Acta Cryst. (1969). B**25**, 1696

The Crystal Structure of Potassium Pentasulphate $K_2S_5O_{16}$

BY R. DE VRIES AND F. C. MIJLHOFF

Laboratory for Inorganic Chemistry, University of Amsterdam, Holland

(*Received* 17 *June* 1968 *and in revised form* 23 *August* 1968)

Crystals of $K_2S_5O_{16}$ are orthorhombic, space-group *Pbcn*, with $a=9{\cdot}19$, $b=10{\cdot}891$ and $c=14{\cdot}522$ Å. The unit cell contains eight K^+ and four $S_5O_{16}^{2-}$ ions with the central sulphur atom on a twofold axis. As in $S_3O_{10}^{2-}$ the anion consists of a chain of SO_4 pseudo-tetrahedra, sharing an oxygen atom, the S–O bridge distances being alternately short and long. The S–O bridge bond length to the terminal group is 0·14 Å greater than the single-bond length calculated by the Schomaker–Stevenson equation.

Introduction

The investigation of compounds of the formula $K_2O.nSO_3$ was started in order to obtain a better insight into the chemical constitution of various polysulphates formed on reaction of SO_3 with K_2SO_4. During this reaction two liquid phases are formed (Weber, 1884), the upper layer being SO_3. The denser layer has a composition $K_2O.nSO_3$ with n about 8 to 10, from which upon standing, solid polysulphates with n about 5 to 6 crystallize, liberating SO_3.

Experimental

A small needle (diameter about 0·2 mm) of the very hygroscopic material was isolated and sealed in a thin-walled glass capillary. A zero-level Weissenberg photograph about [100], superposed with Al-powder lines ($a=4{\cdot}0491$ Å at 20°), was prepared for calibration purposes using copper radiation. The dimensions of the b and c axes as listed in Table 1 were derived from the glancing angles of the $0kl$ reflexions by a least-squares procedure. Owing to the needle shape, no suitable calibration photograph for computing the a axis could be made. The length of the a axis was derived from a precession photograph containing the $hk0$ reflexions, with the known b axis as reference. Systematically absent reflexions ($0kl$ for $k=2n+1$, $h0l$ for $l=2n+1$ and $hk0$ for $h+k=2n+1$) uniquely determine the space group to be *Pbcn* (No. 60).

A set of equi-inclination Weissenberg photographs with three different exposure times for each layer was made about [100], levels 0 to 7, at room temperature with molybdenum radiation. The reflexions $hk0$, $hk1$ and $hk2$ were recorded with a precession camera by use of molybdenum radiation.

The intensities of the reflexions were measured with a densitometer and converted to structure factor moduli in the usual way, with allowance for spot-shape variations. Several reflexions occuring more than once on different photographs enabled us to put all structure factors on a common relative scale. Corrections for absorption effects were deemed unneccessary.

Table 1. *Crystal data of* $K_2S_5O_{16}$

The indicated errors are three times the standard deviations

Cell dimensions:	$a=9{\cdot}19\pm0{\cdot}04$ Å*
	$b=10{\cdot}891\pm0{\cdot}003$ Å
	$c=14{\cdot}522\pm0{\cdot}004$ Å
Space group:	*Pbcn*
Number of molecules per cell:	$Z=4$
Calculated density:	d(X-ray) = 2·26 g.cm^{-3}
Absorption coefficient:	$\mu=1{\cdot}4$ cm^{-1} (Mo radiation)

* *Note added in proof:* – Recently we found accidentally a crystal more suitable for obtaining a precise value for the a axis, *viz.* $9{\cdot}172\pm0{\cdot}003$Å, 2 ‰ less than our estimate. Recalculation of the distances results in S–O distances 0·001Å shorter and S–S distances 0·002Å longer than those listed in Table 4. The angles are not significantly affected.

Determination of the structure

Initially it was not known with which of the polysulphates ($K_2O.nSO_3$) we were dealing. Since only fourfold and eightfold positions occur in the space group *Pbcn* the number of molecules per cell must be a multiple of four. Calculated density values which agree approximately with those of K_2SO_4 (2·24 – 2·61 g.cm^{-3}) and $K_2S_2O_7$ (2·27 g.cm^{-3}) were found only with $n=4,5$ and 6 (1·89, 2·26 and 2·62 g.cm^{-3} respectively).

If n is odd, one sulphur atom of the anion must be at a special position, and if n is even, one oxygen atom of the anion must be at a special position. The space group *Pbcn* offers special positions with point symmetry $\bar{1}$ or 2. The former would require the anion to have a linear S–O–S or O–S–O arrangement which is very unlikely. It is therefore assumed that the anion has C_2 symmetry with its odd atom at the special position 4(c). Assuming an oxygen atom ($n=4$ or 6) at a twofold axis, a strong Patterson peak in the plane $y=0$, representing the distance between symmetry-related sulphur atoms bound to this oxygen atom, should be found at about 2·9 Å (*cf.* $S_3O_{10}^{2-}$, Eriks & MacGillavry, 1954) from the origin. Since no such peak was found, we assumed the compound to have $n=5$ and the formula $K_2S_5O_{16}$, with a sulphur atom at the special position 4(c).

By systematically scanning the Patterson function for Harker peaks positional coordinates were found for two sulphur atoms and one potassium atom in the general position 8(d) and one sulphur atom in the special position 4(c).

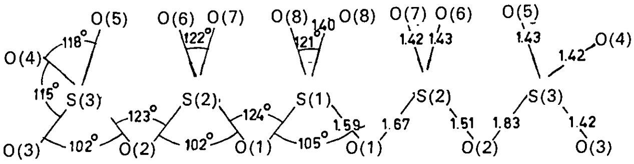

Fig. 1. Numbering of the atoms and interatomic distances and angles in the $S_5O_{16}^{2-}$ ion.

The oxygen atoms were found by Fourier analysis, starting with the structure factors the signs of which could be derived with reasonable confidence from the sulphur and potassium position found from the Patterson. The structure was further refined by the least-squares method, finally with the use of anisotropic individual temperature factors. Rather large discrepancies were found for about twenty very strong reflexions, F_{obs} being systematically smaller than F_{calc}, indicating extinction effects. The weighting scheme was changed so as to give these reflexions a low weight (about 10%) and the least-squares refinement was repeated till convergence. The final agreement index R

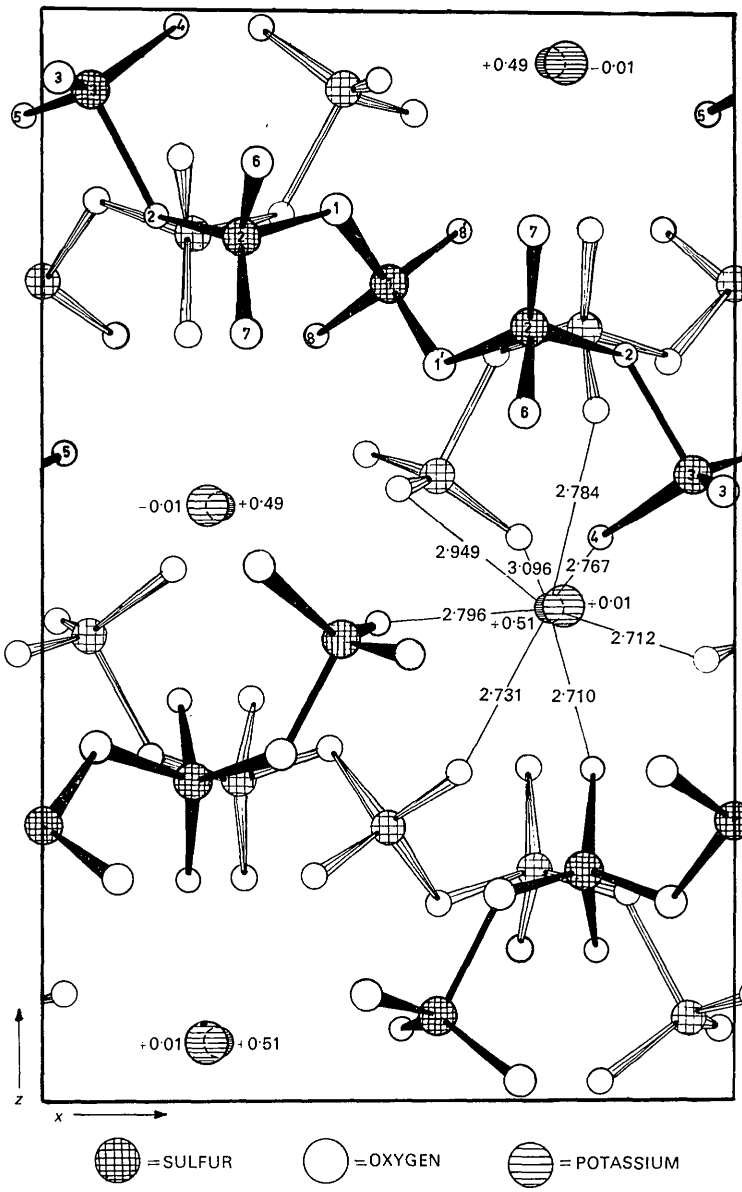

Fig. 2. Projection of the unit cell along [010]. The y axis is pointing downwards. The numbers next to the potassium atoms are their y coordinates.

is 0·094 for 1017 observed reflexions. A list of structure factors is available on request.

In Table 2 the atomic coordinates, and in Table 3 the thermal parameters given by the temperature factor $\exp[-2\pi^2(U_{11}a^{*2}h^2+\ldots+2U_{12}a^*b^*hk+\ldots)]$, and their respective standard deviations are listed. The atoms are labelled in accordance with Figs. 1 and 2. In order to distinguish between the angles around the central sulphur atom S(1), two of the oxygen atoms are primed in Fig. 2.

Discussion of the structure

Atomic distances are listed in Table 4, bond angles in Table 5 and oxygen–oxygen distances in the SO_4 groups in Table 6. The contribution of the uncertainty of the estimate of the a-axis to the variance of the distance is given by

$$v_a=[a(\Delta x)^2/r]^2\sigma_a^2 .$$

If we take $\sigma_a=0{\cdot}013$ the correction proves to be negligible in all cases except the S(1)–S(2) distance, which has been corrected in this way. The influence on the standard deviations of the angles has been estimated by calculating the angles twice, first with $a=9{\cdot}19$ and then with $a=9{\cdot}19\pm0{\cdot}013$. The discrepancies were regarded as the error resulting from the uncertainty in the a axis alone. Again the contribution to the variance proved to be negligible. The distances between K and O atoms shorter than 3·7 Å are indicated in Fig. 2. Their standard deviations are all about 0·009 Å. The K^+ ions are situated close to the b and c glide planes, forming layers at approximately $y=0$ and $y=\frac{1}{2}$, with the $S_5O_{16}^{2-}$ chains in between. They are surrounded by eight oxygen atoms if distances shorter than 3·7 Å are considered. The largest K–O separation is 3·10 Å.

The two halves of the $S_5O_{16}^{2-}$ ion are related by a twofold axis passing through the central sulphur atom. The S–O (bridge) distances are alternately short and long going from S(1) along the chain. The bridge angles S–O–S and O–S–O are about 123° and 102° respectively. The angles between the non-bridging oxygen atoms and S(1) and S(2) are about 122°. The O–O and S–O distances belonging to the SO_4 groups at the ends of the anion chains indicate that the tetrahedral configuration around the terminal sulphur atoms is distorted. The sulphur atoms are shifted from the centres of the pseudo-tetrahedra towards the three non-briding oxygen atoms, giving nearly C_{3v} symmetry at the terminal sulphur atoms. The angles between the bond O(2)–S(3) and the bonds from S(3) to O(3), O(4) and O(5) are about 100°; the dihedral angles between the planes through O(2), S(3) and each of the three other oxygen atoms are about 120°. The O(2)–S(3) bond is exceptionally long (1·83 Å), which is much geater than the assumed single bond separation of 1·69 Å, calculated by the Schomaker–Stevenson equation (Schomaker & Stevenson, 1941). This indicates a large contribution of the sulphur d_{z^2} orbital to the S–O σ-bond. Since the terminal group is almost planar it may be considered as a SO_3 molecule weakly bound to the chain.

As the dihedral angle between the planes O(1)–S(1)–O(1′) and S(1)–O(1′)–S(2) is 67° the configuration around the S(1)–O(1) bond is almost staggered. This

Table 2. *Atomic coordinates and standard deviations of the asymmetric unit in fractions of cell edges*

	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$
S(1)	0·0000	0·1679	0·2500	0·00000	0·00031	0·00000
S(2)	0·2169	0·3478	0·2955	0·00033	0·00023	0·00016
S(3)	0·4306	0·2514	0·4268	0·00031	0·00025	0·00019
K^+	0·2430	0·0098	0·0476	0·00031	0·00020	0·00013
O(1)	0·077	0·257	0·322	0·0009	0·0007	0·0004
O(2)	0·345	0·265	0·314	0·0010	0·0008	0·0005
O(3)	0·488	0·371	0·439	0·0011	0·0007	0·0006
O(4)	0·310	0·223	0·484	0·0010	0·0008	0·0006
O(5)	0·529	0·154	0·405	0·0012	0·0009	0·0008
O(6)	0·203	0·443	0·362	0·0011	0·0007	0·0006
O(7)	0·208	0·372	0·200	0·0011	0·0008	0·0005
O(8)	0·104	0·105	0·198	0·0012	0·0008	0·0007

Table 3. *Thermal parameters in* 10^{-4} Å^2

	U_{11}	σ	U_{22}	σ	U_{33}	σ	$2U_{12}$	σ	$2U_{23}$	σ	$2U_{31}$	σ
S(1)	157	21	170	14	233	15	0	0	0	0	40	33
S(2)	227	16	237	10	163	8	−66	23	−6	18	−183	24
S(3)	146	13	215	10	313	11	5	25	−61	21	−124	24
K^+	233	12	233	9	208	7	−84	20	54	16	50	25
O(1)	165	41	344	38	155	26	−76	78	41	61	−7	59
O(2)	336	51	376	44	208	33	42	84	−157	66	7	71
O(3)	388	57	252	36	451	47	−279	81	−164	71	−279	94
O(4)	278	53	476	52	338	42	−264	87	480	77	197	79
O(5)	392	67	422	50	809	75	493	100	−273	108	−353	120
O(6)	470	63	245	37	442	49	207	85	−153	70	−511	93
O(7)	525	68	420	46	225	33	−555	95	196	68	−289	85
O(8)	310	57	408	49	514	54	346	87	−338	89	53	98

Table 4. *Interatomic distances and standard deviations in* Å*

	r	σ		r	σ
S(1)–O(8)	1·403	0·010	S(3)–O(2)	1·826	0·008
S(1)–O(1)	1·587	0·008	S(3)–O(3)	1·416	0·009
S(2)–O(1)	1·668	0·008	S(3)–O(4)	1·415	0·009
S(2)–O(2)	1·507	0·009	S(3)–O(5)	1·425	0·011
S(2)–O(6)	1·427	0·009	S(1)–S(2)	2·873	0·005
S(2)–O(7)	1·415	0·008	S(2)–S(3)	2·931	0·004

* See footnote page 1696.

Table 5. *Bond angles and standard deviations in the* $S_5O_{16}^{2-}$ *ion*

	α	σ		α	σ
O(8)–S(1)–O(8′)	121·1°	0·8°	O(2)–S(2)–O(7)	109·2°	0·5°
O(1)–S(1)–O(1′)	104·6	0·6	O(2)–S(3)–O(3)	101·5	0·5
O(1)–S(1)–O(8)	110·5	0·5	O(2)–S(3)–O(4)	101·7	0·5
O(1)–S(1)–O(8′)	104·6	0·5	O(2)–S(3)–O(5)	97·5	0·6
O(1)–S(2)–O(2)	101·8	0·5	O(3)–S(3)–O(4)	115·0	0·6
O(6)–S(2)–O(7)	121·6	0·5	O(3)–S(3)–O(5)	118·2	0·6
O(1)–S(2)–O(6)	102·0	0·5	O(4)–S(3)–O(5)	117·5	0·6
O(1)–S(2)–O(7)	107·0	0·5	S(1)–O(1)–S(2)	123·9	0·4
O(2)–S(2)–O(6)	113·0	0·5	S(2)–O(2)–S(3)	122·8	0·5

Table 6. *Oxygen–oxygen distances in the* SO_4 *groups and their standard deviations in* Å

	r	σ		r	σ
Around S(1)					
O(1)–O(1′)	2·51	0·014	O(1)–O(8)	2·46	0·012
O(8)–O(8′)	2·44	0·021	O(1)–O(8′)	2·37	0·013
Around S(2)					
O(1)–O(2)	2·47	0·012	O(6)–O(7)	2·48	0·012
O(1)–O(6)	2·41	0·012	O(2)–O(7)	2·38	0·012
O(1)–O(7)	2·48	0·011	O(2)–O(6)	2·45	0·012
Around S(3)					
O(2)–O(3)	2·52	0·012	O(4)–O(5)	2·43	0·014
O(2)–O(4)	2·53	0·011	O(3)–O(5)	2·44	0·012
O(2)–O(5)	2·46	0·014	O(3)–O(4)	2·39	0·013

is not the case for the S(2)–O(1) and the S(2)–O(2) bonds, the corresponding dihedral angles being about 88°. The crystal structure of $(NO_2^+)_2S_3O_{10}^{2-}$ was determined by Eriks & MacGillavry (1954) and refined by Cruickshank (1964). There are many similarities between the $S_3O_{10}^{2-}$ and the $S_5O_{16}^{2-}$ ion; the terminal groups in the two anions are almost identical. Although in the former anion the S–O bridge bond in the terminal group is 0·1 Å shorter, it is also exceptionally long. Since Cruickshank's estimated standard deviations of the bond lengths are about 0·05 Å the question of whether the difference might be significant can only be settled if a more accurate structure determination of a $S_3O_{10}^{2-}$ compound is carried out. At present the S–O bridge bond in the terminal group of $S_3O_{10}^{2-}$ may be regarded as intermediate between the S(3)–O(2) and S(2)–O(1) bond lengths in $S_5O_{16}^{2-}$. The S–O (bridge) distance (1·54 Å) to the central sulphur atom in $S_3O_{10}^{2-}$ is between those of S(1)–O(1) and S(2)–O(2) in $S_5O_{16}^{2-}$.

The non-bridging S–O separations in $S_3O_{10}^{2-}$ are 1·42 Å for the end group and 1·38 Å for the central sulphur atom, and about the same distances are found in $S_5O_{16}^{2-}$. The bond angles we find agree favourably with those of $S_3O_{10}^{2-}$, but the O–S–O bridge angle (101°) in $S_3O_{10}^{2-}$ is closer to the O(1)–S(2)–O(2) angle (102°) than to the central bridge angle (105°).

The authors wish to express their gratitude to Professor H. Gerding for initiating this research, Mr A. Kreuger for his skilful preparation of the photographs and Professor C. H. MacGillavry and Dr C. Romers for their advice in preparing this paper.

References

Cruickshank, D. W. J. (1964). *Acta Cryst.* **17**, 684.

Eriks, K. & MacGillavry, C. H. (1954). *Acta Cryst.* **7**, 430.

Schomaker, V. & Stevenson, D. P. (1941). *J. Amer. Chem. Soc.* **63**, 37.

Weber, R. (1884). *Ber. dtsch. chem. Ges.* **17**, 2497.