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Hydrogen Bond Studies. XXI.* The Crystal Structure of Sulphuric Acid Monohydrate

BY INGER TAESLER AND IVAR OLOVSSON

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

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The crystal structure of $H_2SO_4.H_2O$ has been determined from three-dimensional single-crystal X-ray data obtained at -135 °C. The crystals are monoclinic, space group $P2_1/c$, with four formula units in a cell with the dimensions: $a=7{\cdot}062$, $b=6{\cdot}948$, $c=8{\cdot}139$ Å, and $\beta=106{\cdot}22°$. The structure can be considered as consisting of H_3O^+ and HSO_4^- ions. The HSO_4^- ions are linked by hydrogen bonds (2·657 Å) to form infinite chains. These chains are coupled together by hydrogen bonds from the H_3O^+ ions (2·538, 2·566, and 2·649 Å) in such a way that infinite 'double-layers' are formed. The S–O distances within the HSO_4^- ion are 1·434, 1·449, 1·462, and 1·560 Å.

Introduction

The freezing point curves of the H_2SO_4–H_2O system indicate six intermediate compounds: $H_2SO_4.H_2O$, $H_2SO_4.2H_2O$, $H_2SO_4.3H_2O$, $H_2SO_4.4H_2O$, $H_2SO_4.6{\cdot}5H_2O$, and $H_2SO_4.8H_2O$ [Giauque, Hornung, Kunzler & Rubin (1960). For references to the many earlier studies of the system see this paper and Gable, Betz & Maron (1950)].

The melting point of sulphuric acid monohydrate has been reported as 8·49 °C (Kunzler & Giauque, 1952). From various physical measurements, including proton magnetic resonance (Richards & Smith, 1951), Raman (Millen & Vaal, 1956), and infrared spectroscopy (Savoie & Giguère, 1964), it has been concluded that sulphuric acid monohydrate is ionic in the solid state.

An X-ray diffraction study of crystalline sulphuric acid monohydrate has previously been reported by Bourre-Maladière (1958) who, contrary to the authors mentioned above, has interpreted the structure as molecular. Since the compound is of great chemical interest and very little detail is given in that paper, it has been considered worth while to perform a more detailed investigation.

The present work involves a determination of the crystal structure of sulphuric acid monohydrate from single-crystal X-ray diffraction data obtained at -135 °C.

Experimental

The crystals were grown from sulphuric acid solutions sealed in glass capillaries (diameter 0·2 mm, wall thickness about 0·02 mm). Sulphuric acid, *pro analysi*, was distilled as described by Kunzler (1953) and diluted with distilled water. The composition was determined by titration with sodium hydroxide. After the capillaries had been filled a new analysis was made of the main solution. The composition was found to be within the limits 49·8 and 50·2 mol.% sulphuric acid.

The single crystals were grown in a modified Weissenberg camera (Olovsson, 1960). During the crystal growth the melting point was found to be about +9 °C, which is in agreement with the published value cited above. Since it was very difficult to induce crystallization of the solution in the capillaries, a small amount of barium sulphate was put into the rear ends. The solutions thus seeded crystallized readily when cooled. The single crystals were grown very slowly just below the melting point and then gradually cooled to about -30 °C before the X-ray photographs were taken.

The crystals grew preferentially along the *a* axis. In order to obtain a crystal oriented along the *b* axis, a capillary with a short part bent almost to a right angle was used (*cf.* Jönsson & Olovsson, 1968). The crystal thus obtained was only used for accurate determination of the cell dimensions.

Equi-inclination Weissenberg photographs, layers 0 to 6, were taken with unfiltered Cu *K* radiation at $-30°$ and at -135 °C, the crystal rotating about the *a* axis. (The photographs indicated the same structure at these two temperatures.) The structure determination was based only on the data obtained at -135 °C. The relative intensities were estimated visually by the multiple-film technique (five films) and comparison with an intensity scale. The intensity range was 1 to 2500. The data were corrected for the Lorentz and polarization effects, and for absorption (cylindrical specimen). For the absorption correction a local modification of the program ERLPA, written by Van den Hende (1962), was used. The linear absorption coefficient for the Cu $K\alpha$ radiation is $\mu=65{\cdot}4$ cm^{-1} and the radius of the crystal was 0·009 cm.

The number of independent reflexions recorded was 732, but 51 of these were too weak to be measured. About 84% of the reflexions within the Cu reflexion sphere were thus recorded. Ten strong reflexions were rejected during the last cycles of least-squares refinement. The intensities of these could not be measured

* Parts XVII to XX will be published in the near future in *Acta Crystallographica* (Section B)

accurately and some of them may also be affected by secondary extinction.

Unit cell and space group

The diffraction symmetry and systematic absences suggest the space group $P2_1/c$ (C_{2h}^5). In the paper by Bourre-Maladière the space group was chosen as $P2_1/a$, which corresponds to an interchange of the present a and c axes.

The unit-cell dimensions were determined from quartz-calibrated zero-layer oscillation photographs taken about the a and b axes with unfiltered Cu K radiation. The cell dimensions and their estimated standard deviations are, at −135 °C:
$a=7{\cdot}062\pm0{\cdot}001$, $b=6{\cdot}948\pm0{\cdot}002$, $c=8{\cdot}139\pm0{\cdot}001$ Å, $\beta=106{\cdot}22\pm0{\cdot}01°$. ($a=4{\cdot}913$ Å for α-quartz at 25 °C; λ(Cu $K\alpha_1$) = 1·54051 Å, λ(Cu $K\alpha_2$) = 1·54433 Å, λ(Cu $K\beta$) = 1·39217 Å).

Hülsmann & Biltz (1934) determined the density of $H_2SO_4.H_2O$ pycnometrically and obtained 1·993 g.cm^{-3} at −78 °C and 2·012 g.cm^{-3} at −192 °C. With four molecules per unit cell the calculated density at −135 °C is 2·011 g.cm^{-3}.

Determination of the atomic coordinates

The positions of the sulphur atom and of the four oxygen atoms belonging to the sulphate group were determined from a three-dimensional Patterson synthesis. The remaining oxygen was located in a three-dimensional F_o synthesis. All the atoms are in the four-fold general positions of the space group $P2_1/c$ (no. 14, *International Tables for X-ray Crystallography*, 1952). The atomic coordinates were improved in another F_o synthesis, after which the atomic coordinates, individual isotropic thermal parameters, and inter-layer scale factors were refined by the method of least squares.

The least-squares calculations were performed on the CD 3600 computer in Uppsala with a modified version of the full-matrix least-squares program by Gantzel, Sparks & Trueblood (1962). In the refinement the function $\Sigma w(|F_o|-|F_c|)^2$ was minimized. The weighting scheme used was $w=1/(a+|F_o|+c|F_o|^2)$, where the final values for a and c were 2·9 and 0·046 respectively. Reflexions too weak to be measured were given zero weight in all calculations.

After some cycles of isotropic refinement the agreement factor $R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$ was 0·119. At this stage a three-dimensional difference synthesis was calculated to determine the positions of the hydrogen atoms. However, no clear indication of their positions could be obtained. Ten reflexions for which F_o was much smaller than F_c were excluded from the data (see above) and a few more cycles of isotropic refinement were performed. The R value decreased to 0·111.

The refinement was completed with three cycles of least-squares calculations using anisotropic temperature factors for all atoms. The atomic coordinates and an overall scale factor were also varied. The relative inter-layer scale factors used were those from the last cycle of isotropic refinement. The total number of parameters refined was 55 as compared with 31 in the isotropic case. In the third cycle the shifts in the parameters were less than one tenth of their estimated standard deviations. The final R value was 0·093.

An (F_o-F_c) synthesis was calculated, based on the reflexions with $\sin\theta/\lambda$ less than 0·5 Å^{-1}. Peaks appeared near the locations predicted for hydrogen. The peaks were, however, somewhat diffuse and other peaks also appeared in the maps. Thus the hydrogen atoms were not located from these maps.

The atomic scattering factors used in the calculations were those given for neutral sulphur and oxygen in *International Tables for X-ray Crystallography* (1962).

Tables 1 and 2 list values for the atomic coordinates and thermal parameters with their standard deviations, obtained from the final least-squares refinement. The observed and calculated structure factors are compared in Table 3.

Table 1. *Atomic coordinates with standard deviations* (×10^4)

	x	y	z
S	2497 (2)	1583 (2)	0416 (1)
O(1)	1699 (6)	4829 (6)	4122 (4)
O(2)	3257 (6)	0686 (6)	2097 (4)
O(3)	4379 (6)	2477 (6)	0076 (5)
O(4)	1125 (7)	3135 (6)	0411 (5)
O(5)	7750 (6)	2005 (6)	3251 (5)

Description and discussion of the structure

General

The structure is shown in Figs. 1–3. Bond distances and angles are listed in Table 4 and are illustrated in Fig. 3. The standard deviations were calculated from the standard deviations of the atomic coordinates; the errors in the cell parameters were then also considered.

Table 2. *Anisotropic temperature factors with standard deviations* (×10^4)

The form of the temperature factor is:
$\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+\beta_{12}hk+\beta_{13}hl+\beta_{23}kl)]$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S	16 (5)	30 (3)	23 (3)	−3 (3)	−30 (4)	1 (3)
O(1)	40 (10)	53 (8)	39 (6)	4 (12)	−25 (11)	24 (10)
O(2)	56 (11)	55 (7)	29 (6)	0 (12)	−35 (11)	−1 (10)
O(3)	14 (11)	100 (9)	69 (7)	−31 (13)	−10 (12)	25 (11)
O(4)	61 (11)	46 (8)	64 (6)	29 (13)	−20 (12)	−7 (10)
O(5)	22 (10)	55 (7)	56 (6)	15 (12)	7 (11)	−12 (11)

Distances corrected for anisotropic thermal motion are not given, since no experimental scaling has been performed.

On the basis of the assignment of the hydrogen atoms (see below) the structure can be described as being built up from HSO_4^- ions and H_3O^+ ions.

Table 3. *Observed and calculated structure factors*

Reflexions marked * were too weak to be measured. The F_o values for these are given as F_{min} for the reflexion in question. Reflexions marked ** were omitted from the last cycles of least-squares refinement.

h	k	l	$\lvert F_o\rvert$	$\lvert F_c\rvert$
0	0	2	46.3**	68.7
0	0	4	34.3	37.9
0	0	6	8.3	8.1
0	0	8	22.2	20.0
0	0	10	7.1	8.3
0	1	1	32.8**	46.8
0	1	2	14.6	18.3
0	1	3	2.1	2.3
0	1	4	43.8	50.4
0	1	5	1.8*	0.2
0	1	6	35.2	38.1
0	1	7	17.2	17.7
0	1	8	22.4	18.7
0	1	9	1.6*	0.4
0	2	0	35.5**	43.1
0	2	1	32.8	35.2
0	2	2	36.4	42.8
0	2	3	2.7	0.1
0	2	4	26.2	26.2
0	2	5	18.8	16.3
0	2	6	24.3	25.7
0	2	7	21.7	24.3
0	2	8	1.9	1.6
0	2	9	9.3	7.8
0	3	1	7.4	2.5
0	3	2	11.8	9.8
0	3	3	29.3	31.2
0	3	4	23.7	23.2
0	3	5	8.3	6.1
0	3	6	10.2	10.4
0	3	7	2.0	2.0
0	3	8	3.6	2.4
0	3	9	9.8	9.9
0	4	0	7.4	7.4
0	4	1	5.5	4.3
0	4	2	2.0	1.7
0	4	3	21.6	20.0
0	4	4	9.3	8.1
0	4	5	3.0	3.2
0	4	6	3.9	1.2
0	4	7	14.9	12.7
0	4	8	9.1	8.3
0	5	1	2.0*	0.4
0	5	2	16.0	16.2
0	5	3	13.1	12.3
0	5	4	31.0	33.4
0	5	5	16.3	15.1
0	5	6	19.7	17.0
0	5	7	1.5	1.3
0	5	8	16.1	17.9
0	6	0	27.7	27.1
0	6	1	5.9	5.3
0	6	2	26.2	28.3
0	6	3	19.8	18.6
0	6	4	3.0	1.3
0	6	5	17.9	15.4
0	6	6	7.9	6.8
0	6	7	1.2*	1.9
0	7	1	26.4	25.2
0	7	2	3.0	3.1
0	7	3	14.2	12.7
0	7	4	16.3	15.0
0	7	5	2.9	1.7
0	7	6	14.2	16.4
0	8	0	10.9	10.1
0	8	1	1.6*	1.6
0	8	2	7.4	6.0
0	8	3	12.4	12.0
0	8	4	2.9	3.0
1	0	-10	7.8	7.0
1	0	-8	23.6	21.1
1	0	2	34.7	37.1
1	0	4	20.0	19.7
1	0	6	50.7**	61.0
1	0	8	34.4	35.3
1	1	-10	11.7	12.3
1	1	-9	10.7	9.3
1	1	-8	9.4	8.7
1	1	-7	16.3	16.6
1	1	-6	8.6	8.9
1	1	-5	2.1	2.3
1	1	-4	21.3	22.5
1	1	-3	16.4	15.8
1	1	-2	53.5**	65.9
1	1	1	7.1	7.6
1	1	2	52.5**	60.8
1	1	3	17.9	16.8
1	1	4	39.6	42.1
1	1	5	27.1	27.5
1	1	6	4.9	4.1
1	1	7	15.3	15.0
1	1	8	4.3	3.6
1	1	9	10.0	9.7
1	2	-10	7.4	7.7
1	2	-9	13.2	10.8
1	2	-8	6.2	5.3
1	2	-7	7.8	8.0
1	2	-6	10.5	9.4
1	2	-5	23.6	25.2
1	2	-4	22.1	22.8
1	2	-3	4.1	3.6
1	2	-2	17.7	17.9
1	2	-1	42.0**	56.5
1	2	0	10.8	10.2
1	2	1	28.4	33.9
1	2	2	46.0**	56.9
1	2	3	4.3	3.4
1	2	4	27.4	27.1
1	2	5	8.8	8.1
1	2	6	15.2	13.2
1	2	7	14.1	13.6
1	2	8	19.6	18.5
1	2	9	10.0	10.7
1	3	-9	13.5	12.4
1	3	-8	15.7	12.6
1	3	-7	11.9	11.5
1	3	-6	3.4	2.9
1	3	-5	28.6	32.9
1	3	-4	5.2	3.4
1	3	-3	25.4	28.0
1	3	-2	16.3	16.3
1	3	-1	22.9	24.4
1	3	0	25.8	28.3
1	3	1	19.5	18.9
1	3	2	26.2	26.5
1	3	3	36.7	40.7
1	3	4	1.6*	0.5
1	3	5	26.1	27.4
1	3	6	4.1	4.5
1	3	7	9.8	8.1
1	3	8	3.3	3.9
1	3	9	5.6	7.8
1	4	-9	12.1	11.1
1	4	-8	12.4	10.8
1	4	-7	10.9	8.9
1	4	-6	23.2	24.5
1	4	-5	10.8	10.3
1	4	-4	33.6	36.9
1	4	-3	16.1	15.7
1	4	-2	26.5	28.5
1	4	-1	6.5	6.4
1	4	0	4.9	4.6
1	4	1	21.6	20.8
1	4	2	8.0	7.6
1	4	3	1.6*	0.2
1	4	4	14.5	14.0
1	4	5	1.7*	0.2
1	4	6	7.3	7.1
1	4	7	2.1	1.3
1	4	8	1.1*	1.1
1	5	-8	10.0	8.8
1	5	-7	5.2	4.2
1	5	-6	5.4	4.2
1	5	-5	1.7*	0.2
1	5	-4	8.8	8.3
1	5	-3	8.6	7.5
1	5	-2	21.3	21.2
1	5	-1	21.1	24.2
1	5	0	15.3	14.9
1	5	1	14.3	14.8
1	5	2	31.6	34.8
1	5	3	5.4	4.5
1	5	4	13.0	12.8
1	5	5	9.2	7.2
1	5	6	8.1	6.8
1	5	7	2.7	2.4
1	6	-7	1.1*	0.9
1	6	-6	20.0	20.4
1	6	-5	7.7	6.0
1	6	-4	26.7	28.1
1	6	-3	14.9	14.4
1	6	-2	18.0	17.0
1	6	-1	1.7*	0.4
1	6	0	18.8	19.1
1	6	1	6.8	6.4
1	6	2	1.7*	1.0
1	6	3	23.0	21.6
1	6	4	15.8	14.0
1	6	5	1.5*	3.2
1	6	6	14.5	16.7
1	7	-6	11.3	11.2
1	7	-5	13.5	12.6
1	7	-4	3.8	2.5
1	7	-3	14.3	11.4
1	7	-2	21.1	17.3
1	7	-1	9.1	7.8
1	7	0	18.9	18.4
1	7	1	5.1	3.7
1	7	2	18.7	17.7
1	7	3	15.6	13.8
1	7	4	10.5	9.8
1	7	5	7.4	8.8
1	8	-4	4.2	4.1
1	8	-3	18.0	19.8
1	8	-2	18.7	19.6
1	8	-1	20.5	22.1
1	8	0	5.4	4.9
1	8	1	18.0	20.3
1	8	2	4.3	2.8
1	8	3	12.6	14.8
2	0	-10	13.8	13.3
2	0	-8	38.2	39.1
2	0	2	10.7	7.4
2	0	4	12.3	8.5
2	0	6	2.5	2.2
2	0	8	8.0	7.0
2	1	-10	4.6	4.7
2	1	-9	12.0	10.1
2	1	-8	6.3	5.9
2	1	-7	13.1	12.1
2	1	-6	11.3	10.1
2	1	-5	14.4	12.7
2	1	-4	24.0	25.9
2	1	-3	22.2	24.7
2	1	-2	14.0	14.1
2	1	1	4.3	5.0
2	1	2	11.7	10.3
2	1	3	3.8	3.5
2	1	4	32.2	33.5
2	1	5	6.9	6.6
2	1	6	25.2	28.9
2	1	7	12.2	11.3
2	1	8	14.5	14.2
2	2	-10	9.6	9.3
2	2	-9	12.9	10.0
2	2	-8	5.2	4.1
2	2	-7	28.8	33.6
2	2	-6	3.0	3.0
2	2	-5	14.6	14.0
2	2	-4	13.0	12.0
2	2	-3	10.8	11.6
2	2	-2	35.0	38.0
2	2	-1	16.8	16.3
2	2	0	3.5	2.5
2	2	1	35.5	39.4
2	2	2	21.4	19.1
2	2	3	21.1	19.9
2	2	4	4.2	1.4
2	2	5	33.2	33.2
2	2	6	12.8	13.4
2	2	7	24.0	22.7
2	2	8	14.8	14.2
2	3	-9	6.2	5.1
2	3	-8	12.4	9.6
2	3	-7	6.7	7.1
2	3	-6	19.1	18.2
2	3	-5	8.5	7.6
2	3	-4	11.7	10.0
2	3	-3	34.0	36.7
2	3	-2	29.2	30.9
2	3	-1	21.7	19.7
2	3	0	1.2*	0.1
2	3	1	25.3	25.8
2	3	2	4.3	2.9
2	3	3	33.0	35.5
2	3	4	5.2	4.1
2	3	5	3.0	3.1
2	3	6	9.2	8.2
2	3	7	15.1	13.3
2	3	8	1.1*	1.1
2	4	-9	13.5	12.9
2	4	-8	1.4*	0.5
2	4	-7	20.1	18.5
2	4	-6	6.9	6.6
2	4	-5	22.3	22.9
2	4	-4	11.9	10.2
2	4	-3	5.9	5.4
2	4	-2	17.5	17.8
2	4	-1	1.4*	0.7
2	4	0	22.5	21.7
2	4	1	21.5	23.8
2	4	2	29.8	32.0
2	4	3	35.9	38.4
2	4	4	26.4	28.2
2	4	5	7.4	5.9
2	4	6	5.9	5.0
2	4	7	22.1	22.6
2	5	-8	17.0	17.8
2	5	-7	1.4*	0.3
2	5	-6	27.4	25.7
2	5	-5	5.2	3.6
2	5	-4	34.4	39.9
2	5	-3	29.7	31.2
2	5	-2	17.0	16.5
2	5	-1	12.1	11.6
2	5	0	13.9	14.0
2	5	1	2.4	2.3
2	5	2	12.8	12.3
2	5	3	1.7*	0.9
2	5	4	17.1	15.6
2	5	5	14.4	13.4
2	5	6	13.4	13.4
2	5	7	5.2	5.4
2	6	-7	3.2	2.0
2	6	-6	7.7	6.9
2	6	-5	17.3	15.3
2	6	-4	15.0	13.9
2	6	-3	13.2	14.1
2	6	-2	24.2	27.2
2	6	-1	4.7	4.2
2	6	0	28.9	31.1
2	6	1	7.3	7.6
2	6	2	26.2	30.5
2	6	3	5.9	5.5
2	6	4	8.5	7.2
2	6	5	3.6	3.9
2	6	6	9.6	11.0
2	7	-6	10.7	11.1
2	7	-5	2.6	2.2
2	7	-4	17.7	16.2
2	7	-3	17.9	16.2
2	7	-2	15.1	14.1
2	7	-1	16.0	15.9
2	7	0	12.4	12.5
2	7	1	28.4	26.2
2	7	2	9.6	9.1
2	7	3	4.2	4.0
2	7	4	8.3	8.8
2	7	5	2.2	2.8
2	8	-4	5.3	5.0
2	8	-3	11.1	12.4
2	8	-2	6.7	6.6
2	8	-1	3.8	3.1
2	8	0	9.9	9.3
2	8	1	1.1*	2.4
2	8	2	2.9	2.5
2	8	3	10.1	13.1
3	0	-10	2.3	1.4
3	0	-8	14.0	15.4
3	0	2	9.5	9.0
3	0	4	13.9	13.0
3	0	6	21.5	23.9
3	0	8	13.5	16.7
3	1	-10	12.4	15.6
3	1	-9	9.3	8.0
3	1	-8	12.5	12.7
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3	6	-4	16.5	14.1
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3	6	-2	8.8	8.4
3	6	-1	4.5	3.7
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3	7	-3	4.5	3.5
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3	8	-3	17.4	20.9
3	8	-2	5.6	5.2
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3	8	0	4.9	5.0
3	8	1	14.3	16.3
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4	0	6	5.6	3.5
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4	1	6	11.7	11.0
4	1	7	1.1*	2.3
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4	2	-8	1.9	1.6
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4	2	-2	21.4	21.4
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4	2	1	11.6	8.1
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4	2	3	24.7	22.8
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4	3	6	9.2	9.2
4	3	7	9.8	13.3
4	4	-9	8.5	9.3
4	4	-8	1.2*	0.5
4	4	-7	22.3	21.7
4	4	-6	1.6*	0.5
4	4	-5	28.6	32.9
4	4	-4	1.6*	0.4
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4	4	-2	16.1	15.4
4	4	-1	20.0	22.7
4	4	0	20.7	19.6
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4	4	2	23.6	22.9
4	4	3	21.4	21.8
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4	4	5	9.2	8.0
4	4	6	7.0	6.9
4	5	-8	7.3	8.1
4	5	-7	4.0	3.3
4	5	-6	18.3	17.5
4	5	-5	1.6*	0.8
4	5	-4	13.1	13.1
4	5	-3	19.3	21.7
4	5	-2	5.4	4.9
4	5	-1	11.4	11.5
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4	6	1	3.3	2.6
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4	7	-5	10.0	10.5
4	7	-4	4.8	4.1
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4	7	0	6.4	5.0
4	7	1	19.3	20.2
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4	7	3	1.6	2.6
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5	0	-8	18.2	20.1
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5	0	2	23.7	23.0
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5	0	6	15.0	16.8
5	1	-9	5.9	4.5
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5	2	-9	17.4	18.5
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5	3	-7	20.3	20.2
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5	7	-1	14.3	14.6
5	7	0	1.0*	0.8
5	7	1	7.9	8.9
6	0	-8	6.0	6.3
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6	0	4	9.6	8.7
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6	1	-8	15.4	17.1
6	1	-7	5.8	5.4
6	1	-6	8.9	8.2
6	1	-5	1.6*	0.1
6	1	-4	19.3	22.4
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6	1	-2	3.0	1.1
6	1	-1	7.9	6.8
6	1	0	24.4	22.0
6	1	1	3.2	0.4
6	1	2	17.8	15.7
6	1	3	22.1	18.3
6	1	4	35.0	34.2
6	1	5	5.5	5.2
6	2	-9	4.8	5.7
6	2	-8	3.1	3.5
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6	2	-3	20.0	20.2
6	2	-2	12.6	11.1
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6	2	0	36.6	37.8
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6	2	2	21.0	17.4
6	2	3	21.5	19.4
6	2	4	1.5*	0.3
6	2	5	11.4	15.3
6	3	-8	4.7	4.3
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6	3	-5	9.3	9.9
6	3	-4	9.4	9.1
6	3	-3	10.3	11.7
6	3	-2	9.4	9.0
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6	3	0	11.1	10.4
6	3	1	27.5	24.8
6	3	2	7.2	4.8
6	3	3	23.7	21.9
6	3	4	3.8	2.6
6	4	-7	12.0	14.2
6	4	-6	7.3	8.6
6	4	-5	16.6	16.4
6	4	-4	3.8	3.8
6	4	-3	1.7*	0.8
6	4	-2	15.4	13.8
6	4	-1	21.4	20.3
6	4	0	17.8	15.3
6	4	1	6.3	4.0
6	4	2	13.3	12.8
6	4	3	6.5	5.6
6	4	4	2.6	3.2
6	5	-7	0.7*	0.1
6	5	-6	19.9	24.3
6	5	-5	1.4*	2.3
6	5	-4	12.6	15.0
6	5	-3	1.6*	1.4
6	5	-2	11.5	10.7
6	5	-1	1.6*	0.5
6	5	0	2.8	3.4
6	5	1	5.8	5.1
6	5	2	10.6	9.3
6	5	3	5.6	6.4
6	6	-5	5.9	6.8
6	6	-4	12.7	14.2
6	6	-3	4.9	4.0
6	6	-2	8.9	8.4
6	6	-1	5.1	4.4
6	6	0	17.4	18.7
6	6	1	4.5	4.5

The hydrogen of the HSO_4^- ion links two oxygen atoms, O(2) and O(3), in neighbouring sulphate groups by a hydrogen bond (O···O distance 2·657 Å). In this way infinite zigzag chains of sulphate groups are formed along the *c* axis. Similar hydrogen bonded chains are also found in other structures containing hydrogensulphate ions (see below).

The oxonium ion takes part in three hydrogen bonds to the oxygen atoms O(1), O(2), and O(4) belonging to different sulphate groups. The sulphate chains are thus linked together and 'double-layers' parallel to the *yz* plane are formed (Figs. 1 and 2). There are no hydrogen bonds between the atoms in two neighbouring 'double-layers'. The shortest distance between atoms in two such 'double-layers' is 3·00 Å.

The hydrogensulphate ion

The S–O distances of the sulphate group (1·560, 1·434, 1·462, and 1·449 Å) clearly indicate that hydrogen is attached only to O(3) (*cf.* Cruickshank, 1961). This is also supported by the angles within the sulphate group (Table 4).

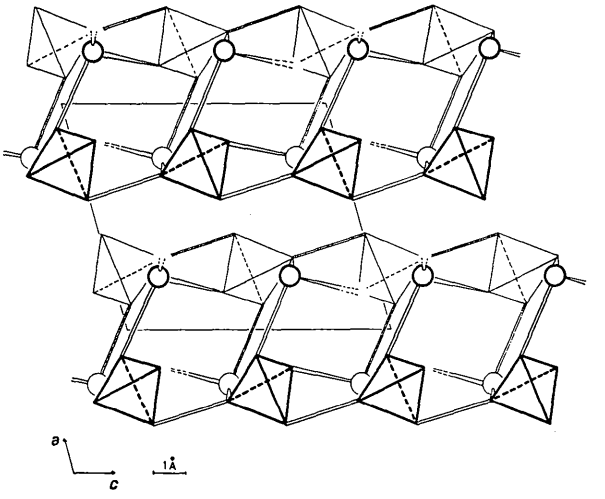

Fig. 2. The structure viewed along the *b* axis. The HSO_4^- ions are represented by tetrahedra. Thick lines represent ions lying around $y=0{\cdot}75$ while thin lines represent those around $y=0{\cdot}25$.

Table 4. *Bond distances and angles with their standard deviations*

Standard deviations of distances are multiplied by 10^3.

Covalent bonds			
S–O(1)	1·434 (4) Å	O(1)–S–O(2)	111·2° (0·2)
S–O(2)	1·462 (4)	O(1)–S–O(3)	108·7 (0·2)
S–O(3)	1·560 (4)	O(1)–S–O(4)	112·4 (0·2)
S–O(4)	1·449 (4)	O(2)–S–O(3)	103·1 (0·2)
		O(2)–S–O(4)	113·0 (0·2)
		O(3)–S–O(4)	107·8 (0·2)
Hydrogen bonds			
O(3)···O(2)	2·657 (5) Å	S–O(3)···O(2)	107·6° (0·2)
O(5)···O(1)	2·566 (5)	S–O(2)···O(3)	126·0 (0·2)
O(5)···O(2)	2·649 (6)	S–O(1)···O(5)	147·6 (0·3)
O(5)···O(4)	2·538 (6)	S–O(2)···O(5)	107·1 (0·2)
		S–O(4)···O(5)	118·1 (0·2)
		O(3)···O(2)···O(5)	124·3 (0·2)
		O(1)···O(5)···O(2)	125·5 (0·2)
		O(1)···O(5)···O(4)	100·9 (0·2)
		O(2)···O(5)···O(4)	106·4 (0·2)

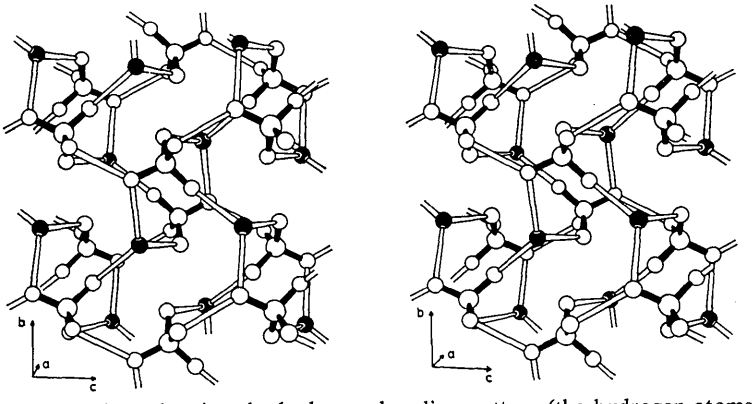

Fig. 1. A stereoscopic pair of drawings showing the hydrogen bonding pattern (the hydrogen atoms are not shown, however). Covalent bonds are filled, hydrogen bonds are open. The oxygen atoms of the H_3O^+ ions are filled. Figs. 1 and 3 have been drawn with the program OR TEP (Johnson, 1965).

The distances and angles of the HSO_4^- ion are in agreement with those found in structures reported earlier. For references to some of these see Jönsson & Olovsson (1968).

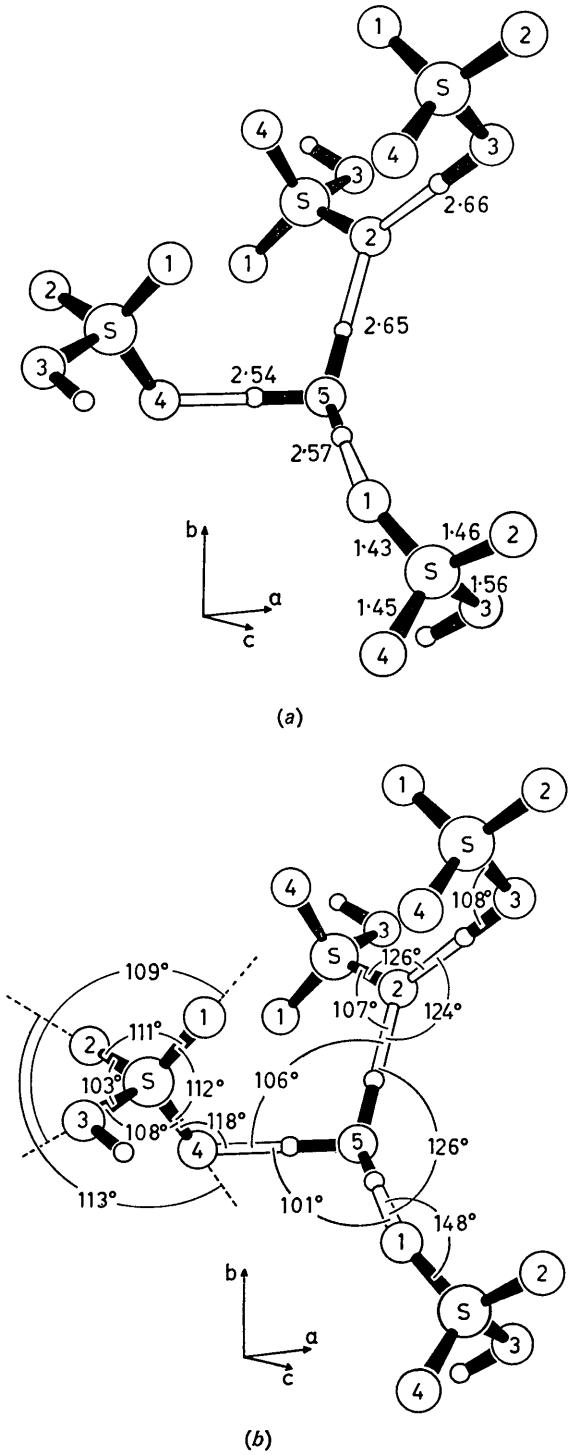

Fig. 3. The bonding situation around the H_3O^+ ion, with (*a*) bond distances and (*b*) angles. The assignment of hydrogen atoms is in accordance with the discussion in the text.

The oxonium ion

As described above, it was not possible to locate the hydrogen atoms unambiguously from the difference synthesis. However, from the existence of an HSO_4^- ion in the structure, it can be inferred that the oxygen atom O(5) must represent an H_3O^+ ion.

The oxonium ion is hydrogen bonded to three different sulphate ions. The hydrogen bond distances from O(5) are: 2·566 Å to O(1), 2·538 Å to O(4), and 2·649 Å to O(2). The difference between the O(5)···O(2) distance and the other two distances can be explained by the difference in coordination number of the oxygen atoms accepting the hydrogen bonds (*cf.* Lindgren & Olovsson, 1968). The coordination numbers are two, two, and three for O(1), O(4), and O(2), respectively (Fig. 3).

The angles formed by the three hydrogen bonds about O(5) are 100·9°, 106·4°, and 125·5°. If the hydrogen atoms are placed on the lines between the hydrogen-bonded atoms, the oxonium ion is seen to be pyramidal. This agrees with the results of earlier work on H_3O^+; for references see Conway (1964) and Giguère (1966).

Fig. 3 shows the bonding situation around the oxonium ion. In the Figure the hydrogen atoms are placed according to the above discussion.

Comparison with earlier results

The structure of sulphuric acid monohydrate has been determined independently of the previous investigation. Although very little detail is given in the earlier study it is clear that essentially the same structure has been found in both investigations. However, there are large differences in the bond distances. In the paper by Bourre-Maladière the reported S–O distances of the sulphate group indicate a structure built of sulphuric acid and water molecules. The interpretation of the hydrogen bonding pattern also differs in the two investigations. However, since no standard deviations of the parameters are given in the earlier report, a comparison of bond distances in the two investigations is of rather little value.

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Direct Determination of the Crystal Structure of $PaOCl_2$*

BY RICHARD P. DODGE,† GORDON S. SMITH, QUINTIN JOHNSON AND ROBERT E. ELSON
Lawrence Radiation Laboratory, University of California, Livermore, California, U.S.A.

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A compound obtained during a reduction of $PaCl_5$ has been studied by single-crystal X-ray diffraction techniques and identified as the oxydichloride, $PaOCl_2$. Crystals of this material are orthorhombic with $a=15{\cdot}25$, $b=17{\cdot}86$, $c=4{\cdot}01$ Å. The space group is *Pbam*, and the unit cell contains twelve $PaOCl_2$ units. Phase determination was by means of the symbolic addition procedure; full-matrix least-squares refinement of diffractometrically measured data resulted in a final R index of 7·6%. The structure consists of infinite polymeric chains which extend along the short c axis and which are cross-linked to one another in the *ab* plane by bridging Cl atoms. The repeating unit of structure along the chain is the twelve-atom aggregate, $Pa_3O_3Cl_6$. The Pa atoms are seven-, eight- and nine-coordinated. The oxygen atoms are three- and four-coordinated; the chlorine atoms, two- and three-coordinated. Pa–O and Pa–Cl bond distances are in the respective ranges 2·19–2·38 Å and 2·74–3·08 Å.

Introduction

During the course of preparing protactinium tetrachloride by hydrogen reduction of the pentachloride, we encountered crystals quite unlike those of the expected product. It appeared likely that the unknown phase was a second modification of $PaCl_4$ or possibly a chloride of mixed oxidation states, *e.g.* Pa_2Cl_9. A crystal-structure determination shows the phase instead to be a complex oxychloride of empirical composition $PaOCl_2$.

We may mention that solution of the crystal structure was effected by the symbolic addition procedure. Prior to that, an attempt by conventional Patterson analysis had been unsuccessful. In retrospect, the lack of success with the latter approach is traceable to a serious misestimate of the number of Pa atoms within the unit cell. On the other hand, this misestimate proved of no handicap in the symbolic addition procedure.

Experimental

Our sample of protactinium, in the form of $PaO_{2\cdot25}$, was received from Oak Ridge National Laboratory. This sample, originally part of a gram-scale lot recovered by investigators at the Atomic Energy Research Establishment, Harwell, England, is now known to contain about 4% Nb [for further details see Stein (1964)]. Preparation of the samples followed lines previously described (Elson, Fried, Sellers & Zachariasen, 1950). $PaO_{2\cdot25}$ was treated with carbon tetrachloride at about 200 °C to produce $PaCl_5$ as well as a less volatile component (probably oxychlorides of Pa^V). Following fractional sublimation, the pentachloride was reacted with hydrogen at 800 °C. Unreacted pentachloride was separated from the less volatile tetra-

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† Permanent address: Chemistry Department, University of the Pacific, Stockton, California.