The Crystal Structure of Potassium Metazirconate and Potassium Metastannate; K_2ZrO_2 and K_2SnO_3: Oxides with Five-co-ordinate Square-pyramidal Zirconium(IV) and Tin(IV)

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Summary Potassium metazirconate and potassium metastannate contain chains of base edge shared MO_5 (where M is Zr or Sn) square pyramids.

As part of the structural study of the ZrO_2–K_2O system, the crystal structure of potassium metazirconate, K_2ZrO_3, has been determined by single-crystal *X*-ray diffraction techniques. A comparison of corresponding Weissenberg photographs of K_2ZrO_3 and the analogous stannate, K_2SnO_3, indicated that the two compounds were isostructural; this was subsequently confirmed by the independent crystal structure determination of the compounds.

Potassium metazirconate was first characterized[1] in 1961, followed by a more extensive study[2] of K_2ZrO_3 and K_2SnO_3 where the two compounds were reported to be isomorphous. In the light of the present structure determination of the two compounds, the structure originally suggested for the metastannate is incorrect.

Single crystals of these extremely hygroscopic oxides were prepared by dissolving MO_2 (where M is Zr or Sn) in K_2O at 1050° under an atmosphere of dry nitrogen and boiling off the excess of solvent.

The compounds crystallize in the orthorhombic system, space group *Pnma*, with unit-cell dimensions $a = 5{\cdot}90 \pm 0{\cdot}02$, $b = 10{\cdot}73 \pm 0{\cdot}02$, $c = 7{\cdot}04 \pm 0{\cdot}02$ Å and $a = 5{\cdot}75 \pm 0{\cdot}02$, $b = 10{\cdot}29 \pm 0{\cdot}02$, and $c = 7{\cdot}11 \pm 0{\cdot}02$ Å; $D_c = 3{\cdot}24$ for K_2ZrO_3 and 3·87 for K_2SnO_3. Totals of 293 and 119 independent reflections for the zirconate and the stannate, respectively, were collected using the Weissenberg technique. The structures were determined using Patterson and Fourier syntheses and refined by the full-matrix least-squares technique to conventional agreement factors for K_2ZrO_3 and K_2SnO_3 of $R = 0{\cdot}089$ and $R = 0{\cdot}138$, respectively. Anisotropic temperature factors were used for all atoms in the zirconate but for tin atoms only in the stannate.

The structure is similar to that reported by Hoppe *et al.*[3] for potassium plumbate, K_2PbO_3. It contains chains of edge-sharing MO_5 square pyramids, with apices oppositely directed, running in the *x*-direction (see Figure). The double pyramidal unit of the chains is shown in the Figure where the six oxygen atoms O(1), O(2), O(3), O(4), O(1)′, and O(2)′ are not coplanar. The metal atoms in each chain are not collinear.

The structure described here for the metazirconate and metastannate differs from that originally suggested by Tournoux in the position of the oxygen atoms. Tournoux's model contained chains of face-shared SnO_6 octahedral units running in the *x*-direction.

In the MO_5 square-pyramidal units found in the present structure, the metal atom is equidistant from the four basal oxygen atoms but the slightly shorter M–O bond to the apical oxygen atom is not quite perpendicular to the plane containing the four basal oxygen atoms. The metal atom lies 0·64 Å above this plane in both compounds. The M–O distances for the four basal oxygen atoms is 2·13 Å and slightly shorter at 1·92 Å, as expected, for the apical oxygen atom. The next nearest oxygen atom to the zirconium (or tin) atom lies at a distance of 4·43 Å which is well outside the co-ordination sphere. The estimated standard deviations for the Zr–O distances are 0·02 Å but are higher for the Sn–O distances chiefly because of the slightly imperfect nature and the size of the crystals available and the consequent lack of data. As expected, the O–O distances for the shared edges are significantly shorter at 2·77 ± 0·02 Å than the unshared edges 2·96 ± 0·02 Å for the zirconate. The corresponding values for the stannate are 2·83 Å and 2·91 Å but poor standard deviations (0·08 and 0·11 Å, respectively) render the evidence inconclusive here. The M–M distances are 3·212 ± 0·002 Å for K_2ZrO_3 and 3·13 ± 0·01 Å for K_2SnO_3. These distances indicate the rather "packed-up" nature of the relatively straight MO_5 chains. The potassium atoms occupy interchain positions having irregular six-fold co-ordination with oxygen atoms. The K–O distances are in the range 2·68—3·01 ± 0·01 Å, the average being 2·89 Å for the zirconate and 2·59—3·27 ± 0·07 Å with an average of 2·82 Å for the stannate. This seems to be normal for this type of compound.[4]

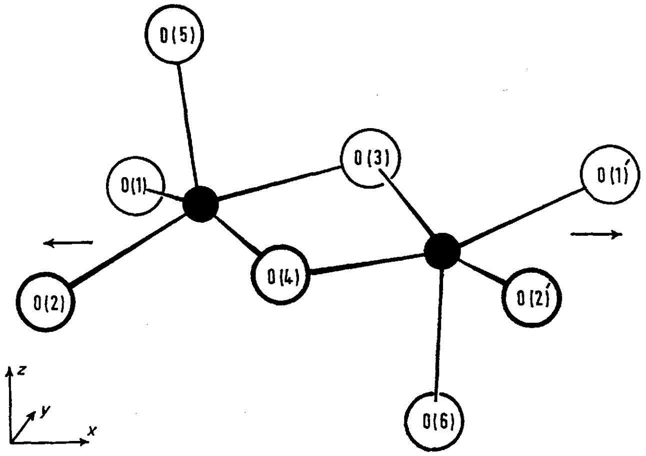

FIGURE. *The idealized double pyramidal unit of the chains in the* K_2ZrO_3 *and* K_2SnO_3 *structures. The unfilled circles represent oxygen atoms and the filled ones zirconium or tin atoms. The metal atoms and apical oxygen atoms* [O(5) *and* O(6)] *lie on the mirror plane. Relevant bond lengths are given in the text.*

The structure found to exist for both potassium metazirconate and potassium metastannate may be used to explain the extreme hygroscopic nature of the compounds where, by absorption of water, the higher, more favourable co-ordination for zirconium(IV) and tin(IV) may be satisfied, but the structure is then disrupted.

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[3] R. Hoppe, H. J. Rohrborn, and H. Walker, *Naturwiss.*, 1964, **51**, 86.
[4] "International Tables for *X*-ray Crystallography, Kynoch Press, Birmingham, 1962, Vol. III.