

Hydrogen-Bond Studies. LVIII. The Crystal Structures of Normal and Deuterated Sulphuric Acid Tetrahydrate, $(\text{H}_5\text{O}_2^+)_2\text{SO}_4^{2-}$ and $(\text{D}_5\text{O}_2^+)_2\text{SO}_4^{2-}$

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The crystal structures of sulphuric acid tetrahydrate ($\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$) and the corresponding deuterated compound have been determined from three-dimensional single-crystal X-ray diffractometer data recorded at -190°C . The crystals are tetragonal, space group $P\bar{4}2_1c$, with two formula units in a cell with the following dimensions: $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$: $a = 7.484$ (1), $c = 6.349$ (1) Å; $\text{D}_2\text{SO}_4 \cdot 4\text{D}_2\text{O}$: $a = 7.482$ (1), $c = 6.353$ (1) Å. The water molecules are bonded together in pairs by a very short hydrogen bond of length 2.431 (3) Å in the normal and 2.426 (3) Å in the deuterated compound, so forming H_5O_2^+ , and D_5O_2^+ ions. The H_5O_2^+ and SO_4^{2-} ions are hydrogen bonded to one another to form a three-dimensional network. A twofold axis passes through the centre of the $\text{O} \cdots \text{H} \cdots \text{O}$ bond of the H_5O_2^+ ion whose conformation is *gauche*. The S–O bonds in the SO_4^{2-} ion are all equivalent, 1.480 (2) Å.

Introduction

This work is part of a systematic study of the solid hydrates of strong acids currently in progress at this Institute. References to earlier work can be found in a paper by Lundgren (1972).

In aqueous sulphuric acid which has a molar ratio $\text{H}_2\text{SO}_4:\text{H}_2\text{O}$ of approximately 1:4, the existence of the following ions has been proposed by various investigators (*cf.* Robertson & Dunford, 1964): H_5O_2^+ , H_7O_3^+ , H_9O_4^+ and $\text{H}_{11}\text{O}_5^+$.

The present X-ray work shows that solid $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ contains H_5O_2^+ ions in which the hydrogen bond is possibly symmetric. In order to obtain some information concerning the potential function of this bond, the isotope effect on substitution of H by D has also been studied. The crystal structure determinations described below are based on single-crystal X-ray diffractometer data obtained at -190°C .

Experimental

(a) $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$

Sulphuric acid (*pro analysi*) was distilled as described by Kunzler (1953). A solution with molar ratio $\text{H}_2\text{SO}_4:\text{H}_2\text{O} = 1:4.00$ was prepared by diluting sulphuric acid with distilled water. Small amounts of the solution were sealed in thin-walled glass capillaries (diameter 0.2 mm, wall thickness about 0.02 mm). The composition of the solution was checked by titration with sodium hydroxide immediately before and after the capillaries were filled. Sulphuric acid solutions generally have a very strong tendency to supercool. However, in previous work on the mono- and dihydrates (Taesler & Olovsson, 1968, 1969), it was found that barium sulphate was effective in inducing crystallization. Accordingly, a small amount of barium sulphate was added at the ends of the capillaries.

Single crystals were grown from the above samples in a semi-automatic 2-circle Stoe–Philips X-ray diffractometer (Weissenberg geometry), modified for low-temperature work. The low-temperature equipment was analogous to that developed earlier for a Weissenberg camera (Olovsson, 1960). During the crystal growth the melting point was observed to be about -28°C , in agreement with the value -28.36°C reported by Gable, Betz & Maron (1950). The crystals grew preferentially along the [110] direction.

(b) $\text{D}_2\text{SO}_4 \cdot 4\text{D}_2\text{O}$

The deuterium compound was prepared by diluting commercial D_2SO_4 (CIBA, isotropic purity > 99 at. % D) with D_2O (99.9 at. % D) to the molar ratio $\text{D}_2\text{SO}_4:\text{D}_2\text{O} = 1:3.98$. The isotropic purity of the sample was checked by infrared spectroscopy (Lindgren, 1971). Small amounts of the solution were again sealed in thin-walled glass capillaries together with a small amount of barium sulphate as described above. However, the deuterated compound showed an even stronger tendency to supercool. Special capillaries having a larger diameter at the rear end (0.1 cm) were therefore used to assist crystallization.

Single crystals were grown as described above. During the crystal growth the melting point was observed to be about -39°C , some 11° lower than for $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$; no earlier reports of the melting point seem to exist. As above, the crystals grew preferentially along the [110] direction.

For each of the compounds ten layers were recorded about the [110] direction at -190°C using Cu $K\alpha$ radiation. The capillary axes coincided within a couple of degrees with the rotation axis. Details of the measurement technique are described by Jönsson (1971). 219 (219) independent reflexions were recorded. This corresponds to about 86% (86%) of the reflexions within the copper reflexion sphere (values within pa-

rentheses refer to the deuterated compound). The data were corrected for the Lorentz, polarization and absorption effects. The μR value is approximately 0.40 (0.32). No corrections for extinction effects were made.

Apart from the diffractometer measurements, equi-inclination Weissenberg photographs were also recorded at -190°C for both compounds. The multiple film method was then employed and a total of 250 independent reflexions measured by visual comparison with an intensity scale. The results below are based on the diffractometer data.

Weissenberg photographs taken at different temperatures indicated no phase transformation between the melting point and -190°C .

Unit cell

The unit-cell dimensions at -190°C were determined from quartz-calibrated zero-layer oscillation photographs recorded about [001] and [110] for $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ and about [110] for $\text{D}_2\text{SO}_4 \cdot 4\text{D}_2\text{O}$ using unfiltered Cu K radiation. The cell parameters were fitted to 61 (44) observed θ values by a least-squares procedure using the program *CELSIUS*. This and other programs referred to in the following are described briefly by Liminga (1967) and by Nahrngbauer (1967). The following values were obtained for $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ (the standard deviations given within parentheses refer to the last digit):

$$a = 7.484 (1), \quad c = 6.349 (1) \text{ \AA}, \quad U = 355.61 \text{ \AA}^3,$$

and for $\text{D}_2\text{SO}_4 \cdot 4\text{D}_2\text{O}$:

$$a = 7.482 (1), \quad c = 6.353 (1) \text{ \AA}, \quad U = 355.64 \text{ \AA}^3,$$

$$(a = 4.913, c = 5.405 \text{ \AA} \text{ for } \alpha \text{ quartz at } 22^\circ\text{C}, \lambda(\text{Cu } K\alpha_1) = 1.54051, \lambda(\text{Cu } K\alpha_2) = 1.54433, \lambda(\text{Cu } K\beta) = 1.39217 \text{ \AA}).$$

With two units of $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ in the cell the calculated density is 1.589 g.cm^{-3} at -190°C . The experimental value obtained by Hülsmann & Biltz (1934) is

1.588 g.cm^{-3} at -183°C . The calculated density for $\text{D}_2\text{SO}_4 \cdot 4\text{D}_2\text{O}$ is 1.682 g.cm^{-3} . No experimental value has been reported.

Space group and structure determination

The diffraction symmetry $4/mmm$ and systematic absences $h00$ for $h=2n+1$ and hhl for $l=2n+1$ suggest the space group $P4_2/c$ (No. 114, *International Tables for X-ray Crystallography*, 1952).

With two formula units of $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ in the cell, the special twofold positions $2(a)$: $(0,0,0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ may be chosen arbitrarily for sulphur. The oxygen atoms were subsequently determined from three-dimensional electron density maps based on sulphur. In the structure obtained one independent sulphate oxygen O(1) and one water oxygen O(2) occurs in the cell, each in general eightfold positions. The refinements were performed in the same way for $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{D}_2\text{SO}_4 \cdot 4\text{D}_2\text{O}$ except when stated otherwise. The values given in parentheses below refer to the deuterated compound.

The preliminary oxygen coordinates were first improved in a series of electron density calculations. The atomic coordinates, individual isotropic thermal parameters and the scale factor were subsequently refined by the method of least-squares until the parameter shifts were less than 0.1σ . The full-matrix program *LALS* was used to perform the refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$. The weights were calculated using the expression: $w = \sigma^{-2}(F) = (\sigma_c^2(F^2)/4F^2 + 0.0001F^2)^{-1}$, where σ_c is based on counting statistics. Three (five) reflexions with $I < 2\sigma(I)$ were considered to be insignificantly different from the background and thus given zero weight in the refinement. The final discrepancy index, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, was 0.077 (0.071). At this point a three-dimensional difference synthesis was computed, using only reflexions with $\sin \theta / \lambda < 0.5 \text{ \AA}^{-1}$, to locate the hydrogen atoms. Somewhat diffuse

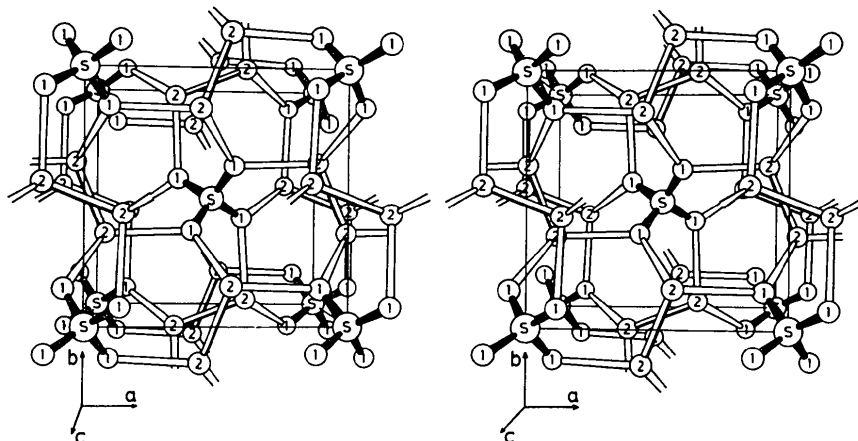


Fig. 1. A stereoscopic illustration of the structure of $(\text{H}_3\text{O}_2^+)_2\text{SO}_4^{2-}$. The covalent bonds within the SO_4^{2-} ions are filled, the hydrogen bonds are open. The oxygen atoms are numbered 1–2 as in the text. Hydrogen atoms are not included.

peaks were found in both the normal and the deuterated case. The hydrogen coordinates used below were calculated as described in the section 'Assignment of hydrogen atoms'.

A series of least-squares refinements was performed including the hydrogen atoms with fixed parameters. The hydrogen atoms were given a Debye-Waller factor of $B=5.0 \text{ \AA}^2$. After three cycles the R value dropped to 0.071 (0.064).

A difference synthesis indicated anisotropy for the sulphur and oxygen atoms. A series of anisotropic least-squares refinements was therefore performed. The scale factor and the parameters for all atoms except hydrogen were refined. The total number of parameters refined was now 22 as compared with 10 in the isotropic case. After three cycles the R value was 0.031 (0.042). In the deuterated case four reflexions were excluded from the data set at this stage. These were evidently extinction-affected reflexions. A further two cycles produced a final R value 0.033. In the last cycle all shifts were less than 0.1σ . The final atomic coordinates and thermal parameters with their standard deviations are listed in Tables 1 and 2. The r.m.s. components of thermal displacement along the principal axes of the ellipsoids of vibration are also given in Table 2. The observed and calculated structure factors are listed in Table 3.

Table 1. Atomic coordinates with standard deviations ($\times 10^5$)

The atomic coordinates of the hydrogen and deuterium atoms are not determined experimentally but are based on chemical assignment as described in the text.

$\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$

	x	y	z
S	0	0	0
O(1)	13616 (20)	8858 (20)	13262 (25)
O(2)	5982 (18)	34901 (18)	58014 (22)

Hydrogen atoms

H(1)	300	26750	69020
H(2)	19450	35470	60010
H(3)	0	50000	58000

$\text{D}_2\text{SO}_4 \cdot 4\text{D}_2\text{O}$

	x	y	z
S	0	0	0
O(1)	13701 (21)	8823 (21)	13206 (28)
O(2)	5995 (20)	34938 (19)	57965 (26)

Deuterium atoms:

D(1)	320	26810	69010
D(2)	19490	35450	59950
D(3)	0	50000	57950

The final R value obtained from the refinements based on film data was 0.080 (0.089). The corresponding atomic coordinates agreed within twice the combined standard deviations with those obtained from the diffractometer data.

The atomic scattering factors used in the above calculations for sulphur and oxygen were those suggested

by Hanson, Herman, Lea & Skillman (1964) and for hydrogen those of Stewart, Davidson & Simpson (1965). All calculations were made on the CDC 3600 computer in Uppsala.

Description and discussion of the structure

A stereoscopic drawing of the structure is given in Fig. 1. Bond distances and angles with their standard deviations are provided in Fig. 2. The corrections to the bond distances for anisotropic thermal motion, assum-

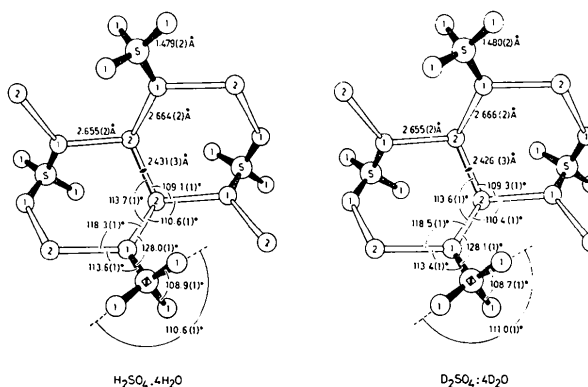


Fig. 2. Bond distances and angles with standard deviations in $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{D}_2\text{SO}_4 \cdot 4\text{D}_2\text{O}$. The orientation is the same as in Fig. 1. A twofold axis passes through the middle of the $\text{O}(2) \cdots \text{O}(2)$ hydrogen bond and a fourfold inversion axis passes through the sulphur atom. Both axes are normal to the plane of the paper.

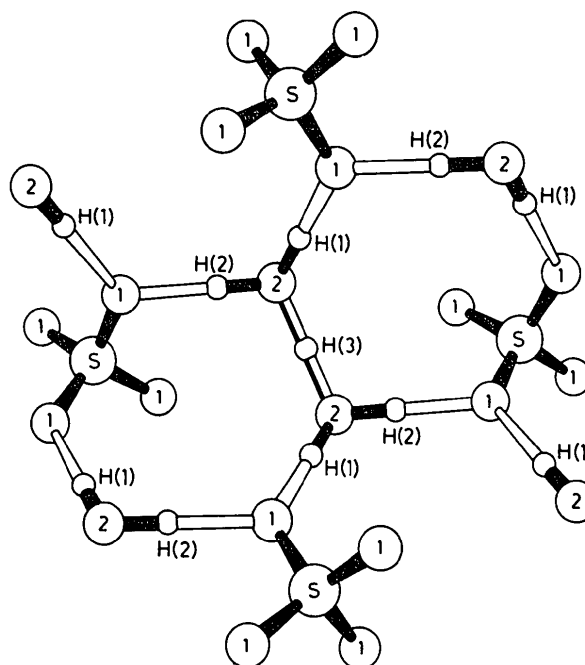


Fig. 3. The assignment of hydrogen atoms based on chemical evidence (see text).

ing riding motion and independent motion, are <0.008 and <0.017 Å, respectively. These calculations were made using the program *ORFFE*.

Assignment of hydrogen atoms

The water oxygen, O(2), is pyramidally surrounded by three oxygen neighbours at possible hydrogen bond distances, 2.431, 2.655 and 2.664 Å (2.426, 2.655 and 2.666 Å), respectively (Fig. 2). The first of these bonds is formed between two O(2) atoms related by a two-fold axis passing through the centre of the bond. All S–O distances in the sulphate group are equal, 1.479 Å (1.480 Å), which is close to the average value found in compounds containing SO_4^{2-} ions (see below). It is therefore clear that both protons of the sulphuric acid have been transferred to the water molecules. This is also evident from the shortness of the $\text{O}(2)\cdots\text{O}(2)$ bond, since hydrogen bonds between normal H_2O molecules are about 2.76 Å. There is one extra proton per $2\text{H}_2\text{O}$ and the only possible location for this proton is on the twofold axis through the centre of the $\text{O}(2)\cdots\text{O}(2)$ bond. The two hydrogen atoms of each water molecule are involved in hydrogen bonds to two different sulphate ions. The assignment of the hydrogen atoms is illustrated in Fig. 3. The hydrogen atoms have been placed on the lines between the hydrogen bonded atoms, two of them, H(1) and H(2), on the bonds $\text{O}(2)\cdots\text{O}(1)$ and $\text{O}(2)\cdots\text{O}(1)'$ at 1.02 Å from O(2) and the third, H(3), in the middle of the $\text{O}(2)\cdots\text{O}(2)$ bond. The hydrogen positions so derived corresponded closely with the peaks found in the difference maps.

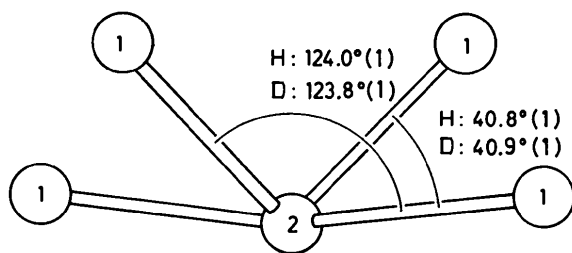


Fig. 4. Dihedral angles of the H_5O_2^+ ion in $\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$ and $\text{D}_2\text{SO}_4 \cdot 4\text{D}_2\text{O}$. The view is along the $\text{O}(2)\cdots\text{O}(2)$ direction.

The peak heights were: $\text{H}(1)=0.41$ (0.45), $\text{H}(2)=0.58$ (0.49) and $\text{H}(3)=0.74$ (0.87) $\text{e} \cdot \text{Å}^{-3}$. Other peaks (all less than 0.27 (0.35) $\text{e} \cdot \text{Å}^{-3}$) could be definitely excluded as possible hydrogen positions. Only calculated hydrogen positions were used in the structure refinements.

Using the above assignment the structure may be described as follows. Pairs of water molecules are hydrogen bonded to one another to form H_5O_2^+ ions. These H_5O_2^+ ions are hydrogen bonded to the SO_4^{2-} ions, so forming a three-dimensional network. Each sulphate ion is hydrogen bonded to eight H_5O_2^+ ions, each sulphate oxygen being involved in two hydrogen bonds.

The sulphate ion

The sulphate ion forms an almost regular tetrahedron (Fig. 2). The average O–S–O angle is 109.5° . A four-fold inversion axis passes through the centre of the sulphur atom and all S–O distances are equivalent, 1.479(2) Å [1.480(2) Å]. After correcting for assumed riding motion, the S–O distances become 1.488(2) Å [1.488(2) Å]. This is in close agreement with the earlier published results (Taesler & Olovsson, 1969).

It is interesting to note that the sulphur atom, the sulphate oxygen O(1) and its two hydrogen bonded neighbours O(2) and O(2)' are all coplanar, no atom deviating by more than 0.02 Å from the least-squares plane through the four atoms (calculated according to Blow, 1960). A similar situation has also been found in $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ (Taesler & Olovsson, 1968, 1969).

The H_5O_2^+ and D_5O_2^+ ion

Although a twofold axis passes through the centre of the $\text{O}(2)\cdots\text{O}(2)$ bond, it is not possible from the present investigation to ascertain whether the bond is truly symmetrical. The conformation of the H_5O_2^+ and D_5O_2^+ ion is *gauche*; the dihedral angles are given in Fig. 4.

The existence of H_5O_2^+ ions in solution was first suggested by Huggins (1936) and the presence of H_5O_2^+ has been demonstrated in several solid hydrates of inorganic acids: $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$ (Olovsson 1968), $\text{HCl} \cdot 2\text{H}_2\text{O}$, $\text{HCl} \cdot 3\text{H}_2\text{O}$, (Lundgren & Olovsson, 1967a,b)

Table 2. Anisotropic thermal parameters with standard deviations ($\times 10^5$)

The form of the temperature factor is $\exp(-\beta_{11}h^2 \dots -2\beta_{12}hk - \dots)$. The root-mean-square components R_i ($\times 10^3$ Å) of thermal displacement along the ellipsoid axes are also listed.

$\text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$									
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
S	180 (14)	180 (14)	652 (25)	0	0	0	72 (3)	72 (3)	116 (2)
O(1)	579 (27)	436 (25)	1130 (42)	56 (23)	-393 (27)	-152 (26)	97 (5)	109 (3)	175 (3)
O(2)	427 (23)	562 (27)	917 (37)	-51 (23)	75 (19)	110 (22)	104 (4)	125 (3)	143 (3)
$\text{D}_2\text{SO}_4 \cdot 4\text{D}_2\text{O}$									
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
S	149 (15)	149 (15)	580 (26)	0	0	0	65 (3)	65 (3)	109 (3)
O(1)	554 (29)	436 (26)	1153 (48)	130 (26)	-384 (30)	-111 (28)	93 (4)	111 (4)	175 (3)
O(2)	421 (24)	535 (28)	867 (39)	-119 (25)	91 (21)	81 (25)	94 (5)	131 (4)	137 (3)

HBr.2H₂O and HBr.3H₂O (Lundgren, 1970). The first compound possesses a centre of symmetry at the centre of the O...O bond, whereas in HBr.3H₂O there is a twofold axis at the centre of the O...O bond. In the remaining three compounds, however, the environments at the two ends of H₃O₂⁺ ions are not equivalent. The conformation of the H₃O₂⁺ ion is *trans* in HClO₄.2H₂O and HBr.3H₂O but *gauche* in HCl.2H₂O, HCl.3H₂O, HBr.2H₂O, H₂SO₄.4H₂O and D₂SO₄.4D₂O. The O...O distances are all very similar in these compounds: 2.424 (9), 2.473 (18), 2.414 (7), 2.434 (10), 2.410 (13), 2.431 (3) and 2.426 (3) Å respectively.

The bonding arrangement about the oxygen atom O(2) is pyramidal (Fig. 2) and the O(1)...O(2)...O(2) and O(1)...O(2)...O(1) angles close to tetrahedral. In HClO₄.2H₂O, HCl.3H₂O and HBr.3H₂O the bonding arrangement is also pyramidal, whereas in HCl.2H₂O and HBr.2H₂O the arrangement is pyramidal at one end but almost planar at the other.

The O...O hydrogen bond distances between the H₃O₂⁺ and SO₄²⁻, 2.655 and 2.664 Å (2.655 and 2.666 Å), are considerably longer than those between H₃O⁺ and HSO₄⁻ in H₂SO₄.H₂O, 2.538, 2.566 and 2.649 Å, and those between H₃O⁺ and SO₄²⁻ in H₂SO₄.2H₂O, 2.520–2.590 Å. A similar comparison between HClO₄.H₂O (Lee & Carpenter, 1959; Nordman, 1962) and HClO₄.2H₂O gives the same result. This is of course to be expected if the extra proton in H₃O₂⁺ is

shared approximately equally between the two oxygen atoms.

The isotope effect

The variation of the isotope effect with hydrogen bond length is of great relevance to a discussion of the nature of the hydrogen bond. Unfortunately, very few complete structure determinations have so far been performed in which both the normal and the corresponding deuterated compound have been studied. However, in short O...O hydrogen bonds (2.5–2.6 Å) an expansion has been observed on substitution of H by D (*cf.* Tellgren & Olovsson, 1971). This effect appears to decrease as the hydrogen bond becomes weaker. In the present compound an insignificant change from 2.431 (3) to 2.426 (3) Å is observed in the short O(2)...H(3)...O(2) bond length on deuteration. This is also true for the longer O(2)–H(1)...O(1) and O(2)–H(2)...O(1)' bond lengths: 2.664 (2) and 2.655 (2) Å as compared to 2.666 (2) and 2.655 (2) Å in the deuterated compound. Corresponding angles are also equal within 2σ in the two cases.

The O(2)...O(2) bond length falls within the range of possible symmetric hydrogen bonds, although no definite conclusion may be drawn from the crystallographically observed symmetry. According to Rundle (1964) virtually no isotope effect should occur if the hydrogen bond is of the symmetric single potential well

Table 3. Observed and calculated structure factors

The five columns are in order *h*, *k*, *l*, |F_o| and |F_c|. Reflexions marked by an asterisk were deleted from the refinement.

(a) H₂SO₄.4H₂O

Observed and calculated structure factors for H₂SO₄.4H₂O. The table shows columns for h, k, l, |F_o|, and |F_c|. Reflexions marked with an asterisk (*) are those deleted from the refinement. The data is presented in a grid-like format with rows corresponding to different (h, k, l) reflections.

(b) D₂SO₄.4D₂O

Observed and calculated structure factors for D₂SO₄.4D₂O. The table shows columns for h, k, l, |F_o|, and |F_c|. Reflexions marked with an asterisk (*) are those deleted from the refinement. The data is presented in a grid-like format with rows corresponding to different (h, k, l) reflections.

type. On this basis it could be suggested that the hydrogen bond within the H_5O_2^+ ion is of this type. It is, however, uncertain whether this is a sufficiently definitive test to eliminate the possibility that the bond is of the statistically symmetric double-potential type.

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The Crystal Structure of Zinc Isopropylxanthate

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The crystal structure of zinc isopropylxanthate, $\text{Zn}(\text{S}_2\text{COiso-C}_3\text{H}_7)_2$ has been determined. The final R value was 6.8%. The crystal is triclinic, space group $P\bar{1}$, with $a=10.915$ (3), $b=13.167$ (4), $c=10.393$ (2) Å, $\alpha=100.89$ (2), $\beta=100.42$ (2), $\gamma=101.33$ (7)°, $Z=4$. The four zinc isopropylxanthate

molecules in the unit cell are linked together by the $-\text{Zn}-\text{S}-\text{C}-\text{S}-\text{Zn}-$ bridges to form a tetramer with a 16-membered ring. The tetramer is centrosymmetric about the centre of the ring. Four isopropylxanthate groups (bridging groups) make up the ring formation, and each of the other four (chelating groups) coordinates to a zinc atom. The coordination of the four sulphur atoms about each zinc atom forms a distorted tetrahedron, the Zn-S distances ranging from 2.307 to 2.408 Å.

Introduction

Although the sulphur coordinations around a zinc atom in some zinc salts of dithioacids form distorted tetrahedra, in the crystalline state (Ito, Igarashi & Hagihara, 1969), the modes of molecular aggregations are varied as shown schematically in Fig. 1. In zinc ethylxanthate, $\text{Zn}(\text{EX})_2$ (Ikeda & Hagihara, 1966), the molecules aggregate into two-dimensional networks with 16-membered rings [Fig. 1(a)]. In zinc diethyldithiophosphate, $\text{Zn}(\text{EP})_2$ (Ito *et al.*, 1969), only one half

of the phosphate groups take part in bridge formation, forming infinite linear zigzag chains [Fig. 1(b)]. On the other hand, dimeric structures with an 8-membered ring [Fig. 1(c)] are reported for zinc diethyldithiocarbamate, $\text{Zn}(\text{EC})_2$ (Bonamico, Mazzone, Vaciago & Zambonelli, 1965), zinc dimethyldithiocarbamate, $\text{Zn}(\text{MC})_2$ (Klug, 1966) and zinc diisopropyldithiophosphate, $\text{Zn}(\text{isoPP})_2$ (Lawton & Kokotailo, 1969). In organic solvents, however, the $\text{Zn}(\text{EC})_2$ and $\text{Zn}(\text{EP})_2$ molecules are monomeric (Bonamico *et al.*, 1965; Ito *et al.*, 1969).