The Cu atom has an almost linear [2] coordination by O atoms [O(1)–Cu–O(3) = 178·1 (5)°]. Such a coordination is usual for monovalent Cu (*cf.* Wells, 1984). A comparable example is the structure of Cu_2O with a symmetry-restricted linear [2] coordination and Cu–O distances of 1·84 Å (Eichhorn, Spilker & Fischer, 1984).

The coordination polyhedron of the As atom is a tetrahedron, built up by four crystallographically different O atoms. As shown in Table 2, the four As–O distances are equal within two e.s.d.'s. Also the range of variation of the O–O distances [2·71 (1) to 2·80 (1) Å] within the AsO_4 tetrahedron is small.

The PbO_6 coordination polyhedra and the AsO_4 tetrahedra are connected in two dimensions, resulting in a formal [$PbAsO_4$] sheet parallel to (001). These sheets are combined *via* strong Cu–O bonds involving the monovalent Cu atom to form a network structure.

The main features of the atomic arrangements are represented in Fig. 1.

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Structure of Deuterated Triammonium Hydrogendisulfate,† $(ND_4)_3D(SO_4)_2$. Phases (III′) and (VI)

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Abstract. Phase (III′): $M_r = 260{\cdot}3$, monoclinic, $P2$, $a = 10{\cdot}087\ (2)$, $b = 5{\cdot}835\ (1)$, $c = 15{\cdot}542\ (2)$ Å, $\beta = 101{\cdot}71\ (2)°$, $V = 895{\cdot}7$ Å^3, $Z = 4$, $D_x = 1{\cdot}930$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}60$ mm^{-1}, $F(000) = 521{\cdot}84$, $T = 189 \pm 7$ K, $R = 0{\cdot}028$ for 2156 unique reflections. Phase (VI): triclinic, $P1$, $a = 10{\cdot}123\ (1)$, $b = 5{\cdot}846\ (1)$, $c = 15{\cdot}476\ (1)$ Å, $\alpha = 89{\cdot}98\ (1)$, $\beta = 101{\cdot}78\ (1)$, $\gamma = 90{\cdot}01\ (1)°$, $V = 896{\cdot}6$ Å^3, $Z = 4$, $D_x = 1{\cdot}928$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}7107$ Å, $\mu = 0{\cdot}60$ mm^{-1}, $F(000) = 521{\cdot}84$, $T = 233 \pm 7$ K, $R = 0{\cdot}035$ for 4367 unique reflections. The structures in phases (III′) and (VI) have pseudo $P2/c$ symmetry. It has been found that the ferroelectric polarization observed in phase (VI) is mainly caused by the arrangement of the distorted SO_4^{2-} ions. The polarization along $\mathbf{c}^*$ is expected to be easily reversed by slightly changing the SO_4^{2-} geometries.

Introduction. Triammonium hydrogendisulfate, $(NH_4)_3H(SO_4)_2$, at 0·1 MPa shows successive phase transitions and has six phases (I), (II), (III), (IV), (V), (VII) (Gossner, 1904; Fischer, 1914; Gesi, 1976*a*; Gesi & Ozawa, 1977; Suzuki, 1979; Suzuki, Oshino, Gesi & Makita, 1979; Gesi, 1980); phase (VII) shows ferroelectricity (Gesi, 1980). Another ferroelectric phase, (VI), exists at a hydrostatic pressure higher than about 500 MPa (Gesi, 1976*b*).

The deuterated crystal also exhibits complicated successive phase transitions; the six isostructural phases at 0·1 MPa are designated (I), (II), (III), (VI), (III′) and (VII) with descending temperature (Osaka, Makita & Gesi, 1977; Gesi, Ozawa, Osaka & Makita, 1980). The ferroelectric phase (VI) appears at 0·1 MPa, showing an isotope effect. Recently, phases (IX) and (VIII) were found at hydrostatic pressures higher than about 300 MPa and about 450 MPa (Osaka, Makita & Gesi, 1980).

Gesi (1977) suggested that the modified Mitsui (1958) model was effective for explaining the dielectric behaviour of $(NH_4)_3H(SO_4)_2$. However, the details of the phase transitions and the origin of the spontaneous polarization are not explained well. The O–H···O hydrogen bonds, which link neighbouring SO_4^{2-} ions, are influenced by deuteration; the O···O bond length is

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† Tri($^2H_4$) ammonium deuteriumbis(sulfate).

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0·02 Å longer and the D atom is in the symmetric double-minimum potential well (Suzuki & Makita, 1978; Tanaka & Shiozaki, 1981). They seemed to be closely related to the ferroelectricity (Tanaka & Shiozaki, 1981).

In this paper the crystal structures of $(ND_4)_3D(SO_4)_2$ in phases (III′) [(III)] and (VI) are reported.

Experimental. *Phase* (III′).* Crystals provided by Dr K. Gesi, ellipsoidal, 0·33 × 0·29 × 0·29 mm; Rigaku automatic four-circle diffractometer, graphite monochromator; cell dimensions from 17 reflections, $21 < \theta < 32°$; no absorption correction $(\sin\theta/\lambda)_{\max} = 0·650\ \text{Å}^{-1}$, h −13 to 13, k −7 to 0, l −20 to 20; three standard reflections, $125·09 \leq F(060) \leq 139·10$, $133·11 \leq F(0,0,16) \leq 138·45$, $204·77 \leq F(10,0,0) \leq 212·57$; 6557 reflections; Laue group $2/m$ with $R_{\text{int}} = 0·02$; unobserved reflections $F < 3\sigma(F)$; structure solved by key shift method (Ito, 1973, 1976) using 96 reflection data and Fourier syntheses, D atoms located from difference syntheses; refinement on F (2156 unique reflections), 340 parameters, D atoms with isotropic thermal parameters, anisotropic thermal parameters for other atoms; $wR = 0·040$, $S = 0·99$, $w = [\sigma^2(|F_o|) + (0·03|F_o|)^2]^{-1}$; $(\Delta/\sigma)_{\max} = 2·6$ (for non-hydrogen atoms); $(\Delta\rho)_{\max}$ and $(\Delta\rho)_{\min}$ 0·4 and $-0·4\ \text{e Å}^{-3}$; f' and f'' from *International Tables for X-ray Crystallography* (1974); *UNICS*III (Sakurai & Kobayashi, 1979), local version of *RADIEL* (Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979), *ORTEP* (Johnson, 1976), local unpublished programs.

The temperature of the sample was controlled by the cooling unit designed by Kido & Konno (1980).

Phase (VI). Crystal, hemi-spherical-like, 0·3 × 0·3 × 0·2 mm (two samples), cylinder-like 0·35 × 0·35 × 0·35 mm (two samples); graphite (or LiF) monochromator; cell dimensions from 31 reflections, $26·27 \leq \theta \leq 32·16°$; $(\sin\theta/\lambda)_{\max} = 0·836\ \text{Å}^{-1}$, h −15 to 16, k −8 to 7, l −24 to 24; three standard reflections, $F(060)$ within ±4·1%, $F(0,0,16)$ within ±3·4%, $F(10,0,0)$ within ±2·1%; 6053 unique reflections; $\sum[F(hkl) - F(h\bar{k}l)]/\sum F(hkl) = 0·035$; 673 parameters; $wR = 0·041$, $S = 1·00$, $w = [\sigma^2(|F_o|) + (0·026|F_o|)^2]^{-1}$; $(\Delta/\sigma)_{\max} = 0·8$ (for non-hydrogen atoms); $(\Delta\rho)_{\max}$ and $(\Delta\rho)_{\min}$ 0·5, $-0·4\ \text{e Å}^{-3}$.

The appearance of phases (VI) and (VII) at about 0·1 MPa was confirmed by the dielectric measurements.

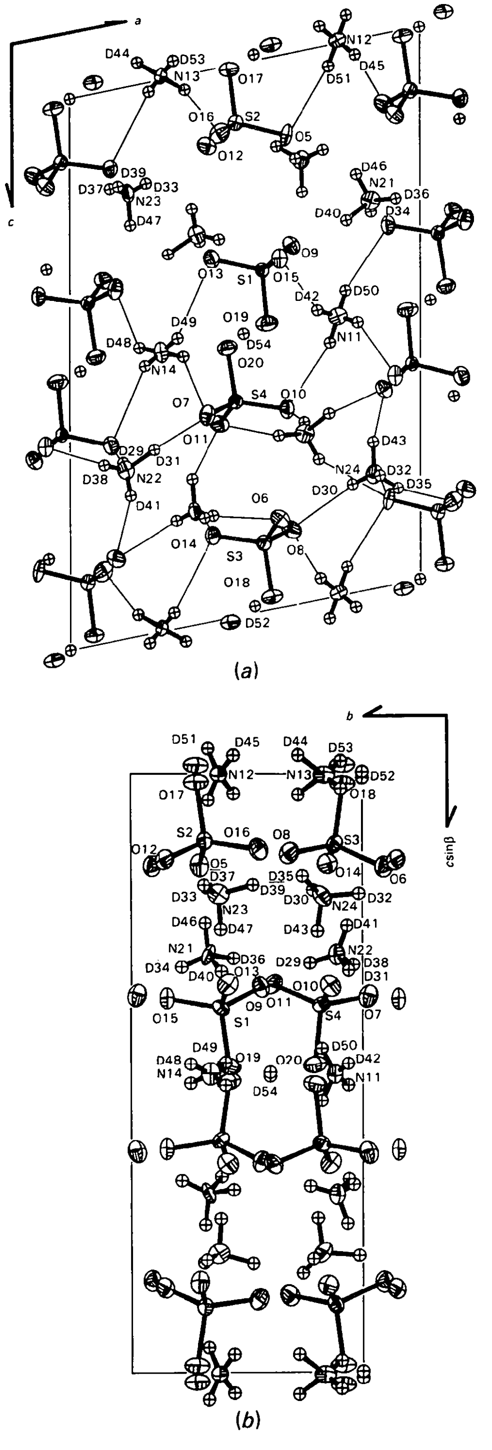

Fig. 1. Crystal structure for $(ND_4)_3D(SO_4)_2$ in phase (III′) viewed (*a*) along **b**, (*b*) along **a**.

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* Cell parameters for $(NH_4)_3H(SO_4)_2$ were published (Davis & Johnson, 1984) when we were preparing this paper. Davis & Johnson claimed that the true unit cell is triclinic, $P1$ or $P\bar{1}$ ($a = 5·87$, $b = 10·17$, $c = 8·27$ Å, $\alpha = 101·1$, $\beta = 111·1$, $\gamma = 89·9°$, $V = 450·7\ \text{Å}^3$, $Z = 2$); they said nothing about the phase transition. Their proposal may be correct; however, we used the monoclinic unit cell for the following reasons: (1) the crystal structure at room temperature was previously determined successfully by adopting the monoclinic $A2/a$ unit cell (Suzuki & Makita, 1978); (2) we obtained a reasonably good internal agreement factor, 0·02, between $F(hkl)$ and $F(h\bar{k}l)$ for phase (III′). At least the monoclinic unit cell must be a good approximation.

Table 1. *Atomic parameters in phase* (III′) *for non-deuterium atoms*

Positional parameters are multiplied by 10^4. Thermal parameters are given as the equivalent isotropic temperature factors (Å^2): $B_{eq} = \frac{4}{3}(B_{11}/a^{*2} + B_{22}/b^{*2} + B_{33}/c^{*2})$.

	x	y	z	B_{eq}
S(1)	2872 (1)	2836†	3890 (1)	1·3
S(2)	2121 (1)	2154 (1)	1110 (1)	1·4
S(3)	2900 (1)	−2230 (3)	−1159 (1)	1·4
S(4)	2109 (1)	−2820 (3)	−3834 (1)	1·4
O(5)	3560 (2)	1926 (7)	1517 (2)	1·9
O(6)	3363 (3)	−119 (7)	−1535 (2)	2·0
O(7)	1303 (3)	−785 (6)	−3688 (2)	2·1
O(8)	3673 (3)	−4196 (7)	−1307 (2)	2·1
O(9)	3691 (3)	4568 (7)	3534 (2)	1·8
O(10)	3558 (2)	−2419 (7)	−3514 (2)	1·9
O(11)	1646 (3)	−4900 (7)	−3488 (2)	1·9
O(12)	1301 (3)	427 (7)	1420 (2)	2·0
O(13)	1428 (2)	3139 (8)	3495 (2)	2·0
O(14)	1448 (2)	−2535 (7)	−1475 (2)	1·9
O(15)	3359 (3)	521 (6)	3737 (2)	1·7
O(16)	1675 (3)	4476 (7)	1242 (2)	2·3
O(17)	1939 (3)	1797 (8)	137 (2)	2·3
O(18)	3126 (3)	−1879 (8)	−159 (2)	2·5
O(19)	2996 (3)	3185 (7)	4870 (2)	2·4
O(20)	1872 (3)	−3088 (7)	−4838 (2)	2·2
N(21)	4057 (4)	2304 (7)	−3005 (3)	1·8
N(22)	1007 (4)	−2150 (9)	2991 (3)	1·7
N(23)	933 (3)	−7252 (9)	−1990 (3)	1·8
N(24)	3978 (4)	7232 (9)	2017 (3)	1·9
N(11)	5000	−2239 (11)	5000	1·7
N(12)	5000	2770 (11)	0	1·5
N(13)	0	7339 (12)	0	1·6
N(14)	0	2394 (12)	5000	2·0

† Parameter fixed to define the origin.

Table 2. *Bond distances* (Å) *and bond angles* (°) *for* SO_4^{2-} *ions in phase* (III′)

S(1)—O(9)	1·482 (4)	S(1)—O(13)	1·472 (2)
S(1)—O(15)	1·473 (4)	S(1)—O(19)	1·517 (4)
O(9)—O(15)	2·415 (5)	O(9)—O(13)	2·419 (4)
O(9)—O(19)	2·459 (5)	O(13)—O(19)	2·387 (4)
O(13)—O(15)	2·444 (5)	O(15)—O(19)	2·432 (5)
O(9)—S(1)—O(13)	110·0 (2)	O(9)—S(1)—O(15)	109·6 (2)
O(9)—S(1)—O(19)	110·2 (2)	O(13)—S(1)—O(15)	112·2 (2)
O(13)—S(1)—O(19)	106·0 (2)	O(15)—S(1)—O(19)	108·9 (2)
S(2)—O(5)	1·467 (2)	S(2)—O(12)	1·447 (4)
S(2)—O(16)	1·455 (4)	S(2)—O(17)	1·500 (4)
O(5)—O(12)	2·417 (4)	O(5)—O(16)	2·384 (5)
O(5)—O(17)	2·420 (4)	O(12)—O(17)	2·356 (5)
O(12)—O(16)	2·417 (6)	O(16)—O(17)	2·377 (5)
O(5)—S(2)—O(16)	109·3 (2)	O(5)—S(2)—O(12)	112·1 (2)
O(5)—S(2)—O(17)	109·3 (2)	O(12)—S(2)—O(16)	112·8 (2)
O(12)—S(2)—O(17)	106·1 (2)	O(16)—S(2)—O(17)	107·1 (2)
S(3)—O(6)	1·479 (4)	S(3)—O(8)	1·432 (4)
S(3)—O(14)	1·458 (2)	S(3)—O(18)	1·538 (4)
O(6)—O(8)	2·416 (6)	O(6)—O(14)	2·408 (5)
O(6)—O(18)	2·428 (5)	O(8)—O(14)	2·410 (4)
O(8)—O(18)	2·391 (5)	O(14)—O(18)	2·406 (4)
O(6)—S(3)—O(8)	112·2 (2)	O(6)—S(3)—O(14)	110·2 (2)
O(6)—S(3)—O(18)	107·1 (2)	O(8)—S(3)—O(14)	113·0 (2)
O(8)—S(3)—O(18)	107·2 (2)	O(14)—S(3)—O(18)	106·8 (2)
S(4)—O(7)	1·482 (4)	S(4)—O(10)	1·464 (2)
S(4)—O(11)	1·443 (4)	S(4)—O(20)	1·538 (4)
O(7)—O(10)	2·430 (4)	O(7)—O(11)	2·437 (5)
O(7)—O(20)	2·397 (5)	O(10)—O(20)	2·420 (4)
O(10)—O(11)	2·418 (5)	O(11)—O(20)	2·401 (5)
O(7)—S(4)—O(10)	111·2 (2)	O(7)—S(4)—O(11)	112·8 (2)
O(7)—S(4)—O(20)	105·1 (2)	O(10)—S(4)—O(11)	112·6 (2)
O(10)—S(4)—O(20)	107·5 (2)	O(11)—S(4)—O(20)	107·3 (2)

Discussion. *Phase* (III′). The crystal structure of $(ND_4)_3D(SO_4)_2$ in phase (III′) at 189 ±7 K and 0·1 MPa is shown in Fig. 1 and Table 1.†

Strong correlations were found among the parameters connected with pseudo-inversion symmetry which appears in phase (II). The correlation-matrix elements were larger than 0·8 in the final stage of the refinement, which may cause the high Δ/σ ratio. The pseudo-inversion symmetry connects two SO_4^{2-} ions; for example, S(1)—O(9)—O(13)—O(15)—O(19) and S(2)—O(12)—O(5)—O(16)—O(17). Pseudo glide planes also exist at $y = \frac{1}{4}$ and $y = \frac{3}{4}$.

Table 2 gives bond distances and bond angles for the SO_4^{2-} ions. Each SO_4^{2-} ion is distorted and has some electric dipole moment. S(1)—O(19) and S(2)—O(17) bond distances are longer by 0·043 (5) Å than the others because the O(17) and O(19) atoms are bonded to the D atoms. The electric moments caused by the distortion of the SO_4^{2-} ions are arranged in an antiparallel way in the (010) plane, so no polarization arises perpendicular to **b**. This is consistent with the sublattice model suggested by Gesi (1977) for explaining the temperature–pressure dependence of the dielectric constants of $(NH_4)_3H(SO_4)_2$.

Phase (VI). The crystal structure in phase (VI) at 233 ±7 K and 0·1 MPa is shown in Fig. 2 and Table 3.†

The structure in phase (VI) is also $P2$-like as expected from the pseudo $2/m$ Laue symmetry. Pseudo n-glide symmetries exist at $y = \frac{1}{4}$ and $y = \frac{3}{4}$. Pseudo inversion symmetries are also found; for example, two SO_4^{2-} ions, S(5)—O(13)—O(26)—O(28)—O(29) and S(4)—O(16)—O(30)—O(14)—O(23), are closely interrelated by a pseudo inversion symmetry. The correlation-matrix elements between S(5) and S(4), O(13) and O(16) *etc.* were larger than 0·8. The glide symmetries in phase (II) remain in phase (VI) as the pseudo glide symmetries.

The bond distances and bond angles for SO_4^{2-} ions are listed in Table 4. Comparisons of bond distances S(5)—O(13) with S(1)—O(9), S(3)—O(18) with S(6)—O(12), S(8)—O(35) with S(4)—O(16) and S(7)—O(19) with S(2)—O(11) show the former to be longer than the latter by 0·022 (5) ~ 0·060 (5) Å. The electric dipole moments caused by the distorted SO_4^{2-} ions seem not to be entirely cancelled out in the (010) plane. The calculated magnitude of the c^* component, 0·3 $\mu C\,cm^{-2}$, is nearly the same as that observed, 1 $\mu C\,cm^{-2}$ (Osaka, Makita & Gesi, 1977); $\mathbf{P}(e) = \sum 1{\cdot}5e \times (\mathbf{r}_S - \mathbf{r}_O)/V$, where V, $\mathbf{r}_S$ and $\mathbf{r}_O$ represent the volume

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† Lists of structure factors, anisotropic thermal parameters, D-atom parameters and bond distances and bond angles for N—D···O hydrogen bonds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42801 (49 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and atomic position vectors of S and O, and the charges on S and O atoms are assumed to be +6·0 e and −1·5 e respectively. In the reversed-polarization state the roles of the SO_4^{2-} ions connected with the pseudo twofold axis are interchanged. It seems to be easy to reverse the polarization along **c***, since the structure has pseudo twofold symmetry. This is consistent with the fact that the ferroelectric hysteresis is observed along **c*** (Osaka, Makita & Gesi, 1977). It is found that the ferroelectric polarization of $(ND_4)_3D(SO_4)_2$ is mainly caused by the arrangement of the distorted SO_4^{2-} ions.

In phases (III′) and (VI) almost all N—D···O bonds are normal (Table 5). However, in phase (II) all N—D···O bonds of $ND_4(2)^+$ in general positions seem to be bifurcated (Tanaka & Shiozaki, 1981). The N—D···O bond networks of ND_4^+ ions on pseudo twofold axes are remarkably different, accompanying the (III′)–(VI) phase transition.

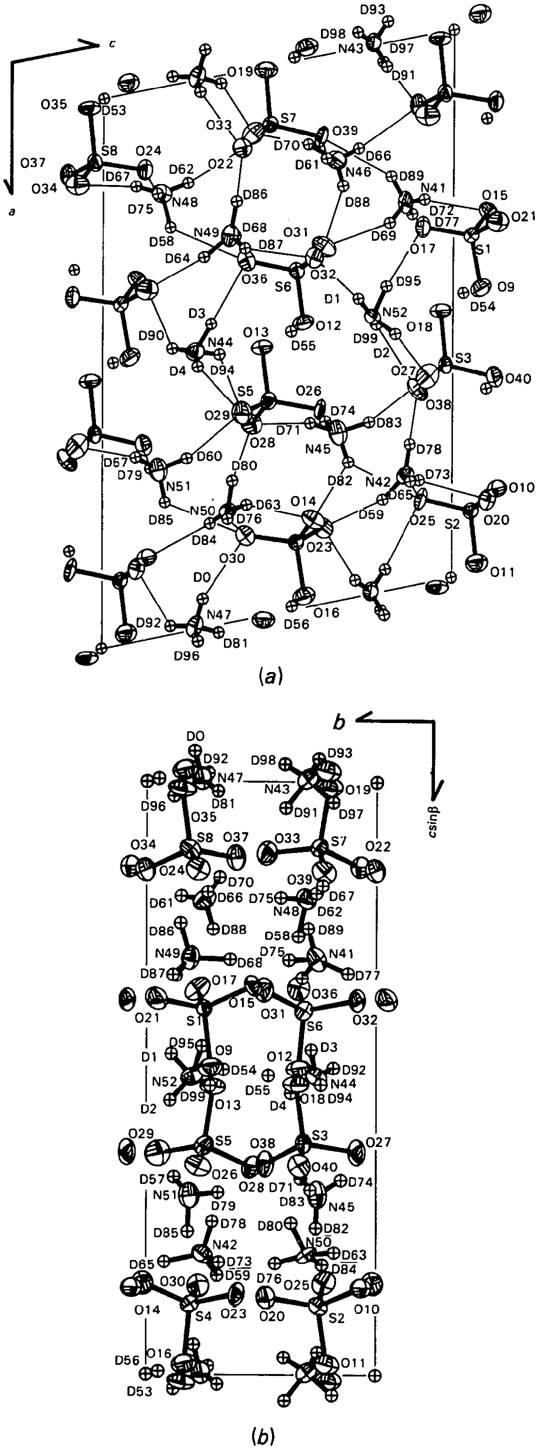

Fig. 2. Crystal structure for $(ND_4)_3D(SO_4)_2$ in phase (VI) viewed (*a*) along **b**, (*b*) along **a**.

Table 3. *Atomic parameters in phase* (VI) *for non-deuterium atoms*

Positional parameters are multiplied by 10^4. Thermal parameters are given as the equivalent isotropic temperature factors (Å^2): $B_{eq} = \frac{4}{3}(B_{11}/a^{*2} + B_{22}/b^{*2} + B_{33}/c^{*2})$.

	x	y	z	B_{eq}
S(1)	367†	7189†	3862†	1·4
S(2)	381 (2)	12181 (3)	−1105 (1)	1·7
S(3)	−377 (2)	2831 (3)	6136 (1)	1·5
S(4)	5385 (2)	7772 (3)	−1144 (1)	1·5
S(5)	4597 (2)	7178 (3)	6173 (1)	1·8
S(6)	−4633 (2)	2830 (3)	3902 (1)	1·7
S(7)	4608 (2)	12172 (3)	1141 (1)	1·5
S(8)	9578 (1)	7789 (2)	1178 (1)	1·9
O(9)	639 (5)	6909 (10)	4857 (3)	2·6
O(10)	1146 (5)	10320 (8)	−1419 (3)	2·2
O(11)	559 (6)	11817 (10)	−131 (3)	2·9
O(12)	−4440 (5)	3067 (9)	4870 (3)	2·5
O(13)	4398 (5)	6794 (9)	5171 (3)	2·6
O(14)	5876 (6)	9827 (9)	−1496 (3)	2·7
O(15)	845 (5)	5044 (7)	3485 (3)	1·9
O(16)	5625 (6)	8009 (10)	−141 (3)	2·8
O(17)	−1054 (5)	7470 (9)	3540 (3)	2·5
O(18)	−525 (6)	3166 (10)	5136 (3)	2·7
O(19)	4474 (6)	11733 (10)	137 (3)	2·9
O(20)	852 (5)	14453 (8)	−1251 (3)	2·2
O(21)	1118 (6)	9245 (9)	3701 (3)	2·8
O(22)	3809 (5)	10394 (8)	1465 (3)	2·2
O(23)	6155 (5)	5734 (7)	−1307 (3)	2·1
O(24)	11050 (5)	7453 (9)	1509 (3)	2·3
O(25)	−1079 (4)	11922 (9)	−1498 (3)	2·3
O(26)	6050 (4)	7429 (9)	6521 (3)	2·3
O(27)	−898 (6)	533 (8)	6279 (4)	3·0
O(28)	4110 (5)	5113 (8)	6541 (3)	2·4
O(29)	3838 (6)	9178 (10)	6301 (4)	3·1
O(30)	3948 (5)	7410 (9)	−1450 (3)	2·4
O(31)	−3857 (6)	4575 (8)	3555 (3)	2·7
O(32)	−4131 (5)	521 (7)	3721 (3)	2·1
O(33)	4127 (6)	14443 (9)	1242 (3)	2·9
O(34)	9069 (6)	9743 (8)	1517 (4)	2·9
O(35)	9416 (6)	8140 (10)	168 (3)	2·8
O(36)	−6057 (5)	3057 (9)	3530 (3)	2·4
O(37)	8809 (5)	5796 (8)	1315 (4)	2·3
O(38)	−1186 (5)	4506 (8)	6489 (3)	2·5
O(39)	6058 (4)	11966 (9)	1550 (3)	2·3
O(40)	1046 (5)	3014 (8)	6522 (3)	2·4
N(41)	−1564 (5)	2277 (10)	3035 (4)	2·2
N(42)	−1527 (6)	7236 (10)	−11982 (4)	2·0
N(43)	−2495 (6)	12671 (10)	6 (4)	1·9
N(44)	2503 (7)	2304 (11)	5002 (4)	2·2
N(45)	−3444 (7)	12234 (11)	−2995 (5)	2·6
N(46)	6475 (7)	7163 (12)	2023 (4)	2·4
N(47)	2522 (6)	7288 (10)	7 (4)	2·1
N(48)	11536 (7)	12736 (11)	2009 (4)	2·3
N(49)	−6519 (6)	17768 (10)	−6981 (4)	2·1
N(50)	3448 (5)	12693 (10)	−1968 (3)	1·8
N(51)	1470 (7)	7819 (11)	7025 (5)	2·6
N(52)	−2479 (6)	7712 (11)	5009 (4)	1·9

† Parameters fixed to define the origin.

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Table 4. *Bond distances* (Å) *and bond angles* (°) *for* SO_4^{2-} *ions in phase* (VI)

S(1)—O(9)	1·517 (5)	S(1)—O(15)	1·504 (5)
S(1)—O(17)	1·432 (5)	S(1)—O(21)	1·470 (6)
O(9)—O(15)	2·434 (7)	O(9)—O(17)	2·403 (6)
O(9)—O(21)	2·378 (8)	O(15)—O(17)	2·405 (7)
O(15)—O(21)	2·486 (7)	O(17)—O(21)	2·398 (8)
O(9)—S(1)—O(15)	107·3 (3)	O(9)—S(1)—O(17)	109·1 (3)
O(9)—S(1)—O(21)	105·5 (3)	O(15)—S(1)—O(17)	109·9 (3)
O(15)—S(1)—O(21)	113·4 (3)	O(17)—S(1)—O(21)	111·4 (3)
S(2)—O(11)	1·496 (5)	S(2)—O(20)	1·444 (5)
S(2)—O(25)	1·487 (4)	S(2)—O(10)	1·474 (5)
O(10)—O(11)	2·362 (7)	O(10)—O(20)	2·455 (7)
O(10)—O(25)	2·419 (7)	O(11)—O(20)	2·382 (7)
O(11)—O(25)	2·408 (6)	O(20)—O(25)	2·419 (7)
O(10)—S(2)—O(11)	105·3 (3)	O(10)—S(2)—O(20)	114·5 (3)
O(10)—S(2)—O(25)	109·6 (3)	O(11)—S(2)—O(20)	108·2 (3)
O(11)—S(2)—O(25)	107·6 (3)	O(20)—S(2)—O(25)	111·2 (3)
S(3)—O(18)	1·537 (5)	S(3)—O(27)	1·476 (5)
S(3)—O(38)	1·453 (5)	S(3)—O(40)	1·446 (5)
O(18)—O(27)	2·431 (8)	O(18)—O(38)	2·453 (7)
O(18)—O(40)	2·397 (6)	O(40)—O(38)	2·413 (7)
O(40)—O(27)	2·411 (7)	O(27)—O(38)	2·372 (7)
O(18)—S(3)—O(27)	107·6 (3)	O(18)—S(3)—O(38)	110·3 (3)
O(18)—S(3)—O(40)	106·9 (3)	O(27)—S(3)—O(38)	108·1 (3)
O(27)—S(3)—O(40)	111·2 (3)	O(38)—S(3)—O(40)	112·7 (3)
S(4)—O(14)	1·448 (6)	S(4)—O(16)	1·528 (5)
S(4)—O(23)	1·474 (5)	S(4)—O(30)	1·451 (5)
O(14)—O(16)	2·410 (7)	O(14)—O(23)	2·420 (7)
O(14)—O(30)	2·422 (8)	O(16)—O(23)	2·390 (7)
O(16)—O(30)	2·388 (6)	O(30)—O(23)	2·408 (7)
O(14)—S(4)—O(16)	108·1 (3)	O(14)—S(4)—O(23)	111·9 (3)
O(14)—S(4)—O(30)	113·4 (3)	O(16)—S(4)—O(23)	105·5 (3)
O(16)—S(4)—O(30)	106·6 (3)	O(23)—S(4)—O(30)	110·9 (3)
S(5)—O(13)	1·539 (5)	S(5)—O(26)	1·467 (4)
S(5)—O(28)	1·462 (5)	S(5)—O(29)	1·435 (6)
O(13)—O(26)	2·424 (6)	O(13)—O(28)	2·408 (7)
O(13)—O(29)	2·394 (8)	O(26)—O(28)	2·391 (7)
O(26)—O(29)	2·422 (7)	O(28)—O(29)	2·412 (8)
O(13)—S(5)—O(26)	107·4 (3)	O(13)—S(5)—O(28)	106·7 (3)
O(13)—S(5)—O(29)	107·1 (3)	O(26)—S(5)—O(28)	109·4 (3)
O(26)—S(5)—O(29)	113·1 (3)	O(28)—S(5)—O(29)	112·7 (4)
S(6)—O(12)	1·477 (5)	S(6)—O(31)	1·455 (6)
S(6)—O(32)	1·489 (5)	S(6)—O(36)	1·445 (5)
O(12)—O(31)	2·399 (7)	O(12)—O(32)	2·388 (7)
O(12)—O(36)	2·365 (6)	O(31)—O(32)	2·406 (6)
O(31)—O(36)	2·390 (8)	O(32)—O(36)	2·419 (7)
O(12)—S(6)—O(31)	109·8 (3)	O(12)—S(6)—O(32)	107·3 (3)
O(12)—S(6)—O(36)	108·1 (3)	O(31)—S(6)—O(32)	109·6 (3)
O(31)—S(6)—O(36)	111·0 (3)	O(32)—S(6)—O(36)	111·1 (3)
S(7)—O(19)	1·553 (5)	S(7)—O(22)	1·467 (5)
S(7)—O(39)	1·480 (4)	S(7)—O(33)	1·434 (6)
O(19)—O(22)	2·419 (7)	O(19)—O(33)	2·409 (8)
O(19)—O(39)	2·437 (6)	O(22)—O(33)	2·423 (7)
O(22)—O(39)	2·434 (7)	O(33)—O(39)	2·401 (7)
O(19)—S(7)—O(22)	106·4 (3)	O(19)—S(7)—O(33)	107·5 (3)
O(19)—S(7)—O(39)	106·9 (3)	O(22)—S(7)—O(33)	113·3 (3)
O(22)—S(7)—O(39)	111·4 (3)	O(33)—S(7)—O(39)	111·0 (3)
S(8)—O(24)	1·487 (5)	S(8)—O(34)	1·399 (6)
S(8)—O(35)	1·552 (5)	S(8)—O(37)	1·441 (5)
O(24)—O(34)	2·414 (8)	O(24)—O(35)	2·409 (6)
O(24)—O(37)	2·428 (7)	O(34)—O(35)	2·379 (8)
O(34)—O(37)	2·336 (7)	O(35)—O(37)	2·419 (8)
O(24)—S(8)—O(34)	113·5 (3)	O(24)—S(8)—O(35)	104·9 (3)
O(24)—S(8)—O(37)	112·1 (3)	O(34)—S(8)—O(35)	107·4 (3)
O(34)—S(8)—O(37)	110·7 (4)	O(35)—S(8)—O(37)	107·8 (3)

Table 5. *Interatomic distances* (Å) *and angles* (°) *for* O—D···O *bonds*

(*a*) Phase (III′)

O(19)—O(20)	2·536 (6)	O(17)—O(18)	2·544 (6)
O(19)—D(54)	1·27 (5)	O(18)—D(52)	0·74 (5)
O(20)···D(54)	1·28 (5)	O(17)···D(52)	1·84 (5)
O(19)—D(54)···O(20)	169 (4)	O(18)—D(52)···O(17)	159 (5)

(*b*) Phase (VI)

O(9)—O(18)	2·563 (8)	O(12)—O(13)	2·564 (8)
O(9)—D(54)	0·62 (8)	O(12)—D(55)	0·87 (7)
O(18)···D(54)	2·04 (8)	O(13)···D(55)	1·70 (7)
O(9)—D(54)···O(18)	145 (9)	O(12)—D(55)···O(13)	174 (6)
O(11)—O(35)	2·528 (8)	O(16)—O(19)	2·547 (8)
O(35)—D(53)	1·02 (6)	O(16)—D(56)	0·81 (7)
O(11)···D(53)	1·51 (6)	O(19)···D(56)	1·74 (7)
O(35)—D(53)···O(11)	174 (6)	O(16)—D(56)···O(19)	171 (6)

The computations were performed using the HITAC M-200H computer system at Hokkaido University Computing Center, and the FACOM M-160F computer at the Institute for Solid State Physics, The University of Tokyo.

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