The Crystal Structure of Potassium Metazirconate, K_2ZrO_3, and Its Tin Analogue, K_2SnO_3*

B. M. GATEHOUSE AND D. J. LLOYD

Chemistry Department, Monash University, Clayton, Victoria, Australia 3168

Structural information concerning compounds existing in the K_2O–ZrO_2 system has been extended by a single-crystal structure determination of potassium metazirconate, K_2ZrO_3; a compound which crystallises in the orthorhombic system *Pnma* with unit cell dimensions of $a = 5.93$ Å, $b = 10.48$ Å, and $c = 7.03$ Å. The structure contains chains of edge-sharing ZrO_5 square pyramids, with apices oppositely directed, running in the x direction. Single crystal studies on the analogous tin compound K_2SnO_3 show that it is isostructural with K_2ZrO_3 and so a previously proposed model must be considered in error.

This is the first report of a compound which has five-coordinate zirconium atoms and, to our knowledge, the first reported compound containing five-coordinate square pyramidal tin atoms.

Introduction

Solid state studies of phases in the K_2O–ZrO_2 system were initiated when an attempt was made to solve the structure of potassium metazirconate via the isostructural tin analogue, K_2SnO_3 (*1*). However, the model proposed gave poor agreement between observed and calculated structure factors (*R* factor > 30%) and must, in view of the present work, be considered incorrect.

More recently the crystal structure of the ortho-rhombic 1:2 compound beta-potassium dizirconate, β-$K_2Zr_2O_5$ was reported (*2*). Until then, the instability of the compounds with respect to water and the resulting difficulties involved in their handling and characterisation had led to inadequate and often conflicting reports of chemical and physical properties. Characterization by powder photography is hampered by the difficulties involved in the preparation and preservation of homogeneous samples and rigorous control of conditions is needed to make this technique useful.

Single crystal X-ray diffraction techniques have been used here to determine the structure of the 1:1 compound, potassium metazirconate K_2ZrO_3.

Experimental

The preparation of single crystals of compounds in this system is made difficult by the high volatility

of K_2O, formed in this case by decomposition of an oxygenated salt of potassium. This together with the apparent dependence of the products of a reaction on the temperature, rate of escape of K_2O, vessel shape, time of reaction, and other factors renders the results of these reactions unpredictable. It seems that this will remain the case until some of the above observations are explained and more rigorous control of reaction conditions is available.

In this study clear, rod shaped single crystals of hygroscopic potassium metazirconate were produced by dissolution of ZrO_2 in excess K_2O formed from the decomposition of potassium nitrate at 1000°C under an atmosphere of dry nitrogen in Pythagoras furnace-ware. In this way, potassium oxide acts as a solvent from which K_2ZrO_3 and other potassium zirconates may be satisfactorily crystallised. Examination of preparations under a binocular microscope with facility for polarized light allows different compounds, if present, to be distinguished and their suitability for single crystal structure determination established.

From a successful preparation of potassium metazirconate a sound, representative crystal of dimensions $0.07 \times 0.03 \times 0.03$ mm was examined and found suitable for single crystal structure analysis. It was subsequently mounted in a fine, thin walled pyrex capillary tube under dry paraffin oil and wedged firmly in the desired orientation; in this case with the a (needle) axis parallel to the tube.

Single-crystal oscillation and Weissenberg photo-

TABLE I

K$_2$ZrO$_3$ AND K$_2$SnO$_3$ FRACTIONAL ATOMIC POSITIONAL PARAMETERS[a]

K$_2$ZrO$_3$

Atom	Point position	x	y	z
Zr	4c	0.2730(6)	0.25	0.1598(4)
K	8d	0.264(1)	0.5857(5)	0.1143(6)
O	4c	0.175(5)	0.75	0.390(3)
O	8d	0.015(3)	0.121(1)	0.234(4)

K$_2$SnO$_3$

Atom	Point position	x	y	z
Sn	4c	0.267(5)	0.25	0.163(1)
K	8d	0.266(9)	0.588(2)	0.113(2)
O	4c	0.19(2)	0.75	0.40(1)
O	8d	0.02(2)	0.113(5)	0.23(1)

[a] Errors are in parentheses.

graphs were used to determine systematic absences and cell dimensions: multiple film pack Weissenberg intensity series were collected for $h = 0$, 1–5 using CuKα radiation. A total of 293 independent reflections were indexed in the orthorhombic space group Pnma using unit cell dimensions $a = 5.93(2)$ Å, $b = 10.48(2)$ Å, and $c = 7.03(2)$ Å. After reflection intensities were estimated by visual comparison with a calibrated film strip and converted to structure factors, a three-dimensional Patterson synthesis was produced. Assuming four formula weight units in the unit cell, a solution was found for the position of the zirconium atoms in the cell using the Harker

heavy-atom method. This, when used to phase reflections and generate a three-dimensional Fourier synthesis, indicated the position of all other atoms in the structure. Scattering curves used for K$^+$, Zr, and O, corrected for dispersion effects in the case of the metals, were those of Cromer and Waber (3).

At this stage, a three-dimensional difference Fourier synthesis contained no unusual features so refinement of atomic positional parameters, individual scale factors and individual anisotropic temperature factors by the least-squares procedure was used to obtain the final model. Another difference Fourier calculated for this final model revealed no maxima or minima of significance which, together with the good agreement of observed and calculated structure factors (a conventional agreement factor of $R = 0.087$) indicated a correct model.

Final fractional atomic coordinates and individual temperature factors are listed in Tables I and II, respectively, while Table III contains selected interatomic distances. The list of observed and calculated structure factors is given in Table IV.

To clarify the contradiction in structures reported for K$_2$ZrO$_3$, single crystals of potassium metastannate K$_2$SnO$_3$ were prepared in an analogous manner to the zirconate and although they were slightly imperfect, were examined using X-ray diffraction techniques. K$_2$SnO$_3$ has the unit cell $a = 5.74$ Å, $b = 10.34$ Å, $c = 7.14$ Å and space group Pnma. Great similarities in the single-crystal diffraction patterns with respect to both reflection position and intensity indicate that K$_2$SnO$_3$ and K$_2$ZrO$_3$ are isostructural. Weissenberg intensity data was collected from a slightly imperfect crystal of the metastannate and an independent structure determination using 119 reflections, refining to a con-

TABLE II

K$_2$ZrO$_3$ AND K$_2$SnO$_3$ THERMAL PARAMETERS

K$_2$ZrO$_3$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Zr	0.012(1)	0.0050(2)	0.0087(4)	0.0	−0.0004(8)	0.0
K	0.019(2)	0.0054(4)	0.013(1)	−0.000(1)	−0.001(1)	0.0009(5)
O(4)	0.02(1)	0.003(2)	0.015(5)	0.0	0.009(6)	0.0
O(8)	0.007(7)	0.007(1)	0.025(5)	−0.004(3)	0.006(4)	−0.001(3)

K$_2$SnO$_3$

Atom	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	0.016(5)	0.0046(5)	0.009(1)	0.0	0.009(8)	0.0
K	3.2(5)					
O(4)	1.0(15)					
O(8)	2.2(18)					

15

TABLE III

K₂ZrO₃ AND K₂SnO₃ INTERATOMIC DISTANCES (Å) INCLUDING E.S.D.'s[a,b]

Zr–Zr	3.212(3)	Sn–Sn	3.13(4)
Zr–O	4 × 2.13(2)	Sn–O	2 × 2.21(7)
	1 × 1.92(2)		2 × 2.03(7)
			1 × 1.93(7)
O(I)–O(II)	2.77(3)	O(I)–O(II)	2.83(7)
O(I)–O(III)	2.96(3)	O(I)–O(III)	2.92(14)
O(I)–O(V)	3.19(3)	O(I)–O(V)	2.94(8)
O(III)–O(V)	3.43(3)	O(III)–O(V)	3.55(8)

[a] See Fig. 3.

[b] All relevant angles are simply calculated from bond lengths given in this table.

ventional agreement factor of $R = 0.138$, confirmed this idea.

The results of this determination are given for comparison in the respective tables for K₂ZrO₃. A list of observed and calculated structure factors is given in Table V.

Discussion

The interest in the structure of potassium meta-zirconate lies in the strings of slightly distorted edge-sharing ZrO₅ square pyramids which run through the structure in the x direction (see Figs. 1 and 2). This unusual stereochemistry, while previously unreported for Zr(IV) and Sn(IV), has been found to exist for the lead atoms in the closely related

TABLE IV

Observed and Calculated Structure Factors for K₂ZrO₃

H	K	L	F(OBS)	F(CAL)
0	2	0	20.5	-18.0
0	4	0	7.9	6.6
0	6	0	31.9	-32.2
0	8	0	12.4	12.8
0	10	0	4.1	-5.3
0	12	0	10.7	10.7
0	1	1	15.9	-16.7
0	3	1	23.4	22.5
0	5	1	5.9	-5.3
0	7	1	8.7	8.6
0	9	1	13.0	-13.8
0	13	1	1.5	-1.7
0	0	2	14.4	-13.9
0	2	2	8.9	9.1
0	6	2	4.9	4.7
0	8	2	7.3	-7.4
0	10	2	2.0	3.2
0	1	3	12.0	11.1
0	3	3	16.3	15.4
0	7	3	5.6	-6.0
0	9	3	4.1	-4.9
0	0	4	20.7	-21.6
0	2	4	6.4	6.7
0	4	4	7.6	-7.5
0	6	4	16.9	16.5
0	12	4	7.0	-7.7
0	1	5	7.7	8.6
0	3	5	15.5	-16.8
0	5	5	9.2	9.7
0	7	5	4.7	-5.3
0	9	5	8.8	8.1
0	11	5	4.5	-5.0
0	0	6	5.3	5.9
0	2	6	10.8	-11.4
0	4	6	10.8	11.1
0	8	6	7.1	6.6
0	10	6	4.9	-5.4
0	1	7	9.7	-9.2
0	5	7	9.4	-8.0
0	7	7	6.7	6.6
0	0	8	3.8	3.2
0	4	8	1.6	-3.0
0	6	8	1.9	-2.3
1	0	1	3.7	-4.1
1	1	1	7.7	-7.4
1	2	1	3.5	2.6
1	3	1	29.7	28.1
1	4	1	2.6	-2.7
1	5	1	5.9	-6.3
1	6	1	2.5	2.8

H	K	L	F(OBS)	F(CAL)
1	7	1	3.6	3.8
1	9	1	13.6	-12.0
1	0	2	35.1	-35.5
1	2	2	6.4	6.7
1	3	2	3.1	-3.4
1	4	2	5.3	-5.2
1	6	2	20.8	22.2
1	8	2	4.9	-5.3
1	10	2	1.9	2.5
1	12	2	9.9	-8.9
1	1	3	15.8	15.1
1	2	3	1.6	-3.0
1	3	3	26.4	-25.4
1	4	3	3.2	3.7
1	5	3	11.6	12.5
1	6	3	3.8	-2.8
1	7	3	8.0	-8.8
1	9	3	12.8	12.5
1	11	3	5.9	-6.0
1	0	4	10.0	9.6
1	2	4	12.4	-14.1
1	3	4	2.0	2.5
1	4	4	11.8	12.3
1	6	4	6.3	-6.9
1	8	4	8.6	8.3
1	10	4	6.1	-6.0
1	1	5	6.7	-7.0
1	3	5	5.0	-5.5
1	5	5	5.3	-5.3
1	7	5	5.7	5.0
1	9	5	1.6	2.9
1	11	5	1.6	-2.4
1	0	6	8.5	8.9
1	1	6	2.0	-0.2
1	6	6	6.7	-6.6
1	1	7	5.5	-5.6
1	3	7	8.0	7.7
1	5	7	4.8	-5.0
1	7	7	3.8	3.5
1	0	8	4.6	-5.1
1	2	8	8.6	8.3
1	4	8	7.4	-7.5
1	6	8	3.3	3.9
2	1	0	6.0	6.2
2	0	1	2.8	3.6
2	6	0	5.0	4.7
2	2	0	12.5	12.9
2	3	0	14.0	-11.6
2	4	0	16.4	-15.3
2	5	0	5.6	5.4

H	K	L	F(OBS)	F(CAL)
2	6	0	23.6	24.0
2	7	0	3.1	-3.1
2	8	0	4.9	-5.3
2	9	0	3.9	4.8
2	10	0	5.4	4.7
2	12	0	10.2	-10.7
2	1	1	3.3	4.0
2	2	1	2.1	-2.1
2	3	1	27.9	-27.4
2	4	1	2.6	2.6
2	5	1	11.1	10.5
2	6	1	3.3	-3.0
2	7	1	3.6	-3.0
2	9	1	9.8	10.0
2	11	1	5.2	-4.9
2	0	2	2.7	-1.0
2	2	2	7.7	-7.9
2	3	2	1.3	2.3
2	4	2	9.9	10.7
2	6	2	2.8	-3.0
2	8	2	2.0	-3.4
2	12	2	2.4	2.3
2	1	3	2.3	-1.9
2	3	3	6.2	-7.4
2	5	3	4.0	-4.5
2	9	3	5.9	5.8
2	0	4	18.9	22.2
2	1	4	3.3	-3.5
2	2	4	4.3	-4.5
2	3	4	4.2	4.8
2	6	4	15.1	-13.8
2	7	4	1.9	2.2
2	8	4	4.4	4.5
2	9	4	2.0	-2.8
2	0	5	3.7	-4.0
2	1	5	9.6	-9.9
2	2	5	1.8	2.3
2	3	5	14.2	11.9
2	5	5	6.5	-6.9
2	6	5	2.3	2.8
2	7	5	7.8	6.3
2	9	5	7.7	-7.7
2	0	6	7.8	-7.1
2	1	6	1.9	2.7
2	2	6	10.1	9.6
2	4	6	8.6	-7.8
2	8	6	6.7	-6.7
2	1	7	9.8	8.3
2	2	7	1.8	-2.3
2	5	7	6.0	6.2

H	K	L	F(OBS)	F(CAL)
2	7	7	5.3	-6.1
2	2	8	1.5	-2.4
3	0	1	6.8	7.5
3	1	1	2.0	2.9
3	2	1	3.6	-3.5
3	3	1	14.2	-13.6
3	4	1	2.9	2.6
3	5	1	3.5	2.8
3	6	1	4.3	-4.6
3	8	1	2.1	2.1
3	9	1	8.2	6.9
3	12	1	1.2	1.8
3	0	2	20.4	20.4
3	2	2	5.8	-5.7
3	3	2	5.1	4.9
3	4	2	4.8	4.4
3	6	2	12.4	-13.8
3	8	2	4.2	4.0
3	9	2	3.5	-3.1
3	10	2	1.9	-2.1
3	12	2	5.6	5.9
3	0	3	7.8	-8.0
3	1	3	7.9	-8.1
3	2	3	4.6	4.8
3	3	3	12.1	13.8
3	4	3	3.3	-3.4
3	5	3	6.5	-6.8
3	6	3	5.8	5.0
3	7	3	5.9	5.0
3	8	3	4.1	-3.3
3	9	3	8.6	-7.5
3	10	3	1.4	2.0
3	11	3	3.7	3.5
3	0	4	4.9	-5.6
3	1	4	4.8	4.4
3	2	4	8.7	8.2
3	3	4	1.7	-2.4
3	4	4	7.3	-7.2
3	5	4	3.0	2.7
3	6	4	3.7	4.0
3	7	4	2.9	-2.8
3	8	4	6.2	-5.1
3	9	4	1.4	1.9
3	10	4	3.9	3.8
3	1	5	4.2	4.9
3	5	5	4.2	3.7
3	7	5	4.2	-3.5
3	0	6	6.6	-5.8
3	6	6	4.7	4.5

TABLE IV—*continued*

H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)
3	1	7	4.3	3.2	4	4	1	2.6	-1.9	4	0	6	2.2	2.9	5	0	3	5.0	4.8
3	2	7	1.7	-1.6	4	5	1	3.7	-3.4	4	1	6	3.5	-2.8	5	1	3	3.6	3.3
3	3	7	5.3	-4.6	4	6	1	4.1	4.9	4	2	6	7.0	-5.4	5	2	3	4.2	-3.6
3	4	7	1.3	1.9	4	7	1	4.7	4.5	4	4	6	5.9	5.4	5	3	3	5.4	-5.9
3	5	7	3.1	3.0	4	9	1	7.3	-7.0	4	5	6	3.0	-2.7	5	4	3	3.9	3.6
3	6	7	1.1	-1.3	4	0	2	4.5	-5.1	4	6	6	2.7	-2.6	5	5	3	3.6	3.0
3	7	8	2.9	3.0	4	1	2	2.5	2.8	4	7	6	1.6	1.9	5	6	3	4.4	-3.9
3	1	8	2.0	-2.2	4	2	2	3.3	3.9	4	1	7	4.1	-3.9	5	7	3	2.6	-2.2
3	2	8	4.4	-5.1	4	8	2	3.8	-3.6	4	2	7	2.6	2.6	5	8	3	2.2	2.1
3	3	8	2.0	-2.0	4	3	3	6.5	7.0	4	4	7	2.2	-2.6	5	9	3	3.4	3.4
4	1	0	6.2	-6.6	4	0	4	7.4	-7.7	5	0	1	4.1	-4.3	5	0	4	1.7	2.3
4	2	0	4.4	-5.0	4	1	4	1.6	2.2	5	2	1	2.2	2.1	5	1	4	3.0	-2.8
4	3	0	8.4	8.3	4	3	4	6.4	-5.7	5	3	1	5.2	5.4	5	2	4	3.5	-3.6
4	4	0	1.5	1.6	4	4	4	2.0	-2.3	5	4	1	2.0	-2.1	5	3	4	2.7	2.9
4	5	0	4.3	-4.5	4	6	4	7.5	6.7	5	6	1	3.2	3.3	5	4	4	3.3	3.3
4	6	0	11.0	-11.9	4	9	4	2.6	3.0	5	9	1	2.9	-3.1	5	5	4	3.3	-2.9
4	7	0	4.2	4.4	4	0	5	4.9	4.0	5	0	2	8.4	-9.1	5	7	4	1.2	2.0
4	8	0	6.1	4.6	4	1	5	5.1	4.3	5	1	2	2.5	2.4	5	8	4	1.6	2.3
4	9	0	4.9	-5.0	4	3	5	4.9	-7.9	5	2	2	2.9	3.0	5	1	5	3.1	-2.6
4	11	0	1.5	1.9	4	4	5	3.8	3.2	5	3	2	5.5	-5.5	5	5	5	2.3	-2.2
4	2	1	6.1	-7.3	4	5	5	5.1	4.8	5	4	2	2.4	-2.5	5	0	6	3.4	3.1
4	1	1	5.3	-7.4	4	6	5	3.6	-3.2	5	5	2	2.4	2.5					
4	2	1	3.3	3.0	4	7	5	1.8	-2.8	5	6	2	7.3	6.8					
4	3	1	9.2	9.9	4	8	5	1.7	1.9	5	9	2	2.6	2.9					

structure of potassium metaplumbate K_2PbO_3 (4). Distortions in the square pyramid are such that the metal atom lies 0.64 Å above an almost square base of four oxygen atoms. The Zr–O distance is longer at 2.13 Å for the basal oxygen atoms than for the apical oxygen atom at 1.92 Å as may be expected. The closest approach of the next-nearest oxygen atom to zirconium atom is 4.43 Å—well outside the coordination sphere. The O–O distances for a shared base edge of the square pyramids are significantly

shorter [2.77(2) Å] than the unshared distances [2.96(2) Å] and the distance from the apical oxygen atom to one pair of basal oxygen atoms in the polyhedron is 3.37(3) Å and to the other pair is 3.19(3) Å. The Zr–Zr distance at 3.212(2) Å is close to the corresponding distance in h.c.p. metallic zirconium (3.179, 3.231 Å) (5). Potassium ions occupy interchain sites with irregular sixfold coordination to oxygen atoms. Relevant distances are given in Table III.

TABLE V

Observed and Calculated Structure Factors for K_2SnO_3

| H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)	H	K	L	F(OBS)	F(CAL)
0	2	0	6.4	-6.1	0	5	7	2.5	-2.5	1	6	8	1.1	1.3	3	0	1	1.0	1.2
0	4	0	3.9	3.2	0	7	7	2.0	2.3	1	1	9	1.7	1.7	3	1	1	.8	1.3
0	6	0	10.8	-9.4	0	3	5	4.1	-4.7	2	1	0	1.2	1.2	3	3	1	3.9	-3.3
0	8	0	4.7	4.4	1	1	1	2.7	-2.3	2	2	0	4.8	4.3	3	0	2	4.5	5.0
0	12	0	2.6	3.0	1	3	1	7.9	6.7	2	3	0	2.9	-2.5	3	2	2	1.9	-2.0
0	1	1	5.0	-5.7	1	5	1	2.2	-2.1	2	4	0	4.8	-4.4	3	4	2	1.8	1.6
0	3	1	7.5	6.8	1	9	1	2.8	-2.7	2	6	0	6.2	5.6	3	6	2	3.7	-3.4
0	5	1	3.0	-2.9	1	0	2	7.7	-8.6	2	8	0	1.9	-2.1	3	8	2	1.8	1.4
0	7	1	3.5	3.4	1	2	2	2.5	2.6	2	12	0	2.2	-2.4	3	0	3	1.7	-1.2
0	9	1	4.0	-3.8	1	4	2	1.9	-2.1	2	1	1	1.7	2.0	3	1	3	2.5	-2.8
0	0	2	4.1	-4.3	1	6	2	6.2	5.3	2	3	1	7.1	-6.6	3	3	3	3.6	3.6
0	2	2	2.4	3.0	1	8	2	2.4	-1.9	2	5	1	3.6	2.9	3	5	3	2.3	-2.2
0	8	2	2.0	-2.2	1	12	2	1.8	-2.0	2	9	1	1.9	2.6	3	9	3	1.6	-2.0
0	1	3	2.1	3.0	1	1	3	4.0	4.5	2	2	2	2.0	-2.3	3	0	4	1.1	-1.8
0	3	3	3.1	3.6	1	3	3	6.0	-6.5	2	4	2	2.8	2.7	3	2	4	2.3	2.3
0	0	4	5.1	-5.9	1	5	3	3.7	3.8	2	3	3	1.0	-1.4	3	4	4	2.0	-2.0
0	2	4	1.9	2.3	1	7	3	2.3	-2.8	2	0	4	4.5	5.1	3	0	6	1.3	-1.2
0	6	4	3.5	4.2	1	9	3	2.8	3.2	2	6	4	2.7	-3.2	3	3	7	2.1	-1.4
0	1	5	2.5	3.2	1	11	3	1.5	-1.9	2	1	5	2.4	-2.8	3	0	8	1.1	1.2
0	5	5	2.8	3.0	1	0	4	2.8	3.0	2	3	5	2.3	3.0	3	2	8	1.9	-1.6
0	7	5	2.0	-2.1	1	2	4	3.5	-4.1	2	5	5	1.4	-2.1	4	2	0	2.0	-1.8
0	9	5	2.6	2.4	1	4	4	3.7	3.7	2	7	5	1.3	1.9	4	3	0	1.6	2.0
0	11	5	1.2	-1.6	1	8	4	2.4	2.3	2	9	5	2.0	-1.8	4	6	0	3.0	-3.1
0	0	6	2.0	2.3	1	10	4	1.1	-1.9	2	0	6	1.9	-2.0	4	3	1	2.7	2.4
0	2	6	4.4	-3.6	1	1	5	1.8	-1.9	2	2	6	2.7	2.6	4	0	4	1.8	-2.2
0	4	6	3.2	3.4	1	0	6	2.2	1.6	2	4	6	2.3	-2.4	4	3	5	1.6	-2.2
0	6	6	2.2	-1.9	1	3	6	2.3	1.7	2	8	6	1.9	-1.7	4	2	6	2.1	-1.7
0	8	6	2.7	2.1	1	0	8	2.1	-1.6	2	1	7	2.6	2.2	4	4	6	2.4	1.7
0	10	6	1.3	-1.8	1	2	8	3.3	2.2	2	5	7	1.9	1.8	4	1	7	1.5	-1.1
0	1	7	3.4	-3.2	1	4	8	3.1	-2.0	2	7	7	1.9	-1.6					
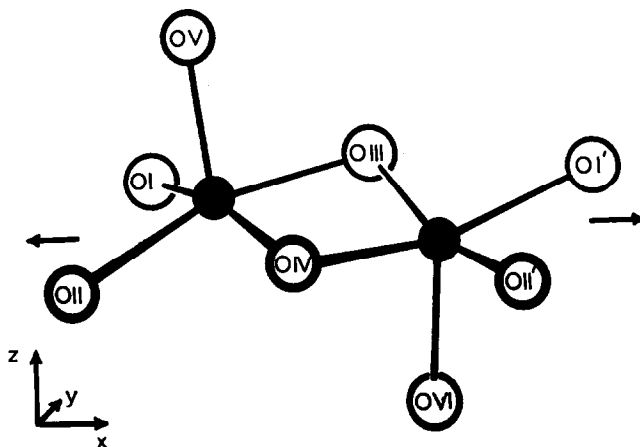
FIG. 1. The idealised double pyramidal unit in the K_2ZrO_3 chain structure. Filled circles represent zirconium atoms and unfilled ones represent oxygen atoms. Zirconium atoms and oxygen atoms O(V) and O(VI) lie on a mirror plane.
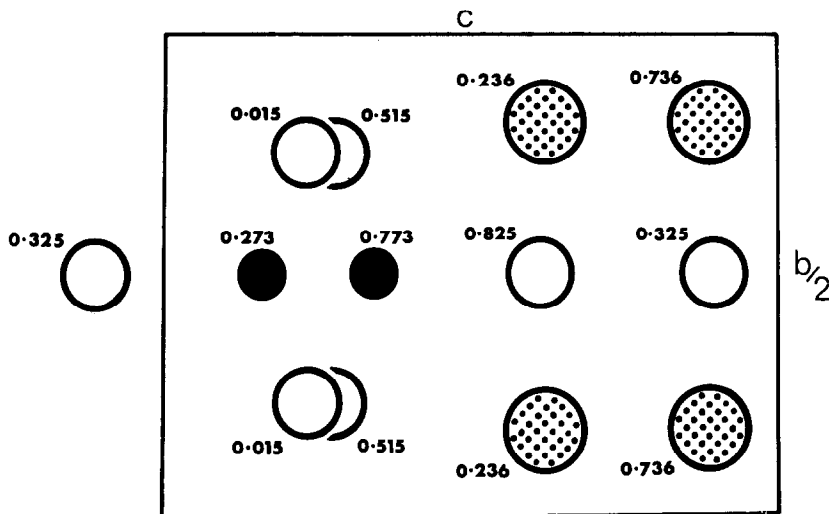

FIG. 2. A (100) projection of the K_2ZrO_3 structure showing a view down the chains of edge-sharing ZrO_5 square pyramids. Filled shaded and open circles represent zirconium, potassium, and oxygen atoms, respectively.
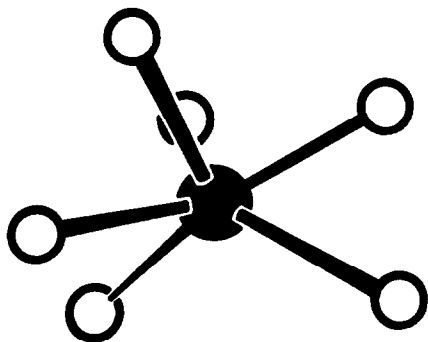

FIG. 3. A perspective representation of the irregular sixfold coordination of oxygen atoms (open circles) to potassium atoms (filled circle) in K_2ZrO_3.

The large errors in the x parameters of each atom (Table I) and the high standard deviations in bond lengths (Table III) for K_2SnO_3 are attributed to the relative lack of accurate data in the a-axis direction. This is a consequence of the imperfection and instability of the crystals of this compound which were available.

The structure shown here to exist for potassium metazirconate may be used to explain the hygroscopic nature of the compound where, by absorption of water, the higher, more favourable coordination state for Zr(IV) may be satisfied with the consequent disruption of the structure.

This report has shown that the chemistry of zirconium has been extended to at least five co-

ordination and, as explained in the recent report of the structure of β-$K_2Zr_2O_5$ (2) indications are that the extension may go to even lower coordination in the solid state. Considering the five-coordination found in potassium metazirconate, it should be possible to design a ligand which, in forcing square-pyramidal stereochemistry on a central metal, will simulate the geometry exhibited by zirconium in this compound.

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