

## Structure of Tetrapotassium Tetrakis(oxalato)zirconate(IV) Pentahydrate

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**Abstract.**  $K_4[Zr(C_2O_4)_4] \cdot 5H_2O$ , monoclinic, space group  $P2_1/c$ , with  $a = 10.624$ ,  $b = 12.385$ ,  $c = 15.984$  Å,  $\beta = 94.43^\circ$ ,  $Z = 4$ . The coordination around the Zr atom is dodecahedral. The Zr—O(oxalato) bonds range from 2.166 (2) to 2.221 (2) Å. The packing is primarily dominated by Coulomb interactions between  $K^+$  ions and oxalato O atoms. The three-dimensional network is completed by hydrogen bonds acting between water molecules and oxalato groups.

**Introduction.** A description and discussion of the crystal structure of  $K_4[Hf(C_2O_4)_4] \cdot 5H_2O$  (Tranqui, Boyer, Laugier & Vulliet, 1977) and the present determination have confirmed strict isomorphism between these Zr and Hf oxalato complexes. Therefore, only a brief report on the  $K_4[Zr(C_2O_4)_4] \cdot 5H_2O$  structure is given.

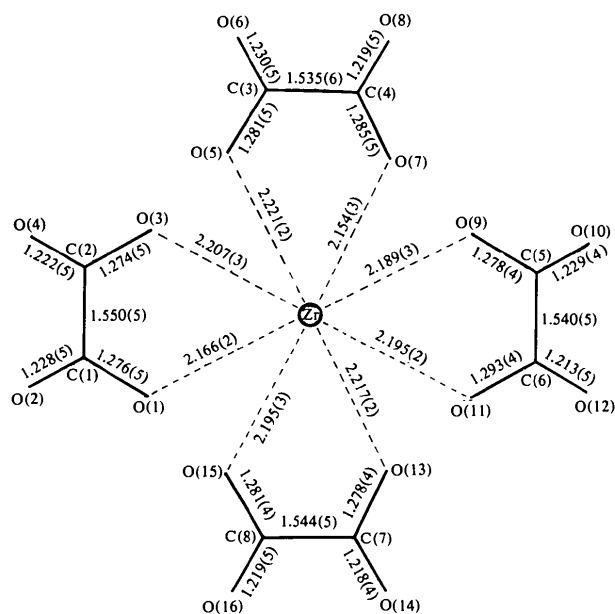


Fig. 1. The coordination around the Zr atom with bond distances (Å).

The intensities of 4258 independent reflexions were collected (Mo  $K\alpha$  radiation, graphite monochromator,  $\omega$  scan up to  $\theta = 30^\circ$ ). The structure was solved by Patterson and Fourier methods. A difference synthesis located the H atoms which were included in the structure factor calculations only. Full-matrix least-

Table 1. Final positional parameters ( $\times 10^5$ ) for non-hydrogen atoms

	x	y	z
Zr	23685 (3)	15172 (3)	32796 (2)
K(1)	50897 (9)	-6015 (8)	30954 (6)
K(2)	87259 (8)	15621 (7)	25275 (6)
K(3)	61085 (10)	32649 (9)	58981 (7)
K(4)	1699 (9)	77133 (7)	51146 (6)
O(1)	12579 (23)	15106 (23)	20848 (16)
O(2)	11319 (30)	10777 (26)	7225 (18)
O(3)	36138 (24)	11180 (22)	22802 (18)
O(4)	37258 (31)	6736 (28)	9372 (21)
O(5)	43251 (24)	13096 (22)	38535 (18)
O(6)	55571 (27)	12299 (28)	50551 (22)
O(7)	23816 (25)	18119 (25)	46083 (18)
O(8)	34629 (35)	18533 (31)	58657 (21)
O(9)	25956 (23)	-2356 (21)	33810 (18)
O(10)	17825 (27)	-18351 (22)	37128 (19)
O(11)	5956 (22)	7924 (20)	36251 (17)
O(12)	-4074 (26)	-6814 (25)	40178 (23)
O(13)	9179 (23)	27942 (20)	33522 (18)
O(14)	4032 (26)	45136 (23)	31224 (23)
O(15)	32266 (24)	31002 (21)	30819 (19)
O(16)	29816 (27)	48784 (23)	29598 (23)
O(W1)	18770 (32)	84672 (31)	15127 (24)
O(W2)	39428 (30)	74340 (29)	24725 (21)
O(W3)	17253 (37)	57389 (29)	46930 (23)
O(W4)	45671 (39)	-13789 (30)	7490 (26)
O(W5)	22462 (42)	-9556 (39)	58585 (33)
C(1)	17181 (37)	12138 (31)	14071 (24)
C(2)	31535 (37)	9772 (30)	15285 (26)
C(3)	45406 (35)	13861 (29)	46509 (27)
C(4)	33825 (40)	17165 (32)	51084 (26)
C(5)	17236 (33)	-8516 (29)	36146 (24)
C(6)	5111 (32)	-2295 (30)	37771 (24)
C(7)	11644 (33)	37771 (28)	31839 (25)
C(8)	25740 (34)	39713 (30)	30609 (25)

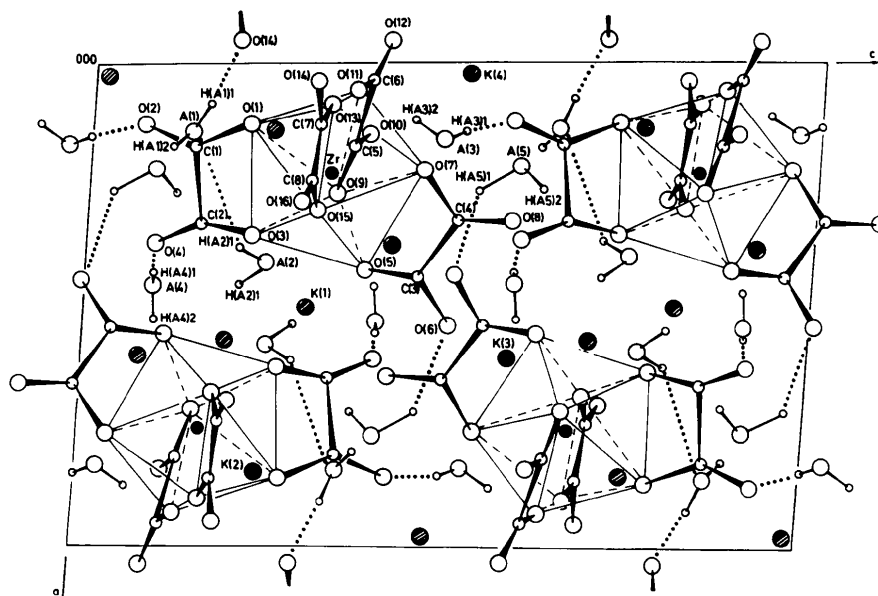


Fig. 2. The projection along *b* showing the dodecahedral coordination around the Zr atom and the hydrogen bonds. *A* denotes oxygen atoms belonging to the water molecules.

squares refinement led to an *R* of 0.04. Atomic coordinates are given in Table 1.\*

**Discussion.** The Zr atom is in dodecahedral coordination (Figs. 1 and 2). The Zr—O distances range from 2.166 (2) to 2.221 (2) Å. There is no significant difference between the geometries of these Zr and Hf tetrakis(oxalato) anions.

The crystal structure is a three-dimensional network of dodecahedra connected by hydrogen bonds between oxalato groups and water molecules (Table 2 and Fig. 2). Coulomb interactions between K<sup>+</sup> ions and oxalato O atoms dominate the molecular packing.

In Tranqui *et al.* (1977) the H atom positions were not included; therefore complete information on the hydrogen-bond system in the present structure is given (Table 2). Each water molecule acts as a donor of one

Table 2. *Hydrogen bonds (values in Å and degrees)*

<i>X</i> —H... <i>Y</i>	<i>X</i> ... <i>Y</i>	<i>X</i> —H	H... <i>Y</i>	∠ <i>X</i> —H... <i>Y</i>
O( <i>W</i> 1)—H(OW1)1...O(14)	2.847 (5)	0.88	1.97	176
O( <i>W</i> 2)—H(OW2)1...O( <i>W</i> 1)	2.882 (6)	1.01	1.98	146
O( <i>W</i> 3)—H(OW3)1...O(2)	2.886 (5)	0.97	1.92	173
O( <i>W</i> 4)—H(OW4)1...O(4)	2.730 (6)	0.82	1.95	156
O( <i>W</i> 5)—H(OW5)1...O(6)	2.867 (6)	1.03	2.04	134

Relation between atom numbering in this paper and that in Tranqui *et al.* (1977)

O( <i>W</i> 1)	O(22 <i>W</i> )	O( <i>W</i> 4)	O(25 <i>W</i> )
O( <i>W</i> 2)	O(24 <i>W</i> )	O( <i>W</i> 5)	O(23 <i>W</i> )
O( <i>W</i> 3)	O(21 <i>W</i> )		

proton only. Four water molecules are hydrogen bonded to oxalato O atoms. A further water molecule, O(*W*2), forms a hydrogen bond with O(*W*1).

\* Lists of structure factors, thermal parameters and hydrogen atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33421 (40 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

#### Reference

TRANQUI, D., BOYER, P., LAUGIER, J. & VULLIET, P. (1977). *Acta Cryst.* B33, 3126–3133.