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Reinvestigation of Crystalline Sulfuric Acid and Oxonium Hydrogensulfate

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Abstract

The crystal structures of H_2SO_4 and $(H_3O)(HSO_4)$ have been refined with good accuracy (R = 0.021 and 0.033, respectively) making a discussion of hydrogen bonding now possible. In sulfuric acid, the S—O and S—OH distances are 1.426 (1) and 1.537 (1) Å, respectively, and the structure is characterized by layers of hydrogen-connected SO_4 tetrahedra forming 4^4 nets. In oxonium hydrogensulfate, the HSO_4^- tetrahedra form infinite hydrogen-bonded chains which are linked by H_3O^+ ions to form double layers.

Comment

Many new acidic sulfates of mono- and divalent metals have recently been synthesized and structurally characterized (Kemnitz, Trojanov & Worzala, 1993; Kemnitz, Werner, Trojanov & Worzala, 1994; Kemnitz, Werner, Worzala, Trojanov & Strutschkov, 1995; Kemnitz, Werner, Worzala & Trojanov, 1995; Trojanov, Kemnitz, Werner & Worzala, 1995; Werner, Kemnitz, Trojanov, Strutschkov & Worzala, 1995). The structures of these compounds are characterized by such structural elements as HSO_4^- ions and, in some cases, H_2SO_4 molecules. In order to compare the characteristics of the hydrogen-bonding systems in the new metal hydrogen sulfates of mono- and divalent metals with those of H_2SO_4, (I), and $(H_3O)(HSO_4)$, (II), it was necessary to have precise data for the crystal structures of (I) and (II), including the H-atom positions. The crystal structure of pure sulfuric acid determined from X-ray data without H-atom positions has already been published (Pascard-Billy, 1965; Yu & Mak, 1978). Neutron diffraction experiments based on polycrystalline sulfuric acid revealed the protons with good positional accuracy (Moodenbaugh *et al.*, 1983). The structure of oxonium hydrogensulfate, without H-atom positions, was determined (R = 0.093) using Weissenberg measurements (Taeslar & Olovsson, 1968).

A comparison of our results with those of previous crystal structure determinations confirms the basic structures; however, it also shows some differences due to the higher accuracy of the present work. This provides the basis for a detailed discussion of the structures. The atoms in the structures have been labelled in the same manner as already used by us in a number of recent publications on alkaline earth hydrogen sulfates and differs, therefore, from previous papers on sulfuric acid (Yu & Mak, 1978) and oxonium hydrogensulfate (Taeslar & Olovsson, 1968). For comparison, the data from these other publications are included in Table 3.

In sulfuric acid, the S atom is located on a twofold axis (Fig. 1). The S—O and S—OH distances found in this work [1.426 (1) and 1.537 (1) Å] are, surprisingly, in much better agreement with those determined by Pascard-Billy (1965) (R = 0.12) than with the refinement carried out later by Yu & Mak (1978) (R = 0.099). The structure consists of layers of $SO_2(OH)_2$ tetrahedra connected *via* hydrogen bonds to form 4^4 nets (Wells, 1993) as a result of the two donor and two acceptor functions of the four O atoms of the H_2SO_4 molecule (Fig. 2).

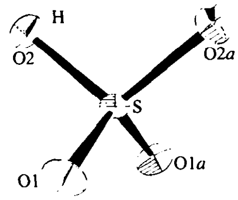

Fig. 1. *ORTEP*II (Johnson, 1976) drawing of H_2SO_4 with displacement ellipsoids at the 50% probability level.

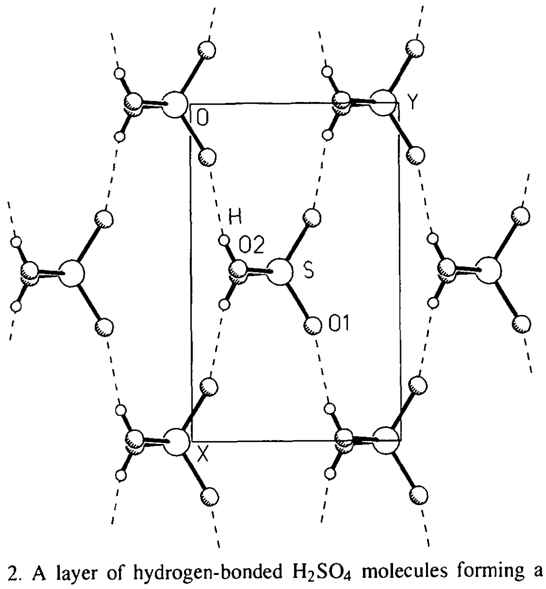

Fig. 2. A layer of hydrogen-bonded H_2SO_4 molecules forming a 4^4 net.

As a result of the X-ray determination of the H-atom positions, the bond relations in the SO_4 tetrahedra and the donor–acceptor distances of the hydrogen bonds, the structure of oxonium hydrogensulfate is un-

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doubtedly ionogenic (Fig. 3). This is in full agreement with the conclusions of Taeslar & Olovsson (1968) and contradicts those of Bourre-Maladière (1958). HSO_4^- ions form infinite chains in the z direction *via* O4—H1···O1(x, $\frac{1}{2}-y$, $z-\frac{1}{2}$) hydrogen bonds. The chains are connected by H_3O^+ ions to form double layers of hydrogen-connected SO_4 tetrahedra (Fig. 4). Three hydrogen bonds of medium strength originating from O5 of the oxonium ion are formed [O5—H2···O2($1-x$, $1-y$, $-z$), O5—H3···O3(x, $\frac{1}{2}-y$, $\frac{1}{2}+z$), O5—H4···O1(x, $y+1$, z)] with O···O distances ranging from 2.556 (1) to 2.660 (1) Å and are directed to three HSO_4 tetrahedra (Table 4). O5 acts three times as a donor in the hydrogen-bonding system while O4 does so only once. At least one of the three remaining O atoms has to act as a double acceptor; this is realised by O1. The S—O and O···O bond distances and angles have been discussed in detail by Taeslar & Olovsson (1968). However, these values need small corrections as all S—O distances in this work are somewhat longer whereas the S—OH distance is slightly shorter. Consequently, there are differences in the donor–acceptor distances as determined by Taeslar & Olovsson (1968) and found in the present work which are significant for O5···O2 [2.556 (1) and 2.538 (1) Å]. The O···O distances for O atoms of the same function (O5···O2 and O5···O3) are almost identical. The pyramidal geometry of the oxonium ion considered on the assumption that the H atoms are situated along the lines O5···$O_{acceptor}$ (Taeslar & Olovsson, 1968) can be confirmed, the highest distortion from the ideal tetrahedral angle being H3—O5—H4 [118.3 (18)°]. For a comparison of the structures of the oxonium ion and the hydrogensulfate ion, a good example is given by the recently determined structure of $K(H_3O)(HSO_4)$ (Kemnitz *et al.*, 1994). The close relationship of both structures can be demonstrated by almost identical O···O distances for the hydrogen bonds originating from the oxonium ions [2.516 (1)–2.631 (1) Å] as well as the bond lengths in S2 chains [2.597 (1) Å]. The same structure relationships have been found in $Na(H_3O)(HSO_4)_2$ (Trojanov *et al.*, 1995) which is isotypic with the potassium oxonium derivative.

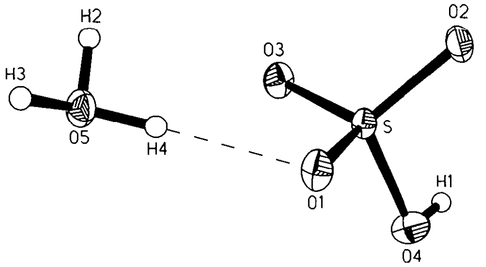

Fig. 3. *ORTEP*II (Johnson, 1976) drawing of $(H_3O)(HSO_4)$ with displacement ellipsoids at the 50% probability level.

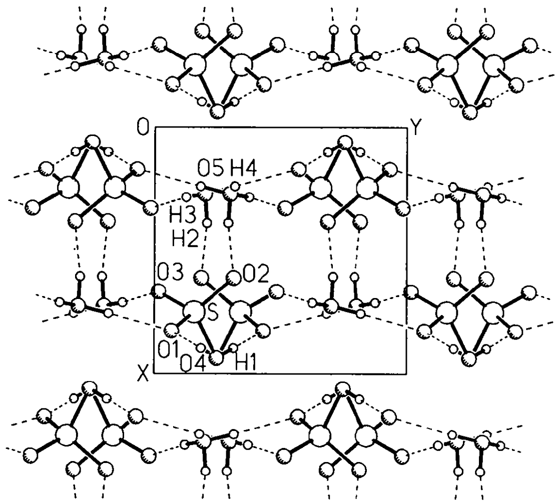

Fig. 4. Double layers in the structure of $(H_3O)(HSO_4)$.

Experimental

The synthetic work and handling of the compounds was carried out under strictly inert conditions using dry nitrogen. 100% H_2SO_4 was prepared from 65% oleum and 98% H_2SO_4. Crystals of H_2SO_4 were slowly grown at 279–281 K. Purity was proved by determining the melting point. The experimental value of 283.5 K seems to be in good agreement with the literature (Lichty, 1908). Oxonium hydrogensulfate was obtained from 86% sulfuric acid by dilution of 98% acid with water. Crystals grew slightly below the melting point of this compound (281.5 K). Crystallization should preferably occur where the dystectic state of the system H_2SO_4/H_2O (ratio 1:1, ~84.5% H_2SO_4) is reached, which allows the crystals of the compound to separate due to the presence of the liquid phase (saturated sulfuric acid). Crystals of both compounds suitable for X-ray analysis were selected in a cool nitrogen stream using a polarization microscope. For measurements, they were quickly transferred to the diffractometer and exposed to cooled nitrogen.

Compound (I)

Crystal data

H_2SO_4
$M_r = 98.08$
Monoclinic
$C2/c$
$a = 8.181$ (2) Å
$b = 4.6960$ (10) Å
$c = 8.563$ (2) Å
$\beta = 111.39$ (3)°
$V = 306.31$ (12) Å^3
$Z = 4$
$D_x = 2.127$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 11$–$12.5°$
$\mu = 0.866$ mm^{-1}
$T = 113$ (2) K
Irregular
0.8 × 0.5 × 0.5 mm
Colourless

Data collection

Stoe–Stadi four-circle diffractometer
θ–2θ scans
Absorption correction: none
453 measured reflections
453 independent reflections
425 observed reflections [$I > 2\sigma(I)$]

$\theta_{\max} = 29.99°$
$h = -11 \rightarrow 9$
$k = -6 \rightarrow 0$
$l = -12 \rightarrow 9$
3 standard reflections frequency: 1260 min intensity decay: 0.5%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0212$
$wR(F^2) = 0.0623$
$S = 1.139$
450 reflections
29 parameters
All H-atom parameters refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0269P)^2 + 0.5004P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.446$

$\Delta\rho_{\max} = 0.386$ e Å^{-3}
$\Delta\rho_{\min} = -0.325$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.029 (4)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Compound (II)

Crystal data

$(H_3O)(HSO_4)$
$M_r = 116.09$
Monoclinic
$P2_1/c$
$a = 7.0770$ (10) Å
$b = 6.9550$ (10) Å
$c = 8.150$ (2) Å
$\beta = 106.18$ (3)°
$V = 385.26$ (12) Å^3
$Z = 4$
$D_x = 2.002$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 9$–$12.5°$
$\mu = 0.724$ mm^{-1}
$T = 160$ (2) K
Irregular
1.0 × 0.8 × 0.5 mm
Colourless

Data collection

Stoe–Stadi four-circle diffractometer
θ–2θ scans
Absorption correction: none
2384 measured reflections
2384 independent reflections
2224 observed reflections [$I > 2\sigma(I)$]

$\theta_{\max} = 40°$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 14$
3 standard reflections frequency: 150 min intensity decay: 6.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0332$
$wR(F^2) = 0.1075$
$S = 1.126$
2364 reflections
72 parameters
All H-atom parameters refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0604P)^2 + 0.0491P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.073$

$\Delta\rho_{\max} = 1.10$ e Å^{-3}
$\Delta\rho_{\min} = -1.25$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 3.25 (9)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (I)*

$U_{\rm iso}$ for H atom, $U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for S and O atoms.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
S	0	0.07450 (9)	1/4	0.0097 (2)
O1	−0.15928 (13)	−0.0822 (2)	0.17792 (13)	0.0173 (2)
O2	0.00920 (13)	0.2733 (2)	0.11080 (12)	0.0157 (2)
H	0.088 (4)	0.328 (5)	0.128 (3)	0.035 (7)

Table 2. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2) for (II)*

$U_{\rm iso}$ for H atoms, $U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for S and O atoms.

	x	y	z	$U_{\rm iso}/U_{\rm eq}$
S1	0.75032 (2)	0.15816 (2)	0.04183 (2)	0.01100 (8)
O1	0.82689 (8)	0.06899 (8)	0.21041 (6)	0.01500 (10)
O2	0.61382 (8)	0.31432 (8)	0.04153 (8)	0.01707 (11)
O3	0.66823 (8)	0.01651 (8)	−0.08874 (6)	0.01629 (11)
O4	0.93770 (8)	0.24719 (9)	0.00759 (7)	0.01874 (12)
O5	0.72575 (8)	0.69970 (8)	0.17478 (7)	0.01579 (11)
H1	0.898 (3)	0.314 (2)	−0.078 (2)	0.024 (4)
H2	0.608 (3)	0.707 (3)	0.105 (3)	0.036 (5)
H3	0.712 (3)	0.625 (3)	0.266 (2)	0.034 (5)
H4	0.756 (3)	0.818 (3)	0.193 (2)	0.028 (4)

Table 3. *S—O bond lengths (Å) for (I) and (II)*

(I)	This work	Yu & Mak (1978)	Pascard-Billy (1965)
S—O1	1.426 (1)	1.419 (5)	1.426 (15)
S—O2	1.537 (1)	1.528 (5)	1.535 (15)
(II)	This work	Taeslar & Olovsson (1968)	
S—O1	1.467 (1)	1.462 (4)	
S—O2	1.453 (1)	1.449 (4)	
S—O3	1.448 (1)	1.434 (4)	
S—O4	1.558 (1)	1.560 (4)	

Table 4. *Hydrogen-bonding geometry (Å, °) for (I) and (II)*

D—H···A	D—H	H···A	D···A	D—H···A
(I)				
O2—H···O1$^{\rm i}$	0.66 (3)	1.99 (3)	2.648 (2)	170 (3)
(II)				
O4—H1···O1$^{\rm ii}$	0.82 (2)	1.84 (2)	2.657 (1)	170 (2)
O5—H2···O2$^{\rm iii}$	0.87 (2)	1.70 (2)	2.556 (1)	171 (2)
O5—H3···O3$^{\rm iv}$	0.93 (2)	1.64 (2)	2.565 (1)	174 (2)
O5—H4···O1$^{\rm v}$	0.85 (2)	1.81 (2)	2.660 (1)	174 (2)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}+y, z$; (ii) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (iii) $1-x, 1-y, -z$; (iv) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (v) $x, 1+y, z$.

For both compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: SK1004). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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$(NH_4)_2(VO)(VP)O_7$, a Layered Structure Comprising Tetrahedral VPO_7 Groups

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Abstract

The new mixed-valence ammonium vanadophosphate $(NH_4)_2(VO)(VP)O_7$ (diammonium phosphorus divanadium octaoxide) is isostructural with $K_2VO(X_2O_7)$ (X = P, V). Its structure consists of $[V_2PO_8]_\infty$ layers of corner-sharing VO_5 pyramids and VPO_7 groups, interleaved with NH_4^+ ions. The unusual features of this structure are the existence of the VPO_7 groups involving VO_4 and PO_4 tetrahedra, and the simultaneous presence of $V^{IV}O_5$ and V^VO_4 polyhedra, observed here for the first time in this class of compounds. The VPO_7 groups are statistically distributed in the framework. Magnetic measurements and bond-valence calculations confirm the mixed-valence character of this phase and show that the VO_5 pyramids and VO_4 tetrahedra are occupied by V^{IV} and V^V, respectively.

Comment

Ammonium vanadium phosphates are of great interest in the field of catalysis as their decomposition products can exhibit high activity, as shown for β-$(NH_4)VO_2(HPO_4)$ (Pulvin, Bordes, Ronis & Courtine, 1981). Apart from the aforementioned phase, very few crystal structures of ammonium vanadium phosphates have been reported to date (Haushalter, Chen, Soghomonian, Zubieta & O'Connor, 1994; Amoros & Lebail, 1992; Krasnikov *et al.*, 1983). We report here the hydrothermal synthesis and crystal structure of a mixed-valence vanadium phosphate, $(NH_4)_2(V^{IV}O)(V^VP)O_7$, isotypic with the diphosphate $K_2VOP_2O_7$ (Gorbunova, Linde, Lavrov & Tananaev, 1980) and with the divanadate $K_2VOV_2O_7$ (Galy & Carpy, 1975).

The atomic coordinates (Table 1) clearly show that $(NH_4)_2(VO)(VP)O_7$ is isotypic with $K_2VOX_2O_7$ (X = P, V). Thus, in the first instance, the structure can be described as $[V_2PO_8]_\infty$ layers interleaved with NH_4^+ ions. In each $[V_2PO_8]_\infty$ layer, there are corner-sharing VO_5 pyramids and $(V,P)O_7$ groups forming five-sided voids (Fig. 1). Such results reflect only an average structure, since they would imply that one vanadium atom, V2,

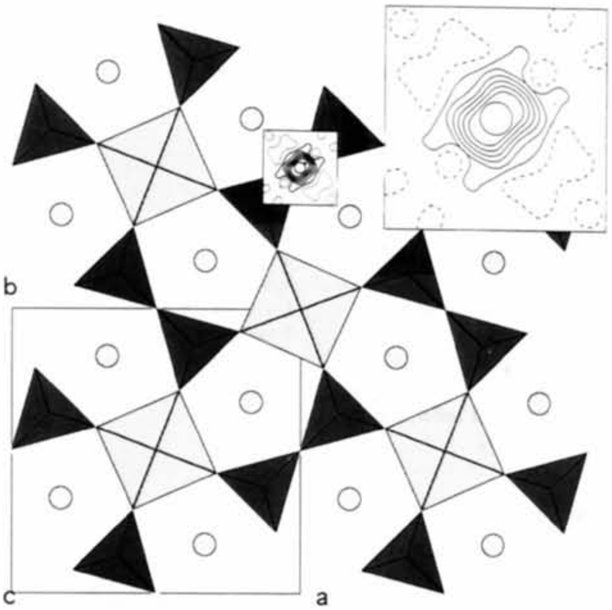

Fig. 1. Projection of $(NH_4)_2(VO)(VP)O_7$ along the c axis; inset: difference Fourier map at the bridging O4 site.