The Crystal Structure of Potassium Tetrathionate, K₂S₄O₆*

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Abstract

The crystal structure of potassium tetrathionate, $K_2S_4O_6$, has been determined from two equivalent sets of X-ray diffractometer data collected with Mo $K\alpha$ radiation, and refined to $R = 0.033$ for 5033 observed reflections, and $R = 0.034$ for all 5450 data. The structure is monoclinic, space group Cc, with $a = 22.081$ (5), $b = 7.991$ (2), $c = 10.108$ (3) Å, $\beta = 102.28$ (2)°, $Z = 8$. The two tetrathionate ions in the asymmetric unit of the structure are comparable in geometry, though there is rotational displacement of SO_3 groups about the terminal S–S bonds. In both ions, the central bond is shorter [2.013 (9), 2.020 (4) Å] while the other bonds range from 2.096 (3) to 2.136 (4) Å. The twelve S–O bonds vary between 1.434 (7) and 1.454 (10) Å. The S skeleton of both ions is bent at nearly a right angle about the central S–S bond. The structure is held together by an extensive network of ionic interactions between the O atoms and K ions, where the distances vary from 2.610 (5) to 3.269 (16) Å.

Introduction

In the course of a study at CANMET of the constituents of waste effluent from sulfide mining operations, the structure of potassium trithionate was redetermined (Stewart & Szymański, 1979). The tetrathionate ion, which is also present in this waste as a thiosalt contaminant, is oxidized in lakes and rivers producing serious environmental problems, because the end-product of oxidation is sulfuric acid. In order to provide precise molecular information for the interpretation of UV and IR spectral data, and for the study of the oxidation processes of this contaminant, the crystal structure of potassium tetrathionate, $K_2S_4O_6$, was determined.

The tetrathionate ion has been previously examined crystallographically as barium tetrathionate dihydrate (Foss, Furberg & Zachariasen, 1954) and sodium

tetrathionate dihydrate (Foss & Hordvik, 1964). However, as both these structures had been refined by Fourier methods from projection data (and even *twinned* projection data in the case of $Na_2S_4O_6.2H_2O$), it was felt that a more precise determination of the geometry of the tetrathionate ion was necessary.

Potassium tetrathionate has been examined morphologically by Rammelsberg (1881), Baker (in Shaw, 1883), Fock (1891) and most recently by Tunell, Merwin & Ksanda (1938). This last investigation also included determination of the unit cell and probable space group by Weissenberg techniques. The space group was correctly identified as Cc (rather than $C2/c$) based upon morphological evidence and the determination of the presence of piezoelectric and pyroelectric effects. Regrettably, this work came to the attention of the present authors after the structure had been determined.

Experimental

Crystal data

Potassium tetrathionate, $K_2S_4O_6$; formula weight: 302.46; crystal system: monoclinic; systematic absences: $hkl, h + k = 2n + 1$; $h0l, l = 2n + 1, (h = 2n + 1)$; possible space groups: $C2/c$ (No. 15) or Cc (No. 9), Cc suggested by intensity statistics and confirmed by the structure analysis; cell dimensions: $a = 22.081$ (5), $b = 7.991$ (2), $c = 10.108$ (3) Å, $\beta = 102.28$ (2)°, $V = 1742.69$ Å³, at 298 K; λ(Mo $K\alpha_1$) = 0.70930 Å; $Z = 8$; density: $D_{calc} = 2.305$, $D_{obs} = 2.28$ (2) Mg m⁻³ (Berman balance, in toluene); linear absorption coefficient: μ(Mo $K\alpha$) = 1.99 mm⁻¹; intensity data: 5450 reflections measured twice ($2\theta < 80°$), 5033 observed with $I > 1.65\sigma(I)$.

An acicular crystal (in c) was cut with a knife to give a tabular shape, approximately $0.17 \times 0.50 \times 0.55$ mm along a^*, b, and c. After preliminary photographic work, the crystal was mounted on a four-circle diffractometer in a general orientation. The cell dimensions were determined from a least-squares fit for

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62 reflections in the range $51 < 2\theta < 60°$ (Mo $K\alpha$ radiation) of the 2θ, χ, ω values (Busing, 1970). Intensity data were collected using graphite-mono-chromated Mo $K\alpha$ radiation to a maximum of $2\theta = 80°$ using a θ–2θ scan mode at $2°$ min^{-1} in 2θ. The 2θ scan width was $2°$, increasing with the α_1–α_2 dispersion. Background counts were measured on either side of the peak for a total of 40 s. Both the $\pm h,k,l$ and $\pm h,k,\bar{l}$ segments were collected. Absorption corrections were applied using a Gaussian integration procedure (Gabe & O'Byrne, 1970), and the data were reduced, with the application of Lp corrections, and averaged over the two sets to provide a unique set of 5450 structure factors, of which 5033 were considered observed at the 10% significance level $[I > 1.65\sigma(I)]$. The internal agreement factor (R_{int}) between the two absorption-corrected data sets was 0.015.

Solution of the structure

Intensity statistics showed unambiguously that the structure was noncentrosymmetric. This was unexpected in view of the presence of eight molecules in the unit cell in the possible space groups $C2/c$ and Cc, and necessitated for the solution of the structure the presence of two molecules in the asymmetric unit in space group Cc.

Early attempts to solve the structure with *MULTAN* 72 (Main, Woolfson & Germain, 1970, with updates up to 1974), were unsuccessful. The problem was traced to the magnitudes of the E's produced during the normalization. A number of these were improbably large for a noncentrosymmetric structure, irrespective of the scaling techniques employed in the program. Finally, the normalization program *NORMSF* in the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) was used, and the E's so produced were fed into *MULTAN*. The second E map tried showed the whole structure apart from three O atoms. These were found from a Fourier synthesis phased on the partial structure.

A low-angle $(2\theta < 35°)$ data set of 592 reflections was used to refine the structure isotropically to $R = 0.076$. Subsequent refinement using the full data set, anisotropic thermal parameters and an isotropic extinction parameter *(Larson, 1970) lowered R to 0.033* for the 5033 observed reflections and $R = 0.034$ with the unobserved reflections included.

The scattering curves used were S^0 and K^{1+} (Cromer & Mann, 1968). For O, the formal charge of -2 of the tetrathionate ion was considered as distributed over the six O atoms of the ion. A scattering curve of $O^{-1/3}$ was prepared from the O^0 and O^{1-} curves taken from the same source. The anomalous-dispersion corrections (Cromer & Liberman, 1970) were included in the refinement. The inverse structure had a higher residual,

$R = 0.036$, and was discarded. After the solution of the structure with *MULTAN*, all calculations were performed using the XRAY system of programs (Stewart *et al.*, 1972).

The refined positional parameters are listed in Table 1.*

Description of the structure

The structure is illustrated in Fig. 1, with the labelled atoms referring to the coordinates quoted in Table 1. The S skeleton of both tetrathionate ions is bent out of planarity about the middle S–S bond [plane S(1)–S(2)–S(3) to plane S(2)–S(3)–S(4) = $87.6°$, plane S(5)–S(6)–S(7) to plane S(6)–S(7)–S(8) = $88.9°$]. The direction of principal extension of the first tetrathionate ion is along **b**, and of the second, along **c**.

The two tetrathionate ions of the asymmetric unit are not identical. Their geometries are illustrated in Fig. 2.* It can be seen that both ions have a shorter S–S bond in the middle [S(2)–S(3) = 2.013 (9), S(6)–S(7) = 2.020 (4) Å], and longer bonds at the ends [S(1)–S(2)

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and angles in the tetrathionate ions with e.s.d.'s, and details of the coordination geometry of K–O polyhedra have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34481 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* $(\times 10^4)$

	x	y	z
S(1)	1000*	6972 (1)	1000*
S(2)	1857 (1)	8123 (1)	955 (1)
S(3)	2082 (1)	9502 (1)	2657 (1)
S(4)	1636 (1)	1820 (1)	2064 (1)
O(1)	512 (1)	8173 (3)	505 (3)
O(2)	1020 (1)	5602 (3)	79 (2)
O(3)	1015 (1)	6481 (3)	2387 (2)
O(4)	1031 (1)	1662 (4)	2354 (3)
O(5)	2036 (2)	2975 (3)	2939 (4)
O(6)	1628 (2)	1990 (3)	645 (3)
K(1)	627 (1)	−871 (1)	3838 (1)
K(2)	145 (1)	3860 (1)	2640 (1)
K(3)	2189 (1)	5691 (1)	4406 (1)
K(4)	4259 (1)	3427 (1)	514 (1)
S(5)	4425 (1)	1679 (1)	4323 (1)
S(6)	3476 (1)	2089 (1)	4183 (1)
S(7)	3393 (1)	1390 (1)	6057 (1)
S(8)	3538 (1)	3644 (1)	7217 (1)
O(7)	4498 (1)	1871 (3)	2938 (2)
O(8)	4563 (1)	9 (3)	4857 (3)
O(9)	4752 (1)	2963 (3)	5218 (2)
O(10)	3225 (1)	3244 (3)	8299 (2)
O(11)	4201 (1)	3842 (3)	7679 (2)
O(12)	3259 (1)	4970 (3)	6323 (3)

* Coordinate held invariant to fix origin.

= 2·113 (9), S(3)—S(4) = 2·124 (6) Å for the first ion; S(5)—S(6) = 2·096 (3), S(7)—S(8) = 2·136 (4) Å for the second]. The S—O bonds range from 1·434 (7) to 1·454 (10) Å with a mean of 1·446 Å. The angles around the terminal S atoms are somewhat distorted from tetrahedral, the individual values varying between 99·5 and 115·3°.

As in the structure of potassium trithionate (Stewart & Szymański, 1979) there is extensive coordination in this structure via S—O···K ionic bonding. The coordination of the four K ions to 3·4 Å is shown in Fig. 3.*
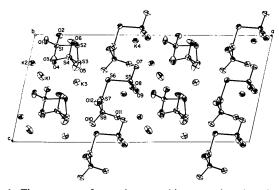
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* See deposition footnote.

Fig. 1. The structure of potassium tetrathionate projected on the ac plane. The x and z coordinates of S(1) were arbitrarily fixed at 0·1 to define the origin. The ellipsoids are drawn at 50% probability (Johnson, 1965).
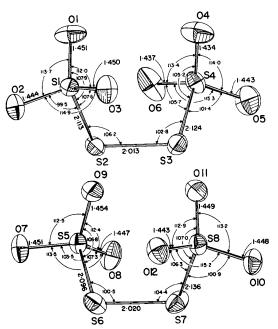

Fig. 2. The geometries of the two independent tetrathionate ions. The e.s.d.'s of the bond lengths vary from 0·003 to 0·012 Å; those of the angles are 0·2° or less. Precise details have been deposited.

Discussion

Although the four terminal S—S bonds in the two tetrathionate ions are of various lengths with no apparent fixed pattern, it is clear from the shortness of both central S—S bonds that some degree of stronger bonding is involved in these two bonds. The geometry of the two ions was compared in detail with the least-squares best-molecular-fit program (*BMFIT*) of Yeun & Nyburg (1979) to find out to what extent the two ions retained the same configuration despite the different interactions of the four terminal SO_3 groups with neighboring K ions. The best weighted least-squares fit was obtained by matching the S skeleton of the first ion [S(1)—S(2)—S(3)—S(4)] to a mirrored skeleton of the second ion in reverse order [S(8)—S(7)—S(6)—S(5)]. With this configuration, O(1), O(2), O(3) matched well with O(11), O(10), O(12), but there was a large discrepancy between the other matching SO_3 groups [O(4), O(5), O(6) with O(9), O(7), O(8)]. It was found that this was as a result of a rotation of about 20° of one group about the S—S bond. It appears, then, that the conformation of the SO_3 groups is not an intrinsic property of the tetrathionate ion, but one which is susceptible to change with the requirements of ionic coordination in which these groups are involved.

Similar rotations, but to a lesser degree, were found in the comparison of the tetrathionate ions reported here, with the two previous examinations of the same

Fig. 3. The coordination polyhedra of potassium ions out to 3·4 Å. (a) K(1), (b) K(2), (c) K(3), (d) K(4). Precise details of the geometry, including e.s.d.'s and symmetry code, have been deposited.

ions in different structures. The overall geometry of all four tetrathionate ions (two in the present structure, and one each in $Na_2S_4O_6.2H_2O$ and $BaS_4O_6.2H_2O$) is very similar. In sodium tetrathionate dihydrate (Foss & Hordvik, 1964), the center of the middle S–S bond is on a twofold axis. Thus there are only two S–S and three S–O distances to be determined in the structure. The central S–S bond is 2·02 (1) Å and the terminal bond is 2·12 Å. The S–O bonds are 1·46 (3), 1·46 (3) and 1·45 (2) Å. The torsional SSS/SSS angle is 90·4 ± 1. The earlier structure determination of barium tetrathionate dihydrate (Foss, Furberg & Zachariasen, 1954) showed S(1)–S(2) = 2·10, S(2)–S(3) = 2·02, S(3)–S(4) = 2·13 Å, all ±0·03 Å, with the S–O distances varying from 1·36 (4) to 1·45 (4) Å. Again the SSS/SSS torsional angle is 90°. Though somewhat less precisely determined, the angular geometries of these two tetrathionate ions are in good agreement with the geometries of the two ions in the structure reported here.

One interesting structural feature in a comparison of the three tetrathionate structures is the chirality of the ions found. $BaS_4O_6.2H_2O$ crystallizes in space group $P2_1/c$, and so both right-handed and left-handed tetrathionate ions exist in the structure. The present structure (space group Cc) contains a left-handed [S(1)–S(4)] ion, a right-handed [S(5)–S(8)] ion, and the mirror image of each of these. However, $Na_2S_4O_6.2H_2O$ crystallizes in space group $C2$, and has only the right-handed form in the crystal examined (this from the coordinates published – no attempt was made to define the absolute configuration). It appears, then, that the formation of this salt from solution must involve a classical crystallization of a racemate into right-handed and left-handed crystals, or a selective inversion to produce one (or other) form during crystallization.

The mean S–O bond length of 1·446 Å in the present structure compares very well with the mean S–O bond (1·444 Å) found in potassium trithionate (Stewart & Szymański, 1979). The shortest and longest S–O bonds in the present structure [S(4)–O(4) = 1·434 (7), S(5)–O(9) = 1·454 (10) Å] are about the same as the shortest and longest in potassium trithionate [1·440 (1), 1·455 (2) Å].

From Fig. 3 and the details of the angular geometry* it can be seen that the coordination polyhedra around the K ions are very irregular, the coordination numbers for the four ions, out to 3·4 Å, being 6, 9, 6 and 8 respectively. The K–O distances vary from 2·610 (5) to 3·269 (16) Å. These polyhedra serve as interionic bridges, linking the tetrathionate ions throughout the structure.

The thermal parameters obtained in the refinement* are reasonable, with the possible exception of those O atoms bonded to S(4) [O(4), O(5), O(6)], which are

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* See deposition footnote.

somewhat large [especially $U_{11} = 0.124$ Å² for O(6)]. However, a count of the O–K interactions in which the four SO_3 groups are involved shows that the total numbers of such bonds (and presumably restraining forces) are 8, 5, 8 and 7 for the four groups. The second SO_3 group is thus the least restrained, and the orientation of the thermal ellipsoids, as shown in Fig. 1, shows that this group is undergoing a rotational libration about the S(3)–S(4) bond. It has also been pointed out that it is this SO_3 group which is displaced relative to the corresponding group in the second tetrathionate ion, by a twist of some 20°. It is therefore quite probable that the SO_3 groups are free to rotate in solution, as in the liquid there would be no specific restraining forces to prevent such a rotation. However, the shape of the tetrathionate S skeleton, in terms of the greater electron density in the middle S–S bond and the torsional SSS/SSS near a right angle, appears to be now well established. These structural features have important implications in the study of the mechanism of oxidation of tetrathionate to sulfuric acid, which is known to occur in the waste effluent of sulfide mining operations.

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