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

$$B_{eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ca	0.21979 (7)	1/4	0.1149 (2)	0.70 (1)
V(1)	0.37954 (5)	3/4	0.1489 (1)	0.321 (9)
V(2)	0	1/2	0	0.404 (9)
P(1)	0.18974 (8)	3/4	0.1134 (2)	0.46 (2)
P(2)	0.43270 (8)	1/4	0.1366 (2)	0.36 (2)
O(1)	0.3662 (2)	0.4378 (4)	0.1278 (4)	0.65 (3)
O(2)	0.2632 (3)	3/4	−0.0424 (6)	0.77 (6)
O(3)	0.4929 (3)	3/4	0.0081 (7)	1.23 (6)
O(4)	0.2514 (3)	3/4	0.2875 (5)	0.59 (5)
O(5)	0.4442 (2)	3/4	0.3759 (5)	0.59 (5)
O(6)	−0.0186 (3)	1/4	0.1750 (5)	0.77 (6)
O(7)	0.1283 (2)	0.5533 (4)	0.1084 (4)	0.79 (4)

Table 2. *Selected geometric parameters* (Å, °)

Ca—O(7)	2.342 (3)	O(5^{ii})· · ·O(6)	2.430 (5)
Ca—O(7^{i})	2.342 (3)	O(5^{ii})· · ·O(6^{vi})	3.276 (1)
Ca—O(1)	2.405 (3)	O(5^{ii})· · ·O(7^{vi})	2.905 (4)
Ca—O(1^{i})	2.405 (3)	O(5^{ii})· · ·O(7)	2.784 (4)
Ca—O(4^{ii})	2.430 (4)	V(2)—O(6)	2.071 (3)
Ca—O(2^{iii})	2.519 (5)	O(6)· · ·O(6^{vi})	4.142 (7)
Ca—O(5^{ii})	2.911 (4)	O(6)· · ·O(7^{vi})	2.884 (5)
V(1)—O(1)	2.020 (3)	O(6)· · ·O(7)	2.895 (4)
O(1)· · ·O(1^{iv})	4.011 (7)	V(2)—O(6^{vi})	2.071 (3)
O(1)· · ·O(2)	2.777 (4)	O(6^{vi})· · ·O(7^{vi})	2.895 (4)
O(1)· · ·O(3)	2.832 (4)	O(6^{vi})· · ·O(7)	2.884 (5)
O(1)· · ·O(4)	2.836 (4)	V(2)—O(7^{vi})	2.015 (3)
O(1)· · ·O(5)	2.922 (4)	O(7^{vi})· · ·O(7)	4.031 (5)
V(1)—O(1^{iv})	2.020 (3)	V(2)—O(7)	2.015 (3)
O(1^{iv})· · ·O(2)	2.777 (4)	P(1)—O(2)	1.545 (4)
O(1^{iv})· · ·O(3)	2.832 (4)	O(2)· · ·O(4)	2.420 (6)
O(1^{iv})· · ·O(4)	2.836 (4)	O(2)· · ·O(7)	2.545 (4)
O(1^{iv})· · ·O(5)	2.922 (4)	O(2)· · ·O(7^{iv})	2.545 (4)
V(1)—O(2)	2.164 (4)	P(1)—O(4)	1.545 (4)
O(2)· · ·O(3)	3.281 (6)	O(4)· · ·O(7)	2.523 (4)
O(2)· · ·O(4)	2.420 (6)	O(4)· · ·O(7^{iv})	2.523 (4)
O(2)· · ·O(5)	3.995 (7)	P(1)—O(7)	1.536 (3)
V(1)—O(3)	1.911 (5)	O(7)· · ·O(7^{iv})	2.527 (6)
O(3)· · ·O(4)	3.992 (7)	P(1)—O(7^{iv})	1.536 (3)
O(3)· · ·O(5)	2.779 (7)	P(2)—O(1)	1.533 (3)
V(1)—O(4)	2.083 (4)	O(1)· · ·O(1^{i})	2.413 (5)
O(4)· · ·O(5)	2.811 (5)	O(1)· · ·O(3^{vii})	2.537 (5)
V(1)—O(5)	1.898 (4)	O(1)· · ·O(6^{viii})	2.491 (4)
V(2)—O(5^{v})	2.008 (2)	P(2)—O(1^{i})	1.533 (3)
O(5^{v})· · ·O(5^{ii})	4.016 (5)	O(1^{i})· · ·O(3^{vii})	2.537 (5)
O(5^{v})· · ·O(6)	3.276 (1)	O(1^{i})· · ·O(6^{viii})	2.491 (4)
O(5^{v})· · ·O(6^{vi})	2.430 (5)	P(2)—O(3^{vii})	1.495 (5)
O(5^{v})· · ·O(7^{vi})	2.784 (4)	O(3^{vii})· · ·O(6^{viii})	2.464 (7)
O(5^{v})· · ·O(7)	2.905 (4)	P(2)—O(6^{viii})	1.542 (4)
V(2)—O(5^{ii})	2.008 (2)		

O(1^{iv})—V(1)—O(1)	166.2 (2)	O(7^{vi})—V(2)—O(5^{v})	87.6 (1)
O(2)—V(1)—O(1)	83.1 (1)	O(7^{vi})—V(2)—O(5^{ii})	92.4 (1)
O(2)—V(1)—O(1^{iv})	83.1 (1)	O(7^{vi})—V(2)—O(6)	89.8 (1)
O(3)—V(1)—O(1)	92.2 (1)	O(7^{vi})—V(2)—O(6^{vi})	90.2 (1)
O(3)—V(1)—O(1^{iv})	92.2 (1)	O(7)—V(2)—O(5^{v})	92.4 (1)
O(3)—V(1)—O(2)	107.1 (2)	O(7)—V(2)—O(5^{ii})	87.6 (1)
O(4)—V(1)—O(1)	87.5 (1)	O(7)—V(2)—O(6)	90.2 (1)
O(4)—V(1)—O(1^{iv})	87.5 (1)	O(7)—V(2)—O(6^{vi})	89.8 (1)
O(4)—V(1)—O(2)	69.4 (2)	O(7)—V(2)—O(7^{vi})	180.0
O(4)—V(1)—O(3)	176.5 (2)	O(4)—P(1)—O(2)	103.1 (2)
O(5)—V(1)—O(1)	96.4 (1)	O(7)—P(1)—O(2)	111.5 (1)
O(5)—V(1)—O(1^{iv})	96.4 (1)	O(7)—P(1)—O(4)	109.9 (2)
O(5)—V(1)—O(2)	159.2 (2)	O(7^{iv})—P(1)—O(2)	111.5 (1)
O(5)—V(1)—O(3)	93.7 (2)	O(7^{iv})—P(1)—O(4)	109.9 (2)
O(5)—V(1)—O(4)	89.8 (2)	O(7^{iv})—P(1)—O(7)	110.8 (2)
O(5^{ii})—V(2)—O(5^{v})	180.0	O(1^{i})—P(2)—O(1)	103.9 (2)
O(6)—V(2)—O(5^{v})	106.9 (1)	O(3^{vii})—P(2)—O(1)	113.9 (2)
O(6)—V(2)—O(5^{ii})	73.1 (1)	O(3^{vii})—P(2)—O(1^{i})	113.9 (2)
O(6^{vi})—V(2)—O(5^{v})	73.1 (1)	O(6^{viii})—P(2)—O(1)	108.3 (2)
O(6^{vi})—V(2)—O(5^{ii})	106.9 (1)	O(6^{viii})—P(2)—O(1^{i})	108.3 (2)
O(6^{vi})—V(2)—O(6)	180.0	O(6^{viii})—P(2)—O(3^{vii})	108.5 (3)

Symmetry codes: (i) $x, \frac{1}{2} - y, z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, z - \frac{1}{2}$; (iii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} + z$; (iv) $x, \frac{3}{2} - y, z$; (v) $x - \frac{1}{2}, \frac{3}{2} - y, \frac{1}{2} - z$; (vi) $-x, 1 - y, -z$; (vii) $1 - x, 1 - y, -z$; (viii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$.

Data were collected with ω–$4/3\theta$ scans of width $(1 + 0.35\tan\theta)°$ and with and a slit aperture of $(1 + \tan\theta)$ mm. The refinements in $Pn2_1a$ (other setting of $Pna2_1$) failed. Calculations were performed using a MicroVAXII computer with the *SDP* system (B. A. Frenz & Associates, Inc., 1982).

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: DU1094). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hydroxylammonium Sulfate

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Abstract

The structure of (NH$_3$OH)$_2$SO$_4$ consists of sulfate and hydroxylammonium ions, which are connected by O—H· · ·O and N—H· · ·O hydrogen bonds. The bond distances fall within normal limits. All O atoms of the sulfate group are involved in two hydrogen bonds.

Comment

The X-ray structure determination of the title compound was undertaken as part of a project concerning the structural studies of double-sulfate compounds of transition elements. The hydroxylammonium group, NH_3OH^+, can be included in the double sulfates instead of some monovalent metals. So far the crystal structures of compounds containing hydroxylammonium groups have not been widely examined. In our previous work, the crystal structure of hydroxylammonium scandium sulfate sesquihydrate was presented (Mirčeva & Golič, 1995).

Hydroxylammonium sulfate was used as the starting reagent for the preparation of the double sulfates and as a result of this we studied its structure. Our particular interest concerned the hydrogen bonding of this compound. The space group and cell parameters were already known (Vilminot, Cot, Avinens & Maurin, 1971). It was found that hydroxlammonium sulfate is isomorphous with the corresponding tetrafluoroberyllate but detailed structural data were not provided.

The structure consists of hydroxylammonium and sulfate ions which are hydrogen bonded. All O atoms are involved in hydrogen bonding; each O atom of the sulfate group forms two hydrogen bonds (Table 3). The geometry of the sulfate ion is as expected (Tanaka & Tsujikawa, 1982; Ishakova, Gasanov, Bondar, Kleinman, Novik & Trunov, 1988; Blackburn & Gerkin, 1994). This ion is not subject to symmetry constraints and forms a slightly irregular tetrahedron. The observed S—O distances and O—S—O angles range from 1.472 to 1.484 Å and from 108.6 to 110.5°, respectively.

The bond distances in the hydroxylammonium groups compare well with the values found in the structures of the corresponding lithium hydroxylammonium sulfate (Vilminot, Anderson & Brown, 1973), aluminium double sulfate (Abden, Will & Weiss, 1981), hydroxylammonium perchlorate (Dickens, 1969), hydroxylammonium chloride (Shi, Wang & Mak, 1987) and hydroxylammonium cyclohexaphosphate (Durif & Averbuch-Pouchot, 1990) as well as in the structure of

the previously mentioned Sc double sulfate. The N—O distances observed in both NH_3OH^+ groups are the same [1.410(1) Å]. The N—H distances in the NH_3 groups vary from 0.81 to 0.89 Å and the H—N—H angles from 107 to 112°.

Fig. 1 gives a stereoscopic view of the unit cell together with the atom-labelling scheme used. Hydrogen bonds are indicated by dotted lines.

Experimental

Well shaped crystals were obtained by recrystallization of $(NH_3OH)_2SO_4$ (commercial product) from the heated, and then slowly cooled, water solution.

Crystal data

$(NH_3OH)_2SO_4$	Mo $K\alpha$ radiation
$M_r = 164.14$	$\lambda = 0.71069$ Å
Monoclinic	Cell parameters from 45
$P2_1/c$	reflections
$a = 7.932(2)$ Å	$\theta = 10–13°$
$b = 7.321(2)$ Å	$\mu = 0.510$ mm^{-1}
$c = 10.403(3)$ Å	$T = 293(1)$ K
$\beta = 106.93(3)°$	Approximately prismatic
$V = 577.9(5)$ Å^3	$0.50 \times 0.41 \times 0.33$ mm
$Z = 4$	Colourless
$D_x = 1.886$ Mg m^{-3}	
$D_m = 1.90(1)$ Mg m^{-3}	
D_m measured by flotation	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.026$
$\omega–2\theta$ scans	$\theta_{max} = 30°$
Absorption correction: none	$h = -11 \rightarrow 11$
	$k = -10 \rightarrow 10$
	$l = -14 \rightarrow 14$
4180 measured reflections	3 standard reflections
1688 independent reflections	monitored every 165
1520 observed reflections	reflections
$[I > 2.5\sigma(I)]$	intensity decay: 1.09%

Refinement

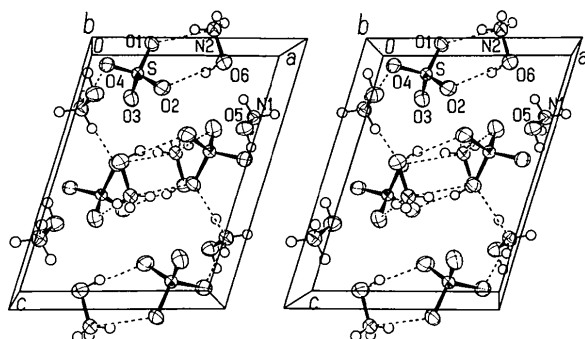|	
Refinement on F	$\Delta\rho_{max} = 0.24$ e Å^{-3}
$R = 0.026$	$\Delta\rho_{min} = -0.52$ e Å^{-3}
$wR = 0.026$	Extinction correction: Larson
$S = 0.363$	(1967)
1578 reflections	Extinction coefficient:
115 parameters	$g = 2.9(3)$
All H-atom parameters refined	Atomic scattering factors from Cromer & Mann
Weighting scheme: empirical $(\Delta/\sigma)_{max} = 0.181$	(1968)

Fig. 1. An *ORTEP*II (Johnson, 1976) stereoview of the unit cell together with the atom-labelling scheme. Displacement ellipsoids are plotted at the 70% probability level.

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

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

	x	y	z	U_{iso}/U_{eq}
S	0.27308(2)	0.19217(3)	0.08728(2)	0.01704(6)
O(1)	0.2982(1)	0.1238(1)	-0.03936(7)	0.0268(2)
O(2)	0.4145(1)	0.3233(1)	0.15036(8)	0.0287(2)

O(3)	0.2766 (1)	0.0401 (1)	0.18056 (8)	0.0287 (2)
O(4)	0.0992 (1)	0.2841 (1)	0.05753 (7)	0.0279 (2)
O(5)	0.9127	0.1888 (1)	0.30823 (8)	0.0269 (2)
N(1)	0.9616 (1)	0.0244 (1)	0.25810 (8)	0.0228 (2)
O(6)	0.6916 (1)	0.3230 (2)	0.04715 (8)	0.0371 (3)
N(2)	0.5909 (1)	0.2880 (1)	−0.08644 (8)	0.0240 (2)
H(1)	0.966 (3)	−0.063 (3)	0.312 (2)	0.030 (4)
H(2)	1.065 (3)	0.037 (3)	0.245 (2)	0.035 (4)
H(3)	0.878 (3)	0.003 (3)	0.182 (2)	0.037 (4)
H(4)	0.977 (3)	0.192 (3)	0.388 (2)	0.035 (4)
H(5)	0.641 (3)	0.212 (3)	−0.118 (2)	0.031 (4)
H(6)	0.495 (3)	0.247 (3)	−0.089 (2)	0.034 (4)
H(7)	0.580 (3)	0.388 (3)	−0.129 (2)	0.035 (4)
H(8)	0.612 (4)	0.318 (4)	0.088 (3)	0.052 (6)

Table 2. *Selected geometric parameters* (Å, °)

S—O(1)	1.4761 (9)	N(1)—O(5)	1.410 (1)
S—O(2)	1.4771 (8)	O(5)—H(4)	0.84 (2)
S—O(3)	1.4717 (9)	N(2)—H(5)	0.81 (2)
S—O(4)	1.4841 (8)	N(2)—H(6)	0.81 (2)
N(1)—H(1)	0.84 (2)	N(2)—H(7)	0.85 (2)
N(1)—H(2)	0.87 (3)	N(2)—O(6)	1.410 (1)
N(1)—H(3)	0.89 (2)	O(6)—H(8)	0.86 (4)
O(1)—S—O(2)	109.54 (5)	H(1)—N(1)—H(3)	110 (2)
O(1)—S—O(3)	110.51 (5)	H(2)—N(1)—H(3)	112 (2)
O(1)—S—O(4)	109.06 (4)	N(1)—O(5)—H(4)	104 (2)
O(2)—S—O(3)	109.42 (5)	O(6)—N(2)—H(5)	109 (1)
O(2)—S—O(4)	109.71 (5)	O(6)—N(2)—H(6)	111 (1)
O(3)—S—O(4)	108.58 (5)	O(6)—N(2)—H(7)	107 (1)
O(5)—N(1)—H(1)	111 (2)	H(5)—N(2)—H(6)	107 (2)
O(5)—N(1)—H(2)	110 (1)	H(5)—N(2)—H(7)	112 (2)
O(5)—N(1)—H(3)	105 (1)	H(6)—N(2)—H(7)	111 (2)
H(1)—N(1)—H(2)	109 (2)	N(2)—O(6)—H(8)	101 (2)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H$\cdots A$	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N(1)—H(1)$\cdots$O(4^i)	1.94 (2)	2.747 (1)	159 (2)
N(1)—H(2)$\cdots$O(3^{ii})	1.98 (3)	2.843 (1)	168 (2)
N(1)—H(3)$\cdots$O(1^{iii})	1.95 (2)	2.806 (1)	161 (2)
O(5)—H(4)$\cdots$O(4^{iv})	1.76 (2)	2.592 (1)	175 (2)
N(2)—H(5)$\cdots$O(3^{iii})	2.12 (2)	2.904 (1)	163 (2)
N(2)—H(6)$\cdots$O(1)	2.00 (2)	2.782 (1)	163 (2)
N(2)—H(7)$\cdots$O(2^v)	2.13 (2)	2.920 (1)	156 (2)
O(6)—H(8)$\cdots$O(2)	1.86 (4)	2.713 (2)	170 (3)

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

$w = W_f W_s$, where $W_f(F_o < 5.0) = (F_o/5.0)^{1.0}$, $W_f(F_o > 11.0) = (11.0/F_o)^{1.5}$, $W_f(5.0 < F_o < 11.0) = 1.0$, and $W_s(\sin\theta < 0.45) = (\sin\theta/0.45)^{2.5}$, $W_s(\sin\theta > 0.95) = (0.95/\sin\theta)^{1.0}$, $W_s(0.45 < \sin\theta < 0.95) = 1.0$, was applied to keep average $\Sigma w(F)^2$ uniform over the ranges of F_o and $(\sin\theta)/\lambda$. Computer programs: *XRAY76* (Stewart *et al.*, 1976).

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