The Atomic Arrangement in Ammonium and Caesium Persulphate $(NH_4)_2S_2O_8$ and $Cs_2S_2O_8$, and the Structure of the Persulphate Group [1].

By

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(With 3 figures.)

1. Introduction.

Among the important consequences of the determination of complete structures of certain crystals is a very definite knowledge of the configuration of various common groups which appear as entities in whole series of compounds, very little changed by association with widely different cations; and also the information gained concerning distances between atoms with the attendant indication of the nature of bonds linking them together. Because of the recent developments in the calculation of the direction and character of interatomic bonds, it becomes still more important to determine experimentally, by means of X-ray crystal analysis, the forms of many groups whose arrangements have hitherto been considered only from the standpoint of the chemist and whose configuration are represented solely by structural formulae. The determination, not only of the spatial arrangement, but also of the actual dimensions of such characteristic configurations as they exist in crystals cannot but clarify these concepts, or, in doubtful cases, indicate fresh possibilities; the more so since an entirely independant method is invoked, whose findings must be supported by the physical properties of the crystalline material.

Such a group, one of the first to be studied and observed again and again, essentially unchanged, in many different compounds is the sulphate group. There are a large number of other sulphur oxygen groups whose structures present interesting features, and which, until lately, have been

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neglected, due perhaps to the complexity of the crystal lattices in which they appear; for instance the sulphite, dithionate, pyrosulphite, thiosulphate, pyrosulphate, and persulphate groups. Three of these, namely, the sulphite[1]), the dithionate[2]) and the pyrosulphite[3]) groups have lately been investigated and reported. The present work was undertaken mainly in order to determine the structure of the persulphate group.

2. Crystallographic Data, Unit Cell and Space Group.

Two isomorphous salts, the persulphates of caesium and ammonium, were chosen as suitable for the investigation. Good crystals of both substances are easily obtained, and the great difference between the scattering powers of caesium and ammonium is of material aid in determining the structures. The compounds were prepared in the laboratory of Professor W. C. Johnson of the Department of Chemistry of this University. The crystallographic data given by Groth[4]) are as follows:

Caesium Persulphate	Ammonium Persulphate
Monoclinic Prismatic	Monoclinic Prismatic
$a : b : c = 1.2978 : 1 : 1.1857$	$a : b : c = 1.2956 : 1 : 1.1872$
$\beta = 103° 7'$	$\beta = 103° 48'$
No distinct cleavage	Imperfect cleavage parallel to (001)
Strong positive birefringence	Positive birefringence
Optical axial plane normal (010)	Optical axial plane (010)
Direction of acute bisectrix as in ammonium salt	The acute bisectrix makes an angle of $26\frac{3}{4}°$ with the c-axis in obtuse angle β.

$$\alpha = 1.4981 \qquad \beta = 1.5016$$
$$\gamma = 1.5866 \qquad 2\,V = 24°$$
$$\text{Density} = 1.982$$

Preliminary oscillation photographs showed that the coordinate system used by Groth corresponded to a cell in which the b-plane is centered. Hence the a and c axes of the true unit cell can be chosen so that they have zone indices [$\bar{1}$01] and [101] in the old system. The transformation formulae are as follows, if the primed characters indicate the old indices, the unprimed ones the new:

$$h = \tfrac{1}{2}\,(-h' + l') \quad k = k' \quad l = \tfrac{1}{2}\,(h' + l').$$

1) W. H. Zachariasen and H. E. Buckley, Physic Rev. **37**, 1295. 1931.
2) M. L. Huggins and Glenn O. Frank, Am. Min. **16**, 580. 1931.
3) W. H. Zachariasen, Physic Rev. **40**, 923. 1932.
4) P. Groth, Chemische Krystallographie II, 726. Leipzig 1908.

The new crystallographic elements become:

$$Cs_2S_2O_8 \qquad a : b : c = 0.9732 : 1 : 0.7733 \quad \beta = 95° 19'$$
$$(NH_4)_2S_2O_8 \qquad a : b : c = 0.9774 : 1 : 0.7671 \quad \beta = 95° 9'$$

The dimensions of the unit cells for the two compounds are:

$$Cs_2S_2O_8 \qquad a = 8.13 \text{ Å} \qquad b = 8.33 \text{ Å} \qquad c = 6.46 \text{ Å}$$
$$(NH_4)_2S_2O_8 \qquad a = 7.83 \text{ Å} \qquad b = 8.04 \text{ Å} \qquad c = 6.13 \text{ Å}$$

These values are accurate to $\frac{1}{2}\%$.

There are two molecules in the unit cell. The densities calculated from the cell dimensions are 3.47 for caesium persulphate and 1.96 for ammonium persulphate. The observed density for the latter compound is 1.982.

Since the unit cell contains so many atoms it is safe to assume that at least some of them are in general positions, so that the general absences recorded may be taken as characteristic for the space group. Reflections $0k0$ are absent in odd orders, indicating that the b-axis is a screw axis rather than a rotation axis. Reflections $h0l$ are absent if $h + l$ is odd, showing that the b-plane is a glide plane with diagonal translation. Hence the space group is $P2_1/n\,(C_{2h}^5)$. The general positions of this space group are:

$$\pm\,(xyz) \pm (x + \tfrac{1}{2},\ \tfrac{1}{2} - y,\ z + \tfrac{1}{2}).$$

Further considerations show that all of the atoms are in general positions. Thus there are eighteen parameters to be determined. It is to be expected also, due to the similarity in dimensions, that there will be little difference between the parameters of the ammonium and caesium salts.

The expression for the structure amplitude becomes:

a) for $h + k + l$ even $\quad F = \quad 4\,\Sigma f_n\, \cos 2\pi\ (hx + lz)\, \cos 2\pi ky$
b) for $h + k + l$ odd $\quad F = -\,4\,\Sigma f_n\, \sin 2\pi\ (hx + lz)\, \sin 2\pi ky.$

All our observations were taken from Laue and oscillation photographs. For the oscillation photographs MoK_a radiation was used, assuming a wave length of .7095 Å for the doublet. The distance from the crystal to the photographic plate was 5.00 cm. During each exposure the crystal was oscillated through an angle of 15°. A very large number of oscillation photographs were taken, so as to record all the possible reflections up to $\sin \Theta/\lambda = .5$. The Laue method was used only on the ammonium compound. Photographs were taken with the incident beam approximately parallel to the three crystallographic axes and also with the beam normal to the a and c faces. The minimum wave length present in the beam was .27 Å.

3. Outline of Method of Attack.

In the caesium compound the scattering power of caesium is very large compared to that of the other atoms. To a first approximation we can therefore consider the intensities of reflections to be due to the caesium lattice alone. Hence it should be possible to determine the three

Table I. F-Curves[1]).

sin Θ/λ	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
Cs	55.0	50.7	43.8	37.6	32.4	28.7	25.8	23.2
S^{+2}	14.0	12.1	10.1	8.8	7.9	6.9	6.0	5.3
O^{-1}	9.0	7.6	5.4	3.9	2.8	2.2	1.8	1.6

parameters of the caesium atoms without encountering great difficulties. Because of the similarity in dimensions it is to be expected that the parameters of the two compounds are nearly the same, so that the location of the caesium atoms simultaneously will give us the approximate positions of the ammonium atoms.

The effect of the sulphur atoms will be small compared to that of the caesium atoms although not entirely negligible. The sulphur contribution was, however, found too small to allow a unique determination of the sulphur parameters.

Considering now the observations from the ammonium compound the conditions are very different. The scattering power of ammonium is small compared to that of sulphur and that of four oxygen atoms, so that we can with good approximation leave the ammonium atoms out of consideration for the time being. Over the greater part of the range of observations the scattering power of sulphur is much greater than that of oxygen. On the other hand there are four oxygen atoms per sulphur atom. It is therefore not entirely obvious that the sulphur lattice may be determined independantly of the oxygen lattice. Nevertheless this can be done by means of the Laue observations. The justification of this statement will be given later (see p. 70).

Having now found the caesium (ammonium) positions and the sulphur positions, the twelve parameters for the oxygen atoms were determined from considerations of the intensities observed in the oscillation photographs of ammonium persulphate.

There are thus three main steps in the determination of the structure:

1. Determination of the caesium parameters, using the oscillation photographs of caesium persulphate.

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1) James and Brindley, Z. Krist. 78, 470. 1931.

2. Determination of the sulphur positions, using the Laue data of ammonium persulphate.

3. Determination of the oxygen positions, using data from oscillation photographs of ammonium persulphate.

These three individual steps will be discussed independantly in the following sections.

4. Determination of the Caesium Positions.

Observed intensities of reflections $hk0$, $0kl$ and $h0l$ for caesium persulphate are given in tables II—IV.

Table II. $Cs_2S_2O_8$. Reflections $hk0$[1].

$h00$	I	F calc. A	B	$h10$	I	F calc. A	B	$h20$	I	F calc. A	B
								020	nil	0	14
				110	w —	89	70	120	m —	149	117
200	w	46	70	210	s	129	165	220	nil	0	2
				310	m	112	92	320	m —	68	49
400	s	141	177	410	w —	52	58	420	nil	0	11
				510	vw	17	8	520	m	138	107
600	m +	88	101	610	m +	69	87	620	nil	0	4
				710	w	85	68	720	nil	8	0
800	m	63	86	810	m	66	75				

$h30$	I	F calc. A	B	$h40$	I	F calc. A	B	$h50$	I	F calc. A	B
				040	s	160	190				
130	w +	77	52	140	nil	0	17	150	w	63	63
230	s	115	127	240	w	36	40	250	s	97	131
330	w +	101	72	340	nil	0	11	350	w	88	88
430	w +	49	52	440	s	120	146	450	vvw	43	52
530	nil	16	3	540	nil	0	17	550	nil	14	14
630	m	65	74	640	w	80	90	650	w	60	85
730	w +	82	57								

$h60$	I	F calc. A	B	$h70$	I	F calc. A	B	$h80$	I	F calc. A	B
060	nil	0	26					080	m	114	123
160	w	104	89	170	nil	53	35	180	nil	0	20
260	nil	0	4	270	m	82	73	280	vw —	27	28
360	vw	50	40	370	w —	75	52				
460	nil	0	22								
560	w	60	97								

1) The calculated amplitudes given in column headed A are for the Cs-contribution alone, those in column B are for the Cs- and S-contribution.

Table III. $Cs_2S_2O_8$. Reflections $0kl$[1]).

$0k0$	I	F calc. A	B	$0k1$	I	F calc. A	B	$0k2$	I	F calc. A	B	$0k3$	I	F calc. A	B
								002	s	175	212				
				011	w	20	27	012	m—	35	52	013	w	46	62
020	nil	0	14	021	s	186	227	022	vw+	0	11	023	s	140	164
040	s	160	190	031	vw	17	27	032	nil	32	38	033	w—	43	66
060	nil	0	26	041	nil	0	22	042	s	144	169	043	nil	0	14
080	m	114	123	051	nil	14	14	052	w	27	44	053	w—	38	38
				061	s	131	149	062	nil	0	22	063	m	109	121
				071	vw	12	17	072	vvw	23	19	073	nil	33	52
				081	nil	0	2								

$0k4$	I	F calc. A	B	$0k5$	I	F calc. A	B	$0k6$	I	F calc. A	B
004	m+	122	139					006	w—	77	77
014	w	53	76	015	vw	57	75	016	vw	58	79
024	nil	0	5	025	m	95	102				
034	vw	49	58	035	w	54	80				
044	m+	107	120	045	nil	0	4				

Table IV. $Cs_2S_2O_8$. Reflections $h0l$[2]).

$h00$	I	F calc. A	B	C	$h01$	I	F calc. A	B	C	$h02$	I	F calc. A	B	C
600	m+	88	101	107	501	m	137	111	149	402	s	123	157	116
400	s	141	177	137	301	m	90	61	100	202	w	6	21	46
200	w	46	70	68	101	m	139	113	96	002	s	175	212	200
					$\bar{1}$01	m	177	133	73	$\bar{2}$02	w	88	113	83
					$\bar{3}$01	nil	48	36	14	$\bar{4}$02	s	109·	134	181
					$\bar{5}$01	m	144	110	115					

$h03$	I	F calc. A	B	C	$h04$	I	F calc. A	B	C
303	m+	107	73	79	204	w+	42	67	77
103	s	74	71	133	004	ms	122	139	110
$\bar{1}$03	m	157	119	130	$\bar{2}$04	m	101	133	148
$\bar{3}$03	nil	0	7	25	$\bar{4}$04	w	65	73	73

As previously stated, the main variations in intensities can be considered, at least to a first approximation, as being due to the caesium

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1) The calculated amplitudes given in column headed A are for the Cs-contribution alone, those in column B are for the Cs- and S-contribution.

2) Column A: Cs-contribution to structure amplitude; Column B: $Cs + S$ contribution to structure amplitude; Column C: All atoms considered.

atoms alone. On that assumption, the expression for the structure amplitude may be taken as:

$$F = \quad 4f_{Cs} \quad \cos 2\pi (hx + lz) \cos 2\pi ky, \text{ if } h + k + l \text{ is even}$$
$$F = -4f_{Cs} \quad \sin 2\pi (hx + lz) \sin 2\pi ky, \text{ if } h + k + l \text{ is odd.}$$

From inspection of observed intensities, it is seen that whenever the expression for the structure amplitude contains the factors $\cos 2\pi\, 2y$, $\cos 2\pi\, 6y$ or $\sin 2\pi\, 4y$, the corresponding reflections are either completely absent or extremely weak. This shows that the y parameter for caesium has a value which hardly can be different from $2\pi y = 45°$. Knowing the value of the y parameter, we are able to get specific information concerning the values of other factors occurring in the expression for the structure amplitude. Considering planes $hk0$ and $0kl$, we are able to write a table showing qualitatively the variations which must occur in the value of $\cos 2\pi hx$, $\sin 2\pi hx$, $\cos 2\pi lz$ and $\sin 2\pi lz$ as follows:

Table V. Values of $\cos 2\pi\, hx$, $\sin 2\pi\, hx$, $\cos 2\pi lz$, $\sin 2\pi lz$.

h	$\cos 2\pi hx$	$\sin 2\pi hx$	l	$\cos 2\pi lz$	$\sin 2\pi lz$
1	small	small	1	very small	large
2	small	large	2	large	small
3	medium	medium small	3	small	large
4	large	small	4	large	small
5	very small	large	5	small	large
6	medium	medium	6	medium	medium
7	medium	nil			
8	medium	medium			

Regarding the hx values in table V, we find that $\cos 2\pi\, 5x$ is very small, while $\sin 2\pi 5x$ is large; likewise, $\cos 2\pi\, 7x$ is medium and $\sin 2\pi\, 7x$ nil, suggesting that $2\pi x$ must be in the neighbourhood of $50°$. Regarding the lz values, it appears that $2\pi lz$ must be close to $80°$. Trying values in these ranges, and using $h0l$ planes also in the testing, we finally come to the conclusion that the only set of parameters which fit the observations are:

$$2\pi x = 52° \qquad 2\pi y = 45° \qquad 2\pi z = 82°.$$

The structure amplitudes calculated with these values are shown in columns A in tables II—IV.

5. Determination of the Sulphur Parameters.

The Laue photograph data presented distinct advantages over the oscillation photograph data in the study of the sulphur lattice. There

were very numerous observations, the majority of which corresponded to high values of sin Θ/λ.

For reflections with high value of sin Θ/λ the scattering power of oxygen and ammonium is small compared to that of sulphur; but by no means negligible. The contribution to the amplitude from the sulphur atoms is characterized by three parameters, the contribution of ammonium and oxygen atoms by 15 parameters. The chance that the contributions from all the individual oxygen and ammonium atoms are in phase is therefore relatively small, so that the greater part of the observed intensity in most cases is due to the sulphur atoms. It would be very dangerous, of course, to assume that the oxygen and ammonium contribution could be neglected for every individual reflection; but it will be a correct assumption if we consider statistically a large number of reflections.

For example, we find when considering reflections $h4l$ and $h2l$, where $h + l$ is odd, that the intensity of reflection $h2l$ is stronger than that of $h4l$ (for constant h and l) in nine out of ten cases. This regularity we must then ascribe to the sulphur contribution. The reason why the regularity does not hold in the tenth case undoubtedly is due to the fact that the oxygen and ammonium contribution for this individual case is exceptionally high. The expression for the contribution from the sulphur atoms to the above reflections are:

$$h4l - 4f_S \sin 2\pi (hx + lz) \sin 2\pi 4y$$
$$h2l - 4f_S \sin 2\pi (hx + lz) \sin 2\pi 2y$$

Only the last factor in the two expressions is different, so that this factor must be responsible for the difference in amplitude of the two sets of planes. Our regularity thus indicates that sin $2\pi 2y$ is considerably greater than sin $2\pi 4y$.

A large number of similar regularities can be found by analogous statistical considerations. A series of such regularities are listed below:

Table VI. Regularities in the Laue photographs.

$h + k + l$ is even	$h + k + l$ is odd
$h3l \; > \; h1l$	$h3l < h1l$
$h5l <<< h3l$	$h4l < h2l$
$h6l \; \approx \; h4l$	$h5l > h3l$
$h7l >>> h5l$	$h6l \gg h4l$
$h8l \; < \; h6l$	$h7l < h5l$
$h9l \; < \; h7l$	$h9l > h7l$

The regularities listed in table VI permit us to draw important conclusions as to the relative values of $\cos 2\pi k y$ and $\sin 2\pi k y$. (It is to be emphasized that reflections which have been compared have always been chosen so that the value of $\sin \Theta/\lambda$ and the value of λ are approximately the same for both reflections.)

The information obtained from table VI is listed below:

Table VII. Relative values of $\cos 2\pi k y$ and $\sin 2\pi k y$.

$\cos 2\pi 3 y$	$>$	$\cos 2\pi y$	$\sin 2\pi 3 y < \sin 2\pi y$
$\cos 2\pi 5 y$	$<<<$	$\cos 2\pi 3 y$	$\sin 2\pi 4 y < \sin 2\pi 2 y$
$\cos 2\pi 6 y$	$\approx$	$\cos 2\pi 4 y$	$\sin 2\pi 5 y > \sin 2\pi 3 y$
$\cos 2\pi 7 y$	$>>>$	$\cos 2\pi 5 y$	$\sin 2\pi 6 y \gg \sin 2\pi 4 y$
$\cos 2\pi 8 y$	$<$	$\cos 2\pi 6 y$	$\sin 2\pi 7 y < \sin 2\pi 5 y$
$\cos 2\pi 9 y$	$>$	$\cos 2\pi 7 y$	$\sin 2\pi 9 y > \sin 2\pi 7 y$

The only value of y which satisfies these relations is $2\pi y = 126°$ (or $54°$, $234°$, $306°$).

Having now found y, we know one of the factors in the expression for the contribution from sulphur, and we are able to draw conclusions with respect to the factor containing the x and z parameters. For example, we find in the photographs that the reflections 621, 641 and 661 are all absent, whereas the reflections 611 and 631 are very strong. The expression for the structure amplitudes (sulphur contribution) for these reflections are (inserting the known value of y):

$6k1$	Structure Amplitude	Int. obs.	$6k1$	Structure Amplitude	Int. obs.
611	$-2.36 fs \cos 2\pi (6 x + z)$	vs	641	$-2.36 fs \sin 2\pi (6 x + z)$	nil
621	$3.80 fs \sin 2\pi (6 x + z)$	nil	651	0	nil
631	$3.80 fs \cos 2\pi (6 x + z)$	vs	661	$-2.36 fs \sin 2\pi (6 x + z)$	nil

There are two ways in which we can explain the observed intensities of reflections $6k1$. Either $\cos 2\pi(6x + z)$ is very large and $\sin 2\pi(6x + z)$ nil, or the contribution from ammonium and oxygen atoms will exactly balance the sulphur contribution for reflections 621, 641 and 661. The latter possibility cannot, of course, be disproved; but it is an unlikely explanation; therefore we will assume that the first interpretation is correct, i. e. $2\pi(6x + z) \approx n \cdot \pi$.

In an analogous manner, it is possible to deduce a whole series of similar relations. It must be emphasized that these conclusions represent only probabilities, not undisputable facts: therefore the attempt must be made to find such values of x and z as satisfy the greatest possible number of the relations listed below:

Table VIII. Conclusions from Laue Photographs.

Observation	$2\pi(hx+lz)$	Observation	$2\pi(hx+lz)$
$\sin 2\pi(6x+z) \approx 0$	$189°$	$\|\sin 2\pi(7x+z)\| > \|\cos 2\pi(7x+z)\|$	$58°$
$\sin 2\pi(8x+2z) \approx 0$	$182°$	$\|\sin 2\pi(5x+z)\| \approx \|\cos 2\pi(5x+z)\|$	$140°$
$\sin 2\pi(10x+3z) \approx 0$	$175°$	$\|\sin 2\pi(9x+2z)\| > \|\cos 2\pi(9x+2z)\|$	$231°$
$\sin 2\pi(x+2z) \approx 0$	$199°$	$\|\sin 2\pi(4x+z)\| > \|\cos 2\pi(4x+z)\|$	$271°$
$\cos 2\pi(x+3z) \approx 0$	$94°$	$\|\sin 2\pi(3x+2z)\| > \|\cos 2\pi(3x+2z)\|$	$297°$
$\sin 2\pi(5x+6z) \approx 0$	$335°[1])$	$\|\sin 2\pi z\| > \|\cos 2\pi z\|$	$255°$
$\cos 2x(x-2z) \approx 0$	$259°$	$\|\sin 2\pi(4x+5z)\| > \|\cos 2\pi(4x+5z)\|$	$31°[1])$
$\sin 2\pi(4x-5z) \approx 0$	$1°$	$\|\sin 2\pi(3x+4z)\| > \|\cos 2\pi(3x+4z)\|$	$90°$
$\sin 2\pi(7x-3z) \approx 0$	$298°[1])$	$\|\sin 2\pi(3x+5z)\| < \|\cos 2\pi(3x+5z)\|$	$342°$
$\cos 2\pi(9x-2z) \approx 0$	$291°[1])$	$\|\sin 2\pi(3x-5z)\| < \|\cos 2\pi(3x-5z)\|$	$312°[1])$
		$\|\sin 2\pi(5x-2z)\| > \|\cos 2\pi(5x-2z)\|$	$95°$
		$\|\sin 2\pi(8x-3z)\| < \|\cos 2\pi(8x-3z)\|$	$347°$
		$\|\sin 2\pi(5x-z)\| < \|\cos 2\pi(5x-z)\|$	$350°$
		$\|\sin 2\pi(6x-z)\| \approx \|\cos 2\pi(6x-z)\|$	$39°$
		$\|\sin 2\pi(7x-3)\| > \|\cos 2\pi(7x-z)\|$	$268°$
		$\|\sin 2\pi(8x-z)\| < \|\cos 2\pi(8x-z)\|$	$137°$

The values $2\pi x = 49°$ and $2\pi z = 255°$ satisfy almost all of these relationships, as shown by the angles listed in the second column. The parameters for sulphur may consequently be taken as:

$$2\pi x = 49° \qquad 2\pi y = 126° \qquad 2\pi z = 255°.$$

6. Determination of the Oxygen Positions.

With the positions of the sulphur and ammonium (caesium) atoms fixed, it now became possible to consider the distribution of the oxygen atoms. Here, twelve parameters are involved. No such direct approach as was used for the heavier atoms seemed at first possible. Of course it is well known that in general the bonds of sulphur are directed towards the corners of a tetrahedron and that the sulphur to oxygen distance is about 1.45—1.50 Å. Such assumptions, if made at this point would greatly facilitate further steps. However, in dealing with a new group such as this, when the purpose is to determine its configuration, it is preferable to proceed with as few assumptions as possible. We have so far made no such assumptions, and it was decided to attempt the further study by means of twodimensional Fourier analysis of electron distribution. Twodimensional Fourier analyses were first used by W. L. Bragg[2] and his collaborators.

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1) Discrepancies.
2) W. L. Bragg, Pr. Roy. Soc. A. **123**, 537. 1929.

The principles underlying the application of this method in the present case are the following: We have been able to determine the positions of the ammonium and sulphur atoms, so that the contributions from these atoms to the structure amplitude are known. When comparing the observed amplitudes with the calculated contribution from ammonium and sulphur, it is found that the agreement is not good. The lack of agreement must be ascribed to the oxygen contribution. As mentioned in the previous section we gave reasons that the oxygen contribution is not overwhelming due to the many parameters involved. Consequently it is to be expected that the sign of the final amplitude will be the same as for the ammonium and sulphur contribution in all but a few cases. Therefore, if we carry through the twodimensional analysis on the basis of the observed amplitudes and the assumption that the signs are the same as for the ammonium plus sulphur contribution, we ought to get a reasonably good representation of the electron density distribution, showing clearly the location of the oxygen atoms. This method of determining directly the parameters for some of the atoms in the lattice was first used by one of us on $NaClO_3$[1]), later on by J. West[2]) on KH_2PO_4.

In the present case we have used only photographic methods and the observed intensities have been estimated visually. Knowing the ammonium and sulphur contribution it was, however, possible to correlate our estimated intensities with numerical values of the amplitudes. Naturally no great absolute accuracy was obtained in that way, although readers familiar with the photographic methods will realise that the relative values of the estimated amplitudes are rather accurate. Of course we fully realised that our procedue, at best, could only lead to approximate determinations of the whereabouts of the oxygen atoms.

We calculated the electron distribution for the structure projected on the (010) face. If ϱ_{xz} is the electron density at a point x, z in this projection, the expression becomes:

$$A \, \varrho_{xz} = \sum_{-\infty}^{\infty} \sum_{-\infty}^{\infty} F_{h0l} \cos 2\pi (hx + lz)$$

where $A = \mathrm{arsin}\,\beta$. In writing the expression for the electron density in the form given above, it has to be remembered that $F_{000} = Z$, the total number of electrons per unit cell.

1) W. H. Zachariasen, Z. Krist. 71, 517. 1929.
2) J. West, Z. Krist. 74, 306. 1930.

The results of our calculations are shown graphically in fig. 1. The curves are drawn through points of equal electron density. In addition to the peaks due to sulphur and ammonium atoms (marked S and NH_4), there are peaks marked 1 and 2. The volumes associated with these two peaks are approximately the same for both, comparable to the volume of the sulphur peak and roughly twice the volume under the NH_4 peak.
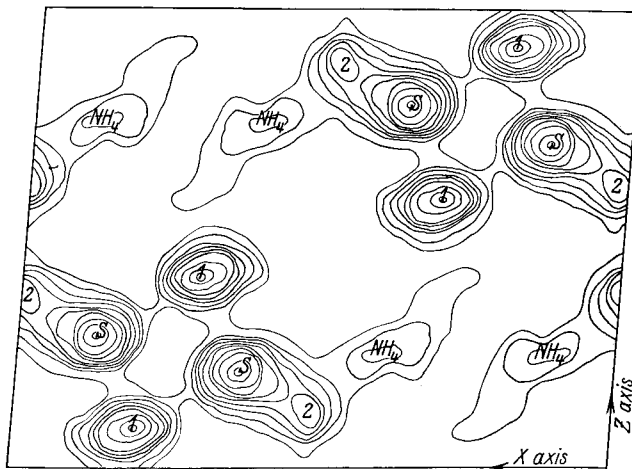

Fig. 1. Shows the electron density distribution projected on the (010) plane. The curves connect points with equal electron density.

It becomes logical therefore to attribute each of the two additional peaks, 1 and 2, to two oxygen atoms in nearly perfect superposition. The approximate values of the x and z parameters of the oxygen atoms were thus obtained. They were: for oxygen atoms corresponding to peak 1 $2\pi x = 75°$, $2\pi z = 330°$, or $2\pi x = 105°$, $2\pi z = 210°$, and for the oxygen atoms corresponding to peak 2 $2\pi x = 5°$, $2\pi z = 220°$. By careful inspection of individual reflections more accurate values were found:

	$2\pi x$	$2\pi z$		$2\pi x$	$2\pi z$
0_I	15°	220°	0_{III}	75°	335°
0_{II}	10°	245°	0_{IV}	105°	215°

It remained now to find the y parameters of the oxygen atoms. This was attempted by means of a two dimensional Fourier analysis of the electron distribution in the xy-plane; but, in this case, the results were not very helpful, since it was difficult to distinguish the diffuse and ill defined peaks of the oxygen atoms. Indeed, the success of the determination of the xz parameters was due to the fact that oxygen atoms

were almost exactly superimposed in the projection, thus giving well defined peaks. However, by making use of the parameters already found, and turning to our data for reflections $hk0$ and $0kl$, the last remaining parameters could be determined. For example, we find that the 120 reflection is of intensity rated very strong. The expression for the amplitude is:

$$3.16 \, NH_4 - 2.88 \, s + 4O \, (\sin 15° \sin 2\pi y_1 + \sin 10° \sin 2\pi y_2 + \sin 75°$$
$$\sin 2\pi y_3 + \sin 105° \sin 2\pi y_4).$$

Inserting the numerical values of the scattering powers, the sum of the ammonium and sulphur contributions totals -11; the first two terms in the oxygen contribution are obviously very small; therefore the values of $\sin 2\pi y_3$ and $\sin 2\pi y_4$ must necessarily be very large and negative in order to explain the observed intensity. This suggests that $2\pi y_3$ and $2\pi y_4$ are in the neighbourhood of 135°. By considerations of this kind, applied to a large number of observations, the y parameters were first approximately found, and then corrected by further structure amplitude calculations. The resulting parameters are:

$$2\pi y_1 = 180° \qquad 2\pi y_2 = 70° \qquad 2\pi y_3 = 150° \qquad 2\pi y_4 = 125°$$

The agreement between calculated structure amplitudes based on the parameters of table IX and the observed intensities, is good throughout the range of observation. This is demonstrated in tables X—XIII. Such discrepancies as appear, small in number and small in degree, may be attributed to errors in the parameter values, and might be improved by further slight changes. However, when there are as many as eighteen parameters involved, this becomes a complicated and arduous process, and it is doubtful whether it is profitable to attempt to continue this labour when the excellent agreement leaves no doubt as to the correctness of the structure.

Table IX. Final Parameter Values.

	$2\pi x$	$2\pi y$	$2\pi z$
NH_4	52°	45°	90°
S	49	126	255
O_I	15	180	220
O_{II}	10	70	245
O_{III}	75	150	335
O_{IV}	105	125	215
Cs	52	45	82

For the sulphur and caesium positions we can claim an accuracy of $\pm 3°$; for the remaining parameters $\pm 5°$.

Table X. $(NH_4)_2S_2O_8$. Reflections $hk0$.

$hk0$	$\sin\theta/\lambda$	Int. obs.	F calc.	$hk0$	$\sin\theta/\lambda$	Int. obs.	F calc.
110	0.089	s	17	420	0.285	nil	11
020	.124	vvw	3	340	.315	nil	6
200	.128	w —	11	430	.317	m —	22
120	.140	vs	54	150	.318	nil	2
210	.143	vs	48	510	.327	nil	2
220	.179	nil	2	250	.336	m —	34
130	.197	w	30	520	.344	m —	18
310	.202	vw —	1	440	.357	ms	37
230	.226	m +	30	350	.366	vw —	2
320	.229	w	20	530	.368	w +	33
040	.248	s	50	060	.373	w +	42
400	.256	w	13	160	.379	w —	13
140	.257	vw +	14	600	.385	m —	27
410	.264	nil	3	610	.390	w	18
330	.268	m	31	260	.395	nil	8
240	.280	s —	43				

Table XI. $(NH_4)_2S_2O_8$. Reflections $0kl$.

$0kl$	$\sin\theta/\lambda$	Int. obs.	F calc.	$0kl$	$\sin\theta/\lambda$	Int. obs.	F calc.
011	0.103	ms	16	042	0.298	w +	33
020	.124	vvw	3	033	.309	trace	6
021	.149	vs	75	051	.322	vw +	26
002	164	s +	49	004	.328	nil	3
012	.175	s +	43	014	.334	m	36
031	.204	vvw	3	043	.350	nil	13
022	.206	m	30	024	.351	vw +	13
032	.248	w	10	052	.352	w +	36
040	.248	s	50	060	.373	w +	42
013	.254	m —	23	034	.377	vw +	25
041	.262	nil	6	061	.382	m	43
023	.276	vw	9	053	.396	vw	7

Table XII. $(NH_4)_2S_2O_8$. Reflections $h0l$.

$h0l$	$\sin\theta/\lambda$	Int. obs.	F calc.	$h0l$	$\sin\theta/\lambda$	Int. obs.	F calc.
10$\bar{1}$	0.099	vs	80	30$\bar{3}$	0.298	w	19
101	.109	ms	20	402	.317	vw	6
200	.128	w —	11	50$\bar{1}$	.324	w	15
002	.164	s +	49	303	.326	w	24
20$\bar{2}$	.199	vw —	0	004	.328	nil	3
30$\bar{1}$	.202	s +	53	501	.338	nil	25
301	.216	m	18	20$\bar{4}$	.341	s	50
202	.217	s	35	204	.363	m	32
10$\bar{3}$	.248	w	13	600	.385	m —	27
400	.256	w	13	50$\bar{3}$	.386	w —	22
103	.260	s +	72	40$\bar{4}$	.398	w —	18
40$\bar{2}$	.292	s +	86				

7. Discussion of the Structure.

Fig. 2 shows a diagram of the complete structure projected on the (010) face.
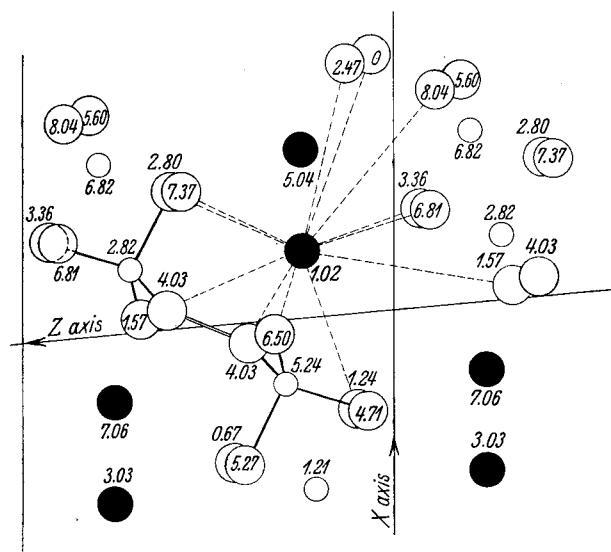

Fig. 2. The atomic arrangement in $(NH_4)_2S_2O_8$ viewed along the b-axis. Large filled circles represent ammonium groups, large open circles represent oxygen atoms and small circles sulphur atoms.

Table XIII. Interatomic Distances.

NH_4 — O_I	3.44 Å	S — O_I	1.51 Å	O_I	— O_I	1.46 Å
	3.59	— O_{II}	1.51	O_I	— O_{II}	2.49
	3.48	— O_{III}	1.52		— O_{III}	2.36
— O_{II}	2.92	— O_{IV}	1.44		— O_{IV}	2.45
	3.42			O_{II}	— O_{III}	2.68
	3.56				— O_{IV}	2.49
	2.95			O_{III}	— O_{IV}	2.27
— O_{III}	3.12					
	2.75					
— O_{IV}	2.95					
	3.16					
	2.84					

Average values:

$NH_4 — O$ 3.18 Å $S—O$ 1.50 Å $O—O$ 2.46 Å

Each ammonium atom is surrounded by 12 oxygen atoms at an average distance of 3.18 Å. The distance calculated on the basis of the ionic radii published by one of us is 3.16 Å[1]).

Sulphur is surrounded by four oxygen atoms at an average distance of 1.50 Å, the four oxygen atoms occupying the corners of a nearly regular tetrahedron. The configuration of around sulphur is thus exactly the same as in the sulphate group. (The S—O distance in Na_2SO_4 was found to be 1.49 Å[2]). However, the SO_4-groups do not appear as independant entities in the structure. The SO_4-groups are linked together in pairs by a valence bond between two oxygen atoms, one from each of two SO_4-groups. Thus the existence of the persulphate group, $(S_2O_8)^{-2}$, has been proved in the most direct manner. The shortest distance between oxygen atoms of different persulphate groups is of the order of 3.4 Å, in agreement with the value 3.45 Å predicted from the ionic radii.
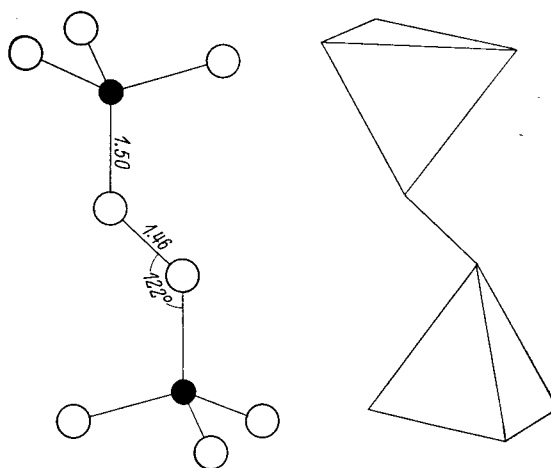

Fig. 3. Shows the structure of the persulphate group.

A drawing of the persulphate group is given in fig. 3, showing clearly the characteristic features of the structure. The distance between the two oxygen atoms linked together by a valence bond is only 1.46 Å. This value is, of course, not very accurate (probably to $\pm$ 0.15 Å). The valence radius of oxygen according to Pauling[3]) (or the "atomic" radius

1) W. H. Zachariasen, Z. Krist. 80, 137. 1931.
2) W. H. Zachariasen and G. E. Ziegler, Z. Krist. 81, 92. 1932.
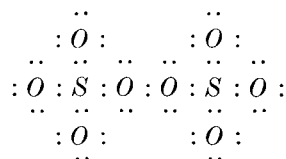3) L. Pauling, Pr. Nat. Acad. Washington 18, 293. 1932.

according to Goldschmidt[1])) is 0.65 Å, in fair agreement with our value of 0.73 Å $\pm$ 0.08 Å. The persulphate group has a center of symmetry, lying halfway between the two linked oxygen atoms. The presence of this center of symmetry may or may not be a characteristic property of the group. The individual interatomic distances within the group is given in table XIII. The angles between the bonds going from sulphur to oxygen atoms are all very close to the tetrahedral angle ($109\frac{1}{2}°$), whereas the angle between the two bonds of the singular oxygen (O_1) is $122°$.

The structural formula for the persulphate group which the chemists give is:

$$
\begin{array}{ccc}
O & & O \\
| & & | \\
O\!-\!S\!-\!O\!-\!O\!-\!S\!-\!O \\
| & & | \\
O & & O
\end{array}
$$
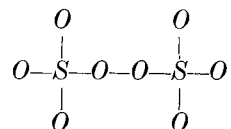
Inasmuch as this formula represents some features of the group, the formula must be said to be correct.

As is the case with all groups of the form $(S_m O_n)^{-2}$, the bonds in the persulphate group may be represented by electron pair bonds, so that the Lewis structural formula becomes:

$$
\begin{array}{c}
:\!\overset{..}{O}\!: \qquad\quad :\!\overset{..}{O}\!: \\[2pt]
:\!O\!:\!S\!:\!O\!:\!O\!:\!S\!:\!O\!: \\[2pt]
:\!\underset{..}{O}\!: \qquad\quad :\!\underset{..}{O}\!:
\end{array}
$$

According to Pauling's[2]) and Slater's[3]) considerations we may interprete the group as: $(S_2^{+2} O_6^{-1} O_2)^{-2}$. The S^{+2} particle can be thought of as having four unpaired electrons, one $3s$ and three $3p$; therefore, if linear combinations of the s and p eigenfunctions are taken, it is capable of forming four bonds directed towards the corners of a tetrahedron. The O^{-1} particle has only one unpaired electron, and therefore should be expected to form only one bond; the neutral oxygen atom on the other hand with two unpaired $2p$ electrons may form two bonds which tend to be at right angles to each other. The angles between these two bonds we found experimentally to be $122°$. The fact that this value is considerably higher than the one to be expected from the above inter-

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1) V. M. Goldschmidt, Geochemische Vert. Gesetze d. El.

2) L. Pauling, J. Amer. Chem. Soc. **53**, 1367. 1931.

3) J. C. Slater, Physic Rev. **37**, 481. 1931.

pretation of the group, may be attributed to the repulsion between other atoms of the group.

The atomic arrangement is in agreement with the known optical properties of the crystal, as will be shown by the following qualitative considerations. The optical anisotropy is due to the fact that all or some of the atoms in the lattice show a different degree of polarisation for different directions of the electric vector, the cause of which is the asymmetrical field produced by the surrounding atoms. Since the field created by a dipole is inversely proportional to the cube of the distance it will be sufficient for qualitative considerations to consider only the nearest neighbours. The twelve oxygen atoms which surround ammonium are evenly distributed over the surface of a sphere, so that the ammonium atoms will be polarized to practically the same extent for all directions of the electric vector. The SO_4-components of the persulphate group conform to a cubic arrangement and consequently contribute nothing to the birefringence. However, the oxygen atoms which are only 1.46 Å apart represent a highly anisotropic configuration, so that this feature of the structure will chiefly be responsible for the birefringence. The connection lines between the two oxygen atoms are all parallel. If the electric vector is parallel to the connection line, the moment induced in one of the atoms will create a comparatively strong field on the other oxygen atom, the field having the same direction as the external field. If on the other hand, the electric vector is perpendicular to the connection line, the moment induced in one of the atoms will create a field in the other opposing the external field. Consequently it is to be expected that the crystal will be optically positive with strong birefringence; the acute bisectrix should be parallel to the connecting line between the two oxygen atoms (O_I), and the axial angle, $2 V$, should be close to zero. The optical properties given by Groth show all these features.

As far as we know, the wave length of the K absorption edge of sulphur in persulphates has not been measured. According to the structure, it should be expected that there only would be one edge, having approximately the same wave length as that of sulphur in the sulphates, probably slightly displaced towards smaller wave lengths.

In conclusion we wish to emphasize that all the eighteen parameters involved have been determined accurately and uniquely without the use of any assumptions whatsoever other than those underlying the theory of diffraction of x-rays by crystals.

The persulphate group is the fifth sulphur-oxygen group the structure of which has been accurately determined. Investigations on further radicals of the same class are in progress in this laboratory. The importance of results of this kind for the understanding of the mechanism of chemical binding needs no comments.

Summary.

In order to determine the size and shape of the persulphate group $(S_2O_8)^{-2}$, the crystal lattice of the two isomorphous compounds, $Cs_2S_2O_8$ and $(NH_4)_2S_2O_8$, was examined. The Laue method and the oscillating crystal method were used.

The size of the unit cell for the two compounds are:

$Cs_2S_2O_8$	$a = 8.13$ Å	$b = 8.33$ Å	$c = 6.46$ Å	$\beta = 95°\ 19'$
$(NH_4)_2S_2O_8$	$a = 7.83$ Å	$b = 8.04$ Å	$c = 6.13$ Å	$\beta = 95°\ 9'$

There are two molecules in the unit cell. The calculated densities are 3.47 and 1.96, whereas the directly determined density for the ammonium compound is 1.982. The space group is $P2_1/n$ (C_{2h}^5). All atoms are lying in general positions: $\pm (xyz) \pm (x + \frac{1}{2},\ \frac{1}{2} - y,\ z + \frac{1}{2})$.

By devising suitable methods of attack it was possible to determine all 18 degrees of freedom accurately and uniquely. The determination of the individual parameters are described in some detail. The final parameter values are given in table IX.

In the lattice two sulphur atoms and eight oxygen atoms are grouped together so as to form the persulphate group. This group may conveniently be described as two SO_4-groups linked together by a covalent bond between two oxygen atoms. The distance between these latter oxygen atoms was found to be 1.46 Å. The sulphur to oxygen distance is 1.50 Å. Ammonium is surrounded by twelve oxygen atoms at an average distance of 3.18 A.

The crystal lattice is in agreement with the optical properties.

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