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Hydrogen Bond Studies. XCIII.* Oxonium Ion in Nitric Acid Monohydrate

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Abstract. $HNO_3.H_2O$, orthorhombic, $P2_1cn$ (non-standard setting of $Pna2_1$, No. 33), $Z=4$, $a=5·4647$ (1), $b=8·6439$ (1), $c=6·2308$ (1) Å, $V=294·32$ Å^3, $D_x=1·829$ g cm^{-3} at 85 K and $a=5·4759$ (2), $b=8·7242$ (2), $c=6·3275$ (2) Å, $V=302·28$ Å^3, $D_x=1·779$ g cm^{-3} at 225 K, $D_m=1·816$ g cm^{-3} at 78 K [Biltz, Hülsmann, & Eickholz. *Nachr. Ges. Wiss. Göttingen* (1935). No. 3, **1**, 95–102]. The crystal structure at both 85 and 225 K consists of H_3O^+ and NO_3^- ions each of which has pseudo-threefold symmetry. The oxonium ion is hydrogen bonded to three different nitrate ions to form infinite layers.

Introduction. Crystals were grown by cooling equimolar aqueous solutions of nitric acid sealed in glass capillaries (m.p. $-36·0$ °C). The intensities and cell dimensions were measured with a Stoe–Philips semi-automatic two-circle diffractometer (Cu $K\alpha$, Ni-filtered, moving crystal-moving detector scan technique) modified for low-temperature studies. Measurements were obtained at 85 and 225 K from two cylindrical crystals (diameter 0·10 mm, length 0·30 mm) mounted about **a** and **c** respectively. Cell parameters were calculated from a least-squares fit of measured 2θ values of 38 axial reflexions. Intensities for layers $0kl$ to $5kl$ were recorded for crystal 1 at 85 K yielding 315 independent reflexions (84 % of the reflexions within the unique octant of the Cu $K\alpha$ sphere). Of these 310 had $I>2\sigma(I)$ where $\sigma(I)$ is based on counting statistics. Three standard reflexions monitored periodically during data collection decreased by 3 % in intensity for which a correction was applied to all intensities. A comparable set of 291 reflexions (287 with $I>2\sigma$) was measured for crystal 2 (layers $hk0$ to $hk5$) at 85 K. No significant variations in the standard reflexions were observed during data collection. A third set of 325 intensities (320 with $I>2\sigma$) was collected for crystal 1 (layers $0kl$ to $5kl$) at 225 K. These were corrected for a 6 % decrease in intensity during data collection. Systematic absences at both 85 and 225 K were $hk0$, $h+k$ odd and $h0l$, l odd. The non-standard space group $P2_1cn$ corresponds to that used previously by Luzzati (1951).

The values of I and $\sigma(I)$ were corrected for Lorentz, polarization and absorption effects ($\mu=19·02$ cm^{-1} for Cu $K\alpha$). With the F_o values obtained from crystal 1 at 85 K, atomic coordinates and anisotropic thermal parameters for the non-hydrogen atoms and an overall scale factor were refined by full-matrix least-squares techniques with the program *UPALS*. The function minimized was $\sum w(|F_o|-|F_c|)^2$ where $w^{-1}=\sigma^2(F)=\sigma_c^2(F^2)/4F^2+(0·01F)^2$ with $\sigma_c^2(F^2)$ based on counting statistics. For unobserved reflexions $w=0$. Trial atomic coordinates were those of Luzzati (1951). A difference synthesis revealed the positions of the three hydrogen atoms. Coordinates and isotropic temperature factors for those atoms were allowed to vary in a subsequent refinement. Comparable structure refinements were performed separately with the data obtained from crystal 2 at 85 K. Interlayer scale factors were calculated by least-squares refinement with the program *INTERSCALE* which was based on 236 reflexions common to both data sets excluding 16 reflexions which appeared to have been seriously attenuated by extinction in both crystals. An isotropic extinction correction (Coppens & Hamilton, 1970) with a variable extinction parameter was included in a final refinement performed separately for each scaled data set. No attempt was made to average F_o values of equivalent reflexions in both data sets because of apparent differences in extinction effects in the two crystals.

For the two data sets from crystal 1 three high-μ-angle, low-detector-angle reflexions suspected to be seriously affected by experimental errors were given zero weight in the final refinements. For data derived from crystal 1 at 85 K, the refinement converged at $R_1=(\sum||F_o|-|F_c||)/\sum|F_o|=0·027$ with reflexions omitted for which $I<2\sigma$ ($R_2=0·030$ for all reflexions) and

Table 1. *Heavy atom coordinates* ($\times 10^5$); *hydrogen atom coordinates* ($\times 10^3$)

	x	y	z	
N	0	9623 (21)	29404 (25)	225 K
	0	9570 (22)	29642 (25)	85 K
O(1)	−17414 (60)	1823 (20)	22364 (29)	
	−17467 (66)	1844 (18)	22185 (25)	
O(2)	21492 (63)	4792 (20)	28156 (31)	
	21590 (67)	4598 (19)	28346 (27)	
O(3)	−4392 (65)	22348 (19)	37742 (32)	
	−4424 (64)	22397 (18)	38406 (27)	
O(*W*)	49174 (54)	26202 (18)	43278 (26)	
	49246 (51)	26163 (20)	44001 (26)	
H(1)	438 (8)	357 (5)	387 (6)	
	457 (15)	352 (7)	383 (10)	
H(2)	390 (8)	185 (5)	384 (7)	
	416 (7)	179 (4)	387 (5)	
H(3)	679 (8)	248 (4)	405 (7)	
	665 (11)	255 (4)	415 (9)	

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* Part XCII: Thomas, Tellgren & Olovsson [*Acta Cryst.* (1974). B**30**, 2540–2549].

$R_w=\{\sum w(|F_o|-|F_c|)^2/\sum w|F_o|^2\}^{1/2}=0{\cdot}040$. For crystal 2 at 85 K values for R_1, R_2 and R_w were 0·027, 0·028 and 0·040, respectively. Corresponding atomic parameters obtained from both crystals are in good agreement. For both the coordinates and thermal parameters of the non-hydrogen atoms, the largest difference was $2{\cdot}6(\sigma_1^2+\sigma_2^2)^{1/2}$ where σ_1 and σ_2 are the standard deviations of the same parameter derived for crystals 1 and 2 respectively. All tables and discussion for the structure are based on the atomic parameters derived for crystal 1.* Similar refinements were performed with the intensities recorded at 225 K except that interlayer scale factors were taken from a refinement with isotropic temperature factors. The values for R_1, R_2 and

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* All tables of structure factors and the atomic parameters derived for crystal 2 at 85 K have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30868 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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

The form of the anisotropic thermal factor is $\exp[-(\beta_{11}h^2+\ldots+2\beta_{12}hk+\ldots)]$. The r.m.s. components R_i ($\times 10^3$ Å) of thermal displacement of the atoms along the ellipsoid axes are included. Isotropic thermal parameters (B, Å^2) are given for the hydrogen atoms.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3	
N	207 (8)	56 (2)	132 (4)	14 (3)	6 (5)	6 (2)	142 (3)	163 (3)	181 (3)	225K
	74 (8)	26 (2)	47 (4)	13 (3)	−1 (5)	3 (2)	83 (6)	97 (5)	117 (5)	85K
O(1)	226 (8)	70 (2)	235 (5)	−5 (3)	−41 (6)	−17 (2)	158 (3)	180 (3)	227 (3)	
	66 (7)	32 (2)	90 (4)	−7 (3)	−6 (5)	−6 (2)	93 (5)	113 (4)	135 (3)	
O(2)	187 (7)	72 (2)	233 (5)	6 (3)	−13 (5)	−14 (2)	162 (3)	170 (3)	220 (3)	
	53 (7)	34 (2)	92 (5)	7 (3)	−14 (5)	−6 (2)	85 (6)	112 (4)	139 (3)	
O(3)	257 (7)	64 (2)	237 (5)	7 (3)	−12 (5)	−34 (2)	145 (3)	197 (3)	228 (2)	
	101 (7)	23 (2)	87 (5)	7 (3)	−5 (4)	−17 (2)	81 (5)	122 (4)	140 (3)	
O(*W*)	216 (7)	62 (2)	162 (4)	−7 (3)	−3 (4)	−3 (2)	154 (2)	181 (3)	183 (3)	
	68 (7)	26 (2)	72 (4)	−5 (3)	−1 (4)	−2 (2)	94 (4)	106 (5)	119 (3)	

H(1)	4·0 (0·8)	H(2)	3·7 (0·8)	H(3)	3·7 (0·8)
	6·5 (1·5)		0·9 (0·6)		3·0 (0·9)

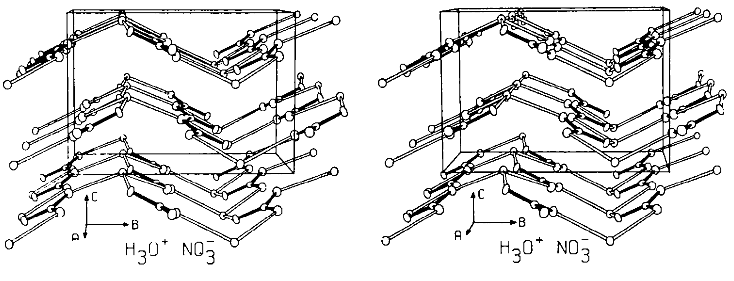

Fig. 1. Stereoscopic view of the crystal structure of $H_3O^+NO_3^-$ at 85K showing the layers. Covalent bonds are filled, hydrogen bonds open. The thermal ellipsoids enclose 50% probability.

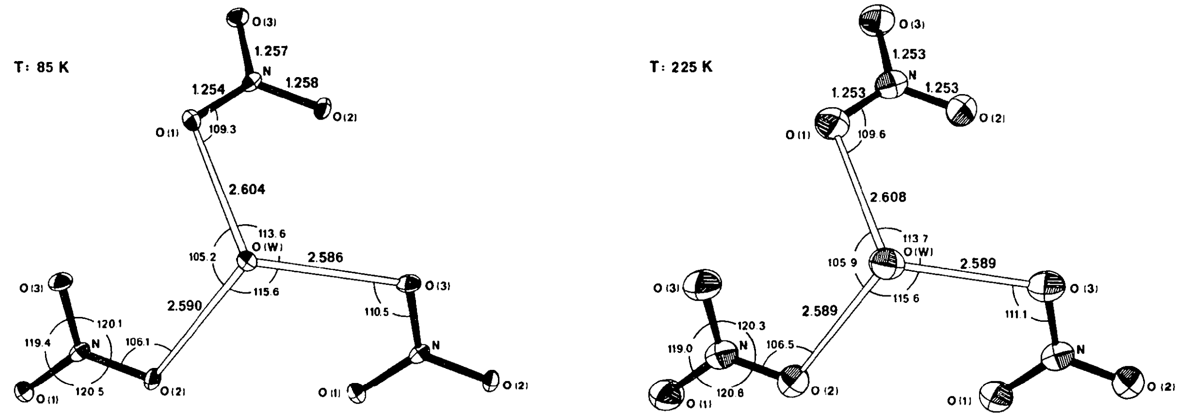

Fig. 2. Bond distances (Å) and angles (°) at 85 and 225 K. The thermal ellipsoids enclose 50% probability. Estimated standard deviations are about 0·2° for bond angles and 0·003 Å for distances.

R_w were 0·026, 0·029 and 0·039, respectively, for the final refinement. Structural parameters corresponding to the enantiomorph ($x = -x$) were refined for each set of data. The values of R for these refinements differed insignificantly from those previously obtained, so the absolute configuration has not been determined.

Scattering factors for N and O were from Hanson, Herman, Lea & Skillman (1965) and for H from Stewart, Davidson & Simpson (1965). An anomalous dispersion correction was included for N and O (Cromer & Liberman, 1970). The programs used for all computations have been described by Lundgren (1974*a*). The final parameters are given in Tables 1 and 2. The value of the extinction parameter g is 2944 (377) and 1986 (287) for the 85 and 225K data, respectively.

Discussion. Luzzati (1951) suggested a crystal structure of acid molecules hydrogen bonded to water molecules although the limited precision of his study prevented any definite conclusions being reached. An n.m.r. study showed that the structure contained oxonium ions (Richards & Smith, 1951). Numerous recent studies of monohydrates of other strong acids have shown the presence of oxonium ions (Lundgren, 1974*b*; Lundgren & Olovsson, 1975). The atomic coordinates derived here agree reasonably well with the less precise values given by Luzzati (1951). The structure consists of H_3O^+ ions hydrogen bonded to NO_3^- ions to form infinite puckered layers perpendicular to **c** (Fig. 1); there are no hydrogen bonds between layers. Bond distances and angles involving only non-hydrogen atoms are shown in Fig. 2. The nitrate group has approximate D_{3h} symmetry as the three N–O distances are similar, and the three bond angles differ only slightly from 120°. The oxygen atoms in the group are nearly equivalent as each accepts one hydrogen bond from the oxonium ion. The average N–O distance of 1·256 Å* is within the range of values generally found in nitrate ions. The nitrogen atom lies in the plane defined by O(1), O(2) and O(3); there is no significant deviation of N from this plane [0·001 (2) Å].

The H_3O^+ ion (Fig. 2) is bonded to three different nitrate groups to form a flat pyramid with the oxonium oxygen atom at the apex. The perpendicular distance between O(*W*) and the base of the pyramid is 1·025 (2) Å. The three O–H···O distances are very similar with an average value of 2·59 Å whereas the bond angles to the acceptor atoms vary from 105·2 to 115·6° with an average value of 111·5°. These values are comparable with an average O–H···O distance of 2·57 Å and an average O···O(*W*)···O angle of 109·3° found in other compounds containing the oxonium ion (Lundgren & Olovsson, 1975). In $H_3O^+NO_3^-$ this arrangement of acceptors gives the H_3O^+ ion an environment with approximate C_{3v} symmetry. The O(*W*)–H distances are 0·88 (6), 0·89 (4) and 0·96 (6) Å; H–O(*W*)–H angles are 117 (5), 101 (6) and 111 (4)°. The limited precision of the distances and angles for bonds involving hydrogen prevents a more detailed analysis of the geometry of the oxonium ion. A neutron diffraction study of $CF_3SO_3H.H_2O$ has shown that its geometry can be nearly regular even in an asymmetric environment (Lundgren, Tellgren & Olovsson, 1974).

Neighbouring layers are related to each other by *c* glide planes and are separated by normal van der Waals contact distances (Fig. 1). The projection of each layer on the *ab* plane has approximate threefold symmetry; the projection of the crystal structure as a whole without the hydrogen atoms appears to have sixfold symmetry (Fig. 3).

The structures at 85 and 225K are nearly identical; corresponding bond distances and angles involving atoms within the same layer do not differ significantly. The N–O distances tend to be slightly shorter at 225K which may reflect the limitations of a harmonic model used for the thermal parameters. From the cell parameters, the mean principal coefficients of linear thermal expansion have been derived for the temperature range 85 to 225K. The values (all $\times 10^6$) for $\bar{\alpha}_a$, $\bar{\alpha}_b$ and $\bar{\alpha}_c$ are 14·6, 66·0 and 110·4 $\deg^{-1}$, respectively. The largest

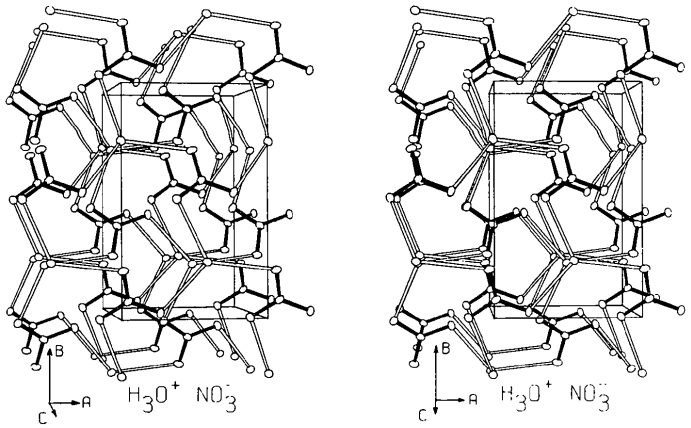

Fig. 3. Stereoscopic drawing of the structure viewed normal to hydrogen-bonded layers of H_3O^+ and NO_3^- at 85K.

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* Distances and angles refer to the 85K data unless stated otherwise.

thermal expansion occurs along **c** in the perpendicular distance between layers.

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Hydrogen Bond Studies. XCIV.* Diaquaoxonium Ion in Nitric Acid Trihydrate

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Abstract. $HNO_3.3H_2O$, orthorhombic, $Z=4$, space group $P2_12_12_1$, $a=9{\cdot}4845$ (4), $b=14{\cdot}6836$ (9), $c=3{\cdot}4355$ (2) Å, $V=478{\cdot}45$ Å^3 at 85K, $D_x=1{\cdot}625$, $D_m=1{\cdot}621$ g cm^{-3} [Biltz, Hülsmann & Eickholz. *Nachr. Ges. Wiss. Göttingen* (1935). No. 3, **1**, 95–102]. The structure contains oxonium ions, each of which is bonded to two water molecules by short hydrogen bonds [2·482 (2) and 2·576 (2) Å] to form $H_7O_3^+$ ions. A longer hydrogen bond [2·800 (2) Å] connects the $H_7O_3^+$ groups with one another to form spirals. These spirals are in turn hydrogen bonded to NO_3^- ions, thus forming a three-dimensional network.

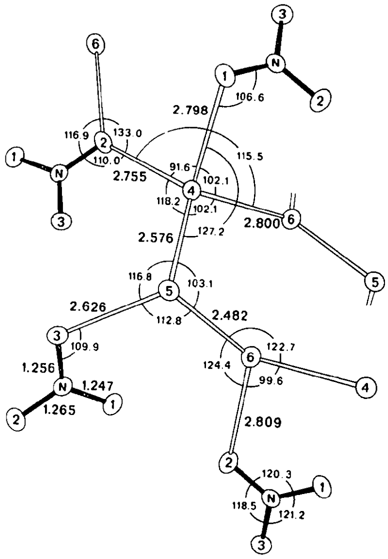

Fig. 1. Bond distances (Å) and angles (°). Estimated standard deviations are about 0·002 Å for distances and 0·1° for angles.

Introduction. Crystals were grown from aqueous solutions of nitric acid (molar ratio 3:1) sealed in thin-walled glass capillary tubes. The crystals grew preferentially with the *c* axis along the axis of the capillary tube. The observed melting point agreed with the value of −18·5°C given by Biltz, Hülsmann & Eickholz (1935).

Collection of intensity data and measurements of cell dimensions were performed at 85K with a semi-automatic Stoe–Philips Weissenberg diffractometer modified for low-temperature work (Cu *Kα*, Ni-filtered, moving-crystal moving-detector scan technique). Two crystals mounted about the [001] and [110] directions, respectively, were used to obtain the cell parameters. Systematic absences were *h*00 *h* odd, 0*k*0 *k* odd, and 00*l l* odd. Layers $0 \leq l \leq 3$ were recorded, yielding 595 independent reflexions, corresponding to 86% of the reflexions within the unique octant of the Cu *Kα* sphere. Of these 19 had $I < 2\sigma(I)$ (where $\sigma(I)$ was based on Poisson counting statistics) and were given zero weight in all least-squares refinements. Four reflexions suspected of being seriously affected by experimental errors were likewise excluded in the final refinement. Three test reflexions for each layer, monitored every 30 reflexions, showed no abnormal variations in inten-