278. *The Structures of Inorganic Oxy-acids: The Crystal Structure of Selenious Acid.*

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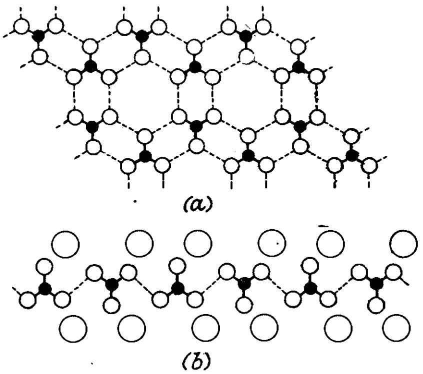
The crystal structure of the orthorhombic form of selenious acid has been determined. The crystals are orthorhombic: $a = 9{\cdot}15$ A., $b = 6{\cdot}00$ A., $c = 5{\cdot}05$ A., space-group $P2_12_12_1$, 4 molecules in the unit cell. The structure consists of pyramidal SeO_3 groups (Se–O, 1·74 A. mean, and mean interbond angle 100°) joined by O–H–O bonds of length 2·56 A. and 2·60 A. There are four such bonds connecting each SeO_3 group to neighbouring groups. The structural schemes in other inorganic oxy-acids are briefly discussed.

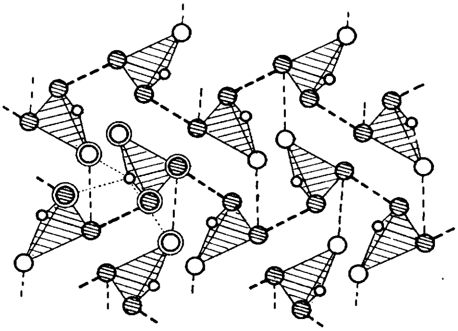
The crystal structures of inorganic oxy-acids H_mXO_n, which include compounds as important as sulphuric and nitric acids, have received very little attention. Only one such structure has been determined, that of the α-modification of iodic acid (Rogers and Helmholz, *J. Amer. Chem. Soc.*, 1941, **63**, 278). Compounds containing hydrogen and an electronegative atom such as nitrogen, oxygen, or fluorine are of particular interest in view of the important part played by the hydrogen in binding together the molecules by means of hydrogen bonds. Rather more is known of the structures of three other groups of compounds closely related to the inorganic oxy-acids, *viz.*, hydroxy-acids [$B(OH)_3$, $Te(OH)_6$], metallic oxy-hydroxides ($AlO{\cdot}OH$, $FeO{\cdot}OH$), and acid salts (*e.g.*, $NaHCO_3$). An electron-diffraction study of nitric acid vapour shows that the free molecule should be represented as an oxy-hydroxy-compound ($OH{\cdot}NO_2$), one N–O bond being appreciably longer than the other two (Maxwell and Mosley, *J. Chem. Physics*, 1940, **8**, 738). This will not, however, necessarily be the case in the crystal, which might consist of symmetrical NO_3^- ions held together by O–H–O bonds. If so, the extended hydrogen-bonded network of composition HNO_3, is to be compared with the infinite hydrogen-bonded $(HCO_3)_n^{n-}$ ion in $NaHCO_3$. In the acid salt KH_2PO_4 there is an infinite 3-dimensional array of PO_4^{3-} ions held together by hydrogen bonds, the K^+ ions being accommodated in the interstices of the $(H_2PO_4)_n^{n-}$ framework. The structure of crystalline H_2SO_4 may be closely related to this $(H_2PO_4)_n^{n-}$ framework.

FIG. 1.



Hydrogen-bond systems in (a) H_3BO_3 *and* (b) $NaHCO_3$.

FIG. 2.



The system of hydrogen bonds in α-HIO_3.

The crystal structures adopted by inorganic oxy-acids must depend on the part played by hydrogen in forming hydrogen bonds between the XO_n groups. In the acid salts so far studied there is at most one (short) O–H–O bond from any oxygen atom, and not all the oxygen atoms are necessarily engaged in hydrogen-bond formation. At the other extreme lie the hydroxy-acids, $X(OH)_n$, in crystals of which there are two (long) O–H–O bonds from every hydroxyl group, as in organic hydroxy-compounds such as resorcinol and pentaerythritol. It is convenient to classify the oxy-acids according to the ratio of H : O atoms, whereupon they fall into four groups :

H : O ratio =	1 : 4.	2 : 7.	1 : 3.	2 : 5.	1 : 2.	4 : 7.	2 : 3.	3 : 4.	1 : 1.
	HIO_4 $H_2S_2O_8$	$H_2S_2O_7$	HIO_3	H_2SO_5	H_2SO_4	$H_4P_2O_7$	H_2SeO_3	H_3PO_4	H_3BO_3 H_6TeO_6
	(*a*)				(*b*)	(*c*)			(*d*)

In group (*d*) there are equal numbers of hydrogen and oxygen atoms, and every oxygen atom takes part in two (long) O–H–O bonds, as shown for boric acid in Fig. 1 (*a*).

In group (*b*) the ratio H : O is 1 : 2, *i.e.*, there could be one O–H–O bond to each oxygen atom as in the acid salts KH_2PO_4 and $(NH_4)_2H_3IO_6$, with the same H : O ratio. The remaining classes are more interesting. In (*a*), with H : O less than ½, there are not enough hydrogen atoms to provide one O–H–O bond to each oxygen atom. One possibility would be that some of the oxygen atoms do not take part in the hydrogen-bonding scheme. For example, HIO_3 might form a chain structure like the $(HCO_3)_n^{n-}$ ion in sodium hydrogen carbonate (Fig. 1*b*). This acid is dimorphic, and the interatomic distances in the α-form have been interpreted as indicating the presence of " bifurcated hydrogen bonds " (Rogers and Helmholz, *loc. cit.*), four of which link each IO_3 group to neighbouring groups. There is, however, another interpretation of the " intermolecular " O–O distances (Wells, *Acta Crystallographica*, 1949, **2**, 128), according to which only half of those regarded by Rogers and Helmholz as hydrogen bonds should be regarded as O–H–O bonds. These are shown as heavy broken lines in Fig. 2, which shows a projection of the structure of α-HIO_3 on one face of the orthorhombic cell. The IO_3 groups are then linked into infinite chains, as would be expected by analogy with the bicarbonate ion.

In group (*c*), with H : O ratio between $\frac{1}{2}$ and 1, there are too many hydrogen atoms to allow only one O–H–O bond from each oxygen atom. If we assume that there will be, as in groups (*b*) and (*d*), one hydrogen bond for each hydrogen atom, then in H_2XO_3, for example, each XO_3 group will be attached to its neighbours by *four* such bonds. We have investigated the structure of one form of selenious acid (which is dimorphic) and find that this is the case. The hydrogen-bonding scheme is illustrated diagrammatically in Fig. 6.

A comprehensive discussion of the crystal structures of these oxy-acids cannot be attempted until the structures of more of the crystalline acids have been determined. It may be noted that other groups of hydrogen-bonded crystals present a similar problem to that of the oxy-acids. For example, in molecular crystals containing CO and NH groups the structural principles are comparatively simple if the molecule contains equal numbers of these groups, for each hydrogen atom joins together one carbonyl and one imino-group of different molecules. If, however, the molecule contains *different* numbers of carbonyl and imino-groups, then there are either too many or too few hydrogen atoms for any such simple structural scheme, and we have classes corresponding to (*a*) and (*c*) in the oxy-acids. So far only crystals (or polymers) with equal numbers of carbonyl and imino-groups have been subjected to detailed structural studies, *e.g.*, diketopiperazine, cyanuric acid, and nylon. The crystal structures of compounds such as oxalylurea would be of the greatest interest.

The Crystal Structure of Selenious Acid.

A solution of selenious acid is prepared by dissolving selenium dioxide in water. On rapid cooling, a supersaturated solution deposits lath-shaped crystals belonging to the triclinic system. Slow crystallisation yields (colourless) orthorhombic crystals. They are prisms with {100}, {110}, and {210} almost invariably present, either {100} or {110} predominating. Some crystals are terminated by {111} and $\{1\bar{1}1\}$, others by combinations of {101}, {111}, and {211}. There is a good (100) cleavage.

Unit Cell and Space-group.—From oscillation and Weissenberg photographs (Cu-K_α radiation) the unit cell dimensions were found to be: $a = 9{\cdot}15$ A., $b = 6{\cdot}00$ A., and $c = 5{\cdot}05$ A. The density was determined pyknometrically as 3·07 g./c.c., indicating 4 molecules in the unit cell. The only systematic absences are the odd orders of $h00$, $0k0$, and $00l$, whence the space-group is $P2_12_12_1$.

Determination of the Structure.—Apart from the hydrogen atoms, which cannot be located directly, there are 4 selenium and 12 oxygen atoms to place in the unit cell. All occupy general (4-fold) positions, the oxygen atoms in sets of four (designated O_1, O_2, and O_3). The approximate positions of the relatively heavy selenium atoms were readily obtained from the relative intensities of the high-order $hk0$ and $h0l$ reflexions, the oxygen scattering being neglected. The relative intensities of the reflexions 10.1.0, 10.2.0, and 10.3.0, and of 840 and 740 suggested a value of x close to 0·205, while those of 170, 270, 370, and 470 showed that $0{\cdot}23 < y_{Se} < 0{\cdot}25$, or $0{\cdot}25 < y_{Se} < 0{\cdot}27$. The approximate parameters derived in this way were: $x_{Se} = 0{\cdot}205$, $y_{Se} = 0{\cdot}245$ (or 0·255), and $z_{Se} = 0{\cdot}11$. A decision was not necessary at this stage between the two possible values for y_{Se}, though when the oxygen atoms are inserted they correspond to different structures. Possible positions for oxygen atoms were found in the following way. Simplified structure factor graphs were made by plotting on a projection of the unit cell the lines along which the function $4 \cos hx . \cos ky$ or $-4 \sin hx . \sin ky$ (for $hk0$ reflexions) is zero, and indicating in which regions it has positive or negative values. From such graphs it is possible to see at a glance the approximate contribution of 4 oxygen atoms placed anywhere in the cell. For certain $hk0$ reflexions with appreciable structure amplitudes the selenium contribution was known to be small; these planes therefore require large contributions from the 12 oxygen atoms. Assuming only that three oxygen atoms will be within a distance of 2 A. of a selenium atom, forming a pyramidal group, only one orientation of the SeO_3 group gave reasonable agreement with these $hk0$ reflexions. This arrangement of oxygen atoms was consistent with a Patterson $h0l$ projection.

Calculations of F_{hk0} showed that the observed F's had a very much smaller range of values, from the strongest to the weakest spots, than the calculated F's, suggesting that the strong reflexions were appreciably reduced by extinction. The observed F_{hk0}'s were therefore placed on an approximately absolute scale and at the same time corrected for extinction by plotting the ratio of $I/I_{obs.}$ against I. Assuming a relation of the form $I_{obs.} = I/(1 + gI)$, the slope of the curve gives g, and the intercept on the $I/I_{obs.}$ axis gives the factor required to put the observed values on an absolute scale. A value of $g = 0{\cdot}001$ was used. At this stage the agreement between calculated and observed F_{hk0} broke down for $k \gg 4$, and it was evidently necessary to alter y_{Se} from the value 0·25. A F_{hk0} projection incorporating about 40 terms was made, a strong artificial temperature factor being applied to the F's to eliminate the possibility of diffraction effects which might give false oxygen positions. (This also, of course, meant that the Se parameters were not known as accurately as if a longer series of F's had been employed, since the F's for planes of large θ are most sensitive to small variations in these parameters.) The approximate oxygen parameters determined in this way were :

	x.	*y*.	
O_2^1	0·10	0·35	(in this projection O_1 and O_2 are superposed).
O_3	$0{\cdot}15_5$	−0·05	

With these oxygen parameters it was possible to decide the direction of shift of F_{Se} from the value $\frac{1}{4}$, since for the *h*40 planes the sign of F_{Se} changes at $y = \frac{1}{4}$. The following figures show that y_{Se} must be taken between 0·24 and 0·245 :

		Contribution to F_{hk0} :			Total F.			
		Oxygen	Se contribution for :					
	$F_{obs.}$.	contribution.	$y = 0{\cdot}24$.	$y = 0{\cdot}245$.	Se 0·24.	0·245.	0·255.	0·26.
140	—	+ 5	− 6	−3	− 1	+ 2	+ 8	+11
340	19	− 5	−14	−7	−19	−12	+ 2	+ 9
540	17	−12	−18	−9	−30	−21	− 3	+ 6
740	<2	+ 8	−14	−7	− 6	+ 1	+15	+22
940	—	+12	− 8	−4	+ 4	+ 8	+16	+20

The agreement was still not sufficiently good for *h*50 and *h*60. It was decided to make a F_{h0l} projection to check the *x* parameters of the oxygen atoms. This definitely showed that O_1 and O_2, which were superposed in the *hk*0 projection, have different *x* parameters (approximately 0·08 and 0·12). The effect of splitting the single (somewhat elliptical) $O_{1,2}$ peak in the *hk*0 projection into two atoms was then tried. Alteration of the $O_{1,2}$ parameters from $x = 0{\cdot}10$, $y = 0{\cdot}35$ to $x_{O_I} = 0{\cdot}12$, $x_{O_{II}} = 0{\cdot}08$ and $y_{O_I} = 0{\cdot}39$ and $y_{O_{II}} = 0{\cdot}31$ immediately improved the agreement for *h*50 and *h*60, as shown by the following figures. (These are given for $y_{Se} = 0{\cdot}243$, the value which appeared to give the best agreement).

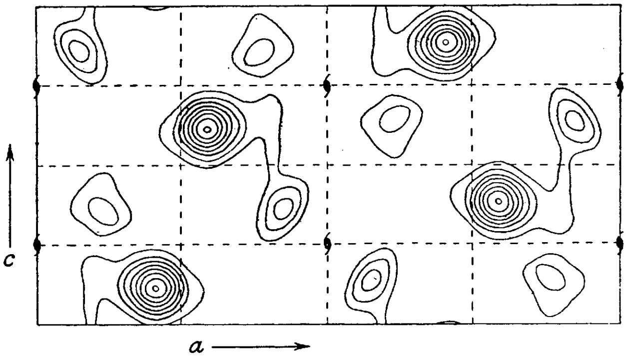
	$F_{obs.}$.	O_1 : *x* 0·10. O_2 : *y* 0·35.	O_1 : *x* 0·11, *y* 0·37. O_2 : *x* 0·09, *y* 0·33.	O_1 : *x* 0·12, *y* 0·39. O_2 : *x* 0·08, *y* 0·31.
150	22	18	19	22·5
350	12	9·5	10·5	12·5
550	10	−0·5	−3·5	−10·5
750	4	−7	−6	−4
160	4	9·5	6·5	1
360	9	8	9	10
560	10	6·5	8·5	14·5
760	8	21	17	11

These *x* parameters also improved the agreement in the case of several pairs of *h*0*l* reflexions, and it was now possible to prepare F_{hk0} and F_{h0l} projections utilising all the experimental data. For these projections a temperature factor of $e^{-2(\sin\theta/\lambda)^2}$ was applied since the series of observed F's was not considered sufficiently convergent. The final projections are shown in Figs. 3 and 4, and the parameters are :

	x.	*y*.	*z*.		*x*.	*y*.	*z*.
Se	0·205	0·243	0·115	O_2	0·08	0·31	−0·135
O_1	0·12	0·39	0·365	O_3	0·155	−0·04	0·133

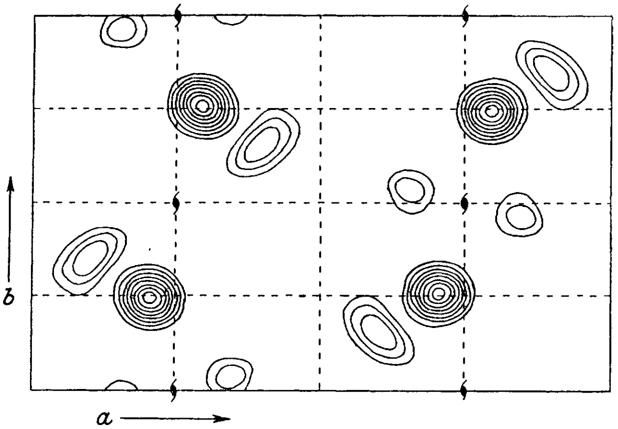
The least certain of these is the *z* parameter of O_3, which has not been determined directly since O_3 is nearly superposed on Se in the *h*0*l* projection. This parameter was estimated by drawing a line through Se in the direction along which the Se peak is extended by O_3, assuming *x* for O_3 as deduced from the *hk*0 projection. Unfortunately, the 0*kl* projection is also valueless from this point of view as the atoms are practically superposed in pairs, O_2 on Se, and O_1 on O_3. Three-dimensional syntheses would give the position of O_3 more accurately, but since there appears to be no doubt about the hydrogen-bond system this extension of the work was not considered to be justified.

FIG. 3.



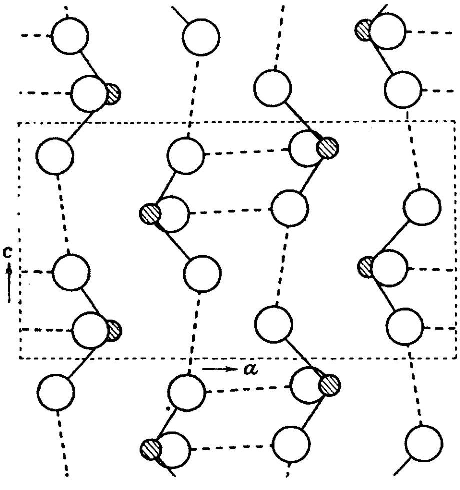
Fourier projection of H_2SeO_3 on (010).

FIG. 4.



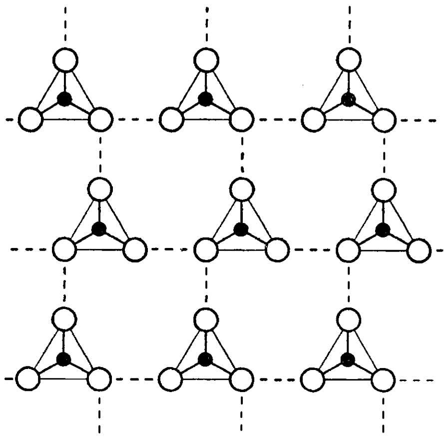
Fourier projection on (001).

FIG. 5.



Projection of the structure of H_2SeO_3 on (010).

FIG. 6.



The system of hydrogen bonds in H_2SeO_3 *(diagrammatic).*

The agreement between calculated and observed structure amplitudes is shown in the following table. The experimental data were obtained from Weissenberg photographs, the intensities being estimated visually, using the multiple-film method. The values of $F_{obs.}$ are the experimental values corrected for extinction as described above. It is considered that the data for the *hk*0 reflexions are the most reliable, as these were obtained from a thin needle of roughly square cross-section. The same extinction correction was applied to the data for the other zones. Absorption corrections, which would be more important for *h*0*l* and 0*kl* reflexions, have not been made.

Observed and Calculated Structure Amplitudes.

	F, obs.	F, calc.
200	77	− 94
400	—	− 2
600	7	+ 5
800	40	− 40
10.0.0	44	+ 55
110	12	+ 9
210	74	− 97
310	22	− 24
410	54	+ 66
510	12	− 11
610	59	− 72
710	17	+ 18
810	51	+ 66
910	—	+ 3
10.1.0	17	− 17
020	86	−103
120	39	− 37
220	66	+ 75
320	20	+ 10
420	44	− 44
520	26	+ 30
620	14	+ 7
720	4	− 7
820	42	+ 47
920	—	− 2
10.2.0	54	− 64
130	22	+ 18
230	51	+ 51
330	33	+ 28
430	76	− 79
530	12	− 9
630	71	+ 76
730	—	− 11
830	44	− 43
930	—	+ 4
10.3.0	7	+ 10
040	68	+ 70
140	—	− 1
240	70	− 70
340	19	+ 22
440	43	+ 39
540	17	− 23
640	13	+ 18
740	2	− 1
840	39	− 43
940	—	− 2
10.4.0	33	+ 45
150	22	+ 21
250	20	− 17
350	12	− 12
450	59	+ 70
550	10	− 8
650	64	− 68
750	4	+ 5
850	29	+ 42

	F, obs.	F, calc.
060	50	− 57
160	4	+ 4
260	50	+ 54
360	9	− 9
460	29	− 27
560	10	+ 11
660	7	− 12
760	8	− 12
170	14	− 20
270	31	+ 35
370	2	+ 8
470	45	− 55
002	6	+ 8
004	90	−106
006	19	− 15
011	83	+ 88
012	37	+ 54
013	41	− 49
014	12	− 5
015	24	− 58
016	13	− 18
021	9	− 10
022	13	− 12
023	8	− 8
024	58	+ 64
025	—	+ 4
026	27	+ 22
031	55	− 91
032	23	− 21
033	39	+ 63
034	—	0
035	45	+ 62
036	12	+ 11
041	26	+ 27
042	15	+ 9
043	17	+ 23
044	45	− 57
045	14	− 20
051	47	+ 27
052	20	+ 18
053	23	− 29
054	—	+ 3
055	55	− 44
061	14	− 16
062	15	− 7
063	13	− 16
064	33	+ 51
071	32	− 37
072	11	− 22
073	—	+ 10

	F, obs.	F, calc.
101	35	+ 28
201	55	+ 61
301	47	− 76
401	40	− 65
501	43	+ 58
601	58	+ 66
701	27	− 26
801	39	− 36
901	24	+ 26
10.0.1	—	+ 3
11.0.1	9	− 8
102	94	− 88
202	19	− 12
302	95	+ 86
402	15	+ 6
502	—	0
602	—	+ 4
702	35	− 46
802	—	− 6
902	35	+ 42
10.0.2	8	+ 5
11.0.2	26	− 46
103	25	+ 26
203	34	− 31
303	57	− 66
403	33	+ 36
503	46	+ 61
603	30	− 45
703	34	− 36
803	20	+ 25
903	25	+ 26
10.0.3	—	+ 3
104	28	− 23
204	46	+ 56
304	13	+ 6
404	13	− 8
504	—	0
604	—	− 6
704	—	− 5
804	23	+ 33
904	13	+ 11
105	10	− 9
205	29	− 36
305	23	+ 30
405	34	+ 51
505	16	− 27
605	30	− 51
705	—	+ 11
106	27	+ 49
206	15	+ 20
306	23	− 44
406	9	− 10

Description of the Structure.—The structure consists of pyramidal SeO_3 groups joined together by hydrogen bonds to form double layers extending parallel to (100), the cleavage plane of the crystals. Fig. 5 shows a projection of the structure along the *b* axis, *i.e.*, viewed along a line lying in the plane of the layers. Within the SeO_3 group the bond lengths and interbond angles are: $Se-O_1$, 1·72 A., $Se-O_2$, 1·75 A., $Se-O_3$, 1·76 A.; O_1SeO_2, 97°, O_1SeO_3, 112°, and O_2SeO_3, 93° (mean about 100°). These may be compared with Se–O distances of 1·73 and 1·78 A. and interbond angles of 90° and 98° (2) in crystalline SeO_2 (McCullough, *J. Amer. Chem. Soc.*, 1937, **59**, 789). Distances between oxygen atoms within a SeO_3 group are: O_1O_2, 2·59 A., O_2O_3, 2·55 A., and O_3O_1, 2·89 A., and the shortest distances between oxygen atoms of different SeO_3, groups are: O_1O_2', 2·60 A., and O_1O_3', 2·56 A. These are the O–H–O bonds shown as broken lines in Figs. 5 and 6. The next shortest intermolecular O–O contact is O_3O_3', 3·12 A., followed by O_1O_3'', 3·21 A., O_1O_2'', 3·28 A., and O_3O_2', 3·51 A. The next nearest neighbours of a selenium atom are three more oxygen atoms at 3·00, 3·08, and 3·09 A., completing a distorted octahedron around Se. The system of hydrogen-bonding is best shown by a projection on (100), the plane of the layer, of the atoms in one double layer (Fig. 6). There are four O–H–O bonds connecting each SeO_3 group (ion) to its neighbours, their length being similar to that found in acid salts.

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