

## On the Crystal Structure of $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$

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The crystal structure of  $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$  has been determined from X-ray diffraction data collected by Weissenberg techniques. The crystals are orthorhombic and the unit cell dimensions, determined from Guinier powder diffraction data, are:  $a = 13.0203 \pm 0.0034 \text{ \AA}$ ,  $b = 4.9451 \pm 0.0013 \text{ \AA}$ ,  $c = 12.0783 \pm 0.0035 \text{ \AA}$ ,  $V = 777.7 \text{ \AA}^3$ .

If the  $a$  and  $b$  axes are interchanged, the cell dimensions are in good agreement with values published by Davies and Donaldson.<sup>1</sup> There are four formula units in the unit cell. The space group is  $Pca2_1$ ,<sup>2</sup> which is the noncentrosymmetric alternative among the groups suggested previously.<sup>1</sup>

Patterson and electron density functions were calculated with  $h0l$ ,  $h1l$ , and  $h2l$  data. Atomic parameters obtained from these calculations and refined by the method of least squares yielded a preliminary  $R$  value

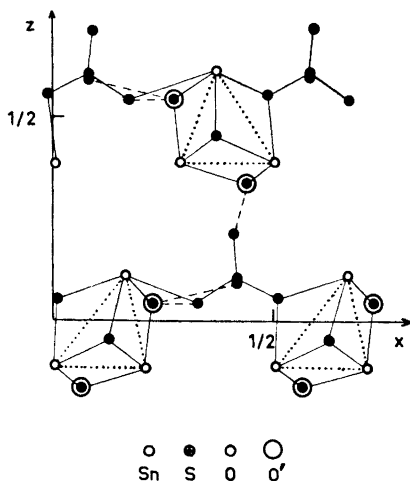


Fig. 1. Projection of the structure of  $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$  on the  $xz$  plane. Tin triangles are marked with dotted lines, coordinated atoms are connected by full lines and O-O distances available for hydrogen bonds are dashed. O' corresponds to an oxygen atom in the next unit cell above or below.

of 13.3%. No correction has yet been made for absorption.

A projection of the structure on the  $xz$  plane is shown in Fig. 1. Three tin atoms form a triangle with Sn-Sn distances of 3.49  $\text{\AA}$ , 3.57  $\text{\AA}$ , and 3.59  $\text{\AA}$ , respectively. One oxygen atom is coordinated to all three tin atoms, while two hydroxide ions are coordinated each to two tin atoms. On the third side of the Sn triangle there is a sulphate oxygen atom coordinated to two tin atoms. The arrangement of tin, oxygen and hydroxide ions yields the ion  $\text{Sn}_3\text{O}(\text{OH})_2^{2+}$ , which is in accordance with that suggested, though not verified, by Davies and Donaldson.<sup>1</sup> It differs from the  $\text{Sn}_3(\text{OH})_4^{2+}$  ion proposed by Tobias<sup>3</sup> from emf measurements by one water molecule. The  $\text{Sn}_3\text{O}(\text{OH})_2^{2+}$  ion is, however, also coordinated to sulphate groups, so that two of the tin atoms are three-coordinated, whereas the third has four oxygen neighbours. The tin triangles form a zig-zag chain running along the  $b$  axis, connection being provided by the coordination of two tin atoms to hydroxide ions in the unit cell below (cf. Fig. 1).

Differential thermal analysis and thermogravimetric analysis indicated different modes of coordinations for the two hydroxide groups since the water is expelled in two steps separated by 65°. This is confirmed by the O-O distances. One of the O-H...O bonds is of the usual linear type with an O-O distance of 2.79  $\text{\AA}$ , whereas for the other there are two O-O distances of 2.61  $\text{\AA}$  and 2.68  $\text{\AA}$ , corresponding to a bifurcated hydrogen bond. The O-O distances of interest are marked in Fig. 1. All the oxygen atoms in the sulphate group are coordinated to other atoms which results in a distortion of the sulphate group.

Further refinement of this structure is in progress and the results will soon be published.

This work has been supported financially by the Swedish Natural Science Research Council, Contract No. 2318.

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Received April 17, 1973.