The Size, Atomic Charges, and Motion of the Sulfate Radical of Symmetry $\bar{4}3m$ in the Crystal of Sulfohalite, $Na_6ClF(SO_4)_2$

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In order to obtain accurate structural data on the sulfate ion with the shape of regular tetrahedron, the crystal structure of the mineral sulfohalite, of Type $H5_3$, has been refined by the method of least squares involving 11 variable parameters with use of a two-dimensional set of data obtained at 10–15 °C through a multiple-film, integration Weissenberg technique. A round rod 0.1 mm thick and with a [101] axis was bathed in an x-ray beam from a Cu target with or without a Ni filter. Visually measured intensities of 61 independent reflections, inclusive of ones unobserved and ones falling in the $K\beta$ region, were used with corrections for absorption, extinction, and dispersion. The resulting structural data: (1) as regards the sulfate ion $S^{8\varepsilon-2}O^{2\varepsilon-}{}_4$, $\varepsilon = 0.47 \pm 15$, leading roughly to $S^{2+}O^-{}_4$, and the radius, $d_{S-O} \sin\alpha$, of a circle lying around the S–O bond in case of rest where the torsionally oscillating O haunts amounts to 0.15 Å, where angle $\alpha = 6.0 \pm 1.1$ ° and distance $d_{S-O} = 1.474 \pm 9$ Å; (2) as regards the crystal lattice, Space Group $O_h^5 - Fm3m$; $a = 10.068 \pm 3$ Å at $12._5 \pm 1.$ °C (or 10.071 ± 3, $25°$—estd.); $B_{Na} = 1.6 \pm 1$, $B_{Cl} = 1.5 \pm 2$, $B_F = 1.1 \pm 3$, $B_S = 0.9 \pm 2$, $B_O = 1.3 \pm 3$, in $Å^2$; $x_{Na} = 0.2232 \pm 5$, $x_O = 0.1655 \pm 5$. Note that Residual $\sum |\Delta_{oc}F| / \sum |F_o| = 5$ %, as against its "experimental" analogue $\sum |\delta F_o| / \sum |F_o| = 3$ %, where δF_o means an experimental error.

1. Structural Study of the Radical Ion

The steady progress of our method and technique of structural research through x-rays has now reached a state under which we can not only analyse a material even with such a complicated structure as protein but also accurately and minutely determine various properties of a material with simple structure. This state of matters allows us possible to perform the study[1] of lattice-energy calculation on such ionic crystals containing radicals as NH_4Cl, $BaSO_4$, and $Na_6ClF(SO_4)_2$, where closer study needs precise and detailed structural data regarding a given radical in particular, namely, the size and shape of it and the distribution of electric charge within it. At the advice of Prof. T. Watanabé and Prof. M. L. Huggins, this study of refining the crystal structure of a sulfate by the modern technique was taken up in order to supply the needs.

With respect to the radical ion SO_4^{2-} the crystal of sulfohalite, $Na_6ClF(SO_4)_2$, is quite suitable for the purpose intended, and was chosen as the fit research material for this structural determination. The primary reason for the suitability is that the sulfate radical and the atoms around it fit together so neatly as to form in a tetrahedral network whose site or local symmetry at Atom S or Radical SO_4^{2-} and lattice symmetry, respectively, are regularly

tetrahedral ($T_d-\bar{4}3m$) and cubic (of the Laue symmetry O_h-m3m), thus the radical shaping into its highest possible symmetry indeed—a situation rarely occurring among moderately simple sulfates at ordinary temperatures. Some of the secondary reasons are that the number of parameters of atomic position or of electrovalency is as few as 1 each within the radical and 1 or 3 without it, respectively, and that the atoms other than O, whose parameters are chiefly aimed to be determined, are neither very "heavy" nor numerous in kind.

The electrovalency of, or partial charge on, an atom of a radical is still at present difficult to determine in every way, more than geometrical properties of it. Yet, it is highly desirable to try getting even a rough estimate of the charge as well as a precise estimate of the size, particularly in the case where a radical displays its most symmetrical shape despite its lying not isolated but arrested; so that such a trial as this study had been hoped for by the chemist public. The purpose of this brief note is to give notice chiefly of the results of this attempt to chemists longing to receive information of such data early, but merely subordinately of the experimental procedure.

2. Experimental Procedure of Structural Analysis

2.1) *The past and the present works.* — The crystal structure of the mineral sulfohalite[2-6] is a unique one and is assigned a Strukturbericht symbol $H5_8$.[4] The refinement of the structure could be accomplished through a regular routine of modern x-ray analysis,[*1] except for a few novelties worthy of particular mention, and so its procedure will now be outlined just briefly, the meaning of the symbols being often left unexplained.

2.2) *Cell dimension.* — The lattice parameter, a, was measured by comparison with a standard sample of powdered NaCl, not only by Taylor and Sinclair's or Nelson and Riley's method of extrapolation[7] but also by a method of observing back-reflection patterns.

2.3) *Intracellular structure.* — The structure has been refined by the method of least squares involving 11 parameters to be adjusted with use of a two-dimensional set of data obtained at 10-15°C through a quadruple-film, integration Weissenberg technique. A round rod 101 ± 3 μm thick and with a [101] axis was bathed in an x-ray beam from a Cu target with or without a Ni filter. Visually measured intensities of 61 independent reflections, inclusive of 8 ones too faint to be observable and 11 ones falling in the Cu$K\beta$ region, were used with corrections[8] for absorption,[9] secondary extinction,[10] and dispersion.[11,12]

The data on relative observed structure factor, F_o' ($=F_o/s$), and its rel-

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evant quantities, on which the subsequent treatment was based, are shown in Table 1, only partially for brevity. An ordinary weighting scheme[13] was followed out, with $w=\sigma^{-2}=(\delta F_o')^{-2}$; Hamilton's scheme[14] was adopted in treating unobserved reflections.

Table 1. Data on F_o' and its relevant quantities.

No.[a]	$h'\,k'\,l'$[b]	$h\;k\;l$[c]	N[d]	$10^2\|F_o'\|$	$10^2\|\delta F_o'\|$	$\|\delta F_o\|/\|F_o\|$[e]
1	2 1 0	1 1 1	3	984	12	0.012
2	0 2 0	0 2 0	4	1102	19	17
3	4 0 0	2 0 2	8	3339	79	24
4	2 3 0	1 3 1	11	1844	28	15
⋮						
9	6 3 0	3 3 3	27	4693	120	26
10	2 5 0	1 5 1	27	1377	19	14
11	8 0 0	4 0 4	32	5258	121	23
12	8 2 0	4 2 4	36	(88<150	46	.523)
⋮						
50	16 6 0	8 6 8	164	304	16	53
51	18 3 0	9 3 9	171	370	98	.265
52	10 11 0	5 11 5	171	(103<180	54	.524)
53	2 13 0	1 13 1	171	(103<180	54	.524)
⋮						
59	16 8 0	8 8 8	192	1243	63	51
60	0 14 0	0 14 0	196	(73<130	38	.521)
61	20 0 0	10 0 10	200	1246	25	20
62	20 2 0	10 2 10	204⎱	These fell outside a film,		
63	4 14 0	2 14 2	204⎰	though $\theta=80.96°<90°$.		

a) The reflections from No. 51 on fell in the $K\beta$ region.

b) A tetragonal description with the c-axis chosen parallel to the cubic [101] zone axis.

c) The ordinary cubic description. Generally:

$$2h=h'-l',\quad k=k',\quad \text{and}\quad 2l=h'+l';$$
$$\text{or}\quad h'=h+l,\quad k'=k,\quad \text{and}\quad l'=-h+l.$$

Here, specifically, $l'=0$ and $h=l$.

d) $N=h^2+k^2+l^2=2h^2+k^2$.

e) The data in parentheses are concerned with the unobserved faint reflections. $\delta F_o'$ is a partial experimental error, but the total one may perhaps, on an average, about twice as large as that in absolute magnitude.

The 11 kinds of parameters to be adjusted were:

(1-5) Isotropic Debye factors for the five elements located each at five kinds of equivalent sites, $B_F,\;B_{Cl},\;B_S,\;B_{Na},\;\&\;B_O$;

(6, 7) Atomic-positional parameters of Na and O, $x_{Na}\;\&\;x_O$ (or $u\;\&\;v$);

(8) Scale factor, $s\;(=1/t)$;

(9) Parameter of extinction, g;

(10) Half angle of oscillation of an S-O bond, α_O;

(11) Parameter of electrovalency on atoms forming SO_4^{2-}, $\varepsilon_{S\&O}$.

The true correction formula[10] for the secondary extinction

$$[F_o(\text{corr.})/F_o's]^2=I_o(\text{corr.})/I_o's^2=1/(1-2g_\theta I_o's^2),$$
$$g_\theta/g=\beta_{2\theta}(\text{effective})=2(1+\cos^4 2\theta)A^*(2\theta)/(1+\cos^2 2\theta)^2 A^*(0),$$

was assumed to hold for the incorporated primary and secondary extinction. $A^{*\prime}$ $(=\mathrm{d}A^*/\mathrm{d}\mu)$ which was estimated for our case of circular cylinder[9b] produced values: $0.8 \lesssim \beta_{2\theta} \lesssim 1.7$, instead of unity, a constant independent of θ according to the old untrue correction formula.

In adopting data on atomic scattering factor,[15-17] the formal ionic valency was assumed, except for the radical-forming atoms; thus, $Na^+{}_6Cl^-F^-(S^{8\varepsilon-2}{}_-O^{2\varepsilon-}{}_4)_2$.[*2] As regards Atoms S and O, additional data[18,19] were referred to also, and a more minute treatment[20,21] was given in the following way.[*3] The atomic scattering factor for S^{z_S+} was formulated as[20]

$$\bar{f}(S^{z_S+})=2f_S(1s)+2f_S(2s)+6\bar{f}_S(2p)+2f_S(3s)+(6-z_S)\bar{f}_S(3p),$$
$$f(3s)\simeq \bar{f}(3p);$$

and that for O^{z_O-} was as[20,21]

$$\bar{f}(O^{z_O-})=2f_O(1s)+2f_O(2s)+\tfrac{1}{2}(3+z_O)\bar{f}_O(2p)$$
$$-\tfrac{1}{2}(1+z_O)[f^{\parallel}{}_O(2p)\cos^2\theta+f^{\perp}{}_O(2p)\sin^2\theta],$$

where such a bonding model for $SO_4{}^{2-}$ shown in Fig. 1 was assumed that contained Atom O in an activated state

$$O^{z_O-}, \ 1s^2 2s^2 2p_z{}^1 2p_x{}^{\frac{1}{2}(3+z_O)} 2p_y{}^{\frac{1}{2}(3+z_O)} \qquad (z_O \leqq 1)$$

and hence with a quite aspherical charge distribution. Values for both the factors were computed and then so modified by adjustment as to fit the known more reliable data.[15,16,18,22]
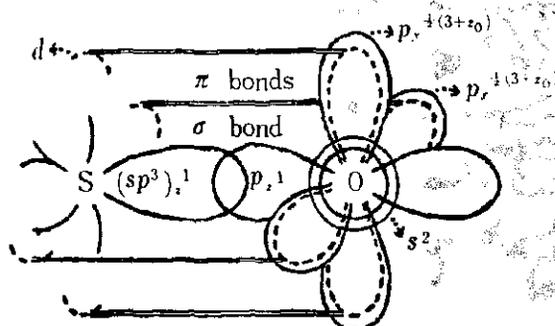
Fig. 1. Bonding model for $SO_4{}^{2-}$. $[S^{z_S+}O^{z_O-}{}_4]^{2-}$, where $z_S-4z_O=-2$, and $-z_S$ or z_O is the number of electrons in excess over that for the neutral atom S or O, resp.

The atomic scattering factor for Atom O oscillating torsionally around an S-O bond was formulated as[23]*4

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*2 A trial to let each of the five valencies vary freely resulted in a difference of a half or more electron units between the input and the output valency value.

*3 In this respect I obtained aid from the late Dr. Y. Tomiie on Oct. 12, 1959.

*4 The 3rd formula of Ref. 23 applied to the case of a (circumference of) circle, for which $\theta_2=\theta_1+2\pi$, was used—though the 1st formula, to lead to a circular disc, could be used instead.

$$2f_0 \exp(-B_0 D) \sum_i \cos(2\pi v' \xi_i) \cdot J_0(8^{\frac{1}{2}} \pi v'' \eta_i),$$

$$\xi_i = 2h + k, \ 2h - k, \ k, \ \& \ k; \quad \eta_i = h + k, \ h - k, \ (3h^2 + k^2)^{\frac{1}{2}}, \ \& \ (3h^2 + k^2)^{\frac{1}{2}};$$

$$\text{for } i = 1, 2, 3, \& 4; \quad \text{respectively}; \quad D^{\frac{1}{2}} = 1/2d_{hkh} = N^{\frac{1}{2}}/2a = \lambda^{-1} \sin\theta,$$

$$v' = v + (1 - \cos\alpha) v^\circ, \quad v'' = v^\circ \sin\alpha, \quad v^\circ = \tfrac{1}{4} - v;$$

$J_0(y)$ being the Bessel function of the 1st kind of the 0th order. — Cf. Fig. 2.
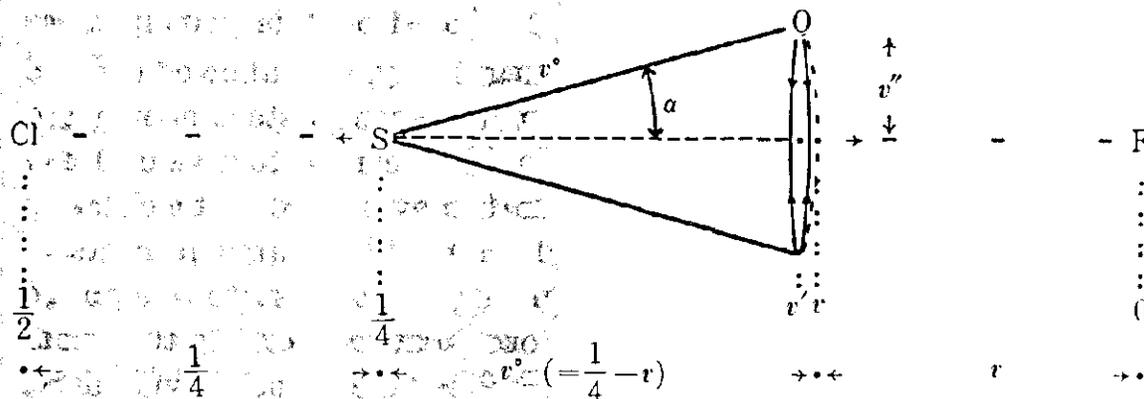
Fig. 2. Geometry of the torsional oscillation of O atom about an S–O bond.

A trial to take into account the tetragonal anisotropy in Na's thermal motion failed because we had in our hand just a single, equatorial, Weissenberg photograph.

3. Resulting Data and Comments on Them

The chief results of analysis are arranged in Table 2.

Table 2. Structural data on sulfohalite, $Na_6ClF(SO_4)_2$, at 10–15 °C.

A. Data on the sulfate radical.

$S^z s^+ O^z o^-_4$, $z_S = 2(4\varepsilon - 1)$, $z_0 = 2\varepsilon$, $\varepsilon = 0.47 \pm 15$.

α (half angle of torsional oscillation) = 6.0 ± 1.1 °.

$d(S\text{–}O) = 1.474 \pm 9$ Å.

B. Data on the crystal lattice.

O_h^5-$Fm3m$ (S. G. No. 225), $Z = 4$ chem. units/cell, a (12.$_5$ ± 1. °C) = 10.068 ± 3 Å
[a(25 °C) = 10.071 ± 3 Å, half the expansivity value of NaCl being assumed.].

		Atomic position F. C. +	Debye factor $B_i / \text{Å}^2$
4F$^-$	in (a)	(0 0 0)	1.1 ± 3
4Cl$^-$	in (b)	$(\tfrac{1}{2}\tfrac{1}{2}\tfrac{1}{2})$	1.5 ± 2
8S^{z}s$^+$	in (c)	$\pm(\tfrac{1}{4}\tfrac{1}{4}\tfrac{1}{4})$	0.9 ± 2
24Na$^+$	in (e)	$\pm(u\,0\,0) \curvearrowright$	1.6 ± 1
32O^{z}o$^-$	in (f)	$\pm(vvv), \pm(v\bar{v}\bar{v}) \curvearrowright$	1.3 ± 3

$u = 0.2232 \pm 5 \simeq \tfrac{1}{4}$, $v = 0.1655 \pm 5 \simeq \tfrac{1}{6}$.

C. Residual (Discrepancy index).

$$R = \sum |F_o - F_c| / \sum |F_o| = 5\%.$$

Compare: $R(\text{exp.}) = \sum |\delta F_o| / \sum |F_o| = 3\%$,

where δF_o means an experimental error.

A few comments will now be added to them.

A) Comments on the radical. — The probable range for the state of electrovalency here estimated experimentally is shown in Fig. 3 as a single-line segment about State $S^{1.76+}O^{0.94-}_4$ near the Lewis electronic state[24a] $S^{2+}O^-_4$. Another plausible range for it expected theoretically from Pauling's electro-neutrality principle[24b] is added there as a double-line segment about State $S^0O^{\frac{1}{2}-}_4$. Pauling's quantitative treatment[25] based on this principle, in com-bination with Huggins's data[26] on electronegativity, ever allowed us[27] to limit the latter range into a narrower one extending about a state shown there as Mark $+$. Pauling's more advanced study,[24c] referring to a value 1.49 Å for d_{S-O}, led to another state with $z_S = 0.29$ marked by $\times$ there; but a checking and slightly modified study of mine[28] based on his[24c] resulted in a state with $z_S = 0.45$ (or 0.64, due to Ref. 26), and, further, in some state in a range 0.16 $\leqq z_S \leqq 2.56$ (between Marks $[$ & $]$ there) if other data concerning the relation[24d] between partial ionic character of bonds[29,30] and electronegativity difference between atoms[24e,26] were taken also into account. A recent review[31] notes five data marked there by $\circ$. It is to be noted, in this connection, that the valency state of this sort must, by nature, largely depend on the condi-tion and situation under which the radical is put and hence be delicately variable or changeable. Let us note, further, that our assumption of the bonding model (Fig. 1) is satisfied with the result that $z_O < 1$. Thus our experimental conclusion should be considered, after all, to conform to the theoretical and other experi-mental ones essentially.

Fig. 3. Electrovalency state within the quite symmetrical ($\bar{4}3m$) SO_4^{2-} in sulfohalite. (The symbols are explained in § 3*A*.)

Numerical data on the thermal motion picturized in Fig. 2 are: the radius of circle, $v''a' = d\sin\alpha = 0.15 \pm 3$ Å; the apparent contraction in bond length, $(v'-v)a' = (1-\cos\alpha)d = 0.008 \pm 2$ Å. — Compare these data with those on the mean-square amplitude of isotropic lattice vibration of Atom O, $\overline{u_x^2}^{\frac{1}{2}}_O$, &c. $= (B_0/8\pi^2)^{\frac{1}{2}} = 0.12 \pm 3$ Å as well as on the uncertainty in bond length, $\delta d_{S-O} = \pm 0.009$ Å. N. B. The radius of circular disc,*4 $2^{-\frac{1}{2}}v''a' = 0.11 \pm 2$ Å. $a' = 3^{\frac{1}{2}}a$.

As for the bond length, see Table 3. Cf., e. g., two collections[32,33] of quite precise data on distorted sulfate radicals and the like.

B) Comments on the lattice. — The known data on the crystal lattice are collected and compared in Table 3. N. B. $t = 1/s = 0.92 \pm 3$, $10^5 g = 2.8 \pm 6$.

Table 3. The known data on d_{S-O}, a, x_{Na}, or x_O.

Source	Date	x_{Na}	x_O	a/Å	d_{S-O}/Å
Watanabé[2]	1934	.225	.165	10.17	1.49₇
Pabst[3]	1934	.226	.164	10.10 ±1	1.50₄
" corrected by Y. S.[a]				10.05₉ ±1	1.49₈
Pabst, *et al.*[6]	1963			10.065	[1.49₉]
Watanabé & Shiono[5][b]	1952?	.222	.163	10.062 ±1	1.51₆
Sakamoto (12.₅°C)	Status 1965	.2232 ±5	.1655 ±5	10.068 ±3	1.474 ±9

Cf. Ref. 32 (1965), on various hydrated sulfates. —   Individual d: 1.473 − 1.496
                                                       ±1   ±2
                                                  Average d: 1.479 − 1.486
                                                       ±1   ±2

a) Combination of Pabst's[3] data 10.08 [kX] for a and 0.001248 for $(\sin\theta)^2/(h^2+k^2+l^2)$ $[=(\frac{1}{2}\lambda/a)^2]$ leads to $\lambda(MoK\bar{a})=0.7122$ kX $=0.7136$ Å, in contrast to the datum 0.71069 Å due to *ITXRC*, Vol. 3 (1962), Tab. 2.2.4.

b) Residual, $R=12.7$ %. Experimental specifications: cylinder with a [001]-axis, Cu radiation, 3-dimensional data in the section $x=y$, visual comparison with an intensity scale, method of the Fourier synthesis.

C) *Comments on reliabiliy.* — Since the magnitudes of total error involving every possible systematic error are likely to be, on an average, about twice those of partial error here allotted to $|\delta F_o|$, the actual value to be expected for R(exp.) might be a little larger one, perhaps 4 %. The fact that R has reached a value of 5 %, which is close to and slightly larger than this value, seems to be satisfactory. Another criterion of reliability, other than R, may be the quantity $|\varDelta_{oc}F/\delta F_o|$, denoted as δ_F, which should be expected for a proper structural model not too much to exceed unity if δF_o were rightly the total error of experiment. In fact it amounts to 6.₁, 5.₅, 5.₄, 4.₉, 4.₇, 4.₄, 4.₄, 4.₀, 4.₀, 3.₉, 3.₄, 3.₃, 3.₂, 3.₂, 3.₂, and 46 values less than 3.₂, and on an average to *ca.* 2, i. e., $\sum \delta_F/m = 1.9_8$, where the number of observations, m, is 61. A second weighting scheme was tried with $w(2nd)=w(1st)(\sum\delta_F/m)^2/\delta_F^2=(1.9_8/\varDelta_{oc}F')^2$ for those 23 reflections of which $\delta_F \geq 2.0$; the data presented in Table 2 are those resulting primarily from the first, ordinary weighting scheme (cf. § 2.-3, par. 2) which afterwards have been modified but slightly on consideration of the closely agreeing results (with R by 0.000₉ less, but $\delta_F = 6.₇$, 7.₄, 6.₀, 4.₈, 4.₈, 4.₄, 4.₂, 4.₃, 3.₆, 5.₄, 4.₀, 2.₅, 4.₀, 3.₈, 2.₆, ⋯, resp., and $\sum\delta_F/m=1.9_8$) from the second scheme. The value for the criterion, similar to mine, proposed by Busing and Levy[34] is $[\sum(\delta_F)^2/(m-n)]^{\frac{1}{2}}=2.7_3$ or 1.6_0 (as against its expectation value of unity) for the 1st or the 2nd weighting scheme, respectively, where $[\delta F_o(\text{mine})]^{-2}=w_i(\text{theirs})$, $m=61$, and n(the number of parameters)$=11$.

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