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The Crystal Structure of Triammonium Hydrogen Disulphate, $(NH_4)_3H(SO_4)_2$

By Shigeru Suzuki and Yasuharu Makita

Department of Applied Physics, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, *Japan*

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The crystal structure of the room-temperature phase of $(NH_4)_3H(SO_4)_2$, which becomes ferroelectric at high hydrostatic pressures or by deuteration, has been determined by X-ray diffractometry. The final R value was 0·045. The crystal is monoclinic, with the space group $A2/a$ and $Z = 4$. Neighbouring SO_4^{2-} ions are linked together in pairs by a hydrogen bond, O—H···O. The H atoms involved in the bonds, it is suggested, are in motion either statistically or dynamically between shallow double potential minima. At least one of two kinds of ammonium ion, $NH_4^+(1)$, is suggested to be ordered. [Crystal data: a = 10·153 (3), b = 5·854 (2), c = 15·410 (6) Å, β = 101·76°, D_c = 1·832 g cm^{-3}.]

Introduction

It has recently been found by Gesi (1976*a*) that triammonium hydrogen disulphate, $(NH_4)_3H(SO_4)_2$, becomes ferroelectric under hydrostatic pressures higher than about 5 kbar in two phases (phases VI and VII) below room temperature. The crystal at 1 atm undergoes successive phase transitions at 140 (Gossner, 1904; Fischer, 1914), −8, −132 and −140°C (Gesi, 1976*b*) and has five phases I, II, III, IV and V altogether (denoted in order of descending temperature). In addition to the dielectric anomaly observed at each phase-transition temperature, there is a broad maximum in the dielectric constant along the c^* axis at around −25°C (Gesi, 1976*b*). One of the interesting features of $(NH_4)_3H(SO_4)_2$ is the fact that the dielectric broad maximum becomes sharp and intense with increasing hydrostatic pressure, and then it splits into two dielectric peaks at about 5 kbar, between which one of the ferroelectric phases appears.

Very recently, it has been found by one of the present authors and coworkers (Osaka, Makita & Gesi, 1977) that deuterated triammonium deuterium disulphate, $(ND_4)_3D(SO_4)_2$, is ferroelectric in two phases below room temperature. This indicates a significant isotope effect on the occurrence of ferroelectric activity similar to the pressure effect. In view of this physical significance, a structure analysis of $(NH_4)_3H(SO_4)_2$, was much desired, although its space group at room temperature had been suggested to be $A2/a$ (Gesi, 1976*b*). The purpose of the present paper is to report the crystal structure of $(NH_4)_3H(SO_4)_2$ determined at room temperature (phase II), which may provide valuable information about the mechanisms of the successive phase transitions.

Experimental

Single crystals of $(NH_4)_3H(SO_4)_2$ were grown by slow evaporation from an aqueous solution which contained 40·6 wt% $(NH_4)_2SO_4$ and 24·0 wt% H_2SO_4. The crystals thus grown were transparent hexagonal plates. Examination by polarization microscope indicated that all the crystals thus obtained were of single domain. In the present study the single-domain crystals were used in all the experiments. Examination of Weissenberg photographs showed that the space group is either Aa or $A2/a$. From the absence of piezoelectric activity, we selected $A2/a$ as the space group, which is consistent with that suggested by Gesi (1976*b*). The lattice parameters were obtained by an extrapolation method (Nelson & Riley, 1945) with a total of 36 reflexions of $h00$, $0k0$, $00l$ and $h0l$ types, which were measured by an X-ray diffractometer with a proportional counter.

Crystal data

$(NH_4)_3H(SO_4)_2$, M_r = 247·3, D_c = 1·832 g cm^{-3}, a = 10·153 (3), b = 5·854 (2), c = 15·410 (6) Å, β = 101·76 (2)°, V = 896·7 Å^3, Z = 4 (λ = 1·5405 Å), where the calculated density, D_c, agrees well with the experimental result, D_m = 1·831, reported by Gossner (1904).

Intensity data were collected on a Rigaku Denki automatic four-circle X-ray diffractometer, controlled by a FACOM U-200 computer, with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·71069 Å). A cylindrical crystal, elongated along **b** with diameter $2r \simeq 0·44$ mm, was used as a specimen. The scanning speed was 8° min^{-1} and the scan range $\Delta 2\theta$ was varied according to the relation: $\Delta 2\theta = (1 + 0{\cdot}5 \tan \theta)^\circ$. The background was measured for 5 s at the beginning and end points of each scan. As a check on the stability of the crystal and the instruments, three standard reflexions, 200, 020 and 004, were monitored every 50 reflexions and no significant variation was noticed in their intensities. The intensity data were collected for $2\theta \leq 70^\circ$ by the ω–2θ scanning technique. Corrections were made for Lorentz and polarization factors. No correction was made for absorption, since the linear absorption coefficient is small ($\mu r = 0{\cdot}12$ for Mo $K\alpha$). 1983 independent reflexions were measured and 236 of these, for which $|F_o| \leq \sigma(|F_o|)$, were assigned zero intensity, where $\sigma(|F_o|)$ is the standard deviation estimated from counting statistics.

Determination and refinement of the structure

The positions of S and O atoms were determined from the three-dimensional Patterson synthesis. A block-diagonal least-squares refinement, based on these atoms, followed by a difference Fourier calculation, gave the positions of two N atoms. Positional parameters and individual isotropic temperature factors were then refined by a block-diagonal least-squares method for non-hydrogen atoms. The quantity minimized was $\Sigma\, w(|F_o| - |F_c|)^2$. The discrepancy index, R, and the weighted discrepancy index, R_w, at this stage were reduced to 0·149 and 0·174 respectively, where R and R_w are defined by $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ and $R_w = [\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, w|F_o|^2]^{1/2}$. Introduction of anisotropic temperature factors reduced the R and R_w values to 0·117 and 0·156 respectively. Comparison between the observed and calculated structure factors suggested that 16 strong reflexions (at low angles of 2θ) out of 1747 were affected by extinction, and were therefore omitted from further refinements. The difference Fourier synthesis at this stage showed the positions of all H atoms, resulting in $R = 0{\cdot}054$ and $R_w = 0{\cdot}064$. In these refinements, unit weight was assigned for all reflexions. In the final stage of refinement, the following weighting scheme was adopted: $w = (41{\cdot}13/F_o)^2$ for $F_o \geq 41{\cdot}13$, $w = 1$ for $F_o < 41{\cdot}13$, and refinements were continued until all parameter shifts became less than one fifteenth of their standard deviations. The final R and R_w values obtained are 0·045 and 0·051, respectively, for 1731 independent reflexions. The positional parameters and their standard deviations thus determined are given in Tables 1 and 2.*

All the calculations in the refinements mentioned above were performed on a HITAC 8800/8700 computer with the *Universal Crystallographic Computation Program System* (Sakurai, 1967). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962), and the dispersion corrections for atomic scattering were neglected.

Table 1. *Fractional coordinates* ($\times 10^4$) *of the non-hydrogen atoms and their e.s.d.'s*

	x	y	z
N(1)	7500	2692 (4)	0
N(2)	6528 (2)	7240 (3)	1988 (1)
S	4615 (1)	2181 (1)	1142 (1)
O(1)	3983 (2)	268 (3)	1495 (1)
O(2)	4427 (2)	1845 (3)	148 (1)
O(3)	6054 (1)	2225 (3)	1504 (1)
O(4)	3985 (2)	4330 (3)	1284 (1)

Table 2. *Fractional coordinates* ($\times 10^3$) *of hydrogen atoms and their e.s.d.'s*

	x	y	z	Bonded to
H(1)	311 (3)	655 (7)	22 (3)	N(1)
H(2)	226 (4)	797 (7)	46 (3)	N(1)
H(3)	723 (4)	708 (7)	172 (3)	N(2)
H(4)	660 (5)	720 (8)	258 (4)	N(2)
H(5)	597 (5)	626 (9)	150 (3)	N(2)
H(6)	617 (5)	860 (9)	163 (3)	N(2)
H(7)	0	0	0	O(2)

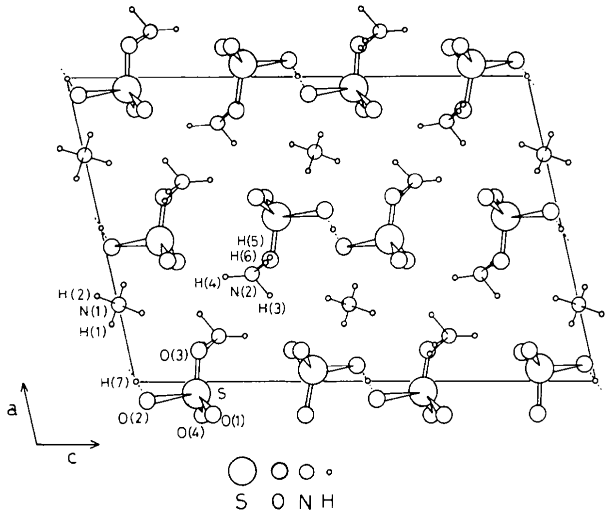

Fig. 1. Crystal structure projected along **b**. Dashed lines indicate hydrogen bonds of type O—H···O. Hydrogen bonds of type N—H···O are not shown because of their complexity.

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* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33163 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Result and discussion

The crystal structure is shown in Figs. 1 and 2. There are 12 ammonium ions and 8 sulphate ions in the unit cell, in which each pair of neighbouring sulphate ions is linked by one hydrogen bond of type O—H···O, thus making four hydrogen bonds of this type. In addition to the O—H···O bond, there is another type of hydrogen bond, N—H···O.

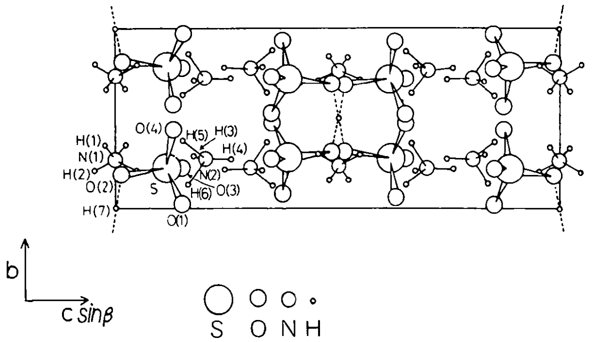

Fig. 2. Crystal structure projected along **a**. Dashed lines indicate hydrogen bonds of type O—H···O.

Table 3. *Interatomic distances* (Å) *and bond angles* (°) *for the ammonium ions*

Greek letters α and β refer to atoms at ($\frac{1}{2}-x, y, -z$) and ($-\frac{1}{2}+x, 1-y, z$) respectively.

N(1β)–H(1)	0·78 (3)	H(1)–N(1β)–H(1α)	110·4 (3·8)
N(1β)–H(2)	0·89 (5)	H(1)–N(1β)–H(2)	103·4 (3·9)
H(1)···H(1α)	1·28 (4)	H(1)–N(1β)–H(2α)	105·4 (4·0)
H(1)···H(2)	1·31 (6)	H(2)–N(1β)–H(2α)	128·4 (3·8)
H(1)···H(2α)	1·33 (6)		
H(2)···H(2α)	1·60 (7)		
N(2)–H(3)	0·90 (5)	H(4)···H(6)	1·65 (7)
N(2)–H(4)	0·89 (6)	H(5)···H(6)	1·40 (7)
N(2)–H(5)	1·02 (5)	H(3)–N(2)–H(4)	123·9 (4·2)
N(2)–H(6)	0·99 (5)	H(3)–N(2)–H(5)	88·4 (3·9)
H(3)···H(4)	1·58 (8)	H(3)–N(2)–H(6)	93·8 (4·0)
H(3)···H(5)	1·34 (6)	H(4)–N(2)–H(5)	130·8 (4·3)
H(3)···H(6)	1·38 (7)	H(4)–N(2)–H(6)	121·2 (4·3)
H(4)···H(5)	1·75 (7)	H(5)–N(2)–H(6)	87·8 (3·9)

Ammonium ions and N—H···O *bond*

Ammonium ions occupy two sets of non-equivalent positions: one set at general positions, NH_4^+(2), and the other at special positions on twofold axes, NH_4^+(1). There are thus four NH_4^+(1) ions and eight NH_4^+(2) ions in the unit cell. The interatomic distances and bond angles for the ammonium ions are given in Table 3, and those of N—H···O bonds are listed in Table 4. Each H atom bonded to N(1) forms a hydrogen bond of the type N—H···O, whereas that bonded to N(2) forms a bifurcated bond of the type N—H···2O. Fig. 3 illustrates the difference Fourier map showing hydrogens of both NH_4^+(1) and NH_4^+(2) ions viewed along **a**. The results of Table 3 and Fig. 3 strongly suggest that NH_4^+(1) ions form slightly distorted tetrahedra having electric dipole moments and are statistically ordered. The ordered state suggested may be attributed, to a certain extent, to the binding force between H and O atoms which can hinder reorientation of the NH_4^+(1) ion. On the other hand, there remains to a certain extent the question whether NH_4^+(2) ions may also be statistically ordered or not, although it is implied from Fig. 3 that they are rather ordered. In order to clarify this, other studies by, for example, neutron diffraction would be desirable.

Sulphate ion and O—H···O *bond*

Bond distances and bond angles of the sulphate ion, SO_4^{2-}, are given in Fig. 4. The S—O(i) bonds (i = 1, 3, 4) are all the same length, 1·450 (3) Å, whereas the S—O(2) bond distance is 1·518 Å. The sulphate ion thus forms a slightly distorted tetrahedron, and carries an electric dipole moment parallel to the S—O(2) bond.

The hydrogen bonds of type O—H···O are shown in Figs. 1 and 2 by dashed lines. Neighbouring SO_4^{2-} ions are linked together in pairs by a hydrogen bond O(2)—H(7)···O(2′), with O(2)···O(2′) = 2·540 (2) Å, ∠O(2)—H(7)···O(2′) = 180°. The angles the hydrogen bond makes with the (100), (010) and (001) planes are 27·9, 58·3 and 10·4°, respectively. The O—O separation in $(NH_4)_3H(SO_4)_2$ is close to, but larger than, that (2·491 Å) of the hydrogen bond in ferroelectric KH_2PO_4 (abbreviated KDP) (Bacon & Pease, 1955). The phase transition of KDP has been much studied, both theoretically and experimentally, in its

Table 4. *Hydrogen-bond distances* (Å) *and bond angles* (°) *of type* N—H···O

N(1)–H(1)···O(4)	147	N(1)–O(4)	2·826	H(1)···O(4)	2·14
N(1)–H(2)···O(3)	148	N(1)–O(3)	3·009	H(2)···O(3)	2·22
N(2)–H(3)···O(1)	132	N(2)–O(1)	3·120	H(3)···O(1)	2·45
N(2)–H(3)···O(4)	162	N(2)–O(4)	3·066	H(3)···O(4)	2·20
N(2)–H(4)···O(1)	134	N(2)–O(1)	2·900	H(4)···O(1)	2·20
N(2)–H(4)···O(3)	116	N(2)–O(3)	3·011	H(4)···O(3)	2·51
N(2)–H(5)···O(4)	136	N(2)–O(4)	3·097	H(5)···O(4)	2·28
N(2)–H(5)···O(3)	122	N(2)–O(3)	3·025	H(5)···O(3)	2·36
N(2)–H(6)···O(1)	127	N(2)–O(1)	3·097	H(6)···O(1)	2·39
N(2)–H(6)···O(3)	152	N(2)–O(3)	3·042	H(6)···O(3)	2·13

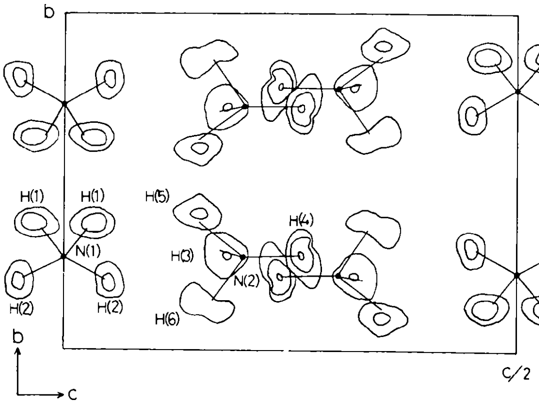

Fig. 3. Difference Fourier map viewed along **a**. Contours are at intervals of 0·1 e Å^{-3}, beginning at 0·2 e Å^{-3}.

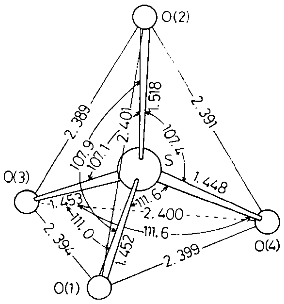

Fig. 4. Bond distances (Å) and bond angles (°) of the sulphate ion.

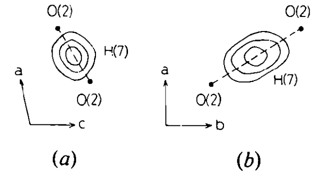

Fig. 5. Difference Fourier maps viewed (*a*) along **b** and (*b*) along **c**. Contours are at intervals of 0·1 e Å^{-3}, beginning at 0·2 e Å^{-3}.

relation to the hydrogen isotope effect. Fig. 5(*a*) and (*b*) shows the difference Fourier maps around the H(7) atom viewed along **b** and **c** respectively. These two maps indicate that the contours are considerably elongated along the O(2)–H(7)···O(2′) bond and thus they are greatly anisotropic.

It is suggested from both the magnitude of the O—O separation and the results shown in Fig. 5 that the H atoms of $(NH_4)_3H(SO_4)_2$ involved in hydrogen bonds are in motion either statistically (*i.e.* in disordered state) or, as an extreme case, dynamically (possibly in the state of tunnelling motion) between shallow double potential minima. The difference in motion of the H atoms between the two cases may be regarded mainly as a difference in the depth of their potential minima at a given temperature. If the former case is correct, there is a possibility that dielectric relaxation may be observed, for example, at certain high frequencies of the microwave region, near the ferroelectric transition (the II–III transition) which is induced at high pressures or by deuteration. If the latter is the case, the H atoms may effectively vibrate anisotropically along the bond axis.

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