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Calcium dipotassium tetraoxalatozirconate(IV) octahydrate

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The Ca and Zr atoms in the title compound, poly[octaaqua-tetra-μ-oxalato-calciumdipotassiumzirconate(IV)], $[CaK_2Zr(C_2O_4)_4(H_2O)_8]$, are chelated by bridging oxalate groups to form a three-dimensional network; the two independent water-coordinated K atoms occupy the space within the network and also interact with the oxalate O atoms to result in eight-coordination for the K atoms. The title compound is isostructural with $[CdK_2Zr(C_2O_4)_4(H_2O)_8]$ [Jeanneau, Audebrand & Louer (2002). *J. Mater. Chem.* **12**, 2383–2389]. All the metal ions occupy special positions with $\overline{4}$ site symmetry.

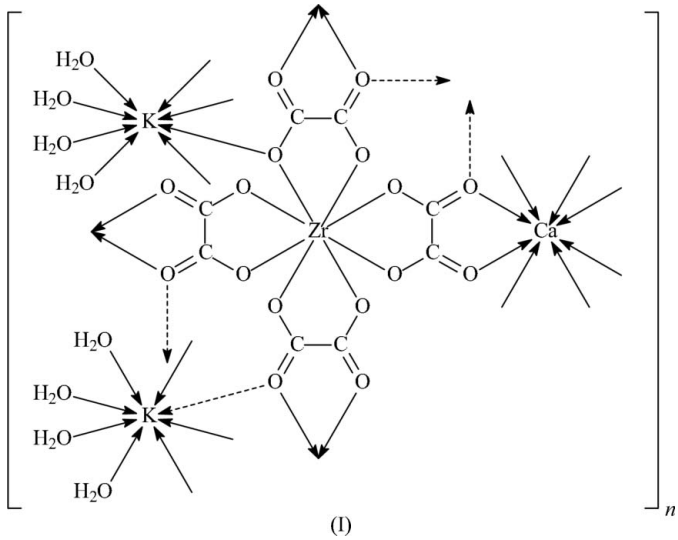
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.037
wR factor = 0.081
Data-to-parameter ratio = 15.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

In the crystal structure of cadmium dipotassium tetraoxalatozirconate octahydrate, $[CdK_2Zr(C_2O_4)_4(H_2O)_8]$ (Jeanneau *et al.*, 2002), the Ca, K and Zr atoms are all eight-coordinate. The Zr atom is chelated by the oxalate dianion, which also chelates to the Ca atoms; the ZrO_8 and CdO_8 polyhedra are linked through the bridging oxalate groups into a three-dimensional network encapsulating the potassium cations, which are also bonded to water molecules.



(I)

The replacement of cadmium by calcium leads to the isostructural calcium dipotassium tetraoxalatozirconate octahydrate, $[CaK_2Zr(C_2O_4)_4(H_2O)_8]$, (I) (Fig. 1); the Zr, Ca and K atoms all lie on different special positions of $\overline{4}$ symmetry. As modeled here, atom Zr1 lies on the Wyckoff 2*a* site and Ca1 on 2*d*, which is the opposite of the Jeanneau *et al.* (2002) model for Zr and Cd in $[CdK_2Zr(C_2O_4)_4(H_2O)_8]$, where a different origin was chosen.

The geometries of the Ca and Zr atoms in (I) are dodecahedral (Fig. 2). The two independent water-coordinated

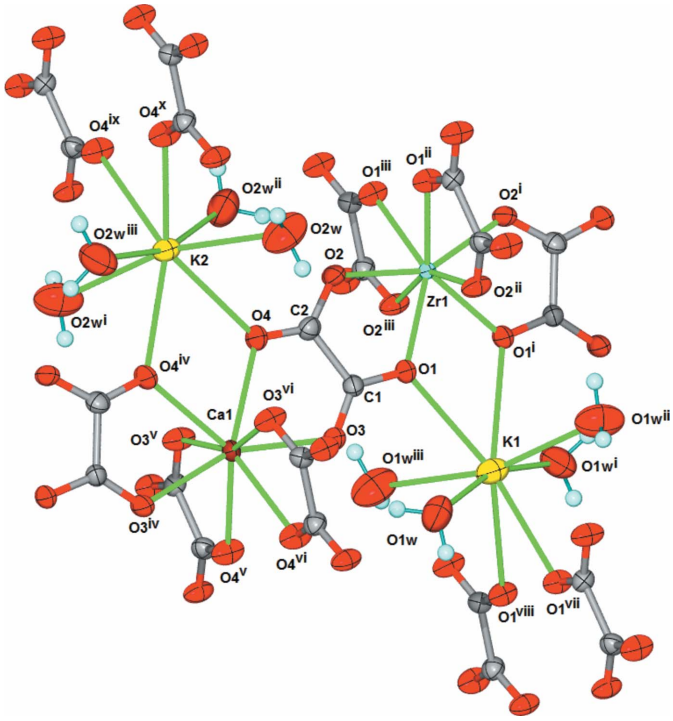


Figure 1
View of a fragment of the network structure of (I), illustrating the coordination geometries of Zr, Ca and K. Displacement ellipsoids are drawn at the 70% probability level, and H atoms are drawn as spheres of arbitrary radii. [Symmetry codes: (i) $2-x, 2-y, z$; (ii) $y, 2-x, -z$; (iii) $2-y, x, -z$; (iv) $1-x, 2-y, z$; (v) $y-\frac{1}{2}, \frac{3}{2}-x, \frac{1}{2}-z$; (vi) $\frac{3}{2}-y, \frac{1}{2}+x, \frac{1}{2}-z$; (vii) $y, 2-x, 1-z$; (viii) $2-y, x, 1-z$; (ix) $y-\frac{1}{2}, \frac{3}{2}-x, \frac{1}{2}-z$; (x) $\frac{3}{2}-y, \frac{1}{2}+x, -\frac{1}{2}-z$.]

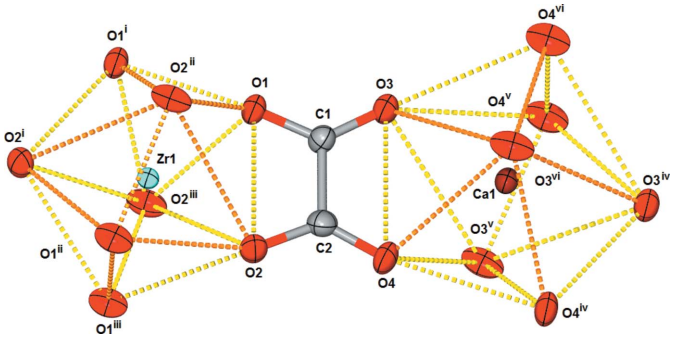


Figure 2
Dodecahedral geometries of Zr and Ca in (I), linked by a doubly chelating oxalate group. Symmetry codes as in Fig. 1.

potassium cations occupy the space within the framework to result in eight-fold coordination for them. The water molecules consolidate the structure through hydrogen bonds (Table 2), each water molecule forming two such bonds.

Experimental

Zirconium oxychloride hydrate, $ZrOCl_2\cdot H_2O$ (0.80 g, 2.5 mmol), oxalic acid (1.0 g, 8.0 mmol) and calcium chloride (0.05 g, 0.5 mmol) were dissolved in water (50 ml). Potassium hydroxide (2 *M*) was added dropwise (approximately 5 ml) until the solution registered a pH of 2. The clear solution was incubated at 323 K for 15 days. A small quantity of crystals of (I) was isolated in about 5% yield based on Zr.

Crystal data

$[CaK_2Zr(C_2O_4)_4(H_2O)_8]$
$M_r = 705.71$
Tetragonal, $I\overline{4}$
$a = 11.342\ (1)$ Å
$c = 8.920\ (1)$ Å
$V = 1147.56\ (16)$ Å^3
$Z = 2$
$D_x = 2.042$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 1.18$ mm^{-1}
$T = 293\ (2)$ K
Block, colorless
0.28 × 0.20 × 0.18 mm

Data collection

Bruker APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.681$, $T_{max} = 0.816$
6454 measured reflections
1302 independent reflections
1199 reflections with $I > 2\sigma(I)$
$R_{int} = 0.046$
$\theta_{max} = 27.4°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.081$
$S = 1.05$
1302 reflections
83 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0434P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.72$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}
Absolute structure: Flack (1983), 603 Fridel pairs
Flack parameter: −0.06 (8)

Table 1
Selected bond lengths (Å).

Zr1—O1	2.234 (2)	K1—O1	2.882 (2)
Zr1—O2	2.175 (3)	K1—O1*w*	2.866 (3)
Ca1—O3	2.404 (2)	K2—O4	2.789 (3)
Ca1—O4	2.521 (3)	K2—O2*w*	2.886 (3)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*w*—H1*w*1···O3	0.85	2.16	2.828 (4)	135
O1*w*—H1*w*2···O2*w*^{i}	0.85	2.19	2.901 (5)	141
O2*w*—H2*w*1···O1*w*^{ii}	0.85	2.16	2.893 (5)	144
O2*w*—H2*w*2···O2^{iii}	0.85	2.12	2.854 (4)	145

Symmetry codes: (i) $x, y, z+1$; (ii) $-x+\frac{3}{2}, -y+\frac{5}{2}, z-\frac{1}{2}$; (iii) $-y+\frac{3}{2}, x+\frac{1}{2}, -z-\frac{1}{2}$.

The H atoms of water molecules were positioned geometrically (O—H = 0.85 Å) and were included in the refinement in the riding-model approximation, with their U_{iso} values fixed at 0.05 Å^2. The water molecules were rotated about their K—O bonds to best fit the electron density.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *SHELXL97*.

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