Acta Cryst. (1962). **15**, 765

The Crystal Structure of Potassium-O-O-dimethyl-phosphordithioate

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(*Received* 18 *October* 1961 *and in revised form* 4 *December* 1961)

The structure of $KS_2P(OCH_3)_2$ has been determined and refined by least-squares adjustment of the combined data of four projections. It consists of $[S_2P(OCH_3)_2]^-$ ions and of potassium ions in an irregular eight-coordination.

Potassium-O-O-dimethylphosphordithioate,

$$K[S_2P(OCH_3)_2]\ ,$$

was prepared some years ago (Ketelaar & Gersmann, 1958) in this laboratory, and preliminary X-ray work has been reported (Gersmann, 1956). The structure analysis is presented in this paper.

Morphology

$K[S_2P(OCH_3)_2]$ crystallizes from dioxane solution in fairly large colourless crystals. Goniometer measurements reveal that these have either orthorhombic or tetragonal symmetry. They show predominantly the bipyramid {111}, with a trace of the prism {110}, the assignment of indices being based on subsequent X-ray determination of the unit cell. The axial ratio is

$$a:b:c=1:1:0{\cdot}67\ .$$

The crystal used for goniometric measurement was somewhat opaque and signals were not accurate to better than 1°.

Optics

The crystals have no pronounced cleavage and their habit is not favourable for optical investigation. However, fragments show clearly that the substance is optically biaxial, the c-axis being parallel to the acute bisectrix.

Cell dimensions, space group etc.

Crystals were cut along [001], [100], [1$\bar{1}$0], and [10$\bar{1}$], and Weissenberg diagrams made about these axes, mainly with Cu K radiation.

The cell edges were determined from least-squares adjustment of $\sin^2\theta$ values of $hk0$ and hhl reflexions, calibrated with an Al powder diagram.

$$a=17{\cdot}21\pm0{\cdot}04,\quad b=17{\cdot}50\pm0{\cdot}04,\quad c=11{\cdot}45\pm0{\cdot}03\ \text{Å}\ .$$

By flotation in mixtures of $CHCl_3$ and CCl_4 the density was found to lie between 1·49 and 1·54 g.cm.$^{-3}$. With 16 molecules $KS_2P(OCH_3)_2$ per unit cell, the X-ray density 1·50 g.cm.$^{-3}$ is calculated.

The reciprocal planes $hk0$, $hk1$, $hk2$; $0kl$, $1kl$, $2kl$; hhl; $h+2,h,l$; $h+4,h,l$ and hkh all show the extinctions characteristic of the space group *Fddd*.

Structure determination

Intensities on three-fold film packs were first estimated visually; films made in the later stage of the analysis were measured on a photometer. When necessary the intensities were corrected for absorption. Apart from space-group extinctions, the intensity distribution shows some peculiar regularities:

(*a*) Reflections with $h+k+l=4n+2$ are all weak or absent. The goniometric structure factor for these is $\sin 2\pi hx \sin 2\pi ky \sin 2\pi lz$, indicating that at least the strongest scatterers have one or more coordinates equal to, or nearly equal to, zero.

(*b*) Many of the strongest reflections have $h+k+l=8n$, which indicates interatomic distances of $\frac{1}{8}$ along the cell diagonal.

(*c*) Some reciprocal planes show tetragonal pseudosymmetry, e.g. $hk0$, $hk2$; also $h,h-2,l$ and $h,h-4,l$, at least for lower values of l.

Consideration of the $hk0$ Patterson summation, expected P–S and P–O distances, and the regularities (*a*), (*b*) and (*c*) led to the following model:

K on 16f, $0y0$, etc., with $y=\frac{1}{8}$;
P on 16e, $x00$, etc., with $x=0{\cdot}18$;
S in general position, 32h, with

$$x=\tfrac{1}{8},\ y=0{\cdot}015,\ z=-0{\cdot}15;$$

O on 32h, with

$$x=0{\cdot}225,\ y=0{\cdot}085,\ z=0\ .$$

N.B. Origin at 222.
No place could be assigned to C at this stage.

On rotating about an axis $[\frac{1}{4}, 0, z]$ through 90°, K then comes approximately at the place of 2 S in the [001] projection, and vice versa, and P at the place

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of two oxygens (see Fig. 3), which would account for the pseudo-tetragonal character. Also the preponderance of $h+k+l=8n$ is explained by the distances $-\frac{1}{8}, \frac{1}{8}, -\frac{1}{8}$, etc., between S and K atoms.

Refinement by Fourier methods

After three [001] electron-density projections and three difference syntheses a reasonable preliminary agreement was reached, with parameters close to those given above (see Gersmann, 1956). The position of C was always doubtful, both in the projections, and in the difference maps, owing to much overlap; it was assumed to be near $x=0{\cdot}275$, $y=0{\cdot}100$, but other positions were also tried, and on the whole the influence of C on calculated structure factors was found to be very small.

A rough confirmation of the z-parameters assumed for S and O was obtained from the $0kl$ reflections; however, this projection is unsuitable for refinement because of the length of the b-axis.

A better prognosis can be given for the face diagonals of the F-centered cell. A model was built of cork balls, put at the proper height z on knitting needles which were set up at the appropriate x, y positions in a flat piece of cork. Only the atoms K, P, S and O were put in. This model showed empty spaces which the CH_3 groups could reasonably be expected to fill. From the model it was apparent that the axis [101] would be the best choice for optimum resolution of the atoms in projection. Moreover, in such a skew projection, two symmetry-related positions project at pseudo-independent positions. By combination, it may then be possible to derive *all* atomic coordinates from one projection (MacGillavry, Hoogschagen & Sixma, 1948).

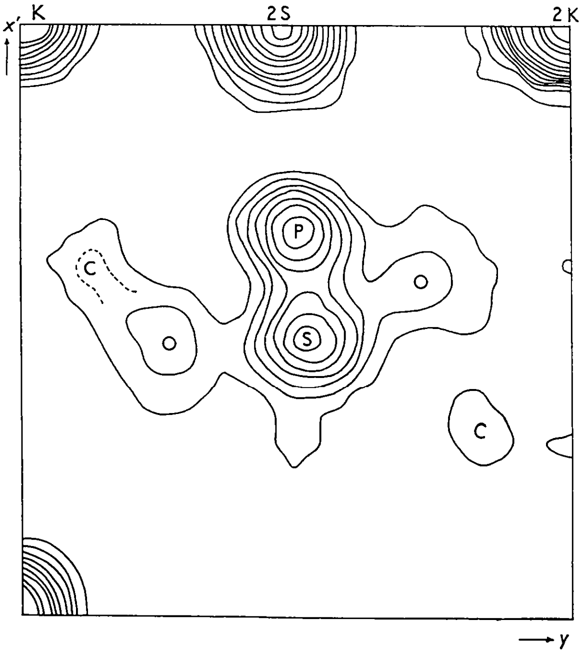

Fig. 1. Electron density of $KS_2P(OCH_3)_2$, projected along [101]. Contour lines on arbitrary scale. Compare Fig. 4 for atomic positions.

The first electron-density map with input S, K, P and O showed the carbon atoms (Fig. 1) near the expected positions. Small parameter adjustments for the other atoms were derived from the map, and two subsequent difference maps calculated. As the last difference map gave no clear indications for further changes, this refinement was stopped.

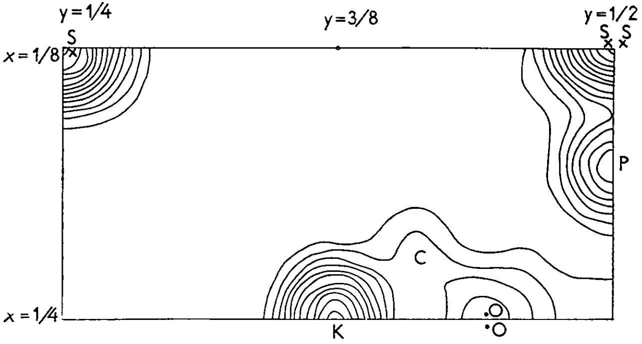

Fig. 2. Final projection of the electron density along [001]. Contours on arbitrary scale. Compare Fig. 3 for atomic positions.

At this point we went back to the $hk0$ reflexions. Because of the many space-group extinctions, their number was extremely small. A Weissenberg diagram from a new crystal with Mo K radiation gave an increase of $\frac{1}{3}$ to a total of 48 reflexions. An electron-density map now showed the carbon atoms at the expected positions, while the false detail of former maps was much reduced (Fig. 2). A last difference map along [001] was computed, without contributions from C, and with $B=3{\cdot}7$ Å^2. This map only indicated that the thermal parameters would increase roughly in the order K, P, S, O. The position of C was not clearly defined. The positional parameters obtained thus far are given in Table 1. Although the R for the various projections was still about 0·25, nearest neighbour distances at this stage were reasonable, except C–O which was found too short, namely 1·34 Å.

Table 1. *Positional parameters of* $KS_2P(OCH_3)_2$, *after refinement by Fourier methods*

Origin at 222

	From *hkh*			From *hk*0	
	x	*y*	*z*	*x*	*y*
K	0	0·123	0	0	0·123
P	0·180	0	0	0·180	0
S	0·125	0·008	0·856	0·122	0·006
O	0·247	0·058	0·025	0·247	0·058
C	0·248	0·090	0·933	(0·248)	(0·090)

An attempt was made to obtain better resolution by cooling the crystal to −150 °C. but a phase transformation then took place, presumably to a monoclinic form which is closely related to the orthorhombic structure. The same transformation appears to occur very slowly at room temperature as shown by X-ray photographs taken of a crystal kept for six years. After removing the outer layers of this crystal, the inner part proved to be unchanged.

Refinement by least squares

It was clear that good refinement by difference syntheses in projection would be virtually impossible. The structure was not considered to be of enough importance to collect 3-dimensional intensity data. An alternative possibility was to refine the available sets of two-dimensional data by computational methods. This was done by using Hirshfeld's least-squares program (F. L. Hirshfeld, private communication) in which the function

$$r=\Sigma w(K^2F_o^2-|F_c|^2)^2/\Sigma wK^4F_o^4\ ,$$

where the w are weights, is minimized with respect to the scale factors K of the various reciprocal-lattice planes, and to the positional and thermal parameters of each atom in the asymmetric unit. The program uses the diagonal approximation.

Because it was *a priori* difficult to assess their relative weights, the sets $hk0$, hhl, $0kl$ and hkh were first refined separately. This allows the determination of the relative weights from the residuals of the last least-squares cycle (Coppens, 1960). Within each set, weights were taken proportional to $1/F_o^3$. For non-observed reflections, a threshold value F_t was estimated from the limit of visibility on the film. Terms

Table 2. *Structural parameters of* $KS_2P(OCH_3)_2$, *after refinement by least squares*

Origin at 222

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$	$B/4$	$\sigma(B/4)$
K	0		0·1207	0·0004	0		0·622 Å²	0·030
P	0·1816	0·0007	0		0		0·838	0·047
S	0·1231	0·0005	0·0077	0·0004	0·8536	0·0009	1·105	0·040
O	0·2515	0·0035	0·0612	0·0016	0·0268	0·0030	2·07	0·22
C	0·2776	0·0029	0·1039	0·0020	0·9120	0·0050	1·80	0·31

Table 3. *Calculated* (F_c) *and observed* (F_o) *structure factors of* $KS_2P(OCH_3)_2$

Origin at $\bar{1}$; 'n.o.' means 'not observed'; K = scaling factor

h	k	l	$\|KF_o\|$	F_c
4	0	0	5.48	- 6.07
8	0	0	23.09	21.52
12	0	0	2.15	- 1.28
16	0	0	10.73	10.93
20	0	0	1.20	0.93
0	4	0	12.15	-11.70
4	4	0	28.98	-32.48
8	4	0	5.23	2.72
12	4	0	10.00	-10.25
16	4	0	3.83	- 3.20
20	4	0	4.53	- 5.45
0	8	0	24.77	23.81
4	8	0	6.67	6.96
8	8	0	9.63	7.40
12	8	0	n.o.	0.77
16	8	0	7.39	7.61
20	8	0	0.75	0.61
0	12	0	6.54	- 5.31
4	12	0	13.08	-12.35
8	12	0	4.06	2.87
12	12	0	6.92	- 5.76
16	12	0	1.43	- 0.97
0	16	0	10.28	10.42
4	16	0	n.o.	- 0.23
8	16	0	3.81	3.76
12	16	0	1.91	- 1.54
16	16	0	4.48	3.88
0	20	0	1.68	- 1.20
4	20	0	3.58	- 3.59
8	20	0	1.91	2.04
2	2	0	14.02	15.89
6	2	0	5.98	0.03
10	2	0	1.87	- 1.42
14	2	0	5.70	- 4.77
2	6	0	n.o.	1.82
6	6	0	7.85	- 7.30
10	6	0	2.43	3.13
14	6	0	5.51	4.31
2	10	0	1.40	0.72
6	10	0	5.98	6.00
10	10	0	5.89	- 4.47
14	10	0	1.68	- 1.28
18	10	0	2.15	- 1.20
2	14	0	4.30	- 3.92
6	14	0	n.o.	- 0.54
10	14	0	n.o.	- 0.31
14	14	0	3.92	3.30
2	18	0	n.o.	0.48
6	18	0	2.15	2.54
10	18	0	2.43	- 1.84
2	22	0	2.15	- 1.88
0	0	4	7.83	- 7.40
0	0	8	14.94	13.84
0	0	12	5.69	- 5.51
0	2	2	12.81	-13.03
0	6	2	4.98	- 3.96
0	10	2	4.98	- 3.36
0	14	2	n.o.	0.78
0	18	2	2.84	- 3.50
0	4	4	16.37	-12.37
0	8	4	1.42	- 1.00
0	12	4	4.98	- 6.07
0	16	4	3.56	- 3.80
0	20	4	1.42	- 1.70
0	2	6	19.21	14.81
0	6	6	9.25	-10.39
0	10	6	9.96	7.74
0	14	6	4.98	- 4.44
0	18	6	3.56	3.96
0	4	8	2.13	- 2.29
0	8	8	10.67	9.98
0	12	8	2.13	- 0.78
0	16	8	4.27	4.93
0	2	10	4.27	1.64
0	6	10	4.27	- 2.32
0	10	10	n.o.	- 0.34
0	14	10	2.13	- 1.24
0	4	12	2.13	- 1.08
0	8	12	4.27	- 4.49
0	12	12	n.o.	- 0.66
0	2	14	4.27	3.18
0	6	14	1.42	- 2.39
2	0	2	8.36	6.73
2	2	2	n.o.	0.10
2	4	2	15.28	-15.14
2	6	2	5.11	4.96
2	8	2	7.90	- 7.92
2	10	2	5.47	- 4.08
2	12	2	9.65	- 8.02
2	14	2	3.41	3.50
2	16	2	2.01	- 1.13
2	18	2	2.01	- 2.59
2	20	2	3.56	- 3.36
4	0	4	22.61	23.59
4	2	4	2.84	1.77
4	4	4	2.48	- 2.36
4	6	4	n.o.	1.08
4	8	4	12.03	10.55
4	10	4	n.o.	0.11
4	12	4	n.o.	0.74
4	14	4	n.o.	- 0.04
4	16	4	4.90	5.54
6	0	6	11.05	- 9.69
6	2	6	n.o.	- 0.92
6	4	6	3.04	- 3.48
6	6	6	2.58	1.40
6	8	6	10.12	- 8.83
6	10	6	3.36	- 1.79
6	12	6	2.89	- 1.44
6	14	6	1.91	1.59
6	16	6	3.92	- 3.76
6	18	6	1.29	- 1.10
8	0	8	5.37	4.24
8	2	8	n.o.	- 0.85
8	4	8	5.47	4.75
8	6	8	n.o.	- 0.27
8	8	8	2.84	2.79
8	10	8	n.o.	- 0.22
8	12	8	2.74	3.43
8	16	8	1.50	1.38
10	0	10	3.77	- 3.65
10	2	10	n.o.	- 0.32
10	4	10	2.74	- 2.52
10	6	10	1.03	0.06
10	8	10	2.74	- 2.93
10	10	10	n.o.	- 0.24
10	12	10	2.06	- 1.65
12	0	12	1.60	2.41
1	1	1	12.39	-15.18
1	3	1	6.61	- 6.52
1	5	1	1.03	1.49
1	7	1	12.08	10.21
1	9	1	9.19	- 7.90
1	11	1	4.54	- 4.08
1	13	1	1.86	- 2.63
1	15	1	4.96	4.79
1	17	1	2.68	- 3.01
1	19	1	1.03	- 1.46
3	1	3	11.26	8.77
3	3	3	2.22	- 2.88
3	5	3	6.61	6.69
3	7	3	8.93	- 7.36
3	9	3	4.34	3.64
3	11	3	3.36	- 2.43
3	13	3	4.65	3.06
3	15	3	n.o.	- 1.34
3	17	3	1.91	0.96
3	19	3	n.o.	- 0.46
3	21	3	2.06	2.23
5	1	5	12.34	- 9.47
5	3	5	n.o.	0.83
5	5	5	1.65	- 0.89
5	7	5	6.35	6.10
5	9	5	6.09	- 5.14
5	11	5	4.18	- 3.23
5	13	5	1.91	- 2.62
5	15	5	3.77	3.52
5	17	5	2.06	- 2.23
7	1	7	4.08	4.67
7	3	7	3.25	1.56
7	5	7	n.o.	0.51
7	7	7	6.61	- 4.00
7	9	7	3.66	4.30
7	11	7	n.o.	- 0.42
7	13	7	n.o.	0.50
7	15	7	1.86	- 1.32
7	17	7	1.55	2.13
9	1	9	n.o.	0.34
9	3	9	4.65	3.93
9	5	9	4.54	- 3.93
9	7	9	n.o.	- 0.18
9	9	9	n.o.	0.44
9	11	9	1.60	1.54
9	13	9	3.61	- 3.16
11	1	11	4.18	3.36
11	3	11	1.03	0.68
11	5	11	n.o.	- 0.37
11	7	11	3.41	- 2.27
11	9	11	2.74	2.98
1	1	3	2.24	- 1.49
1	1	5	7.51	7.03
1	1	7	10.28	8.45
1	1	9	3.29	- 2.88
1	1	11	n.o.	- 0.67
1	1	13	4.08	2.88
2	2	4	9.36	- 7.66
2	2	6	1.98	- 0.53
2	2	8	3.16	2.53
2	2	10	n.o.	- 0.28
2	2	12	n.o.	- 1.14
3	3	1	11.34	-18.43
3	3	5	8.43	7.54
3	3	7	9.49	7.63
3	3	9	5.01	- 4.96
3	3	11	n.o.	- 1.66
3	3	13	3.82	3.07
4	4	2	1.32	1.43
4	4	6	n.o.	0.25
4	4	8	11.73	- 8.52
4	4	10	n.o.	- 0.15
4	4	12	4.22	3.37
5	5	1	3.82	1.78
5	5	3	n.o.	- 2.33
5	5	7	7.78	- 6.00
5	5	9	2.63	- 1.70
5	5	11	n.o.	- 1.05
5	5	13	2.24	- 1.30
6	6	2	2.37	1.57
6	6	4	6.19	4.92
6	6	8	3.42	- 1.91
6	6	10	n.o.	0.41
6	6	12	n.o.	0.96
7	7	1	5.80	5.72
7	7	3	1.84	- 1.27
7	7	5	n.o.	0.34
7	7	9	n.o.	1.04
7	7	11	n.o.	0.35
7	7	13	1.32	- 1.04
8	8	2	n.o.	- 1.53
8	8	4	6.85	5.64
8	8	6	1.84	- 0.27
8	8	10	n.o.	0.16
8	8	12	1.05	- 1.00
9	9	1	2.24	- 1.88
9	9	3	1.71	1.00
9	9	5	3.16	2.24
9	9	7	3.95	3.66
10	10	2	2.24	- 2.39
10	10	4	2.90	2.36
10	10	6	n.o.	- 1.34
10	10	8	2.63	- 1.82
11	11	1	n.o.	- 1.26
11	11	3	n.o.	2.64
11	11	5	n.o.	- 1.85
11	11	7	2.37	0.88
12	12	2	n.o.	0.68
12	12	4	n.o.	- 0.39
12	12	6	n.o.	0.17
12	12	8	2.37	- 2.44
13	13	1	2.77	3.08
13	13	3	n.o.	1.75
13	13	5	4.08	- 3.09
13	13	7	3.42	- 2.97
14	14	2	n.o.	1.54
14	14	4	2.24	- 2.08
14	14	6	n.o.	0.76
15	15	1	n.o.	1.40
15	15	3	n.o.	- 0.40

with $|F_c|^2 < K^2F_t^2$ were left out; the other terms were given half weight.

Although the heavy overlap of atoms within each projection would seem to make the use of the diagonal approximation a doubtful procedure, the structure did refine. The sets were merged after assessment of their relative weights. For reflections which occur in more than one reciprocal-lattice plane, a weighted average of the individual F_o values was included only once in the computations. The total number of reflections, including unobserved, was then 248, with which the 11 positional, 5 individual isotropic thermal, and 4 scale parameters were refined. The final r was 14·8%, the conventional $R = 16{\cdot}5\%$, for observed values only.

The results of the computation are given in Table 2. By comparison with Table 1 it is seen that for the positions of K, P, S and O the only significant shift is in y_K; on the other hand the positional parameters of carbon show large shifts. The drop in R factor must be largely due to the introduction of individual temperature factors. A list of calculated and observed structure factors is given in Table 3; interatomic distances, calculated from the positional parameters in Table 2, are listed in Table 4. All distances involving K or P, which atoms lie on twofold axes, occur twice (left hand side of Table 4).

Table 4. *Interatomic distances in the structure of* $KS_2P(OCH_3)_2$, *calculated from the positional parameters given in Table* 2

	Distance	σ*		Distance	σ*
P–S	1·960 Å	0·013 Å	O–O	2·23 Å	0·04 Å
P–O	1·64	0·05	S–O	3·11	0·05
O–C	1·58	0·06	S′–O	2·87	0·05
K–O	2·82	0·03	S–S	3·36	0·02
K–S	3·35	0·01	P–C	2·65	0·04
K–S′	3·51	0·01			
K–S″	3·45	0·01			

* In the standard deviation, the σ of the cell constants have also been taken into account.

The interatomic distances are all reasonable, except C–O which is much too long. It must be borne in mind that the carbon atom proved difficult to locate by Fourier methods where the same distance came out too short. The uncertainty of the position of the carbon atom might perhaps have to do with the phase transformation mentioned above.

The P–O distance of 1·64 Å compares well with

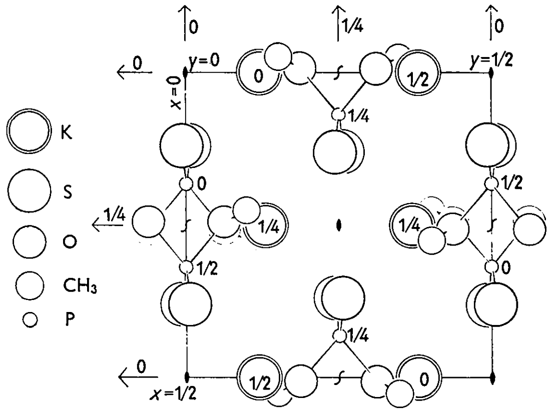

Fig. 3. Structure of $KS_2P(OCH_3)_2$ projected along the c-axis. In view of the face-centering only one quarter of the cell is shown. For clarity, overlapping $S_2P(OCH_3)_2$-ions at $y = \frac{1}{4}$ have been left out.

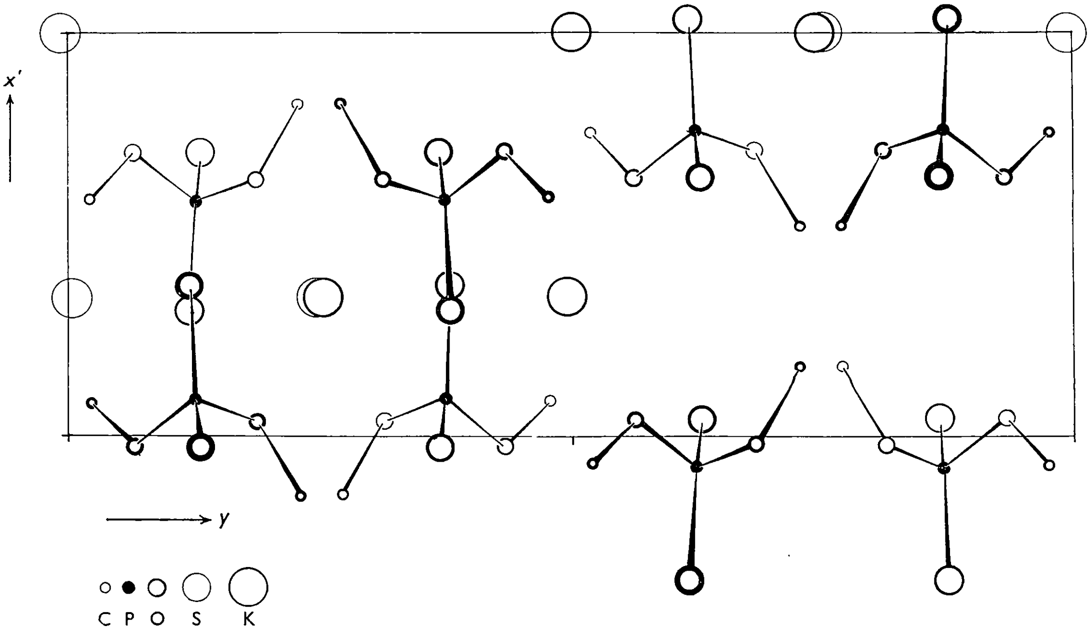

Fig. 4. The structure projected along [101]. On the left, all the atoms in the cell are drawn, for comparison with the electron density map Fig. 1. On the right, part of the atoms have been left out in order to avoid confusing overlap.

single-bond P–O distances found e.g. in metaphosphates—Romers, Ketelaar & MacGillavry (1951); Ondik, Block & MacGillavry (1961); Jost (1961). The P–S bond has the same length as found for double-bonded S in P_4S_5, P_4S_7 and P_4S_{10}—Van Houten & Wiebenga (1957).

Discussion

The structure is shown in Figs. 3 and 4. The packing of the potassium ions and the $S_2P(OCH_3)_2$ groups is such that the former are surrounded by six sulphur and two oxygen atoms forming a distorted tetragonal anti-prism. This is best seen in Fig. 5 which gives the coordination of a K ion viewed along the *b*-axis. Two potassium ions share the base of this anti-prism, formed by four S-atoms. The upper S-corners of the anti-prism are shared with two other potassium ions. Each PS_2O_2 tetrahedron shares its S–S edge with two K-polyhedra, and two of its S–O edges each with the coordination of another K ion. In this way, each sulphur takes part in the coordination of three potassium ions; the oxygen atoms are coordinated to one K^+ only. This might indicate that most of the charge of the anion is located on the sulphur atoms, as expected from considerations of the bonding type similar to those given by Romers, Ketelaar & MacGillavry (1951).

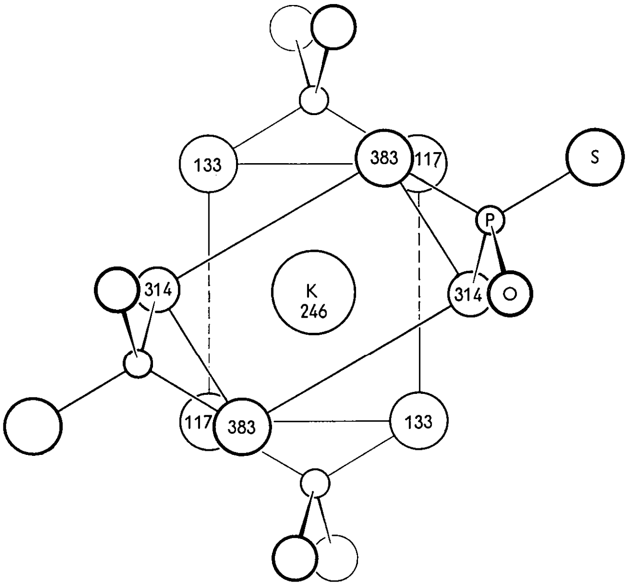

Fig. 5. Coordination of the potassium ion, viewed along the *b*-axis. For clarity's sake, carbon atoms have been left out.

We thank Mr A. Kreuger of the Netherlands Organization for Pure Research (ZWO) for expert help in making the X-ray pictures. Mr H. Arnoldy carried out part of the calculations.

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