

ment résolu: $D_x\text{WO}_3$ par Wiseman & Dickens (1973). Dans le cas présent, la distance Sb—O dans le tunnel varie de 1,86 (3) à 3,05 (3) Å.

La position relative des deux polyèdres de coordination des atomes Sb(1) et Sb(2) laisse entre eux une lacune vraisemblablement occupée par les deux paires non liées E_1 et E_2 .

Tout ceci conduit à comparer $\text{Sb}_2\text{Mo}_{10}\text{O}_{31}$ aux bronzes de molybdène préparés jusqu'à présent avec les seuls métaux alcalins. Du point de vue structural, la ressemblance est encore plus nette avec les bronzes de tungstène de type HTB (hexagonal tungsten bronzes) avec cependant quelques différences: tout d'abord la présence incontestable de l'atome d'oxygène O(8) à l'intérieur des tunnels impose une composition chimique fixée. En effet, il n'a pas été possible de préparer des phases plus pauvres en antimoine, phénomène rare dans les séries de bronzes de tungstène, mais toutefois plus banal dans les bronzes de molybdène, ce qui traduit leur moindre stabilité.

D'autre part, la conductivité électrique (mesurée de 300 à 450 K sur un barreau fritté par la méthode du pont de Wheatstone) est de type semiconducteur avec une énergie d'activation de 0,23 eV (Parmentier, 1977). Or les bronzes de molybdène connus de composition comparable ont une conductivité métallique.

Conclusion

Le composé $\text{Sb}_2\text{Mo}_{10}\text{O}_{31}$ dans lequel Sb et Mo possèdent leur coordination habituelle, peut être con-

sidé comme un bronze de molybdène, bien qu'il n'en ait pas toutes les propriétés.

En effet, les octaèdres MoO_6 s'assemblent pour former des tunnels hexagonaux de type HTB dans lesquels s'insèrent des chaînes Sb—O—Sb—E—Sb.

C'est à notre connaissance le premier composé du molybdène à montrer une structure de ce type. La singularité de ce composé est sans doute liée au rôle stéréochimique de la paire non liée de l'antimoine, permettant la stabilisation de l'ion Sb^{3+} en position excentrée dans un site volumineux tout en conservant sa coordination caractéristique.

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A Redetermination of the Crystal Structure of Potassium Trithionate, $\text{K}_2\text{S}_3\text{O}_6$ *

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Abstract

The crystal structure of potassium trithionate, $\text{K}_2\text{S}_3\text{O}_6$, has been redetermined from two sets of four-circle diffractometer X-ray intensity data, and refined to $R = 0.042$ for 3010 observed reflections, and $R = 0.066$ for all 4309 data. The structure is orthorhombic, space group $Pnam$, with $a = 9.794$ (1), $b = 13.690$ (1), $c =$

5.742 (1) Å, $Z = 4$. The earlier structural results have been confirmed, though the present refinement shows that the symmetry within the trithionate ion is significantly different from the approximate mm symmetry previously claimed. The two S—S bonds are not of equal length [2.064 (1), 2.097 (1) Å], while one S—O bond is appreciably longer than the other five. Both K ions are nine-coordinated, the K—O distances varying from 2.646 (2) to 3.244 (1) Å, while each O is coordinated to three K ions.

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Introduction

The waste effluent from the flotation circuit, processing Cu, Pb, Zn, pyritic sulfide ores (as typified by Brunswick Mining and Smelting and Heath Steele orebodies, New Brunswick, Canada) contains various thiosalts as undesirable constituents. Although the majority of these salts are oxidized to sulfuric acid and neutralized prior to waste disposal, this process is not complete, and the subsequent formation of more acid from the remaining thiosalts in lakes and rivers is a serious environmental problem. As part of an overall program of decreasing such industrial pollution, a systematic study of the thiosalt contaminants was undertaken at CANMET. The trithionate ion is one of the constituents of thiosalt waste in the above-mentioned process, and this paper reports on the re-examination of the crystal structure of potassium trithionate, $K_2S_3O_6$.

The structure was originally determined by Zachariassen (1934) by a trial-and-error method of comparison of intensities from oscillation photographs with calculated structure amplitudes for the proposed structure. Although Zachariassen found the two S—S bonds to be 2.14 and 2.17 Å, and the S—O bonds to be of various lengths, the probable errors associated with this determination were such that he proposed a trithionate ion with *mm* symmetry and with S—S and S—O bonds of 2.15 and 1.50 Å. In order to facilitate interpretation of UV and IR spectral data, and as an aid to studies examining the oxidation of the trithionate ion, a detailed structure determination of potassium trithionate was carried out to determine the molecular geometry more precisely.

Experimental

An acicular crystal showing the forms {100} and {210} was cut perpendicular to the needle axis (*c*) to give a tabular shape (0.10 × 0.34 × 0.38 mm along **a**, **b** and **c** respectively). Preliminary photographic examination, using a precession camera, confirmed the systematic absences for the space group found by Zachariassen, *Pnam* (No. 62, *Pnma* with *a, c, b*), and also permitted for space group *Pna2*₁ (No. 33). The non-standard space-group setting used by Zachariassen was retained in order to conform both to the earlier work and to the subsequent literature references to it. The crystal was mounted on a four-circle X-ray diffractometer in a general orientation and the cell dimensions were refined by a least-squares technique (Busing, 1970), from the 2θ , χ and ω values of 70 reflections in the range $60^\circ > 2\theta > 52^\circ$. The parameters were refined as a triclinic cell, and the deviation from orthogonality was 0.002° . The cell data are given below.

Two equivalent segments of intensity data (*hkl* and $\bar{h}kl$) were collected using a θ - 2θ scan mode, with

graphite-monochromated Mo *K* α radiation to a limit of $2\theta = 100^\circ$. The 2θ scan width was 2° plus the α_1 - α_2 dispersion. The scan rate was 2° min^{-1} , and the background counts were measured on either side of the peak for approximately the same time as was used for the scan. Three reference reflections were measured every 50 measurements in order to monitor crystal alignment and instrument stability. No significant variation was noted during the data collection.

After application of absorption corrections using a Gaussian integration procedure (Gabe & O'Byrne, 1970), the data sets were averaged into a single set. Standard deviations were calculated from counting statistics and from the relative agreement of the two measurements. The final data set contained 4309 reflections, of which 3010 were considered observed on the criterion that $I > 1.65\sigma(I)$. The overall disagreement factor $[\sum (I - \bar{I}) / \sum I]$ between the two sets was 0.015. Structure factors were derived by application of the Lorentz and polarization factors, with $\sigma(F)$ set to $\frac{1}{2}\sigma(I)(I \text{ Lp})^{-1/2}$. The quantity minimized in the least-squares refinement was $\sum w(\Delta F)^2$, where $w = 1/\sigma^2(F)$.

Crystal data

Potassium trithionate, $K_2S_3O_6$; formula weight: 270.39; crystal system: orthorhombic; cell dimensions: $a = 9.794$ (1), $b = 13.690$ (1), $c = 5.742$ (1) Å, 298 K; $\lambda(\text{Mo } K\alpha_1) = 0.70930$ Å; systematic absences: $0kl, k + l = 2n + 1$; $h0l, h = 2n + 1$; possible space groups: *Pnam* (No. 62) or *Pna2*₁ (No. 33), *Pnam* confirmed by the structure analysis; density: $D_{\text{calc}} = 2.332$, $D_{\text{obs}} = 2.32$ (1) Mg m⁻³; $Z = 4$; linear absorption coefficient: $\mu(\text{Mo } K\alpha) = 1.968$ mm⁻¹; intensity data: 4309 reflections measured twice ($2\theta < 100^\circ$); 3010 observed with $I > 1.65\sigma(I)$.

Structure refinement

The structure would not refine from Zachariassen's coordinates until the data set was restricted to $\sin \theta/\lambda < 0.5$ Å⁻¹ (454 reflections). Isotropic refinement for this reduced data set gave $R = 0.071$. From the atomic coordinates so obtained, and using anisotropic temperature factors in the least-squares refinement, the need for the inclusion of an extinction parameter *g* (Larson, 1970) soon became evident, and with this the structure refined to 0.042 for the 3010 observed data and $R = 0.066$ for all 4309 data included at their observed values.

The calculations were made using the XRAY system of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The scattering curves were taken from Cromer & Mann (1968) for the atomic species K¹⁺ and S⁰. The formal charge of -2 on the trithionate ion was considered as distributed over the six O atoms of the

molecule, so a scattering curve representing $O^{-1/3}$ was prepared from a weighted average of the O^{1-} and O^0 curves from the same source. The anomalous-dispersion corrections were taken from Cromer & Liberman (1970).

Two aspects of the structure refinement appeared unsatisfactory:

(1) Despite the inclusion of an overall extinction parameter, the low-order $00l$ reflections were still showing $F_o < F_c$ as though the extinction correction were insufficient for these data ($00l$, $10F_o$, $10F_c$: 2, 1535, 1773; 4, 1495, 1625; 6, 775, 802).

(2) The anisotropic thermal vibration of O(1) normal to the mirror plane refined to a much larger value than in the other two directions ($U_{33} = 0.111 \text{ \AA}^2$; cf. $U_{11} = 0.017 \text{ \AA}^2$, $U_{22} = 0.041 \text{ \AA}^2$).

An attempt was made to refine the extinction anisotropically (Coppens & Hamilton, 1970) using the least-squares program *XFLS4* [Busing *et al.* (1978); based on *ORFLS* (Busing, Martin & Levy, 1962)]. Neither the type 1 (mosaic-spread-dominated) nor the type 2 (particle-size-dominated) extinction models gave significant improvement over the isotropic model, both in terms of weighted residuals and particularly in terms of agreement in the $00l$ row. The three reflections 002, 004 and 006 were thus excluded from further refinement.

It was suspected that the large thermal displacement of O(1) in the c direction might be caused by positional disorder of this atom above and below the mirror plane at $z = \frac{1}{4}$, $\frac{3}{4}$. A refinement was attempted with 'half-atoms' separated by 0.5 Å, but such a refinement turned out to be very ill conditioned, and the two half-atoms eventually merged. Similarly, refinement in space group $Pna2_1$ with the positional constraints of the mirror plane in $Pnam$ removed was totally unsuccessful, with the z coordinate of O(1) refining back to within 1σ of $z = \frac{1}{4}$ from whichever side of this value it was initially placed. Thus within the limits of the room-temperature X-ray diffractometer data, it was not possible to sort out the possibility of positional disorder, as opposed to large thermal displacement. The structure is here reported as ordered, with O(1) at $z = \frac{1}{4}$.

Table 1. Positional parameters with standard deviations

	x	y	z
K(1)	0.1324 (1)	0.0916 (1)	$\frac{1}{4}$
K(2)	0.1792 (1)	-0.2366 (1)	$\frac{3}{4}$
S(1)	0.0298 (1)	0.3243 (1)	$\frac{1}{4}$
S(2)	0.0907 (1)	0.4711 (1)	$\frac{1}{4}$
S(3)	0.3015 (1)	0.4707 (1)	$\frac{1}{4}$
O(1)	-0.1163 (2)	0.3374 (2)	$\frac{1}{4}$
O(2)	0.3229 (2)	0.5759 (1)	$\frac{1}{4}$
O(3)	0.0807 (2)	0.2790 (1)	0.0411 (2)
O(4)	0.3508 (1)	0.4240 (1)	0.0410 (2)

Table 1 lists the atomic parameters for the anisotropic thermal refinement, and an overall isotropic extinction parameter. A ΔF synthesis, calculated at the end of the refinement, showed residual positive areas (up to 0.4 e \AA^{-3}) in the S—S and S—O bonding regions, but as three critical $00l$ reflections had been excluded from the calculation, no significance was attached to these.*

Description of structure

Fig. 1 shows the structure projected on the ab plane. Within each trithionate ion, O(1), S(1), S(2), S(3), and O(2) lie in the mirror planes at $z = \frac{1}{4}$, $\frac{3}{4}$. K(1) and K(2) also lie on the mirror planes. Only O(3) and O(4) are in general positions. Zachariassen's original determination

* Lists of structure factors, anisotropic thermal parameters and details of the angular geometry of the K—O coordination polyhedra have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34480 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

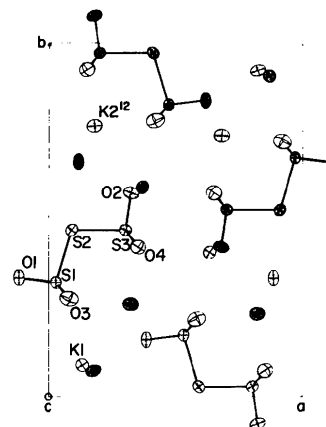


Fig. 1. The structure of potassium trithionate projected on the ab plane. Atoms at $z = \frac{1}{4}$ are stippled, those at $z = \frac{3}{4}$ are shaded. The ellipsoids are drawn at 50% probability (Johnson, 1965). Superscripts used in the diagrams and the text refer to the following symmetry operations: (1) $x, -1 + y, z$; (2) $-x, -y, 1 - z$; (3) $-x, -y, -z$; (4) $-x, -y, \frac{1}{2} + z$; (5) $x, y, \frac{1}{2} - z$; (6) $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} + z$; (7) $\frac{1}{2} - x, -\frac{1}{2} + y, -\frac{1}{2} + z$; (8) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; (9) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$; (10) $-\frac{1}{2} + x, \frac{1}{2} - y, z$; (11) $\frac{1}{2} - x, -\frac{1}{2} + y, -z$; (12) $x, 1 + y, z$.

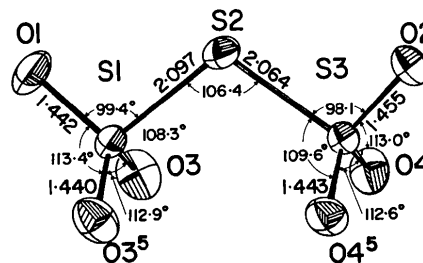


Fig. 2. The geometry of the trithionate ion. The e.s.d.'s of S(1)—O(1) and S(3)—O(2) are 0.002 Å. The e.s.d.'s of the other bonds are 0.001 Å, and of angles are less than 0.1° .

of the structure is thus confirmed, but, in detail, the trithionate ion is significantly different from the *mm* symmetry suggested by the earlier work (see Fig. 2). The S—S bond lengths differ by 0.033 Å (24 σ). Of the six S—O bonds in the molecule, five are virtually equal: S(1)—O(1) = 1.442 (2) Å, S(1)—O(3) = 2 \times 1.440 (1) Å, S(3)—O(4) = 2 \times 1.443 (1) Å. The sixth is very significantly longer, S(3)—O(2) = 1.455 (2) Å. The angular geometry at the terminal S atoms is distorted tetrahedral, with the two 'in-the-plane' O atoms O(1), O(2) being *trans* to the S at the other end of the ion, giving rise to a planar 'zigzag' of O—S—S—O. The longest S—O bond is adjacent to the shorter S—S bond. Thus, there appears to be a degree of conjugation in the chain. Furthermore, the O involved in the shortest K—O distance [K(1)—O(1⁸) = 2.646 (2) Å] is the one with the shorter in-the-plane S—O bond. The distortions from tetrahedral geometry are largest for the two in-the-plane O atoms at the ends of the chain, O(1)—S(1)—S(2) = 99.4 (1)°, O(2)—S(3)—S(2) = 98.1 (1)°. The other geometrical aspects of the trithionate ion are shown in Fig. 2. Both K ions are nine-coordinated by O atoms (Fig. 3*a,b*), the individual K—O distances varying from 2.646 (2) to 3.244 (1) Å. In turn, each O, as well as being bonded to S, is coordinated to three K ions. There are no further K—O distances up to 3.5 Å.*

Discussion

The present refinement confirms the basic structure and coordination model proposed by Zachariassen. However, in detail there are significant differences from the earlier work, and the bond lengths and angles are now known much more precisely. Whether the apparent conjugation of the trithionate ion is maintained in solution is a problem yet to be studied and would

* See previous footnote.

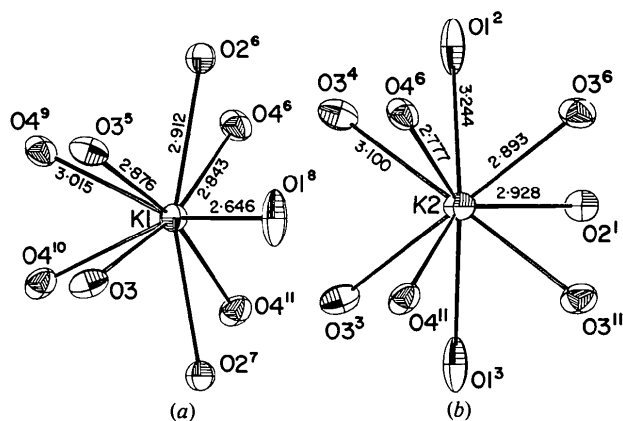


Fig. 3. Coordination polyhedra of potassium ions out to 3.5 Å. (a) K(1), (b) K(2). The e.s.d. of all distances is 0.001 Å, with the exception of the following, where it is 0.002 Å: K(1)—O(1⁸), K(2)—O(2¹), K(2)—O(3⁴), K(2)—O(3⁶).

certainly be important in the mechanism of the oxidation of trithionate to sulfate which occurs in effluent streams.

The individual bond lengths and angles are within the values expected for this type of structure, as is the coordination sphere of the K ions.

The only apparent anomaly is in the thermal parameters of O(1), but even this can be rationalized as follows: for a planar long-chain molecule, the largest thermal displacements would be expected to be a riding motion of the terminal atoms, unless other restraining forces are involved. Thus U_{11} for O(1) should be smaller than U_{22} and U_{33} , particularly since in the *a* direction, O(1) is bonded to S(1) and closely coordinated to K(1). The forces restraining the riding motion are associated with the presence of two K(2) ions at $z = \frac{1}{4}$ and $-\frac{1}{4}$. These K(2)—O(1) bonds are the longest of the K—O coordination distances found in the structure, 3.244 (1) Å, and the K ions do not overlap O(1) in the *c* direction. O(1) is thus reasonably unrestricted in the *c* direction, and the majority of its total thermal displacement appears as a large value for U_{33} . At the other end of the trithionate ion, O(2) is closely overlapped by K(1) in the *c* direction, hence its U_{33} is much smaller.

A similar large thermal displacement for one terminal O was found in the structure of potassium tetrathionate (Stewart & Szymański, 1979).

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