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.

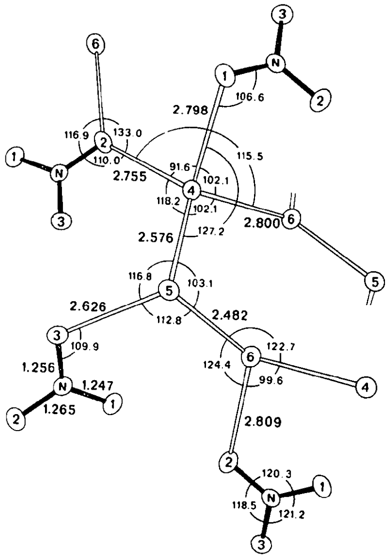

Fig. 1. Bond distances (Å) and angles (°). Estimated standard deviations are about 0·002 Å for distances and 0·1° for angles.

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 $-18{\cdot}5$°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 $K\alpha$, 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 $h00$ h odd, $0k0$ k odd, and $00l$ l odd. Layers $0 \le l \le 3$ were recorded, yielding 595 independent reflexions, corresponding to 86% of the reflexions within the unique octant of the Cu $K\alpha$ 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 intensities. The intensities and standard deviations $\sigma(I)$ were corrected for Lorentz, polarization and absorption effects ($\mu = 16{\cdot}8$ cm^{-1} for Cu $K\alpha$). The crystal form was cylindrical (diameter 0·236 mm, length 0·288 mm).

An overall scale factor, atomic coordinates for the non-hydrogen atoms (Luzzati, 1953), and individual isotropic temperature factors were first refined by full-matrix least-squares procedure using the program *UPALS*. After a refinement with anisotropic thermal parameters a difference synthesis indicated the positions of all seven hydrogen atoms. These were varied in the subsequent refinement with isotropic B factors. An isotropic extinction parameter g (Coppens & Hamilton, 1970) was also included. The final agreement values were: $R = \sum||F_o| - |F_c||/\sum|F_o| = 0{\cdot}026$ (0·030 including zero weighted reflexions); $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0{\cdot}035$.

The atomic scattering factors used were those for neutral N and O given by Hanson, Herman, Lea & Skillman (1965) and for H by Stewart, Davidson & Simpson (1965). An anomalous dispersion correction was included for O (*International Tables for X-ray Crystallography*, 1962). The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ in which $w^{-1} = \sigma^2(F) = \sigma_c^2(F^2)/4F^2 + (0{\cdot}01\ F)^2$ where $\sigma_c^2(F^2)$ is based on counting statistics. Calculations were performed on IBM 370/155 and IBM 1800 computers using programs described by Lundgren (1974*a*). Atomic parameters are given in Table 1 and 2. The final value of the extinction parameter g is 1750 (295).* The U_{33} values of the thermal parameters for the heavy atoms appear to be systematically larger than the corresponding values of U_{11} and U_{22}. Refined individual scale factors from a refinement with isotropic temperature parameters produced considerably reduced U_{33} values. The positional parameters did not change significantly; however, the U values of the nitrogen atom were physically unrealistic, and the R value increased from 0·026 to 0·027. For these reasons the results of the final refinement with an overall scale factor have been preferred.

In an attempt to determine the absolute configuration, a refinement with reversed configuration was per-

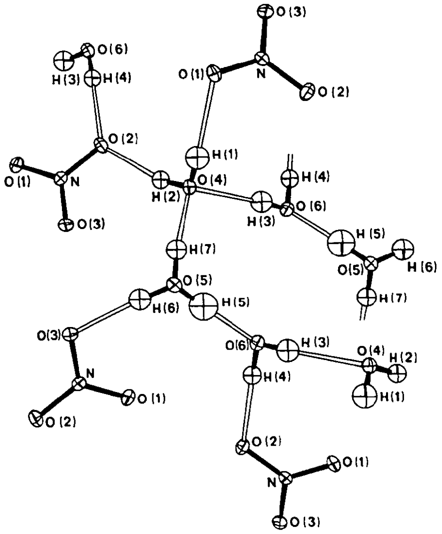

Fig. 2. The $H_7O_3^+$ complex and its environment as obtained from the final refinement. The thermal ellipsoids are scaled to enclose 50% probability.

Table 1. *Atomic coordinates* ($\times 10^5$) (*in the case of hydrogen* $\times 10^3$)

		x	y	z
	N	27245 (15)	33336 (10)	17527 (51)
	O(1)	38761 (13)	30715 (8)	4074 (44)
	O(2)	16738 (13)	28035 (8)	17992 (47)
	O(3)	25831 (13)	41197 (8)	31386 (45)
	O(4)	55047 (13)	64174 (9)	9298 (49)
	O(5)	50699 (13)	48650 (9)	42080 (45)
	O(6)	70284 (14)	39120 (9)	16815 (51)
$H_2O(4)$	H(1)	570 (3)	684 (2)	247 (8)
	H(2)	481 (3)	656 (2)	−30 (9)
$H_2O(6)$	H(3)	771 (3)	380 (2)	328 (10)
	H(4)	691 (3)	340 (2)	67 (8)
$H_3O^+(5)$	H(5)	575 (4)	451 (2)	328 (10)
	H(6)	426 (3)	464 (2)	383 (9)
	H(7)	515 (3)	541 (2)	326 (8)

Table 2. *Anisotropic thermal parameters* ($U_{ij} \times 10^4$ Å^2)

The form of the temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots 2U_{12}hka^*b^* + \ldots)]$. The r.m.s. components ($R_i \times 10^3$ Å) of thermal displacement along the principal axes of the thermal vibration ellipsoids are also listed along with the isotropic thermal parameters (B Å^2) for the hydrogen atoms.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	R_1	R_2	R_3
N	105 (7)	102 (6)	190 (9)	15 (5)	−9 (6)	8 (7)	93 (4)	109 (3)	138 (3)
O(1)	108 (6)	148 (6)	254 (9)	35 (4)	36 (6)	6 (6)	91 (3)	128 (3)	163 (3)
O(2)	109 (6)	140 (6)	315 (8)	−32 (5)	20 (6)	−36 (6)	94 (3)	123 (3)	180 (2)
O(3)	133 (6)	92 (6)	307 (8)	4 (4)	15 (6)	−32 (6)	93 (3)	115 (2)	177 (2)
O(4)	102 (6)	114 (6)	267 (8)	−0 (5)	−23 (6)	−2 (6)	100 (3)	107 (3)	164 (3)
O(5)	120 (6)	117 (6)	280 (9)	−12 (5)	22 (6)	−0 (6)	103 (3)	114 (3)	168 (3)
O(6)	116 (6)	131 (6)	282 (8)	11 (4)	−13 (6)	−29 (6)	105 (3)	114 (3)	170 (3)

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

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* A table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30885 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

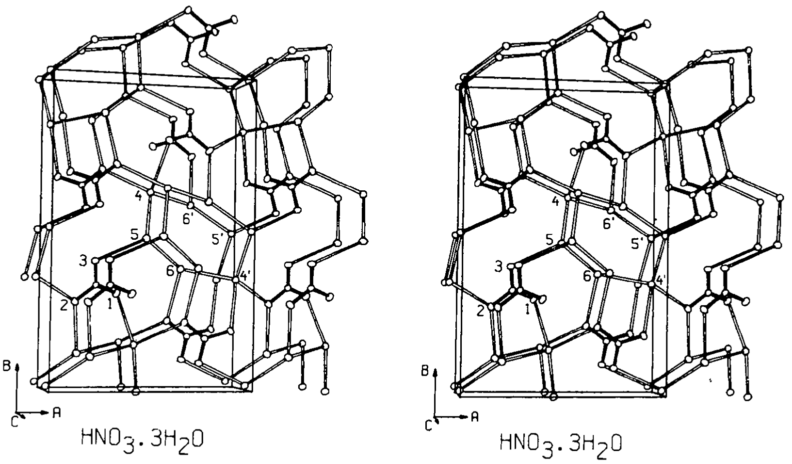

Fig. 3. A stereoscopic drawing of the crystal structure of $H_7O_3^+NO_3^-$. The oxygen atoms in the asymmetric unit have been labelled 1–6. (Atoms marked with primed numbers do not belong to the asymmetric unit.) The thermal ellipsoids are scaled to enclose 50% probability.

formed. There were no significant changes in the *R* values or magnitudes of the structural parameters. Additional refinements were performed for both configurations using the real $\Delta f'$ and imaginary $\Delta f''$ anomalous dispersion terms of Cromer & Liberman (1970) for O and N. *R* values and structural parameters differed insignificantly from those obtained in the previous corresponding refinements.

Discussion. The crystal structure of $HNO_3.3H_2O$ as originally determined by Luzzati (1953) was formulated as $H_3O^+(NO_3^-).2H_2O$. The structure has been reinvestigated to attain higher precision in the course of the systematic studies of the solid hydrates of strong acids at this Institute. The results of our study agree generally with those of Luzzati. The short hydrogen-bond distances, between O(5) and the other two water oxygens [O(4) and O(6)] as well as the small differences in the N–O distances in the nitrate ion clearly indicate that the extra proton is bonded to O(5) to form H_3O^+ (Fig. 1). This is also confirmed by the refined positions of the hydrogen atoms (Fig. 2). The oxonium ion and the two water molecules, $H_2O(4)$ and $H_2O(6)$, form an unsymmetrical $H_7O_3^+$ ion. The $H_7O_3^+$ ions are linked by weaker hydrogen bonds, 2·800 (2) Å, into spirals running along **c** (Fig. 3). These spirals are connected to nitrate ions *via* hydrogen bonds to form a three-dimensional network.

The formulation $H_7O_3^+NO_3^-$ for the present compound should be understood only as a suitable description of the overall structure. The unsymmetrical $H_7O_3^+$ ion is not isolated but hydrogen bonded to other $H_7O_3^+$ ions as described above. However, it forms a well defined complex since the $H_7O_3^+\cdots H_2O$ hydrogen bonds are 0·22 Å longer than the weakest hydrogen bond within $H_7O_3^+$.

The internal structure of the $H_7O_3^+$ ion is rather unsymmetrical; one of the water molecules is considerably closer to the central oxonium ion than the other. The complex may thus be considered as an intermediate between $H_3O^+.2H_2O$ and $H_5O_2^+.H_2O$ (Lundgren, 1974*b*; Lundgren & Olovsson, 1975).

The central oxonium ion is pyramidally surrounded by the two water oxygens O(4) and O(6) and a somewhat more distant nitrate oxygen O(3); atom O(5) is situated 0·788 (2) Å from the plane defined by O(3), O(4) and O(6). Typically the oxonium ion does not accept a hydrogen bond.

One of the outer water oxygens [O(6)] has a pyramidal environment, and it serves as an acceptor of only one proton (from the oxonium ion). Atom O(6) is situated 0·560 (2) Å from the plane through O(2), O(4) and O(5). The other water oxygen [O(4)] takes part in four hydrogen bonds; in addition to accepting a proton from the oxonium ion it also accepts a proton from O(6) in a neighbouring $H_7O_3^+$ ion. However, this latter hydrogen-bond length is considerably longer than the other hydrogen bonds involving the water oxygens. These features are also typical for $H_7O_3^+$ compounds. The hydrogen-bond acceptor power of the two outer water oxygens in $H_7O_3^+$ is expected to be somewhat reduced. In only two cases known so far ($HClO_4.3H_2O$ and $HNO_3.3H_2O$) does such an oxygen atom serve as a proton acceptor (besides accepting a proton from H_3O^+).

The coordinates of the refined hydrogen atoms give O–H distances in the range 0·81 (3)–0·89 (4) Å and H–O–H angles in the range 101–122°. The O–H$\cdots$O angles vary between 162 and 178°. The e.s.d.'s for all angles involving hydrogen are 2–3°.

The nitrate ion is nearly planar; the distance of the nitrogen atom from the calculated plane through O(1), O(2) and O(3) is 0·007 (2) Å. The differences in the N–O bond lengths (Fig. 1) may be correlated with the number and strength of hydrogen bonds accepted by each nitrate oxygen. The atom O(2), which is the most distant from N, is involved in two hydrogen bonds, whereas the other two oxygen atoms only accept one. O(3) takes part in a stronger hydrogen bond than O(1). Similar effects as discussed above have also been correlated in other hydrogen-bonded structures with NO_3^- ions (*cf.* Narasinga Rao & Parthasarathy, 1973).

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Platinum Compound Binding by Purine and Pyrimidine Bases. I. The Structure of [Cytosine.H^+]$_2$[$PdCl_4^{2-}$]

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Abstract. $[C_4H_6N_3O]_2[PdCl_4]$, monoclinic, $P2_1/c$, $a = 8{\cdot}437$ (2), $b = 13{\cdot}776$ (4), $c = 7{\cdot}191$ (2) Å, $\beta = 111{\cdot}07$ (1)°, $\varrho_o = 2{\cdot}01$, $\varrho_c = 2{\cdot}00$ g cm^{-3}. The dominant structural features are ionic moieties, hydrogen bonding and base stacking. Base–base hydrogen bonding is replaced by Cl–H interactions, but base stacking persists.

Introduction. Since the discoveries by Rosenberg (1971), compounds containing certain platinum metals have been shown to be effective in the treatment of various types of animal and human carcinomas. Several metal-binding modes have been proposed for this interaction, including specific metal-base binding (Howle, Gayle & Smith, 1972), disruption of hydrogen bonding and base stacking in the double helix (Drobnik & Horacek, 1973), and cross strand linkages (Roberts & Pascoe, 1972; Zakharenko & Moshkovskii, 1972). Investigation of the interactions between Pt^{2+} and Pd^{2+} compounds and nucleotides, nucleosides, and nucleotide bases is, therefore, of considerable interest. The simplest model for this system employs the use of bases in which the site of ribose attachment has been blocked with an alkyl group. As the first of this series a proton is placed on cytosine. Since the difference in Pt and Pd chemistry is frequently one of rates and Pd is more suitable for X-ray studies, parallel experiments with Pd^{2+} and Pt^{2+} compounds were carried out, and the Pd^{2+} analog was used in the structural studies where possible.

Brick-red crystals of $[C_4H_6N_3O]_2[PdCl_4]$ were prepared by slow evaporation of a solution made by mixing 3 ml of 0·02*M* cytosine acidified to a *p*H of 1·0 by HCl with 3 ml of 0·02*M* K_2PdCl_4.

Source: Mo $K\alpha$, $\lambda = 0{\cdot}710683$ Å, $2\theta_{\max} = 90°$; θ–2θ scan on a Picker automated diffractometer, $\Delta 2\theta = 1{\cdot}5°$. Number of reflections: 3781 taken, 2498 non-zero, confidence level $= 2\sigma$. $\mu = 17{\cdot}58$ cm^{-1}, transmission factor min and max: 0·393, 0·613; crystal size: 0·66 × 0·53 × 0·33 mm; $R = 0{\cdot}049$, weighted $R = 0{\cdot}059$.

Structure solution was by standard heavy-atom techniques and refinement was by full-matrix least-squares calculations. The function minimized was $\sum w(F_o - F_c)^2$ with weights determined from counting statistics. Scattering factors for Pd^{2+}, Cl^-, and neutral nitrogen, oxygen and carbon were from Cromer & Waber (1965), those for hydrogen were from Stewart, Davidson & Simpson (1965). The effects of anomalous dispersion were included in the structure-factor calculations by addition to F_c (Ibers & Hamilton, 1964). Values for $\Delta f'$ and $\Delta f''$ for palladium and chlorine