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Bis(5-hydroxy-2-hydroxymethyl-4-pyrone-κ^2O^4,O^5)bis(2-hydroxymethyl-5-oxido-4-pyrone-κ^2O^4,O^5)calcium(II) tetrahydrate

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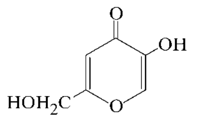
In the title compound, $[Ca(C_6H_5O_4)_2(C_6H_6O_4)_2]\cdot 4H_2O$, which is a kojic acid–$Ca^{2+}$ complex, the Ca atom is on a twofold axis and is octacoordinated by O atoms from four pyrone ligand molecules. The hydroxyl and ketone O atoms of each ligand form a five-membered chelate ring with the Ca atom. The crystal structure is stabilized by partial stacking and O—H$\cdots$O hydrogen bonds.

Comment

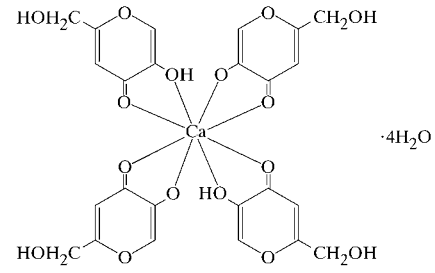
Kojic acid [5-hydroxy-2-hydroxymethyl-4-pyrone, (I)] is a metabolic product of several species of the genus *Aspergillus*. It has been reported that kojic acid is an efficient inhibitor of mushroom tyrosinase and other polyphenol oxidases (Chen *et al.*, 1991), which consequently suppresses biosynthesis of melanin in melanocytes. Kojic acid is also widely known to be an iron chelator (McBryde & Atkinson, 1961; Mitani *et al.*, 2001) and a radical scavenger (Niwa & Akamatsu, 1991). Metal complexes containing kojic acid have been studied in solution (Barret *et al.*, 2001; Malhotra *et al.*, 2001; Buglyó *et al.*, 2000; Yuen *et al.*, 1997; Katoh *et al.*, 1992). However, with regard to the crystal structures of kojic acid–metal chelate complexes, only the methyltin(IV) (Lockhart & Davidson, 1987) and dioxomolybdenum(VI) (Lord *et al.*, 1999) complexes have been reported. To clarify the mode of chelation of kojic acid to the alkaline earth metal, we have analyzed the crystal structure of the kojic acid–Ca^{2+} complex, (II), and present its structure here.

In (II), the Ca atom lies on a twofold axis and is octacoordinated by the O atoms of four pyrone ligand molecules, in which two of the four hydroxyl groups are ionized (Fig. 1 and Table 1). The hydroxyl and ketone O atoms of each ligand form a five-membered chelate ring with the Ca atom. Until now, the crystal structures of only two kojic acid–metal complexes, *viz*. the $\{Me_2Sn\}^{4+}$ and $\{MoO_2\}^{6+}$ complexes, have been analyzed. Although the number of ligand molecules is different in the Ca^{2+} complex, the five-membered rings between the ligand molecule and the metal atom are similar.

In (II), the ketone C═O bond lengths are somewhat longer [1.255 (4) and 1.261 (4) Å] than that in kojic acid [1.244 (1) Å; Lokaj *et al.*, 1991], but they are similar to those in other complexes [$\{Me_2Sn\}^{4+}$ 1.254 (7)–1.267 (7) Å, and $\{MoO_2\}^{6+}$ 1.272 (3) and 1.278 (3) Å].



(I)



(II)

The Ca—O(ketone) bond lengths in (II) are slightly longer [2.483 (2) and 2.494 (2) Å] than the Ca—O(hydroxyl/oxido) distances [2.462 (2) and 2.462 (2) Å]. In the $\{Me_2Sn\}^{4+}$ and $\{MoO_2\}^{6+}$ complexes, the *M*—O(ketone) bond lengths are markedly longer than the *M*—O(hydroxyl) distances [Sn—O(ketone) 2.365 (4)–2.435 (4) Å and Sn—O(oxido) 2.106 (4)–2.145 (4) Å; Mo—O(ketone) 2.236 (2) and 2.286 (2) Å, and Mo—O(oxido) 1.981 (2) and 1.994 (2) Å], which indicates a distinction between Lewis acid–base and ionic bonding for the two types of O atoms. In the case of (II), the complex molecules are connected by strong hydrogen bonding [O2—

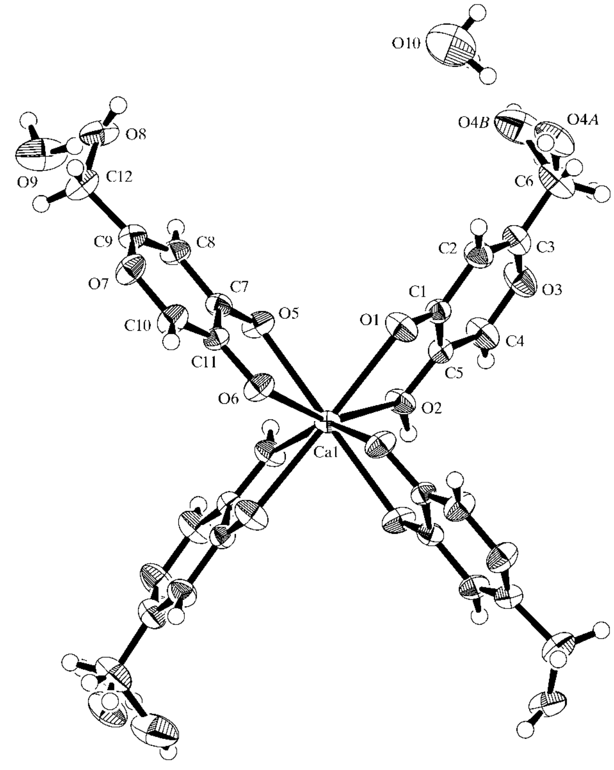


Figure 1
*ORTEP*II (Johnson, 1976) drawing of (II), with the atomic numbering scheme. Ellipsoids for non-H atoms correspond to 50% probability. The occupancy factors of atoms O4*A* and O4*B* are 60 and 40%, respectively.

$H26\cdots O6^{iv}$, with $O2\cdots O6^{iv} = 2.462\,(4)$ Å; see Table 2 for symmetry code], and consequently atom H26 is shared by two hydroxylate anions. Therefore, the Ca—O(hydroxyl/oxido) distances reflect the co-existence of deprotonated O atoms and hydroxyl groups.

The crystal structure of (II) is stabilized by stacking interactions between the pyran rings of neighboring molecules [$O3\cdots C2^{i}$ 3.176 (5) Å and $C2\cdots O3^{i}$ 3.176 (5) Å; symmetry code: (i) $1-x, -y, 1-z$] and hydrogen bonding between chelate complexes and water molecules (Table 2). In the ligand molecules, the hydroxymethyl groups are disordered over two positions (C6—O4*A* and C6—O4*B*). This may be due to comparatively loose packing, in which four water molecules are cocrystallized per Ca^{2+} complex molecule.

Experimental

Yellow pillar-shaped crystals of (II) were obtained by slow evaporation from an 80% ethanol–water solution of kojic acid and calcium nitrate tetrahydrate in a 4:1 molar ratio at room temperature.

Crystal data

$[Ca(C_6H_5O_4)_2(C_6H_6O_4)_2]\cdot 4H_2O$
$M_r = 678.56$
Monoclinic, $C2/c$
$a = 22.020\,(4)$ Å
$b = 6.223\,(4)$ Å
$c = 21.225\,(3)$ Å
$\beta = 91.61\,(1)^\circ$
$V = 2907\,(2)$ Å^3
$Z = 4$

$D_x = 1.550$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 10.1$–12.5°
$\mu = 0.31$ mm^{-1}
$T = 296.2$ K
Pillar, yellow
$0.20 \times 0.10 \times 0.10$ mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.942$, $T_{max} = 0.970$
3773 measured reflections
3332 independent reflections
1748 reflections with $I > 2\sigma(I)$

$R_{int} = 0.062$
$\theta_{max} = 27.5^\circ$
$h = 0 \rightarrow 28$
$k = 0 \rightarrow 8$
$l = -27 \rightarrow 27$
3 standard reflections every 150 reflections intensity decay: 4.3%

Refinement

Refinement on F^2
$R(F) = 0.048$
$wR(F^2) = 0.152$
$S = 1.00$
3332 reflections
217 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2 + 3.2041P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}

The H atoms of the ligand molecules, except for H26 and those of the disordered hydroxymethyl group, were placed in calculated positions and refined as riding. H26, H4*A*, H4*B* and the water H atoms were located from difference Fourier maps and were fixed, except for H26. The long O2—H26 bond [1.24 (2) Å] is due to the strong $O2—H26\cdots O6$ hydrogen bond. Three H atoms bonded to O10 were located as disordered atoms, which exist as H10*A*—O10—H10*B* and H10*A*—O10—H10*C*.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 2000); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976).

Table 1
Selected geometric parameters (Å, °).

Ca1—O1	2.483 (2)	Ca1—O5	2.494 (2)
Ca1—O2	2.462 (2)	Ca1—O6	2.462 (2)
$O1—Ca1—O1^{i}$	167.4 (1)	O2—Ca1—O6	153.62 (7)
O1—Ca1—O2	65.41 (7)	$O2—Ca1—O6^{i}$	116.40 (8)
$O1—Ca1—O2^{i}$	126.41 (8)	$O5—Ca1—O5^{i}$	170.1 (1)
O1—Ca1—O5	75.14 (8)	O5—Ca1—O6	65.25 (7)
$O1—Ca1—O5^{i}$	105.99 (8)	$O5—Ca1—O6^{i}$	124.16 (8)
O1—Ca1—O6	92.21 (8)	$O6—Ca1—O6^{i}$	68.4 (1)
$O1—Ca1—O6^{i}$	77.31 (8)	Ca1—O1—C1	118.9 (2)
$O2—Ca1—O2^{i}$	71.7 (1)	Ca1—O2—C5	118.9 (2)
O2—Ca1—O5	94.26 (8)	Ca1—O5—C7	119.4 (2)
$O2—Ca1—O5^{i}$	77.63 (8)	Ca1—O6—C11	119.2 (2)

Symmetry code: (i) $1-x, y, \frac{3}{2}-z$.

Table 2
Hydrogen-bonding geometry (Å, °).

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
$O8—H8M\cdots O5^{i}$	0.82	1.93	2.715 (3)	160
$O9—H9A\cdots O8$	0.94	1.86	2.708 (4)	149
$O9—H9B\cdots O1^{ii}$	0.94	1.89	2.818 (4)	173
$O10—H10A\cdots O9^{iii}$	0.86	1.94	2.744 (5)	155
$O10—H10B\cdots O4A$	1.00	1.89	2.874 (7)	169
$O10—H10C\cdots O4B$	0.95	1.84	2.670 (10)	144
$O2—H26\cdots O6^{iv}$	1.24 (2)	1.24 (2)	2.462 (4)	168 (3)

Symmetry codes: (i) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$; (ii) $\frac{1}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iii) $x, -y, z-\frac{1}{2}$; (iv) $1-x, y-1, \frac{3}{2}-z$.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1075). Services for accessing these data are described at the back of the journal.

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