The Atomic Arrangement in Potassium Trithionate Crystals $K_2S_3O_6$ and the Structure of the Trithionate Radical $(S_3O_6)^{-2}$.

By

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(With 2 figures.)

1. Introduction. For a considerable length of time we have been making systematic crystal structure investigations with the object of determining the shape and dimensions of inorganic groups. Lately we have concentrated our attention at oxygenic groups formed by atoms in the two first rows of the periodic system. Among these are the sulphur-oxygen radicals. When our systematic work began, the sulphate group was the only one of these radicals the structure of which was known. We have had the opportunity to add the sulphite radical[2]), the pyrosulphite radical[3]) and the persulphate radical[4]) to the list of known groups, while the structure of the dithionate radical[5]) has been determined elsewhere. In this paper we are describing a complete determination of the crystal lattice of potassium trithionate, which we undertook with the purpose of obtaining the structure of the trithionate group.

Crystals of potassium trithionate are described by Groth[6]) as orthorhombic holohedral with axial ratios .7166 · 1 · .4245. The density is given as 2.304.

From the firm de Haën in Hannover we purchased 50 g of the compound and from this sample we were able to obtain the crystal used in the investigation. It was needle-shaped and of approximate dimensions 0.2 × 0.2 × 1.2 mm. Measurements on the goniometer showed the presence of the following forms: (110), (210), (011), (010) and (120). All except the last form are reported by Groth.

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[1]) Some of the results of this paper were published in a note in the March issue of J. chem. Physics **2** (1934) 109.

[2]) Zachariasen, W. H., and Buckley, H. E., Physic. Rev. **37** (1931) 1295.

[3]) Zachariasen, W. H., Physic. Rev. **40** (1932) 923.

[4]) Zachariasen, W. H., and Mooney, R. C. L., Z. Kristallogr. **88** (1933) 63.

[5]) Huggins, M. L., and Glenn O. Frank, Am. Min. **16** (1931) 580.
Helwig, Z. Kristallogr. **83** (1932) 485.
Huggins, M. L., Z. Kristallogr. **86** (1933) 384.

[6]) Groth, P., Chemische Krystallographie **2**, 715. Leipzig 1908.

2. The Unit Cell and Space Group. The oscillation and the Laue method were used. For the former we employed *MoKa* radiation, for which a wave length of .7095 Å was assumed. The distance from the crystal to the photographic plate was 5.00 cm. Due to the fairly long dimensions of the unit cell we found it necessary to use oscillation angles of only 5°, so that a unique determination of the indices of the reflecting planes could be made in every case. Our oscillation data consisted of a complete set of 18 photographs around the *c*-axis, and in addition six photographs around each of the two other principal axes. In this manner we obtained a complete set of intensities, involving reflections from some 600 different crystallographic planes. Great care was taken in estimating the intensities, and any serious errors were ruled out due to the fact that every reflection occured on several plates.

Laue photographs were taken with the beam parallel to the *a* and *b* axes. The minimum wavelength was .26 Å. The Laue photographs served as a sensitive check on the correctness of the unit cell, and gave in many instances useful confirmations of the intensities observed in the oscillation photographs.

The size of the unit cell was found to be:

$$a = 9.77 \pm .04\ \text{Å} \qquad b = 13.63 \pm .04\ \text{Å} \qquad c = 5.76 \pm .02\ \text{Å}.$$

These values correspond to axial ratios .7165 : 1 : .4226, while the Laue photographs independantly gave the ratios .7165 : 1 : 4206.

With four molecules per unit cell we calculate a density of $2.33_5 \pm .02_6$ as against the observed density of 2.304.

The following classes of reflections were absent: $h0l$ if h is odd and $0kl$ if $k + l$ is odd. This shows that the there is a glide plane parallel to the *a*-face with translation $b/2 + c/2$, and also a glide plane parallel to the *b*-face with translation $a/2$. Since the symmetry of the crystals is reported to be holohedral (we could find no observations contradicting this statement), the *c*-face must be a reflection plane. The unit cell contains so many atoms that we safely may assume some of them to occupy general positions. Hence the space group in Pnam (V_h^{16}). All atomic coordinates given in this paper refer to a center of symmetry as origin.

Our next problem is to find how the atoms are distributed between the available positions of the space group. Special positions (four-fold) are centers of symmetry (no degree of freedom) and reflection planes (two degrees of freedom).

In the first place we note that the length of the c-axis is only 5.76 Å. Consequently for atoms lying in general positions interatomic distances cannot be greater than 2.88 Å. In order that equivalent atoms in general positions be separated by reasonable distances, the parameter y cannot be greatly different from zero. We notice further that all even orders from the c-face occur with very great intensity. This observation together with considerations of the intensities for reflections $h0l$ and $0kl$ lead with reasonable certainty to the conclusion that two sets of eight oxygen atoms occupy general positions, while all the remaining atoms are lying in the reflection planes. We have thus 20 parameters to determine:

$$K_{\mathrm{I}}\,(u_1v_1\tfrac{1}{4})\quad K_{\mathrm{II}}\,(u_2v_2\tfrac{1}{4})\quad S_{\mathrm{I}}\,(u_3v_3\tfrac{1}{4})\quad S_{\mathrm{II}}\,(u_4v_4\tfrac{1}{4})\quad S_{\mathrm{III}}\,(u_5v_5\tfrac{1}{4})\quad O_{\mathrm{I}}\,(u_6v_6\tfrac{1}{4})$$

$$O_{\mathrm{III}}\,(u_7v_7\tfrac{1}{4})\quad O'_{\mathrm{I}}\,(x_1y_1z_1) \text{ and } O'_{\mathrm{III}}\,(x_2y_2z_2)$$

Throughout the paper we shall prefer to give all coordinates in angular measure.

3. Determination of the Parameters. Of the 20 parameters involved only two are in the z-direction. Considerations of the observed intensities for the $00l$ reflections show that the values $2\pi z_1 = 2\pi z_2 = 45°$ give good agreement.

It proves to be possible to determine four more of the parameters without serious difficulties, namely the parameters $x_1\, x_2\, y_1\, y_2$.

To determine x_1 and x_2 consider the expressions for the structure amplitudes of reflections $h0l$. Using the known values for z_1 and z_2 the expressions become:

$h00$	$A + B$	$h04$	$A + .50\,B$	$h01$	$-A' - .26\,B'$
$h02$	$-A + .87\,B$	$h06$	$-A$	$h03$	$A' - .71\,B'$
				$h05$	$-A' - .97\,B'$

$$\begin{aligned} \text{where}\quad A &= 4\,\Sigma f\,\cos\,2\pi h u & B &= 8 f_0\,[\cos 2\pi h x_1 + \cos\,2\pi h x_2] \\ A' &= 4\,\Sigma f\,\sin\,2\pi h u & B' &= 8 f_0\,[\sin 2\pi h x_1 + \sin 2\pi h x_2] \end{aligned}$$

In a series like $h00$, $h02$, $h04$, $h06$ (h constant) the terms A and B decrease gradually due to the drop in the scattering powers. From the observed intensities for any such series it is now possible to obtain information about the magnitudes and relative signs of the terms A, B, A' and B'. F. ex. we have the series: 200 vw. 202 w. 204 nil. It follows that the terms A and B both are small and of opposite sign, hence we conclude $|\cos 2\pi 2\,x_1 + \cos 2\pi 2\,x_2|$ is small. In this manner we get the following results:

		calculated
$\lvert \cos 2\pi 2 x_1 + \cos 2\pi 2 x_2 \rvert$	small	.33
$\lvert \sin 2\pi 2 x_1 + \sin 2\pi 2 x_2 \rvert$	small	.12
$\lvert \cos 2\pi 4 x_1 + \cos 2\pi 4 x_2 \rvert$	very large	1.44
$\lvert \sin 2\pi 4 x_1 + \sin 2\pi 4 x_2 \rvert$	very large	1.21
$\lvert \cos 2\pi 6 x_1 + \cos 2\pi 6 x_2 \rvert$	very small	.50
$\lvert \sin 2\pi 6 x_1 + \sin 2\pi 6 x_2 \rvert$	medium large	.87

This list gives uniquely $2\pi x_1 = 30°$ $2\pi x_2 = 130°$.

By a similar procedure values of y_1 and y_2 can be found without difficulty. We found: $2\pi y_1 = 100°$ $2\pi y_2 = 150°$. (It should be mentioned that the accurate values for these four parameters were obtained by using the procedure outlined above on a large number of series of general planes: $hk0$, $hk2$, $hk4$ . . and $hk1$, $hk3$, $hk5$.)

Being now in position to calculate the terms B and B', we are able to get a more detailed information about the terms A and A', which involve the remaining seven parameters in the x-direction. (From an analogous discussion of reflections $0kl$ we get detailed information about similar terms involving the remaining seven parameters in the y-direction.) However, it was not easy to determine the parameter values, and we succeeded only after a great deal of labour.

Due to the similarity in scattering powers it was not possible to distinguish between potassium and sulphur atoms from intensity calculations. However, inspection of the interatomic distances at once told which of the atoms were sulphur atoms and which potassium atoms.

In table I are listed the parameter values. Tables II and III contain about half of the observations we obtained from the rotation photographs. The observed intensities are listed in the columns headed I, while the calculated amplitudes are denoted by F. If only neighbouring reflections are compared, the intensities may be put proportional to the amplitudes (extinction is great) or proportional to the squares of the amplitudes (extinction is small). In the absence of any knowledge of the extinction coefficient the observed intensities are compared directly with the amplitude.

Table I. Parameter Values.

	$2\pi x$	$2\pi y$	$2\pi z$		$2\pi x$	$2\pi y$	$2\pi z$
K_{I}	$47° = u_1$	$32° = v_1$	90°	O_{I}	$-45° = u_6$	$110° = v_6$	90°
K_{II}	$65 = u_2$	$-85 = v_2$	90°	O_{III}	$125 = u_7$	$210 = v_7$	90
S_{I}	$12 = u_3$	$115 = v_3$	90	O'_{I}	$30 = x_1$	$100 = y_1$	$15 = z_1$
S_{II}	$30 = u_4$	$170 = v_4$	90	O'_{III}	$130 = x_2$	$150 = y_2$	$15 = z_2$
S_{III}	$110 = u_5$	$170 = v_5$	90				

Table II. Selected Data from Oscillation Photographs Around c-axis.

$hk0$	$\sin\theta/\lambda$	I	$\|F\|$	$hk1$ I	$hk1$ $\|F\|$	$hk2$ I	$hk2$ $\|F\|$	$hk3$ I	$hk3$ $\|F\|$
010	.037	nil	0	vs	66	nil	0	nil	1
110	.063	nil	29	s	51	w	14	w—	16
020	.073	tr	11	nil	0	m.	32	nil	0
120	.090	vw.	14	m—	30	s	57	wm	30
200	.102	vw.	6	s	83	m	30	s	73
210	.109	vw.	10	vs	81	w—	18	m	48
030	.110	nil	0	vs	114	nil	0	vs	86
130	.121	s	53	vs	77	nil	8	s	65
220	.126	m	36	w	31	vvw	13	nil	18
040	.147	m	84	nil	0	w	53	nil	0
230	.150	m—	51	m	53	vs	167	w—	24
140	.155	nil	3	s	82	w—	27	w—	30
310	.158	vs	148	nil	9	m	70	vw	9
320	.170	tr	13	m—	46	w	41	w—	19
240	.179	w	20	w	27	m	51	nil	12
050	.184	nil	0	vvw	7	nil	0	w	21
330	.189	tr	4	nil	2	vw	5	nil	14
150	.190	vs	154	w	28	w	47	wm	36
400	.205	vs	144	m.	69	vw	29	vw	29
410	.208	vs	124	vw—	18	w—	43	vw—	15
250	.210	nil	6	nil	6	nil	9	nil	4
340	.212	w—	30	w	43	nil	14	nil	14
420	.218	w	35	m.	94	vw.	33	s	95
060	.220	m.	91	nil	0	vw	18	nil	0
160	.226	s	88	m	72	w.	53	w—	38
430	.232	w.	55	m	49	w—	21	w—	30
350	.239	vw	42	wm	50	vw—	12	w—	36
260	.243	ms	58	m—	47	m—	57	w.	52
440	.252	nil	14	nil	9	vvw	7	nil	1
070	.257	nil	0	s.	142	nil	0	s	142
510	.258	m	43	w.	42	wm	48	w	55
170	.262	w	35	w—	53	wm	46	m—	71
520	.266	w.	58	vvw	15	m	86	tr	13
360	.268	w	42	nil	3	nil	2	nil	6
450	.275	s—	92	vw—	29	w—	47	nil	7
270	.276	nil	6	nil	0	nil	3	nil	2
530	.279	w.	71	w.	41	wm	42	w—	29
080	.294	w	31	nil	0	nil	11	nil	0
540	.295	vw	19	w—	33	w	41	w	51
180	.298	w	38	m—	33	m—	93	w.	37

Scale of intensities:

vs s. s s— ms m. m m— wm w. w w— vw. vw vw— vvw tr

Table III. Selected Data from Oscillation Photographs Around *b*-axis.

*h*0*l*	sin θ/λ	*h*0*l*		*h*1*l*		*h*2*l*		*h*3*l*	
		I	|*F*|	*I*	|*F*|	*I*	|*F*|	*I*	|*F*|
001	.087	nil	0	s	66	nil	0	vs	114
101	.105	nil	0	s	51	w.	30	vs	77
002	.174	vs	204	nil	0	w.	32	nil	0
102	.190	nil	0	w —	14	m	57	nil	8
202	.209	w.	30	vw	18	nil	13	vs	167
003	.261	nil	0	nil	1	nil	0	s —	86
103	.279	nil	0	vvw	16	w —	30	m	65
203	.292	s	73	w.	48	vvw	18	vw	24
303	.314	nil	0	vw —	9	vw	19	nil	14
004	.348	vs	229	nil	0	nil	12	nil	0
104	.369	nil	0	nil	1	nil	2	vw —	21
204	.379	nil	6	nil	3	nil	13	vw	59
304	.396	nil	0	m	79	nil	1	nil	7
404	.419	w	65	w.	69	vvw	28	vvw	26
005	.436	nil	0	vw.	54	nil	0	m —	72
105	.459	nil	0	w —	39	nil	12	w —	41
205	.468	w —	56	w —	52	w —	33	w —	40
006	.523	m	157	nil	0	nil	14	nil	0

hkl	*h*4*l*		*h*5*l*		*h*6*l*		*h*7*l*		*h*8*l*	
	I	|*F*|	*I*	|*F*|	*I*	|*F*|	*I*	|*F*|	*I*	|*F*|
0*k*1	nil	0	vw.	7	—		—		—	
1*k*1	vs	82	w.	28	s	72	w	53	m	33
0*k*2	w	53	nil	0	vw	18	nil	0	—	
1*k*2	w	27	w	47	w	53	w.	46	m	93
2*k*2	w.	51	nil	9	m —	57	nil	3	—	
0*k*3	nil	0	w	21	nil	0	m	142	nil	0
1*k*3	vw	30	w.	36	w	38	m	71	w	37
2*k*3	nil	12	nil	4	w	52	nil	2	nil	6
3*k*3	nil	14	w —	36	nil	6	w —	41	w	50
0*k*4	w	53	nil	0	vvw	29	nil	0	—	
1*k*4	nil	5	m —	77	m —	59	vw —	29	w —	45
2*k*4	vw	23	nil	7	w —	43	nil	6	vw	37
3*k*4	vw	19	nil	7	nil	22	w —	36		
4*k*4	nil	7	w.	61	w.	59	w	47		
0*k*5	nil	0	nil	24	nil	0	w	92		
1*k*5	w.	60	vvw	24	vw	54				
2*k*5	nil	28								

Values for the scattering powers were taken from the tables of James and Brindley1) assuming the atoms to be present as K^{+1}, S^{+1}, O^{-1}.

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1) James, R. W., and Brindley, G. W., Z. Kristallogr. 78 (1931) 470.

4. Discussion of Results. Fig. 1 represents a projection of the atomic arrangement on the c-face. In agreement with expectation three sulphur atoms and six oxygen atoms are grouped together in the structure to form the trithionate radicals. Fig. 2 shows the architecture of the radical. The two sulphur atoms S_{I} and S_{III} are each bonded to three oxygen atoms and to the common sulphur atom S_{II}. The latter is only linked to two sulphur atoms S_{I} and S_{III}.

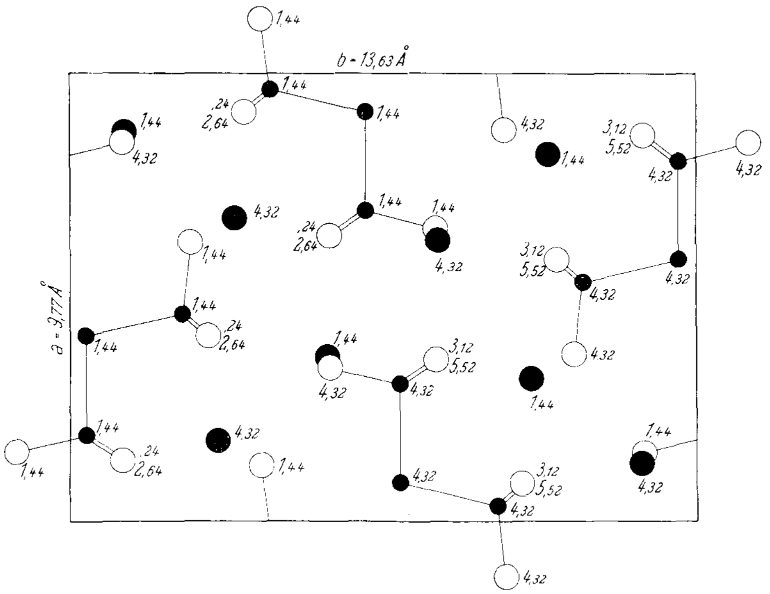

Fig. 1. Projection of the structure of $K_2S_3O_6$ on the c-face. Small filled circles represent sulphur atoms, large filled circles represent potassium atom and open circles oxygen atoms. The attached numbers give the height of the atoms above the c-face. Only the bonds within the trithionate radicals are drawn.

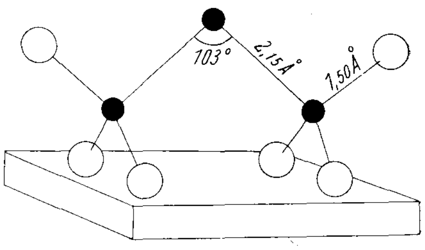

Fig. 2. The structure of the trithionate radical.

The distance from S_{I} or S_{III} to the three oxygen atoms lie between 1.42 Å and 1.57 Å, with an average value of 1.50 Å. The spread in the observed values must be attributed to slight inaccuracy in the parameter values. The distances S_{I}—S_{II} and S_{III}—S_{II} are 2.14 Å and 2.17 Å.

The distances *S—O* and *S—S* observed in other crystals are:

	S—O		*S—S*
$Na_2SO_3$1)	1.39 Å	$FeS_2$5)	2.14 Å
$Na_2SO_4$2)	1.49	$K_2S_2O_5$3)	2.18
$K_2S_2O_5$3)	1.47		
$(NH_4)_2S_2O_8$4)	1.50		

In all these cases one generally supposes that the atoms are linked together by a single electron pair bond. The values given above are not sufficiently accurate to show what effect the number and distribution of the bonds have on the interatomic distances. We can only conclude that this effect is very small.

The set of covalent radii published by Pauling and Huggins6) gives $S:O = 1.70$ Å and $S:S = 2.08$ Å. The lack of agreement for the former distance (there is a similar difficulty with *Si—O*, *P—O*, *Cl—O*) is rather serious in view of the rather accurate predictions of interatomic distances which this set of radii generally permits.

The four bonds of the sulphur atoms S_{I} and S_{III} in the trithionate group are very nearly directed towards the corners of a tetrahedron, while the angle between the two bonds of S_{II} is 103°.

Like all other radicals of the type $(S_mO_n)^{-2}$ we may interpret the trithionate group in terms of only single electron pair bonds, writing $(O_3^{-1}S^{+2}S\,S^{+2}O_3^{-1})^{-2}$. The observed structure would not be in disagreement with such an interpretation.

It is worth noticing that the symmetry of the trithionate radical is fairly high; only one of the reflection planes results from the space group symmetry.

There are two sets of potassium atoms in the structure, K_{I} and K_{II}; the coordination number with respect to oxygen is 9 for both sets. The individual *K—O* distances are:

$K_{\mathrm{I}}—O_{\mathrm{I}}$	2.78 Å	1	$K_{\mathrm{II}}—O_{\mathrm{I}}$	3.08 Å	2
$—O_{\mathrm{III}}$	2.89	2	$—O_{\mathrm{III}}$	2.95	1
$—O'_{\mathrm{I}}$	2.88	2	$—O'_{\mathrm{I}}$	2.85	2
$—O'_{\mathrm{III}}$	2.89	4	$—O'_{\mathrm{I}}$	3.11	2
			$—O'_{\mathrm{III}}$	2.71	2
Average $K_{\mathrm{I}}—O$	2.88 Å		Average $K_{\mathrm{II}}—O$	2.94 Å	

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1) Zachariasen, W. H., and Buckley, H. E., Physic. Rev. **37** (1931) 1295.
2) Zachariasen, W. H., and Ziegler, G. E., Z. Kristallogr. **81** (1932) 92.
3) Zachariasen, W. H., Physic. Rev. **40** (1932) 923.
4) Zachariasen, W. H., and Mooney, R. C. L., Z. Kristallogr. **88** (1934) 63.
5) Parker, H. M., and Whitehouse, W. J., Philos. Mag. **14** (1932) 939.
6) Pauling, L., and Huggins, M. L., Z. Kristallogr. **87** (1934) 205.

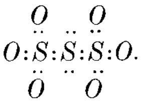
The K—O distance for coordination number 9 found in other crystals varies from 2.88 Å to 3.01 Å, while the value calculated from the ionic radii of the author[1]) is 2.93 Å.

The distance between oxygen atoms belonging to different radicals goes down to 3.21 Å. This is somewhat lower than the value 3.34 Å predicted from the radii of the writer; but nevertheless considerably greater than to be expected from the oxygen radius used by Goldschmidt or Pauling.

Summary. The orthorhombic unit cell of potassium trithionate has dimensions: $a = 9.77$ Å $b = 13.63$ Å $c = 5.76$ Å, and contains 4 molecules $K_2S_3O_6$. The space group is Pnam (V_h^{16}). Two sets of eight oxygen atoms are lying in general positions, while all the remaining atoms are lying in the reflection planes. The values of the 20 parameters involved were rigorously determined from the intensities of reflections observed in oscillation photographs. Their values are give in table I.

Both kinds of potassium atoms have a coordination number of 9, with an average K—O distance of 2.91 Å.

The trithionate group can be represented by the structural formula:



$$\begin{array}{ccccccc} & O & & & & O & \\ & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & \\ O: & S & : & S & : & S & :O. \\ & \cdot\cdot & & \cdot\cdot & & \cdot\cdot & \\ & O & & & & O & \end{array}$$

The S—O distance is 1.50 Å and the S—S distance is 2.15 Å. The angle between the two S—S bonds is 103°.

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[1]) Zachariasen, W. H., Z. Kristallogr. 80 (1931) 137.

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Received August 21st, 1934.