

## The Structure of Deuterated Triammonium Hydrogendisulphate,\* $(\text{ND}_4)_3\text{D}(\text{SO}_4)_2$

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### Abstract

$(\text{ND}_4)_3\text{D}(\text{SO}_4)_2$ ,  $M_r = 260.3$ , monoclinic,  $A2/a$ ,  $a = 10.158$  (1),  $b = 5.860$  (1),  $c = 15.401$  (1) Å,  $\beta = 101.88$  (1)°,  $U = 897.1$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.927$  Mg m<sup>-3</sup>,  $\mu = 0.60$  mm<sup>-1</sup> (Mo  $K\alpha$  radiation).  $R = 0.033$  for 1753 unique observed reflections. The outline of the structure is the same as that of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ . The hydrogen bond  $\text{O}-\text{H}\cdots\text{O}$ , which links two symmetrically equivalent  $\text{SO}_4^{2-}$  ions, is markedly affected by the deuteration. The D in the  $\text{O}-\text{D}\cdots\text{O}$  bond is in a disordered state. Results suggest that the appearance of ferroelectricity in the crystal is closely related to ordering of the D.

### Introduction

It was recently found by Gesi (1976*a*) that triammonium hydrogendisulphate,  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ , had two ferroelectric phases at a hydrostatic pressure higher than about 500 MPa (phases VI and VII). The crystal at 0.1 MPa undergoes successive phase transitions and has five phases (Gossner, 1904; Fischer, 1914; Gesi, 1976*b*). However, no ferroelectric nature is found in any phase at 0.1 MPa (Gesi & Ozawa, 1977). It was recently suggested by Gesi (1977) that the modified Mitsui (1958) model was effective for explaining the dielectric behaviour of a crystal of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ .

Recently it was found by Osaka, Makita & Gesi (1977) that deuterated triammonium hydrogendisulphate,  $(\text{ND}_4)_3\text{D}(\text{SO}_4)_2$ , at 0.1 MPa exhibited successive phase transitions at 263.5, 249, 208 and 173 K; these five phases are designated (II), (III), (VI), (III') and (VII) with descending temperature. Phases (VI) and (VII) show ferroelectric activity (Osaka, Makita & Gesi, 1977). This indicates that the isotope effect on the ferroelectricity is similar to the pressure effect (Gesi, Ozawa, Osaka & Makita, 1978). In order to study the origin of the ferroelectricity in the  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ – $(\text{ND}_4)_3\text{D}(\text{SO}_4)_2$  system, the structure analysis of  $(\text{ND}_4)_3\text{D}(\text{SO}_4)_2$  was undertaken, and the results compared with those of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  (Suzuki & Makita, 1978).

### Experimental and structure analysis

The crystal used was grown by Dr Gesi by the method reported previously (Osaka, Makita & Gesi, 1977). Before the X-ray work, dielectric constants were measured in the temperature range between 163 and 298 K, and the appearance of the ferroelectric phases (VI) and (VII) was confirmed. Examination of X-ray Weissenberg photographs showed that the space group was either  $Aa$  or  $A2/a$ , which is the same as that reported for  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  (Gesi, 1976*b*; Suzuki & Makita, 1978). The lattice parameters were obtained by the least-squares method with 24 Bragg reflections.

Intensity data were collected on a Rigaku Denki automatic four-circle X-ray diffractometer with Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) monochromated by a single crystal of LiF. A spherical crystal with diameter  $2r = 0.35$  mm, which was coated with epoxy resin to prevent deliquescence, was used as the specimen. The  $2\theta$ – $\omega$  scanning range  $\Delta 2\theta$  was varied according to the relation  $\Delta 2\theta = (1.33 + 0.78 \tan \theta)^\circ$ . The background was measured for 60 s at the beginning and end of each scan. In order to check the stability of the sample and instruments, three standard reflections (14,0,0, 4,0,18,  $\bar{1}82$ ) were measured every 18 reflections. No significant variation was found in their intensities. 2032 independent reflection data were collected for  $2\theta \leq 70^\circ$  at 287 K, and the reflection intensities for  $2\theta \geq 60^\circ$  were measured at least twice. Corrections were made for Lorentz and polarization factors. No correction was made for absorption, because the linear absorption coefficient was small ( $\mu_r = 0.105$  for Mo  $K\alpha$ ). 1766 independent reflection data, for which  $|F_o| > \sigma(|F_o|)$ , were used in the following least-squares analysis, where  $\sigma(|F_o|)$ 's are the standard deviations estimated from the counting statistics.

Wilson's (1949) ratio for 2032 Bragg intensities indicated that the structure had inversion symmetry. This is consistent with the fact that the crystal is paraelectric at 287 K. Thus, it is concluded that the space group is  $A2/a$ . The positions of the non-hydrogen atoms were first determined by a Fourier synthesis using the results for  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  (Suzuki & Makita, 1978). Positional parameters and isotropic thermal parameters were then refined by a block-diagonal

\* Tri[(<sup>2</sup>H<sub>4</sub>)ammonium] deuteriumbis(sulphate).

least-squares method for the non-hydrogen atoms. The quantity minimized was  $\sum w(|F_o| - |F_c|)^2$ . The discrepancy index  $R$  and the weighted discrepancy index  $R_w$  at this stage were 0.132 and 0.172, respectively, where  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$  and  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ . On the introduction of anisotropic thermal parameters,  $R$  and  $R_w$  reduced to 0.047 and 0.055 respectively, where 13 strong reflections that seemed to be strongly affected by extinction were omitted from the least-squares calculations. In the above refinement, unit weights were assigned to all independent Bragg reflections. H-atom positions, which were obtained from the difference Fourier synthesis, were then included and least-squares refinements performed; the following weighting scheme was adopted:  $w = 0.25$  for  $|F_o| < 10.3$ ,  $w = 1.0$  for  $10.3 \leq |F_o| \leq 51.3$  and  $w = (51.3/|F_o|)^2$  for  $|F_o| > 51.3$ . In the final stage of the refinement ( $R = 0.034$ ), the split-atom model for the D(7) atom, which was suggested by a difference Fourier synthesis, was assumed. Fig. 1 shows the difference Fourier map around D(7). It indicates that the contours have two separated peaks along the O(2)—D(7)···O(2') bond. In a trial where the position of D(7) was fixed at the centre of symmetry, the isotropic thermal parameter of D(7) converged to a very large value (about  $11 \text{ \AA}^2$ ). The least-squares refinements were continued with the above-mentioned weighting scheme until all parameter shifts become less than one tenth of their standard deviations. The final  $R$  and  $R_w$  were 0.033 and 0.039 respectively. The positional parameters and the thermal parameters thus obtained are listed in Tables 1 and 2.\*

After the least-squares refinement, difference Fourier maps were calculated using the parameters obtained. Residual peak values were less than 3 per cent of those of the electron densities of the corresponding ions.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35954 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters of the non-deuterium atoms and their e.s.d.'s

	$x$	$y$	$z$	$B_{\text{eq}} (\text{\AA}^2)$
N(1)	7500	2687 (3)	0	2.22 (7)
N(2)	6527 (1)	7252 (2)	1989 (1)	2.73 (6)
S	4613 (0)	2190 (1)	1142 (0)	1.89 (1)
O(1)	3978 (1)	272 (2)	1491 (1)	4.56 (7)
O(2)	4422 (1)	1863 (2)	142 (1)	2.78 (6)
O(3)	6056 (1)	2237 (2)	1503 (1)	2.61 (6)
O(4)	3982 (1)	4340 (2)	1289 (1)	3.13 (6)

Table 2. Fractional coordinates ( $\times 10^3$ ) and isotropic thermal parameters of the deuterium atoms and their e.s.d.'s

	$x$	$y$	$z$	$B (\text{\AA}^2)$
D(1)	304 (3)	665 (5)	25 (2)	4.5 (7)
D(2)	231 (3)	785 (4)	36 (2)	4.3 (7)
D(3)	721 (4)	717 (4)	186 (2)	4.4 (6)
D(4)	663 (3)	702 (5)	252 (3)	4.6 (7)
D(5)	610 (3)	640 (5)	178 (2)	4.1 (6)
D(6)	621 (3)	840 (5)	191 (2)	3.6 (6)
D(7)	29 (4)	76 (7)	-7 (3)	1.8 (8)

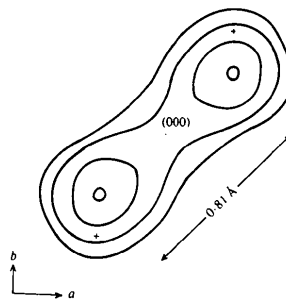


Fig. 1. Difference Fourier map projected on (001). Contours are at intervals of  $0.05 \text{ e \AA}^{-3}$ , beginning at  $0.029 \text{ e \AA}^{-3}$ . The symbol + indicates the position of D(7) converged by least-squares refinement.

Atomic scattering factors and dispersion-correction terms were taken from *International Tables for X-ray Crystallography* (1974). The computations were performed on a FACOM 230-75 computer with *The Universal Crystallographic Computation Program System* (Sakurai, 1967) and *ORTEP II* (Johnson, 1976) at the Hokkaido University Computing Centre. The full-matrix least-squares program *FLS 4* (Busing, Martin & Levy, 1962) was modified slightly for this computation.

## Discussion

The crystal structure is shown in Fig. 2. It is similar to that of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  (Suzuki & Makita, 1978).

Ammonium ions occupy two sets of non-equivalent positions: general positions,  $\text{ND}_4^+(2)$ , and special positions on the twofold axis,  $\text{ND}_4^+(1)$ . The interatomic distances and the bond angles for the deuterated ammonium ions are given in Table 3, and those for N—D···O bonds are listed in Table 4. Comparison of the results with those of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  can be summarized as follows: (1) the shape of the  $\text{ND}_4^+(2)$  ion is almost a regular tetrahedron, which is not the case in  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ ; (2) the N···O distances are not influenced by the deuteration; (3) the shape of the  $\text{ND}_4^+(1)$  ions is slightly distorted from a regular tetrahedron, as in the case of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ .

Bond distances and angles of the sulphate ion,  $\text{SO}_4^{2-}$ , are given in Table 5. They are in agreement with those of  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  within the experimental errors; a sulphate ion forms a slightly distorted tetrahedron having an electric dipole moment parallel to the S—O(2) bond. Thus, the isotope effect does not seriously affect the shape of the  $\text{SO}_4^{2-}$  ions.

Neighbouring  $\text{SO}_4^{2-}$  ions are linked by a hydrogen bond, O(2)—D(7)···O(2'), with O(2)···O(2') = 2.559 (2) Å, and O(2)—D(7) = 0.73 (4) Å, and the angle O(2)—D(7)···O(2') = 174 (5)°. The hydrogen-bond length is seriously influenced by the deuteration.

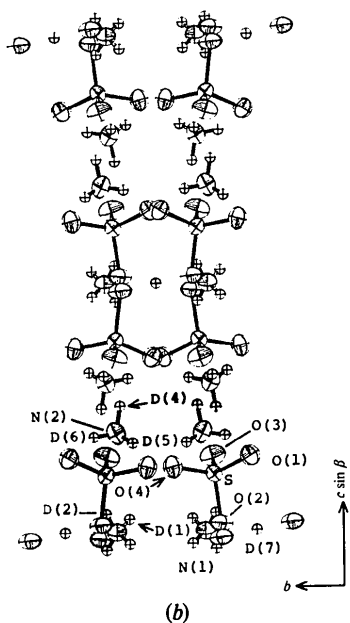
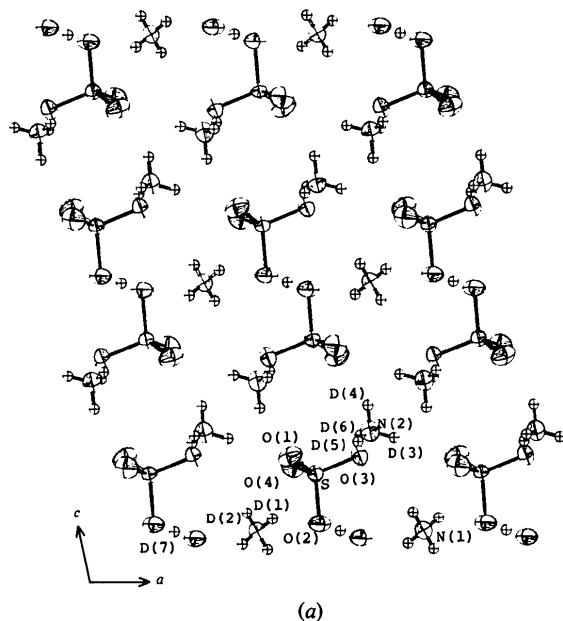


Fig. 2. Crystal structure viewed (a) along *b* and (b) along *a*.

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

$\alpha$  and  $\beta$  refer to atoms at  $(\frac{1}{2} - x, y, -z)$  and  $(-\frac{1}{2} + x, 1 - y, z)$  respectively.

N(1 $\beta$ )—D(1)	0.72 (3)	D(1)···D(1 $\alpha$ )	1.20 (4)
N(1 $\beta$ )—D(2)	0.70 (3)	D(1)···D(2 $\alpha$ )	1.17 (4)
D(1)···D(2)	1.06 (4)	D(2)···D(2 $\alpha$ )	1.25 (5)
D(1)—N(1 $\beta$ )—D(1 $\alpha$ )	114 (3)	D(1)—N(1 $\beta$ )—D(2 $\alpha$ )	111 (4)
D(1)—N(1 $\beta$ )—D(2)	97 (3)	D(2)—N(1 $\beta$ )—D(2 $\alpha$ )	127 (3)
N(2)—D(3)	0.76 (4)	N(2)—D(5)	0.70 (3)
N(2)—D(4)	0.81 (4)	N(2)—D(6)	0.74 (3)
D(3)···D(4)	1.28 (6)	D(4)···D(5)	1.21 (5)
D(3)···D(5)	1.20 (5)	D(4)···D(6)	1.25 (5)
D(3)···D(6)	1.26 (5)	D(5)···D(6)	1.19 (4)
D(3)—N(2)—D(4)	108 (3)	D(4)—N(2)—D(5)	106 (3)
D(3)—N(2)—D(5)	110 (3)	D(4)—N(2)—D(6)	106 (3)
D(3)—N(2)—D(6)	114 (3)	D(5)—N(2)—D(6)	111 (3)

Table 4. *N—D···O hydrogen-bond distances (Å) and angles (°)*

N—D···O	$\angle$ N—D···O	N···O	D···O
N(1 $\beta$ )—D(1)···O(4)	156 (3)	2.831 (2)	2.16 (3)
N(1)—D(2)···O(3)	149 (3)	2.996 (2)	2.38 (3)
N(2)—D(3)···O(1)	139 (2)	3.111 (2)	2.50 (3)
N(2)—D(3)···O(4)	160 (2)	3.059 (2)	2.33 (4)
N(2)—D(4)···O(1)	143 (3)	2.903 (2)	2.21 (4)
N(2)—D(4)···O(3)	120 (3)	3.012 (1)	2.52 (3)
N(2)—D(5)···O(4)	158 (3)	3.100 (2)	2.45 (3)
N(2)—D(5)···O(3)	141 (3)	3.046 (2)	2.48 (3)
N(2)—D(6)···O(1)	141 (3)	3.100 (2)	2.48 (3)
N(2)—D(6)···O(3)	157 (3)	3.029 (2)	2.33 (3)

Table 5. *Bond distances (Å) and bond angles (°) for the sulphate ion*

S—O(1)	1.453 (1)	S—O(3)	1.457 (1)
S—O(2)	1.524 (2)	S—O(4)	1.452 (1)
O(1)—O(2)	2.403 (2)	O(2)—O(3)	2.401 (2)
O(1)—O(3)	2.401 (2)	O(2)—O(4)	2.399 (2)
O(1)—O(4)	2.404 (2)	O(3)—O(4)	2.404 (2)
O(1)—S—O(2)	107.6 (1)	O(2)—S—O(3)	107.3 (1)
O(1)—S—O(3)	111.2 (1)	O(2)—S—O(4)	107.3 (1)
O(1)—S—O(4)	111.7 (1)	O(3)—S—O(4)	111.5 (1)

The O···O length is 0.019 (4) Å longer than that in  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ . This isotope effect is similar in the case of  $\text{KH}_2\text{PO}_4$  (Nakano, Shiozaki & Nakamura, 1973) and also agrees with the empirical law proposed by Olovsson & Jönsson (1976) and Ichikawa (1978). In comparison with the very small effects predicted for potentials of the single-minimum type, a substantial expansion (several hundredths of an Å) is suggested by the calculations of Singh & Wood (1969) for the case of symmetric and asymmetric double-minimum potentials. The difference Fourier map around H(7) for  $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$  indicates that the contours are elongated along the O(2)—H(7)···O(2') bond (Suzuki &

Makita, 1978). However, it was not clear whether the potential for H(7) was the single-minimum or double-minimum type. In the case of  $(\text{ND}_4)_3\text{D}(\text{SO}_4)_2$  the electron density distribution around D(7) has apparently separated into two peaks. This suggests that D(7) is in the symmetric double-minimum potential well. Hence, on deuteration the H-bond situation seems to change as follows: (1) from the symmetric effectively centred H bond,  $\text{O}\cdots(\text{H},\text{H})\cdots\text{O}$ , to the symmetric disordered H bond,  $\text{O}\cdots(\text{D})\cdots(\text{D})\cdots\text{O}$ ; or (2) from the symmetric disordered H bond to that with a higher potential barrier. The above suggests that the bond  $\text{O}(2)-\text{D}(7)\cdots\text{O}(2')$  is involved in the appearance of ferroelectricity.

The O–D and N–D bond lengths obtained are shorter than those from neutron diffraction experiments; this seems to be due to the bonding electrons; further analysis is required on this point.

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## Dimensional Analysis of Laves Phases: Phases with the $\text{MgCu}_2$ Structure

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### Abstract

Equations are derived for the unit-cell dimensions of phases with the  $\text{MgCu}_2$ ,  $\text{MN}_2$ , structure in terms of the coordination number 12 diameters of the component atoms. These are interpreted in terms of the interatomic contacts (4  $M-M$ , 12–6  $M-N$  and 6  $N-N$ ) that control the cell dimensions. Phases with this structure are by no means a homogeneous group and at least seven groups exhibiting different dimensional behaviour are identified; in this respect the grouping of atoms in the Periodic Table is at least as important as the diameter ratio of the component atoms. Relationships between the dimensional equations and the 'near-neighbour diagrams' of Pearson [*Acta Cryst.* (1968), **B24**, 7–9, 1415–1422] are examined.

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### 1. Introduction

#### (a) Laves phases

So much has been written about Laves phases ( $\text{MgCu}_2$ ,  $\text{MN}_2$ , structure and polytypes) that it seems inconceivable that there is anything significant still to be said. We have come to recognize them as the epitome of the 'good metallic phase' in whose structural architecture geometrical principles play a strong role. The occurrence of phases with the  $\text{MgCu}_2$  (cubic) and  $\text{MgZn}_2$  (hexagonal) structures has been discussed by many authors from the point of view of (1) the cell dimensions [mostly as  $D_M - (\sqrt{3}/4)a$  and  $D_N - (\sqrt{2}/4)a$  versus  $D_M/D_N$  for the  $\text{MgCu}_2$  structure], (2) atomic valency and (3) the Periodic arrangement of the

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