)–O(3)″	154.16(12)
H(21)–W(2)–Ba	112.53(15)	W(2)–H(22)–O(1)	162.61(17)
H(21)–W(2)–H(31)	108.94(20)		
H(22)–W(2)–Ba	103.20(17)	W(2)–O(3)″	267.5(1)
H(22)–W(2)–H(31)	108.61(17)	W(2)–O(1)	278.4(1)
H(31)–W(2)–Ba	113.38(8)		
	$\bar{\theta}$ = 109.44		
H(31)–W(3)–H(32)	105.54(21)	W(3)–H(31)–W(2)	178.45(25)
H(31)–W(3)–Ba	118.95(16)	W(3)–H(32)–O(2)	154.49(15)
H(31)–W(3)–Ba′	102.73(17)		
H(32)–W(3)–Ba	130.82(18)	W(3)–W(2)	276.1(1)
H(32)–W(3)–Ba′	70.10(11)	W(3)–O(2)	272.0(1)
Ba–W(32)–Ba′	115.59(3)		
	$\bar{\theta}$ = 107.29		

Note. Ba′ refers to the longer Ba–W distance. W = water oxygen. Distances are given in picometers, angles in degrees.

TABLE IX

SURROUNDING OF O$_{squarate}$ ATOMS

C(1)–O(1)–Ba	135.81(5)	C(2)–O(2)–Ba	151.15(6)
C(1)–O(1)–H(22)	111.02(6)	C(2)–O(2)–H(32)	121.92(5)
Ba–O(1)–H(22)	112.38(6)	Ba–O(2)–H(32)	81.78(5)
	ϑ = 119.74		ϑ = 118.28
C(3)–O(3)–H(11)	117.16(7)	C(4)–O(4)–Ba	121.35(4)
C(3)–O(3)–H(12)	114.22(9)	C(4)–O(4)–Ba'	122.19(5)
C(3)–O(3)–H(21)	138.05(6)	Ba–O(4)–Ba'	114.27(2)
H(11)–O(3)–H(12)	80.57(9)		
H(11)–O(3)–H(21)	93.60(10)		ϑ = 119.27
H(12)–O(3)–H(21)	97.58(10)		
	ϑ = 106.86		

Least-squares planes:
Plane I C(1), C(2), C(3), C(4), O(1), O(2), O(3), O(4)
Equation and deviation see Table VII
Plane II C(2), O(2), Ba, H(32)
Equation: $5.9019x - 0.3519y + 0.4002z = 1.2043$
Deviations in pm: C(2) 7.98, O(2) –13.39, Ba 3.04, H(32) 2.37
Plane III C(1), O(1), Ba, H(22)
Equation: $5.7711x - 0.0515y + 5.0860z = 3.8361$
Deviations in pm: C(1) –3.27, O(1) 6.40, Ba –1.47, H(22) –1.66
Plane IV C(4), O(4), Ba, Ba'
Equation: $4.7035x + 5.7866y + 8.0225z = 8.1115$
Deviations in pm: C(4) 6.57, O(4) –11.93, Ba 2.71, Ba' 2.65
Angles between normals to the planes:
I/II 19.30°, I/III 19.97°, I/IV 53.65°

Note. Distances are given in picometers, angles in degrees; with mean positions of H along the covalent O–H bond. Ba' refers to the longer Ba–O distance.

what shorter than those obtained with the mean positions. Thus showing the dominance of the librations in the anharmonic deformations of the H atoms.

The somewhat short $W(3)$–H(32) bond should be regarded in connection with the different Ba–$W(3)$ distances. One distance is the greatest among all Ba–water bonds and the other is the shortest. A close Ba–H(32) distance also occurs (304.1(2) pm) whereas the other Ba–H distances are much greater (the next shortest is Ba–H(22) 320.6(2) pm).

The HOH angles differ considerably for the three water molecules. With $W(2)$ this angle is somewhat greater than the tetrahedron angle whereas with $W(1)$ and particularly $W(3)$ it well resembles the HOH angle in free water molecules. The surrounding of the water molecules is in good agreement with a tetrahedral arrangement of electron pairs (see Table VIII). Greater deviations are observed only with $W(3)$, but this has to

be considered with respect to the different Ba–$W(3)$ distances.

The majority of the OHO angles are considerably bent. Only $W(3)$–H(31)–$W(2)$ and $W(1)$–H(12)–O(3) are close to 180°.

The C–O bond lengths are close to values known from C=O double bonds pointing to a rather efficient overlap between p_z orbitals of C and O$_{squarate}$ atoms. Assuming sp^2 hybridization of the O$_{squarate}$ atoms, their noncarbon neighbors should be in plane with the C$_4$O$_4^{2-}$, if there is a considerable degree of covalent bonding. The corresponding interplane angles are listed in Table IX. With O(1) and O(2) this angle is about 20°, but the plane formed by C(4), O(4), Ba, and Ba' is inclined to the C$_4$O$_4^{2-}$ plane by almost 54°. O(3) is surrounded by three H atoms and its C(3) neighbor even in an unusual and distorted tetrahedral fashion (see Fig. 2). Thus it is difficult to discuss the extent of covalency between the O$_{squarate}$ atoms and their noncarbon neighbors. It seems that the bonding is more adequately described by assumption of ionic and electrostatic interactions.

In order to prove these considerations the study of hydrogen bonding in other squarates would be very helpful, preferably in structures containing cations with a stronger polarization than Ba^{2+}. ZnC$_4$O$_4$·4H$_2$O (12), which shows two O$_{squarate}$ atoms bound to Zn^{2+} and the other two obviously involved in strong hydrogen bonds, should be very suitable for this purpose.
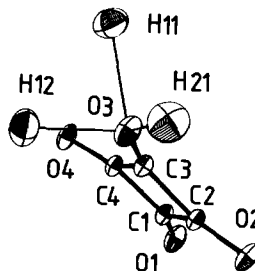

FIG. 2. O(3) is surrounded by three protons and its C(3) neighbor in a distorted tetrahedral fashion.

Acknowledgments

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