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Hydrogen Bond Studies. LXXXVII.* A Neutron Diffraction Study of Ammonium Trihydrogen Selenite

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Abstract. $NH_4H_3(SeO_3)_2$, orthorhombic, $P2_12_12_1$, $a=5{\cdot}8501$ (2), $b=17{\cdot}7772$ (7), $c=6{\cdot}3107$ (3) Å, $V=656{\cdot}30$ Å^3, $Z=4$, $D_x=2{\cdot}785$ g cm^{-3}, $\mu_{obs}=2{\cdot}06$ cm^{-1}. Crystals were prepared from an aqueous solution of SeO_2 and NH_3. The structure consists of two different types of zigzag chains, which are interlinked *via* a third similar hydrogen bond to form a three-dimensional network. The ammonium ions further stabilize the structure by forming four N–H···O hydrogen bonds to oxygen atoms contained in different chains. One of these bonds can be described as a bifurcated hydrogen bond.

Introduction. The space group and unit cell for $NH_4H_3(SeO_3)_2$ were determined in our X-ray study (Tellgren, Ahmad & Liminga, 1972), and are confirmed here.

The intensity data were collected at the Swedish Atomic Energy R2 reactor at Studsvik on a Hilger & Watts four-circle diffractometer controlled by a PDP-8 computer. The experimental arrangement at Studsvik is described briefly elsewhere (Tellgren, Ramanujam & Liminga, 1973). The neutron flux at the specimen was $\sim 10^6$ n cm^{-2} s^{-1} at a wavelength of 1·210 Å.

The crystal used for the data collection had a volume of 30 mm^3. 1093 reflexions with $\sin\theta/\lambda$ up to 0·693 Å^{-1} were collected with the ω–2θ step-scan technique. Of these, 153 had intensities less than $3\sigma_{count}$ and were given zero weight in the refinements together with the six most seriously extinction-affected reflexions. The intensities were corrected for Lorentz and absorption effects. The experimentally determined linear absorption coefficient corresponds to an incoherent scattering cross-section for hydrogen of 45·8 barns. The transmission factors varied between 0·478 and 0·665.

The structure was refined by minimizing $\sum w(F_o^2-F_c^2)^2$ with the full-matrix least-squares program *UPALS*.† Each reflexion was assigned a weight $w=1/\sigma^2(F^2)$, where $\sigma^2(F^2)=\sigma^2_{count}(F^2)+(kF^2)^2$. The constant k was given the value 0·025. The total number of parameters refined was 146, including an isotropic extinction factor $g=5{\cdot}07\ (25)\ .\ 10^4$. [For a detailed description of the refinement procedure see Tellgren, Ramanujam & Liminga (1973).]

The coherent scattering amplitudes used were those compiled by Bacon (1972).

The final R values were $R(F^2)=0{\cdot}061$ (including all reflexions 0·071), $R_w(F^2)=0{\cdot}078$. This corresponds to a conventional $R(F)=0{\cdot}037$.

The final parameters are given in Tables 1 and 2, bond distances and angles in Table 3.†

Table 1. *Atomic coordinates* ($\times 10^4$)

	x	*y*	*z*
Se(1)	2120 (3)	3934 (1)	3062 (3)
Se(2)	7572 (3)	2397 (1)	1735 (2)
O(1)	1727 (5)	4225 (2)	439 (4)
O(2)	4959 (5)	2227 (2)	3004 (6)
O(3)	4901 (4)	4271 (1)	3383 (5)
O(4)	7825 (4)	3330 (1)	1969 (5)
O(5)	774 (5)	4588 (1)	4436 (5)
O(6)	9460 (5)	2052 (2)	3448 (6)
N	2376 (3)	820 (1)	2231 (3)
H(1)	2603 (9)	4702 (3)	148 (8)
H(2)	4851 (9)	2490 (3)	4410 (9)
H(3)	6018 (8)	3861 (3)	2889 (8)
H(4)	3157 (16)	1001 (5)	923 (11)
H(5)	1429 (12)	367 (3)	1894 (12)
H(6)	1340 (12)	1240 (4)	2778 (11)
H(7)	3563 (12)	698 (4)	3351 (12)

Discussion. The present work is part of our series of diffraction studies of hydrogen-bonded ferroelectrics and related compounds. The study was undertaken to obtain detailed information on the hydrogen-bond system for later comparison with $RbH_3(SeO_3)_2$ (Tellgren, Ahmad & Liminga, 1973). The heavy atom structures of these two compounds are isomorphous; the rubidium compound, however, is reported to be antiferroelectric, whereas no ferroelectric properties have been observed in the ammonium compound (Shuvalov, Ivanov, Gordeeva & Kirpichnikova, 1970).

As proposed in the X-ray study, the asymmetric unit consists of an NH_4^+ ion, an $HSeO_3^-$ ion and an H_2SeO_3 molecule. The position of the hydrogen atoms cova-

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† All computer programs used are described in the report UUIC-B13-4-01, which can be supplied by the authors on request.

† The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30476 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

lently bonded to the SeO_3^- groups were predicted from inspection of the Se–O distances. As can be seen from Table 3 the resulting positions were correct. The Se–OH distances vary between 1·746 (3) and 1·752 (3) Å, whereas the Se–O distances are in the range 1·651 (3) to 1·671 (3) Å.

The NH_4^+ ion forms a nearly perfect tetrahedron, with H–N–H angles in the range 108·4 (7) to 110·9 (6)°, and N–H distances between 0·997 (7) and 1·022 (7) Å (Table 3). The thermal ellipsoids for the atoms of the ion give no indication of a free rotation or of any other abnormal thermal motion.

The hydrogen-bond system consists of three O–H···O bonds and four N–H···O bonds, one of which can be described as a bifurcated bond (Figs. 1 and 2, Table 3).

The $H_2Se(1)O_3$ molecules and the $HSe(2)O_3^-$ ions are each connected *via* hydrogen bonds to form two different types of zigzag chains running perpendicular to one another; the first –Se(1)–O(1)–H(1)···O(5)–Se(1)– runs in the [001] direction and the second –Se(2)–O(2)–H(2)···O(6)–Se(2)– runs in the [100] direction. The two chains are interlinked by means of a third hydrogen bond O(3)–H(3)···O(4) (Fig. 1). The features of all three hydrogen bonds are very similar; all are almost linear with O–H distances 1·007 (5), 1·004 (7), 1·027 (5) Å, and H···O distances 1·643 (5), 1·595 (6), 1·532 (6) Å, respectively (Table 3).

The ammonium ions form N–H···O hydrogen bonds with surrounding oxygen atoms contained in both types of chains, thus stabilizing the three-dimensional network. The bonds N–H(5)···O(5), N–H(6)···O(6) and N–H(7)···O(5) (Fig. 2 and Table 3) all follow the general trend for normal hydrogen bonds; stronger bonds with shorter O···H distances are more linear and have slightly longer N–H distances. The differences in this case, however, are very small and are hardly significant.

The remaining bond is somewhat different, as can be seen from Fig. 2. The hydrogen atom H(4) is situated

Table 2. *Anisotropic thermal parameters* ($\times 10^4$)

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

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
Se(1)	140 (4)	012 (1)	124 (3)	001 (1)	−008 (3)	000 (1)	141 (2)	152 (2)	162 (2)
Se(2)	155 (4)	016 (1)	113 (3)	000 (1)	010 (3)	−003 (1)	147 (2)	161 (2)	166 (2)
O(1)	268 (8)	022 (1)	150 (5)	−026 (2)	−043 (6)	015 (2)	154 (4)	170 (4)	245 (4)
O(2)	157 (6)	027 (1)	223 (8)	−018 (2)	029 (6)	−006 (2)	148 (3)	203 (4)	228 (4)
O(3)	137 (5)	019 (1)	213 (6)	−001 (2)	−012 (5)	−005 (2)	153 (3)	171 (3)	209 (3)
O(4)	172 (6)	017 (1)	218 (6)	−002 (1)	044 (6)	002 (2)	158 (3)	167 (3)	218 (3)
O(5)	165 (6)	019 (1)	203 (7)	−003 (2)	028 (5)	−016 (2)	156 (3)	166 (3)	218 (3)
O(6)	203 (7)	021 (1)	235 (8)	018 (2)	−063 (7)	−011 (2)	155 (3)	181 (4)	243 (4)
N	178 (4)	020 (1)	172 (4)	−001 (1)	015 (4)	−001 (1)	172 (2)	181 (2)	190 (2)
H(1)	252 (12)	025 (1)	203 (10)	−014 (4)	002 (11)	013 (3)	175 (6)	208 (6)	227 (6)
H(2)	224 (12)	025 (1)	271 (16)	003 (3)	067 (12)	002 (4)	179 (6)	199 (6)	249 (7)
H(3)	182 (10)	026 (1)	320 (11)	001 (3)	−007 (9)	006 (3)	177 (5)	200 (5)	217 (6)
H(4)	491 (26)	050 (2)	254 (15)	−056 (7)	101 (18)	−013 (5)	204 (8)	239 (7)	343 (9)
H(5)	339 (17)	030 (2)	305 (17)	−014 (4)	007 (16)	−001 (4)	211 (7)	246 (7)	252 (7)
H(6)	342 (20)	035 (2)	282 (16)	016 (5)	001 (15)	−007 (5)	219 (7)	240 (7)	259 (7)
H(7)	305 (16)	038 (2)	329 (18)	015 (5)	−084 (16)	008 (5)	198 (7)	255 (7)	277 (8)

Table 3. *Bond distances* (Å) *and angles* (°) *in* $NH_4H_3(SeO_3)_2$

X	*Y*	*Z*	*X*–*Y*	*Y*···*Z*	*X*···*Z*	∠*X*–*Y*···*Z*
O(1)–	H(1)···	O(5)	1·007 (5)	1·643 (5)	2·644 (4)	172·3 (5)
O(2)–	H(2)···	O(6)	1·004 (7)	1·595 (6)	2·596 (4)	174·3 (5)
O(3)–	H(3)···	O(4)	1·027 (5)	1·532 (6)	2·554 (4)	172·4 (5)
N——	H(4)···	O(4)	0·997 (7)	2·188 (9)	3·063 (3)	145·7 (8)
N——	H(4)···	O(1)	0·997 (7)	2·294 (9)	3·054 (3)	132·2 (8)
N——	H(5)···	O(5)	1·000 (6)	2·069 (7)	3·049 (3)	165·9 (6)
N——	H(6)···	O(6)	1·022 (7)	1·864 (7)	2·881 (3)	173·2 (6)
N——	H(7)···	O(5)	1·014 (7)	1·970 (7)	2·983 (7)	176·9 (6)
Se(1)–O(1)——		H(1)	1·749 (3)	1·007 (5)	2·307 (5)	110·8 (3)
Se(1)–O(3)——		H(3)	1·746 (3)	1·027 (5)	2·287 (5)	108·3 (3)
Se(1)–O(5)···		H(1)	1·651 (3)	1·643 (5)	2·765 (5)	114·2 (2)
Se(2)–O(2)——		H(2)	1·752 (3)	1·004 (7)	2·326 (5)	112·3 (3)
Se(2)–O(4)···		H(3)	1·671 (3)	1·532 (6)	2·851 (5)	125·7 (2)
Se(2)–O(6)···		H(2)	1·663 (3)	1·595 (6)	2·782 (5)	117·2 (2)
H(4)–N——		H(5)	0·997 (7)	1·000 (6)	1·633 (10)	109·7 (6)
H(4)–N——		H(6)	0·997 (7)	1·022 (7)	1·637 (10)	108·4 (7)
H(4)–N——		H(7)	0·997 (7)	1·014 (7)	1·641 (10)	109·4 (7)
H(5)–N——		H(6)	1·000 (6)	1·022 (7)	1·650 (9)	109·3 (6)
H(5)–N——		H(7)	1·000 (6)	1·014 (7)	1·659 (10)	110·9 (6)
H(6)–N——		H(7)	1·022 (7)	1·014 (7)	1·658 (9)	109·0 (6)

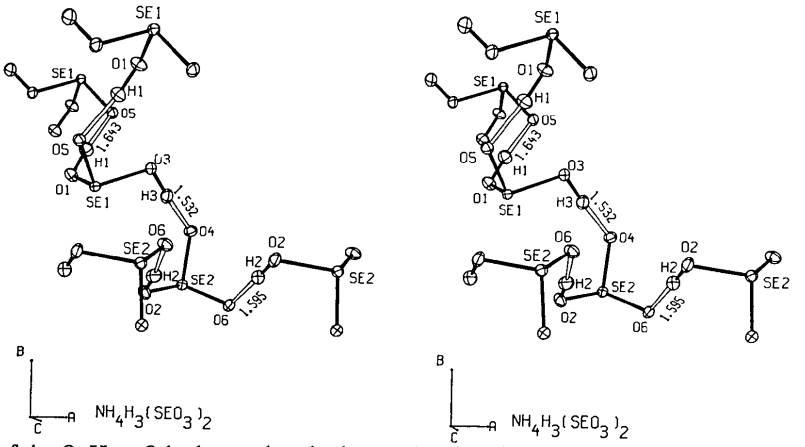

Fig. 1. A stereoscopic view of the O–H···O hydrogen-bond scheme, showing the two types of chains. The ellipsoids are scaled to include 50% probability. Covalent bonds are filled, and H···O hydrogen bonds are open.

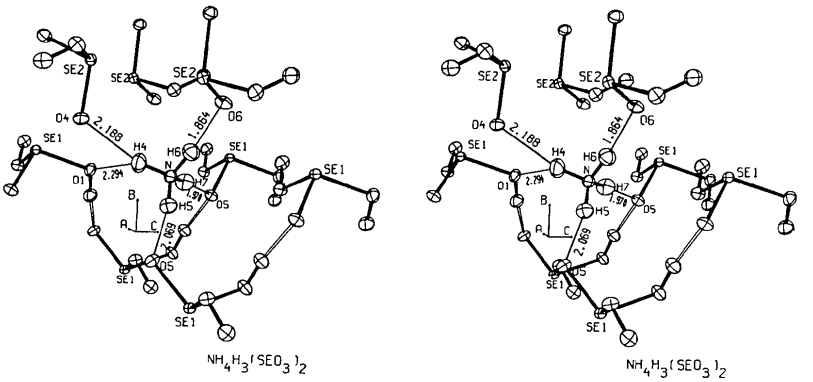

Fig. 2. A stereoscopic pair of drawings showing the ammonium ion and the N–H···O hydrogen bonds. The ellipsoids are scaled to include 20% probability. H···O bonds in N–H···O hydrogen bonds are drawn as single lines.

2·188 (9) Å from O(4) and 2·294 (9) Å from O(1), the N–H···O angles being 145·7 (8) and 132·2 (8)° respectively (Table 3). It is a matter of definition whether or not this should be regarded as a bifurcated hydrogen bond.

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