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The Crystal Structures of Two Potassium Sodium Chloride Dithionates

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The preparation of two mixed salts, $NaK_5Cl_2(S_2O_6)_2$ and $NaK_2Cl(S_2O_6)$, is described. The space groups are $P4/mnc$ and $P4/n$ respectively. The two structures are very similar and by suitably reorientating the unit cells the similarities can be emphasized. This is used to explain the tendency of the two to grow together in an apparently single crystal, and the occurrence of mistakes observed in some specimens. The size and shape of the dithionate ion has been determined: the interatomic distances are S–S 2·08 Å, S–O 1·48 Å, O · · · O 2·46 Å, in confirmation of earlier determinations.

1. Introduction

Buckley (1951) has described a mixed salt prepared from a solution containing potassium dithionate and sodium chloride. The same salt can be grown from a solution containing sodium dithionate and potassium chloride and, in addition, a second, similar mixed salt can be prepared under different conditions. The two salts are similar in their symmetry, optical properties and densities, and show a marked tendency to grow together in the same crystal in aggregates sufficiently large to give rise to the characteristic X-ray diffraction patterns of both salts. Crystals of one of the salts have been prepared which show broadening of the high-order $00l$ and adjacent reflexions, indicating some sort of lattice distortion in the c direction.

2. Preliminary investigation

The crystals were prepared from 4/3 molar solutions of sodium dithionate and potassium chloride. Salt I (identical with the salt described by Buckley) was grown by slowly cooling a solution containing 23% $Na_2S_2O_6$ and 77% KCl, and salt II by similarly treating a solution containing 66% $Na_2S_2O_6$ and 34% KCl (moles % in each case). The range of concentration over which the second salt grows is very much smaller than the corresponding range for salt I and some care was required in order to prepare suitable specimens.

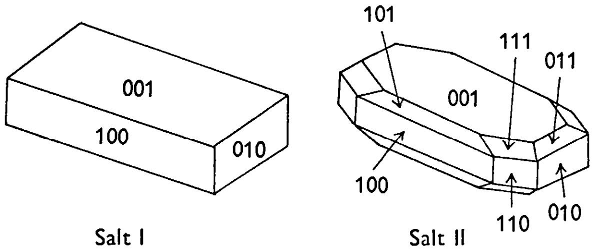

Fig. 1. The forms exhibited by the two salts.

Both salts form rectangular crystals which are uniaxial negative. The forms exhibited by the two salts are shown in Fig. 1. The refractive indices measured by the Becke-line method and the densities determined by flotation in heavy organic liquids are very similar; the values are given in Table 1.

Table 1. *Densities and refractive indices*

	Salt I	Salt II
Density (g.cm.$^{-3}$)	2·396±3	2·416±3
ε	1·507±1	1·511±1
ω	1·526±1	1·531±1

The space groups, determined from oscillation and Weissenberg photographs, were $P4/mnc$ or $P4nc$ for salt I and $P4/n$ for salt II. The ambiguity in the space group of salt I could not be definitely resolved by statistical methods. The tests for centrosymmetry described by Wilson (1951) and Howells, Phillips & Rogers (1950) were inconclusive, but the indications were that the centrosymmetric space group was the more likely. (Atoms in special positions, which contribute to only one-half of the reflexions, have the effect of increasing the dispersion above that for a structure of entirely 'random' atoms.) The average-multiple method (Wilson, 1950; Rogers, 1950) might have been expected to give evidence of a mirror plane, but any results so obtained would have been subject to doubt because of the large allowance for atoms actually lying in the plane and extensive non-crystallographic superposition of atoms in the [001] projection. Salt I does not exhibit any piezo- or pyro-electric effects (Buckley, 1950) and hence it seemed likely that the space group was $P4/mnc$. This conclusion is confirmed by the full structure determination.

The unit-cell dimensions were determined accurately by the method of Farquhar & Lipson (1947). By comparing the 'molecular weights' of the cell contents so determined with the molecular weights of the possible formulae the empirical formula of salt I was determined uniquely as $NaK_5Cl_2(S_2O_6)_2$, two molecules per

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Table 2

	Salt I		Salt II	
Space group	*P*4/*mnc*		*P*4/*n*	
a (Å)	8·5621 ± 6		12·1180 ± 6	
c (Å)	11·5288 ± 6		*5·522 ± 4	
Molecular weight of cell contents (obs.)	1220·4 ± 1·6		1188 ± 2	
Unit-cell contents	2 $NaK_5Cl_2(S_2O_6)_2$	4 $NaK_2Cl(S_2O_6)$	or	2 $NaK_6Cl_5(S_2O_6)$
Molecular weight (calc.)	1219·4	1187·2		1189·8

* At the time that the lattice parameters were measured the only specimens of salt II available exhibited broadening of the high-order 00*l* and adjacent reflexions, so that *c* could not be determined with great accuracy.

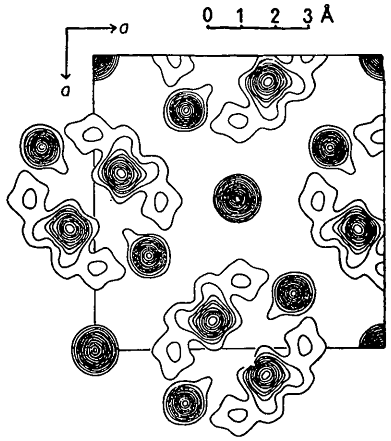

Fig. 2.

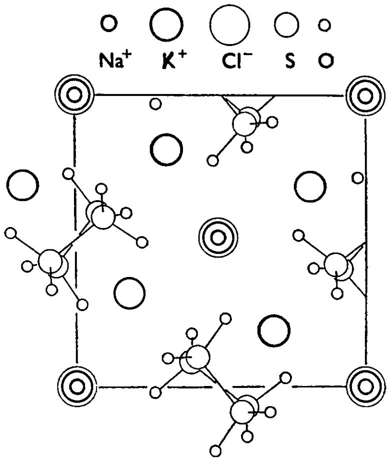

Fig. 3.

Fig. 2. Electron density in the unit cell of salt I projected on (001). The contours are at intervals of 4 e.Å^{-2}, starting at 4 e.Å^{-2}.
Fig. 3. Diagrammatic interpretation of Fig. 2.

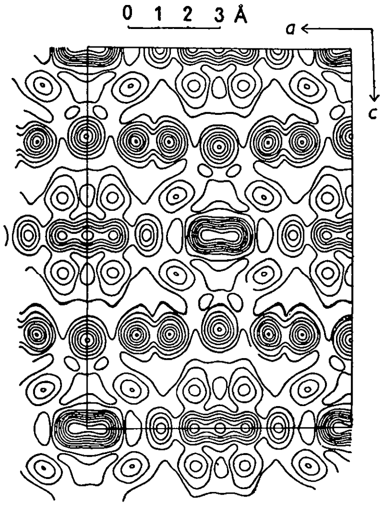

Fig. 4.

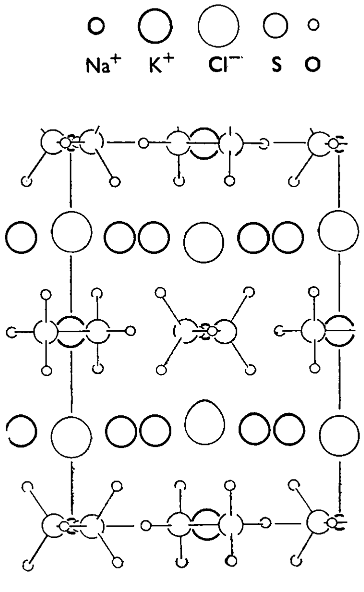

Fig. 5.

Fig. 4. Electron density in the unit cell of salt I projected on (100). The contours in the oxygen peaks are at intervals of 2 e.Å^{-2}. The remaining contours are at 2, 4, 8, 12 etc. e.Å^{-2}.
Fig. 5. Diagrammatic interpretation of Fig. 4.

unit cell. Salt II could be assigned two possible formulae, $NaK_2Cl(S_2O_6)$, four molecules per unit cell or $NaK_6Cl_5(S_2O_6)$, two molecules per unit cell. The latter was rejected as improbable on space-group and packing considerations. The space groups, unit-cell dimensions, unit-cell contents and observed and calculated molecular weights are given in Table 2.

3. The structure of salt I, $NaK_5Cl_2(S_2O_6)_2$

The ions in the unit-cell of salt I cannot be packed in any obvious manner into the space group *P4nc*, but there is a satisfactory arrangement for the space group *P4/mnc* as follows:

$2\,Na^+$ in (a), $0, 0, 0;\ \tfrac12, \tfrac12, \tfrac12$.
$2\,K^+_{(1)}$ in (b), $0, 0, \tfrac12;\ \tfrac12, \tfrac12, 0$.
$4\,Cl^-$ in (e), $0, 0, z;\ 0, 0, \bar z$ etc.
$8\,K^+_{(2)}$ in (g), $x, \tfrac12+x, \tfrac14;\ \bar x, \tfrac12-x, \tfrac14;\ \tfrac12+x, \bar x, \tfrac14;$
$\tfrac12-x, x, \tfrac14;\ x, \tfrac12+x, \tfrac34;\ \bar x, \tfrac12-x, \tfrac34;$
$\tfrac12+x, \bar x, \tfrac34;\ \tfrac12-x, x, \tfrac34$.
$4\,S_2O_6^{--}$ centred at (c), $0, \tfrac12, 0;\ \tfrac12, 0, 0;\ 0, \tfrac12, \tfrac12;\ \tfrac12, 0, \tfrac12$:
symmetry of position $2/m$.

(The letters denoting the positions of the atoms are those given in the *Internationale Tabellen*, 1935.)

The z parameter of the Cl^- ions was assumed to be the equilibrium position between the Na^+ and K^+ in (a) and (b) respectively. This gives the z parameter for the Cl^- ion as 0·235. At the outset the dithionate ion was assumed to be the same size and shape as in rubidium dithionate (Barnes & Wendling, 1938). In the present structure the centre of the ion is at a position of point symmetry $2/m$ and uses the basal plane of the cell as a mirror plane. The orientation about the twofold axis has to be determined.

The hkl reflexions with l odd and the $0kl$ reflexions with both k and l odd will not be affected by the $8\,K^+$ ions in (g). By considering this group of reflexions over a limited range of $\sin\theta$ it was possible to obtain an idea of the orientation of the dithionate ion about the twofold axis. The $8\,K^+$ ions in (g) affect only those reflexions for which l is even and by considering this group over the same range of $\sin\theta$ it was possible to determine the approximate value of the x parameter of the ions. The qualitative intensity data from oscillation photographs were compared with the calculated intensities plotted as a function of the variable parameter (orientation of the dithionate ion about the twofold axis or the x coordinate of the K^+ ion). At this stage a comparison was made between the calculated intensities and the observed intensities recorded in a powder camera, measured with the aid of a recording microphotometer and corrected for Lorentz and polarization factors graphically and for absorption by the tabulated data of Bradley (1935). The agreement was good and the value of the reliability index, $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$, for the first 56 possible reflexions (including 23 reflexions which were too weak to be recorded) was 0·27. The value of R for only those reflexions observed was 0·11. No temperature correction was included in the calculated structure factors.

With the parameters determined in this way the structure factors for the reflexions in the [001] and [100] zones were calculated and compared with the observed structure factors in the same zones measured from the reflexions recorded on multiple-film Weissenberg photographs and corrected for geometrical factors by the method of Goldschmidt & Pitt (1948) and for absorption factors using the figures tabulated by Bradley (1935) for a cylindrical specimen. (The specimens for the Weissenberg photographs were prepared by grinding down large crystals until they were cylindrical in cross section, about 0·3 mm. in diameter, the axis of the cylinder being parallel to the axis of rotation.) The agreement was good, the value of R being 0·19 for the [001] projection and 0·20 for the [100] projection. The calculated structure factors were corrected for the temperature decline obtained from a graph of $\log \Sigma|F_c|\div\Sigma|F_o|$ against $\sin^2\theta/\lambda^2$. The Fourier projections of the electron density in the unit cell projected on the (001) and (100) faces are shown in Figs. 2 and 4 and the diagrammatic interpretations of the projections in Figs. 3 and 5. The maps show all the principal features of the structure, but refinement by the normal Fourier methods was not pursued because of the poor resolution.

4. The structure of salt II, $NaK_2Cl(S_2O_6)$

Reflexions in the [001] and [110] zones were recorded and corrected as above. The principal features of the structure were determined using Bragg & Lipson charts (Bragg & Lipson, 1936) for some of the outstandingly strong and weak reflexions in the two zones. The model proposed from these considerations as the starting point for Fourier refinement was

$2\,Na^+_{(1)}$ in (a), $0, 0, 0;\ \tfrac12, \tfrac12, 0$.
$2\,Cl^-_{(1)}$ in (b), $0, 0, \tfrac12;\ \tfrac12, \tfrac12, \tfrac12$.
$2\,Na^+_{(2)}$ in (c), $0, \tfrac12, z;\ \tfrac12, 0, \bar z$ with $z = 0{\cdot}000$.
$2\,Cl^-_{(2)}$ in (c), $0, \tfrac12, z;\ \tfrac12, 0, \bar z$ with $z = 0{\cdot}500$.
$8\,K^+$ in (g), x, y, z etc. with $x=\tfrac14$, $y=0{\cdot}55$, $z=0{\cdot}500$.
$4\,S_2O_6^{--}$ centred at (d), $\tfrac34, \tfrac34, 0;\ \tfrac14, \tfrac14, 0;\ \tfrac34, \tfrac14, 0;\ \tfrac14, \tfrac34, 0$:
symmetry of position, $\bar 1$.

The axis of the dithionate ion was very nearly parallel to the a edge of the cell; the orientation of the ion about its axis remained to be determined. The [001] projection was refined by successive Fourier projections during which the value of R was reduced from 0·47 to 0·18. The final map is shown in Fig. 6 and the diagrammatic representation of the projection in Fig. 7. The sulphur atom and one of the oxygen atoms in the dithionate ion are not resolved. All the other atoms are quite well resolved in this projection,

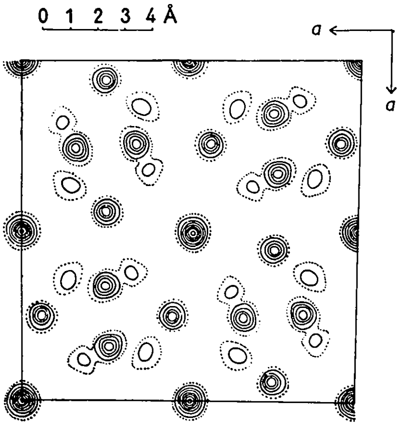

Fig. 6.

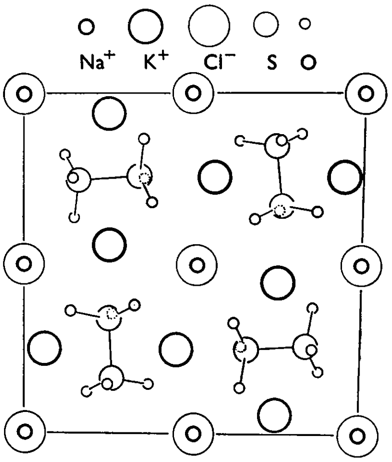

Fig. 7.

Fig. 6. Electron density in the unit cell of salt II projected on (001). The contours (full lines) are at intervals of 5 e.Å^{-2}. The 2 e.Å^{-2} contour is broken.
Fig. 7. Diagrammatic interpretation of Fig. 6.

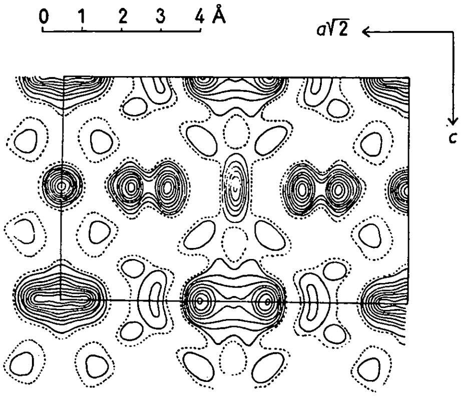

Fig. 8.

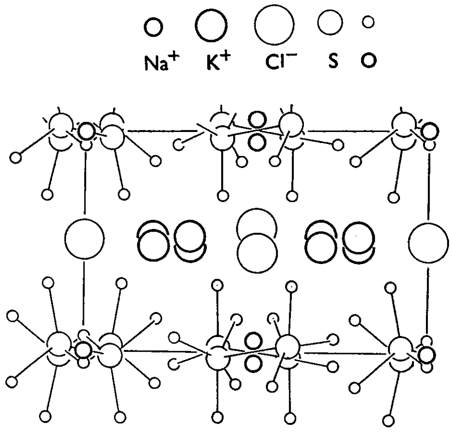

Fig. 9.

Fig. 8. Electron density in the unit cell of salt II projected on (110). The contours (full lines) are at intervals of 5 e.Å^{-2}. The 2 e.Å^{-2} contour is broken.
Fig. 9. Diagrammatic interpretation of Fig. 8.

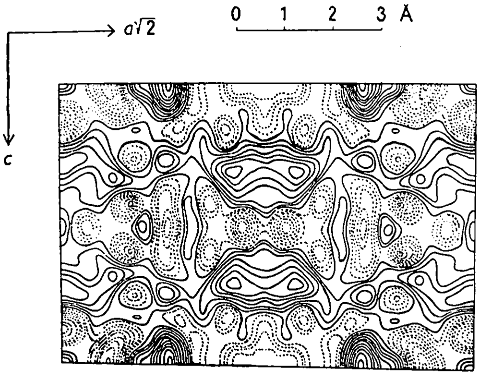

Fig. 10. First projection of $(\varrho_o-\varrho_c)$ on (110) for salt II. The contours are at intervals of $\frac{1}{2}$ e.Å^{-2}. Negative contours broken (zero contour full line).

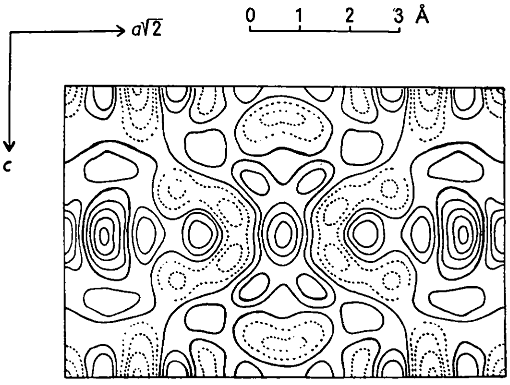

Fig. 11. Final projection of $(\varrho_o-\varrho_c)$ on (110) for salt II. The contours are at intervals of $\frac{1}{2}$ e.Å^{-2}. Negative contours broken (zero contour full line).

Table 3. *Observed and calculated structure factors for salt I*

(1) *hk*0 zone

hkl	F_o	F_c
200	56	+58
400	32	+29
600	31	+40
800	21	+24
10,0,0	47	+46
110	39	−46
210	14	+20
310	143	+165
410	115	+105
510	72	+65
610	56	−49
710	76	+73
810	20	−21
910	15	+24
10,1,0	< 6	− 1
220	96	+106
320	106	−118
420	50	+42
520	23	−18
620	< 9	− 8
720	48	+41
820	56	+39
920	8	+ 8
10,2,0	12	+ 9
330	< 7	+ 3
430	19	+ 8
530	78	+70
630	10	+14
730	10	+12
830	20	−10
930	7	+ 7
10,3,0	12	−19
440	94	+88
540	22	+18
640	53	+53
740	24	−32
840	31	+32
940	30	+28
10,4,0	9	+11
550	33	−22
650	< 10	+ 1
750	25	+26
850	< 7	+ 1
950	19	+20
660	53	+58
760	24	+22
860	< 6	+10
960	11	−11
770	14	+14
870	5	+ 3

(2) 0*kl* zone

hkl	F_o	F_c
020	58	+58
040	29	+29
060	32	+40
080	20	+24
0,10,0	47	+46
011	< 6	+11
031	19	+14
051	30	+31
071	< 9	+ 2
091	24	−20
002	56	+56
022	104	+117
042	23	−24
062	82	−75
082	18	+16
0,10,2	7	− 6
013	< 7	+14
033	31	+28
053	10	−18
073	18	−18
093	25	−16
004	228	+230
024	42	+49
044	67	+65
064	36	+28
084	14	− 7
0,10,4	23	+25
015	35	+39
035	56	+54
055	10	−12
075	9	−11
095	11	− 3
006	17	−19
026	83	−76
046	9	+12
066	61	−35
086	16	+17
017	9	− 9
037	< 9	+ 1
057	11	−10
077	10	−14
097	16	−14
008	167	+165
028	29	+19
048	10	+11
068	13	+15
088	9	−11
019	15	+14
039	19	+12
059	16	+21
079	< 6	+ 7
0,0,10	18	+30
0,2,10	38	+38
0,4,10	12	−11
0,6,10	29	−28
0,1,11	14	−10
0,3,11	< 8	− 7
0,5,11	< 8	− 4
0,7,11	2	− 7
0,0,12	65	+60
0,2,12	10	+ 6
0,4,12	7	+ 6
0,6,12	4	+ 6
0,1,13	< 6	+10
0,3,13	11	+12
0,5,13	5	+ 2
0,0,14	< 6	− 2
0,2,14	19	+19

but the isolated oxygen peaks are not sufficiently well defined for any great confidence to be placed in the parameters derived from the map.

The [110] projection was considered likely to be more profitable than the [100] projection, because of the overlap of the two dithionate ions in the latter. This projection was refined by the Fourier method during which the value of R was reduced from 0·44 to 0·32. The final projection (Fig. 8) shows the main features of the structure, but further refinement by these methods was not possible owing to the lack of resolution. The diagrammatic representation of the projection is shown in Fig. 9.

5. Refinement by the (F_o-F_c) method

Because of the limited resolution in the Fourier projections it was decided to attempt the further refinement of the structures by the (F_o-F_c) method described by Cochran (1951*a*, 1951*b*, 1951*c*). This method was applied to the refinement of the atomic coordinates only, and no attempt was made to refine the atomic scattering curves or to introduce individual temperature factors; it was not considered that the observed structure factors were sufficiently accurate to warrant this. In all cases the refinement by this method reduced the value of R and enabled the atomic

Table 4. *Observed and calculated structure factors for salt II*

(1) *hk*0 zone

hkl	F_o	F_c
110	< 17	−7
130	26	−22
150	115	−111
170	< 16	+2
190	< 16	−8
1,11,0	11	−16
1,13,0	11	+12
1,15,0	15	−11
200	52	+50
220	56	+59
240	144	−148
260	20	+18
280	53	−58
2,10,0	89	+85
2,12,0	22	−19
2,14,0	14	+14
310	< 17	+17
330	21	−12
350	126	−128
370	28	−32
390	19	−21
3,11,0	22	−19
3,13,0	7	+5
3,15,0	21	−21
400	95	+93
420	108	−110
440	54	+63
460	74	−88
480	13	−11
4,10,0	19	+3
4,12,0	28	+24
4,14,0	16	−19

hkl	F_o	F_c
510	129	+149
530	115	+124
550	25	−30
570	41	+33
590	64	+65
5,11,10	46	+49
5,13,0	35	+34
600	19	−16
620	38	+34
640	67	−62
660	< 16	+4
680	77	−81
6,10,0	51	+52
6,12,0	12	−13
6,14,0	4	+13
710	19	+6
730	37	+35
750	54	−52
770	< 15	0
790	28	+19
7,11,0	22	+22
7,13,0	13	+15
800	93	+103
820	102	−97
840	30	−26
860	81	−86
880	13	−12
8,10,0	< 12	−11
8,12,0	9	+8
910	< 16	−5
930	< 16	+1
950	42	−35

hkl	F_o	F_c
970	< 14	+6
990	< 13	+8
9,11,0	9	+8
10,0,0	63	+55
10,2,0	42	+42
10,4,0	24	−18
10,6,0	48	+45
10,8,0	< 12	−6
10,10,0	51	+55
11,1,0	11	−1
11,3,0	15	−10
11,5,0	39	−34
11,7,0	< 12	+8
11,9,0	< 10	+1
11,11,0	4	+2
12,0,0	63	+55
12,2,0	29	−29
12,4,0	24	+27
12,6,0	11	−16
12,8,0	14	+10
13,1,0	27	−11
13,3,0	25	−23
13,5,0	44	−47
13,7,0	6	−12
14,0,0	< 10	+7
14,2,0	12	+11
14,4,0	18	−19
14,6,0	8	+6
15,1,0	14	+20
15,3,0	11	+6

(2) *hhl* zone

hkl	F_o	F_c
110	< 5	−7
220	66	+59
330	20	−12
440	69	+63
550	25	−30
660	< 10	+4
770	< 11	0
880	17	−12
990	< 10	+8
10,10,0	62	+55
11,11,0	7	+2
001	28	+37
111	< 10	+13
221	109	+114
331	24	−16
441	25	−16
551	22	−28
661	100	−82
771	< 11	−2
881	20	+17
991	16	+9
10,10,1	19	−21
11,11,1	18	−3
002	230	+237

hkl	F_o	F_c
112	20	−23
222	17	+20
332	34	−33
442	79	+67
552	15	−15
662	28	+28
772	< 11	+1
882	19	−19
992	9	+7
10,10,2	45	+43
003	< 10	−11
113	< 10	−7
223	86	+76
333	13	−20
443	52	−47
553	< 11	+3
663	73	−63
773	< 10	+1
883	18	+20
993	15	+22
10,10,3	6	−11
004	124	+110
114	23	−26
224	13	+14

hkl	F_o	F_c
334	31	−31
444	< 10	−4
554	10	−11
664	< 9	+2
774	< 8	−6
884	11	−12
994	8	+4
005	28	−26
115	< 10	+3
225	30	+31
335	< 10	−2
445	15	−18
555	8	+5
665	22	−25
775	9	+8
885	< 3	+5
006	39	+39
116	17	−13
226	< 7	0
336	22	−14
446	< 7	−3
556	18	−14
666	< 5	−1

parameters to be determined with more certainty. In the most severe case, the [110] projection of salt II, the reliability index was reduced from 0·32 to 0·17 in four stages of refinement. Figs. 10 and 11 show the first and final $(\varrho_o-\varrho_c)$ projections on (110). The final values of R were:

Salt I, [001] 0·15, [100] 0·15;
Salt II, [001] 0·15, [110] 0·17.

The ambiguities in the z coordinate of some of the atoms in salt II which could not be determined from the [110] projection were resolved by qualitative comparison of the calculated structure factors for the various possible combinations with the observed structure factors in the [100] zone.

Tables 3 and 4 give the observed and final calculated structure factors for the zones refined. A comparison was made between the observed intensities recorded on powder photographs of salt II and the calculated intensities from the final atomic coordinates, and the agreement was good.

6. Atomic coordinates and accuracy

The final coordinates are given in Tables 5 and 6. The accuracy of the coordinates was determined using the formula given by Booth (1947*a*),

$$\sigma(x_r)=\frac{2}{N_r}\left(\frac{\pi}{\lambda p}\right)^2\left(\frac{\pi}{A}\right)^{\frac{1}{2}}\sigma(F)\,,$$

where $\sigma(x_r)$ is the standard deviation of the position of the rth atom, $\sigma(F)$ is the standard deviation of the observed F's, N_r is the atomic number of the rth atom, A is the projected area of the unit cell, λ is the wavelength of the radiation and p is a constant derived from the shape of the atomic peaks. It has been shown (Booth, 1947*b*) that in the neighbourhood of a peak $\varrho(r)=\varrho(0)\exp(-pr^2)$. The value of p found in the present structures is 4·8 for the resolved peaks. Booth quotes a mean value of 4·689 for many organic structures and Cochran (1951*b*) obtained 4·9 for adenine hydrochloride. The formula depends on the independence of the errors in the observed F's and on the atoms being well resolved. Neither of these conditions are completely fulfilled in the present structures, but it is probable that the figures obtained will be of the right order of magnitude. The value of $\sigma(F)$ used was the mean of the standard deviation of the observed F's from two independent observations made of the observed reflexions and the root-mean-square deviation of the observed from the calculated structure factors. The values obtained from the four projections refined did not differ very much amongst themselves and the mean value of 3·6 electrons was used for all projections. From the calculation it can be assumed with some degree of certainty that the value of $\sigma(x_r)$ does not exceed $0{\cdot}30/N_r$ Å.

Table 5. *Atomic parameters for salt I*

Position*	Atom	x	y	z	
(*a*)	2 Na	0·000	0·000	0·000	etc.
(*b*)	2 $K_{(1)}$	0·500	0·500	0·000	etc.
(*e*)	4 Cl	0·000	0·000	0·235	etc.
(*g*)	8 $K_{(2)}$	0·187	0·313	0·250	etc.
(*h*)	8 S	0·077	0·406	0·000	etc.
(*h*)	8 $O_{(1)}$	0·030	0·275	0·000	etc.
(*i*)	16 $O_{(2)}$	0·167	0·590	0·106	etc.

* Letters denoting the positions are those given in the *Internationale Tabellen* (1935).

Table 6. *Atomic parameters for salt II*

Position*	Atom	x	y	z	
(*b*)	2 $Cl_{(1)}$	0·000	0·000	0·500	etc.
(*a*)	2 $Na_{(1)}$	0·000	0·000	0·000	etc.
(*c*)	2 $Cl_{(2)}$	0·000	0·500	0·553	etc.
(*c*)	2 $Na_{(2)}$	0·000	0·500	0·051	etc.
(*g*)	8 K	0·235	0·055	0·523	etc.
(*g*)	8 S	0·165	0·242	0·981	etc.
(*g*)	8 $O_{(1)}$	0·149	0·256	0·714	etc.
(*g*)	8 $O_{(2)}$	0·119	0·329	0·129	etc.
(*g*)	8 $O_{(3)}$	0·131	0·128	0·062	etc.

* Letters denoting the positions are those given in the *Internationale Tabellen* (1935).

7. The size of the dithionate ion

The previous determination of the size and shape o the dithionate ion by Barnes & Wendling (1938) wa

Table 7. *Bond lengths*

All distances are in Ångström units

Salt I				Salt II				B. & W.*
Bond	Length	σ	Mean length	Bond	Length	σ	Mean length	Length
S–S	2·08	0·04	2·08	S–S	2·08	0·04	2·08	2·08
$S–O_{(1)}$	1·47	0·06	1·48	$S–O_{(1)}$	1·50	0·07	1·48	1·50
$S–O_{(2)}$	1·49	0·07		$S–O_{(2)}$	1·44	0·07		
				$S–O_{(3)}$	1·51	0·07		
$O_{(1)}–O_{(2)}$	2·40	0·08	2·43	$O_{(1)}–O_{(2)}$	2·48	0·09	2·48	2·51
$O_{(2)}–O_{(2)}$	2·48	0·08		$O_{(2)}–O_{(3)}$	2·47	0·09		
				$O_{(3)}–O_{(1)}$	2·48	0·09		

* Barnes & Wendling (1938).

carried out using qualitative considerations on rubidium dithionate. The values of the bond lengths obtained from the two structures are given in Table 7 and compared with the values obtained by Barnes & Wendling. The agreement is good and, within the accuracy of the determinations, the findings of the earlier examination are confirmed.

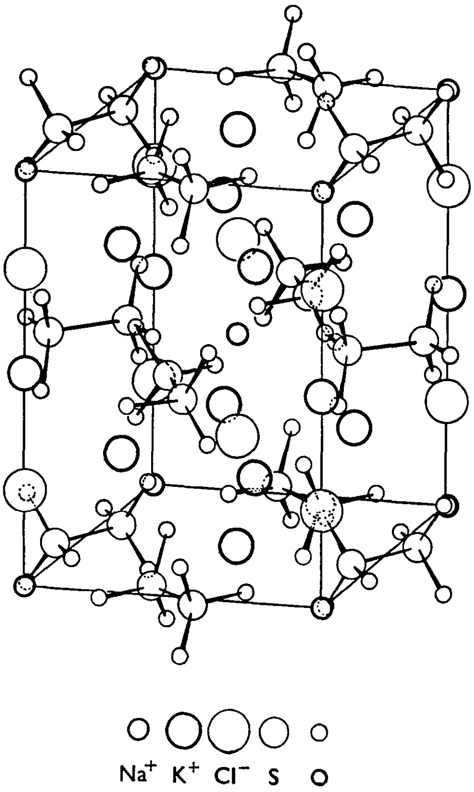

Fig. 12. Diagrammatic representation of the structure of salt I.

8. Ionic coordination

The arrangements of the ions in the two structures are shown in Figs. 12 and 13. The sequence of ions along the *c* edge are Na$^+$–Cl$^-$–K$^+$–Cl$^-$–Na$^+$ in salt I and Na$^+$–Cl$^-$–Na$^+$ in salt II. In both salts the remaining K$^+$ ions are coordinated by two Cl$^-$ ions at a distance of 3·13 Å in salt I and at distances of 3·09 and 3·14 Å in salt II. In addition these K$^+$ ions are coordinated by four oxygen atoms in salt I at a mean distance of 2·89 Å and by six oxygen atoms in salt II at a mean distance of 2·92 Å. The details of the ionic coordination distances and the standard deviations are given in Tables 8 and 9.

9. Discussion of the structures

The two structures are very similar. If the *C*-face centred cell of salt I is compared with the primitive cell of salt II the similarities become more obvious. In this orientation the two *a* parameters differ by less than one part in a thousand. If, in addition, the cell of salt II is doubled along the *c* direction the resemblance is even more striking. The only difference in the sequence along *c* axis then becomes the interchange of the sodium and potassium ions. The projections on the (001) face of the two salts in equivalent orientation are very nearly the same. The projected positions of the potassium ions and the centres of the dithionate ions are effectively the same and the positions of the ion sequences along the *c* direction coincide. What difference there is is almost entirely in the orientation of the dithionate ion about its axis. The diagrammatic projection on (001) of the cell contents of the two salts in equivalent orientation is shown in Fig. 14. From this remarkable similarity it is not surprising that the two salts tend to grow

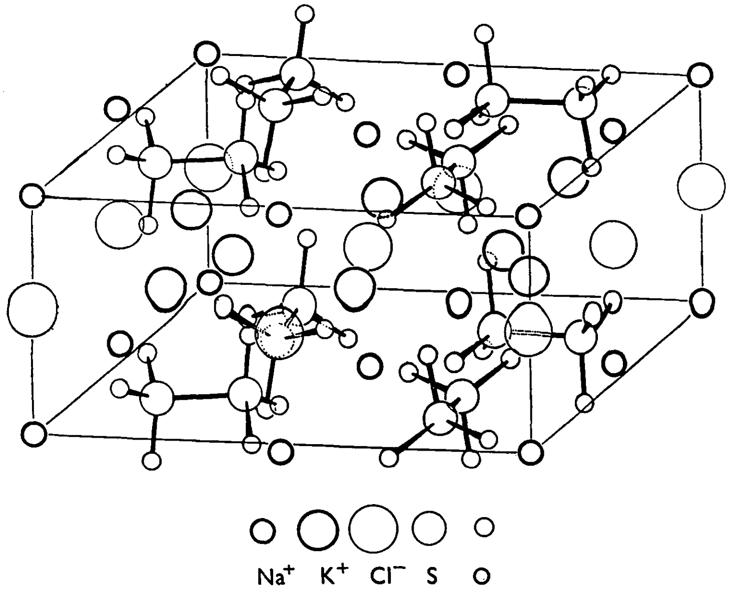

Fig. 13. Diagrammatic representation of the structure of salt II.

Table 8. *Ionic coordination in salt I*

All distances are in Ångström units

Ion	Point position	Neighbour	Point position	C. N.*	Bond length	Standard deviation
Na	(*a*)	Cl	(*e*)	2	2·71	0·03
		$O_{(1)}$	(*h*)	4	2·37	0·05
Cl	(*e*)	Na	(*a*)	1	2·71	0·03
		$K_{(1)}$	(*b*)	1	3·05	0·02
		$K_{(2)}$	(*g*)	4	3·13	0·03
$K_{(1)}$	(*b*)	Cl	(*e*)	2	3·05	0·02
$K_{(2)}$	(*g*)	$O_{(2)}$	(*i*)	2	2·88	0·07
		$O_{(2)}$	(*i*)	2	2·90	0·07
		Cl	(*e*)	2	3·13	0·03
$O_{(1)}$	(*h*)	Na	(*a*)	1	2·37	0·05
$O_{(2)}$	(*i*)	$K_{(2)}$	(*g*)	1	2·88	0·07
		$K_{(2)}$	(*g*)	1	2·90	0·07

* Coordination number.

Table 9. *Ionic coordination in salt II*

All distances are in Ångström units

Ion	Point position	Neighbour	Point position	C. N.*	Bond length	Standard deviation
$Na_{(1)}$	(*a*)	$Cl_{(1)}$	(*b*)	2	2·76	—
		$O_{(3)}$	(*g*)	4	2·25	0·07
$Na_{(2)}$	(*c*)	$Cl_{(2)}$	(*c*)	1	2·77	0·03
		$Cl_{(2)}$	(*c*)	1	2·75	0·03
		$O_{(2)}$	(*g*)	4	2·56	0·08
$Cl_{(1)}$	(*b*)	K	(*g*)	4	3·14	0·03
		$Na_{(1)}$	(*a*)	2	2·76	—
$Cl_{(2)}$	(*c*)	K	(*g*)	4	3·09	0·03
		$Na_{(2)}$	(*c*)	1	2·77	0·03
		$Na_{(2)}$	(*c*)	1	2·75	0·03
K	(*g*)	$O_{(1)}$	(*g*)	1	2·80	0·08
		$O_{(1)}$	(*g*)	1	2·89	0·08
		$O_{(1)}$	(*g*)	1	2·94	0·08
		$O_{(2)}$	(*g*)	1	3·00	0·08
		$O_{(2)}$	(*g*)	1	2·84	0·08
		$O_{(3)}$	(*g*)	1	3·07	0·08
		$Cl_{(1)}$	(*b*)	1	3·14	0·03
		$Cl_{(2)}$	(*c*)	1	3·09	0·03
$O_{(1)}$	(*g*)	K	(*g*)	1	2·80	0·08
		K	(*g*)	1	2·89	0·08
		K	(*g*)	1	2·94	0·08
$O_{(2)}$	(*g*)	K	(*g*)	1	3·00	0·08
		K	(*g*)	1	2·84	0·08
		$Na_{(2)}$	(*c*)	1	2·56	0·08
$O_{(3)}$	(*g*)	K	(*g*)	1	3·07	0·08
		$Na_{(1)}$	(*a*)	1	2·25	0·07

* Coordination number.

together in the same crystal under suitable conditions. Oscillation photographs of such crystals taken about the common *c* axis show a doubling of the spots on the even layer lines. It has been found possible, also, to grow one of the salts epitaxially on a clean (001) face of the other. The indices of the spots occurring on the

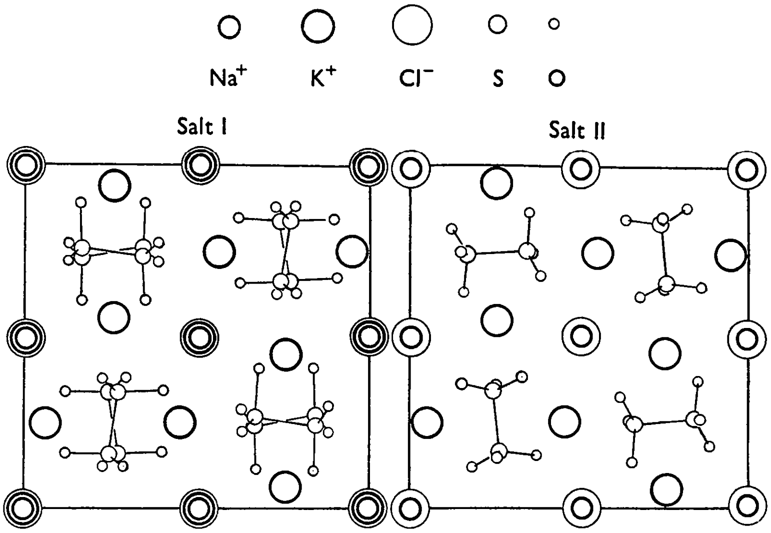

Fig. 14. Diagrammatic projection of the unit cell contents of salt I and salt II, in equivalent orientation, on (001).

oscillation photographs and the orientation of the epitaxial crystals are in agreement with the relation postulated above between the two structures.

The imperfection which occurs in some specimens of salt II reveals itself in the broadening of the high-order $00l$ and adjacent reflexions. This could possibly be accounted for if, in the stacking sequence along the c direction, there was the occasional occurrence of cells of salt I. In view of the overgrowth phenomenon this seems a reasonable explanation, although no detailed measurements have been made to verify it.

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