

Sundaralingam & Jensen's conclusions. The C(1')-O(1') bond is significantly smaller than the C(4')-O(1') bond in all three molecules, the mean C(1')-O(1') bond being 1.414 Å and the mean C(4')-O(1') being 1.454 Å. Angles N(9)-C(1')-O(1') are consistently smaller than angles N(9)-C(1')-C(2'), and angles C(3')-C(4')-C(5') are smaller than angles O(1')-C(4')-C(5').

Apart from the difference in pucker in the sugars, the other big difference in conformation between molecule I and molecules IIA and IIB is in the orientation of the C(5')-O(5') bond about the C(4')-C(5') bond. In both molecules IIA and IIB the conformation is such that C(5')-O(5') is *gauche* to C(4')-O(1') and to C(4')-C(3'), but in inosine I, C(5')-O(5') is *gauche* to C(4')-O(1') and *trans* to C(4')-C(3').

In nucleoside structures, the pyrimidine and purine bases have a tendency to pack in parallel planes about 3.5 Å apart and to prefer hydrogen bonding to each other. Very often nucleoside structures possess a unit-cell dimension of about 4.8 Å, and in many cases, the bases which are parallel and 3.5 Å apart are those which are separated by this lattice translation. Therefore, it is possible to predict that the planes of the bases will make an angle of about 45° with this cell edge. Some examples of this include deoxyadenosine (Watson, Sutor & Tollin, 1965), thymidine (Young, Tollin & Wilson, 1969), and the 5-bromouridine-adenosine complex (Haschemeyer & Sobell, 1965).

The structure of inosine again shows this kind of packing, when the short axis is the *c* axis. The hydrogen bond between the bases is from N(1) to N(7). In the inosine dihydrate structure the bases are again con-

nected by this hydrogen bond but have been rotated about it until they are coplanar and as a result produce sheets of hydrogen bonded bases. These sheets are stacked 3.3 Å apart as mentioned by Bugg *et al.* (1970).

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A Refinement of the Crystal Structure of NH₄NO₃·2HNO₃

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The structure of NH₄NO₃·2HNO₃ has been refined, using the original experimental results of Duke & Llewellyn. The structure consists of NH₄⁺ cations and hydrogen-bonded [O₂NO-H-(NO₃)-H-ONO₂]⁻ anions. The bond lengths in this anion are discussed in detail, and compared with relevant values for other molecules.

Introduction

There has been an increasing interest recently in the group of anions with the general formulae HX₂⁻ and HXY⁻, in which two like or unlike uninegative anions (X⁻, Y⁻) are linked through a hydrogen bond. The study of such species offers many advantages in the investigation of simple isolated hydrogen-bonded

systems. A number of spectroscopic studies have been reported for salts of a number of these anions, but bond length data are lacking in most cases (Tuck, 1968). In addition to the HX₂⁻ species, a small number of anions of the type [H_MX_{M+1}]⁻ are also known. For X = F, the values of *n* range from 2 to 7, and the structure of H₂F₃⁻ has been established by X-ray methods (Forester, Senko, Zalkin & Templeton, 1963).

Anions of this series with $\text{X}=\text{NO}_3$ form an interesting group. A variety of large cations yield salts of $[\text{H}(\text{NO}_3)_2]^-$, and with Ph_4As^+ and Ph_4P^+ , higher species were also observed (Faithful, Gillard, Tuck & Ugo, 1966; Tuck, 1968). Simpler crystalline salts with the stoichiometry $\text{MNO}_3 \cdot \text{HNO}_3$ and $\text{MNO}_3 \cdot 2\text{HNO}_3$ ($\text{M}=\text{K}, \text{Rb}, \text{Cs}, \text{NH}_4$) have been known for many years (Mellor, 1923). The crystal structure of $\text{NH}_4\text{NO}_3 \cdot 2\text{HNO}_3$ was determined by Duke & Llewellyn (1950), who suggested that the structure was very slightly distorted from the orthorhombic space group $P22_12_1$, with $a=6.57$, $b=12.64$ and $c=4.56$ Å. The arrangement of ions was described in terms of NH_4^+ and NO_3^- ions separated by sheets containing HNO_3 molecules, with two HNO_3 molecules linked to a NO_3^- ion by hydrogen bonds. The variation in N—O bond lengths [which has also been remarked upon by Wells (1962)] led Duke & Llewellyn to suggest that this description was in fact an oversimplified one.

The uncertainty in this description prompted us to carry out a refinement of the structure by techniques not available to Duke & Llewellyn. The recent identification of two different structures for the related $[\text{H}(\text{NO}_3)_2]^-$ anion by Dobinson, Mason & Russell (1967), and by Faithful & Wallwork (1967),

raises a number of problems about the relationship of this anion to that discussed in this paper. Our refinement has given atomic coordinates of sufficient precision to permit a more detailed interpretation of the structure than was previously possible.

Refinement procedure

Refinement began with the published atomic coordinates. Of the 467 structure factors listed by Duke & Llewellyn, all except the 040 and 220 values were used; these two remained consistently amongst the strongest F_{calc} and $F_{\text{obs}} \approx \frac{2}{3}F_{\text{calc}}$. Isotropic temperature factors, together with variable coordinate parameters, were first refined as 4×4 blocks by the usual least-squares procedure. After 4 cycles using 80% shifts, the discrepancy index R had fallen from 0.19 to 0.12 and convergence had been attained. At this stage, the largest features of an electron density difference map (based on reflexions with $\sin^2 \theta < 0.36$) were the anisotropic motions of the nitrate groups. At no stage of the refinement was it possible to assign hydrogen atom positions directly.

At this point an analysis of the weighting scheme as a function of both $|F_{\text{obs}}|$ and $\sin \theta$ was carried out

Table 1. Final positional parameters and standard errors (fractional), thermal parameters and standard deviations

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Mean σ_u
O(11)	0.2043 (15)	$\frac{1}{2}$	0	2.19	4.89	3.96	—	—	0.10	0.49
O(12)	0.4902 (13)	0.4468 (6)	0.1871 (21)	3.15	4.98	5.53	-0.08	-1.31	0.50	0.42
O(21)	0.3222 (13)	0.2134 (6)	0.1654 (18)	4.57	5.21	3.80	-0.09	1.29	0.73	0.42
O(22)	0.1106 (12)	0.1736 (6)	0.5147 (21)	4.01	5.20	4.81	-0.44	0.53	1.20	0.40
O(23)	0.2408 (13)	0.3318 (6)	0.4950 (18)	3.82	4.19	3.83	0.24	-0.21	1.00	0.38
N(11)	0.3933 (16)	$\frac{1}{2}$	0	1.89	3.11	3.78	—	—	-0.54	0.52
N(2)	0.2248 (13)	0.2337 (6)	0.3847 (19)	2.47	3.85	3.24	0.54	-0.28	0.07	0.39
NH_4	0.1182 (19)	0	0	B_{iso}	2.74					0.21 (σ_B , Å ²)

Table 2. 'Bonded' distances and angles

N(11)—O(11)	1.242 (1.252)* Å	O(11)—N(11)—O(12)	120.4°
N(11)—O(12)	1.259 (1.273)*	O(12)—N(11)—O(12)	119.3
N(2)—O(21)	1.215 (1.233)*	O(21)—N(2)—O(22)	126.3
N(2)—O(22)	1.221 (1.241)*	O(21)—N(2)—O(23)	117.5
N(2)—O(23)	1.343 (1.353)*	O(22)—N(2)—O(23)	116.2
O(12)···O(23)	2.601 —	N(11)—O(12)—O(23)	110.2
		N(2)—O(23)—O(12)	111.3
Estimated errors			
N—O	0.013 Å		
O···O	0.012		
O—N—O	1.2°		
Other short contacts (< 3.15 Å)			
NH_4^+ —O(12)	3.018 Å	II	
—O(21)	3.105	I	
—O(11)	3.113	III	
—O(22)	3.117	IV	
O(23)—O(21)	3.028	V	I x y z
—O(11)	3.110	I	II $1-x$ $y-\frac{1}{2}$ $\frac{1}{2}-z$
—O(11)	3.143	VI	III $-x$ $y-\frac{1}{2}$ $\frac{1}{2}-z$
O(22)—N(2)	3.013	VII	IV x y $z-1$
—O(11)	3.016	VII	V $1-x$ $\frac{1}{2}-y$ $\frac{1}{2}+z$
—O(12)	3.132	V	VI x y $z+1$
			VII $-x$ $\frac{1}{2}-y$ $\frac{1}{2}+z$

* Denotes a value corrected for the movement of the oxygen atom riding on the nitrogen atom.

and new weights assigned as $\omega = 1/\{1 + [(F_{\text{obs}} - 8.5)/5]^2\}$ instead of the unit weights previously used. Unobserved reflexions were assigned a value of 0.4, all of these values referring to the final scale (1.25 original published value). Self consistent field scattering factors were used for all atoms (*International Tables for X-ray Crystallography*, 1962).

Anisotropic refinement (9×9 blocks) was then undertaken. Only the atoms involved in the NO_3 groups were permitted this freedom, as the ammonium ion appeared to be moving isotropically. After 8 cycles with 40% shifts, convergence was complete and the parameters in Table 1 were obtained. It should be noted that the atom numbering scheme throughout is that used by Duke & Llewellyn. Indicated shifts in coordinates were quite small and averaged 0.002 \AA ; the final discrepancy index R was 0.094. An analysis of the weighting scheme showed $\sum \omega \Delta^2$ to be constant over different ranges of $|F_{\text{obs}}|$ and $\sin \theta$. A final electron density difference map using all reflexion data revealed no interpretable features.

Since estimates of error based on the block-diagonal procedure are known to be optimistic (Geller, 1961), we have arbitrarily increased these estimates by 50% to allow for the neglected interaction terms. Table 2 gives the interatomic distances and angles. Librational corrections were applied with the assumption that the oxygen atoms of each NO_3 entity in the anion ride on the appropriate nitrogen atom. This physically reasonable description is confirmed by the results in

Table 3, so that the NO_3 groups may be regarded as kinematically independent rigid bodies. Table 3 shows the root-mean-square thermal displacement of the atom along the principal axes of vibration, and the three component along the appropriate bond vector. Table 4 gives the equations for the planes through the two different NO_3 groups and the deviations from these planes.

Table 4. Equation of the planes through the nitrate groups

$$\begin{aligned} X, Y, Z \text{ are the coordinates in } \text{\AA}. \\ \text{Plane I} \quad & -0.7851Y - 0.6193Z + 4.9620 = 0 \\ \text{Plane II} \quad & -0.7659X + 0.2995Y - 0.5690Z + 1.2319 = 0 \end{aligned}$$

Deviations from planes	I		II	
	I	II	I	II
O(11)	—	2.10 \AA	—	—
O(12)	—	-0.01	—	—
N(11)	—	1.17	—	—
O(21)	2.38 \AA	0.001	—	—
O(22)	1.79	0.001	—	—
O(23)	0.27	0.001	—	—
N(2)	1.56	-0.004	—	—

Discussion

The structure clearly consists of NH_4^+ cations and $[\text{H}_2\text{N}_3\text{O}_9]^-$ anions (see Fig. 1). The closest approach of the NH_4^+ cation to an anionic oxygen atom is 3.02 \AA , which is greater than the distance usually associated with significant N--O hydrogen bonding.

Table 3. *R.m.s.* thermal displacements of the atoms along the principal axes of vibration, and along the bond vector

	R_1	R_2	R_3	Component	Bond vector
O(11)	0.15 \AA	0.20 \AA	0.22 \AA	0.15 \AA	O(11)-N(11)
O(12)	0.16	0.22	0.25	0.19	O(12)-N(11)
O(21)	0.16	0.22	0.24	0.16	O(21)-N(2)
O(22)	0.18	0.21	0.25	0.18	O(22)-N(2)
O(23)	0.17	0.19	0.23	0.19	O(23)-N(2)
N(11)	0.14	0.17	0.20	—	—
N(2)	0.15	0.18	0.20	—	—

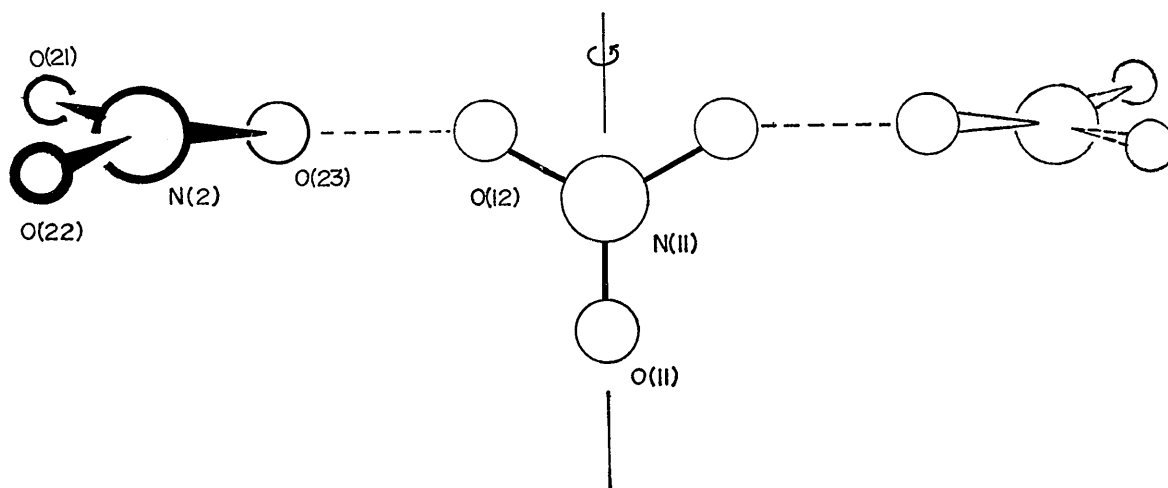


Fig. 1. The $(\text{HNO}_3)_2\text{NO}_3^-$ ion.

Analysis of corresponding N--O angles shows that any such hydrogen bonding would involve non-linear bonds.

The bonding of the anion is of considerable interest. We first note that the outer NO_3 group is rotated through an angle of 83° with respect to the central NO_3 group. Both central and outer NO_3 groups of the anion are planar within experimental error (see Table 4).

The only significant hydrogen bond for which we find evidence is that between O(23) and O(12), for which the O--O distance is $2.601 \pm 0.012 \text{ \AA}$. This distance can be compared with the value of 2.45 \AA reported by Faithful & Wallwork (1967) for the $[\text{H}(\text{ONO}_2)_2]^-$ anion. No meaningful comparison can be made with the O--O distance in the structure reported by Dobinson, Mason & Russell (1967). A comparison of the electrostatic interactions in $[\text{H}(\text{ONO}_2)_2]^-$ (*i.e.* -+-) and the present anion (*i.e.* -+--+ -) suggests that the hydrogen bonding will be weaker in the latter, with a consequently smaller O--O distance in $[\text{H}(\text{ONO}_2)_2]^-$. In the analogous fluorine systems, the F--F distances in HF_2^- and H_2F_3^- are 2.27 and 2.33 \AA respectively (McDonald, 1960; Forester, Senko, Zalkin & Templeton, 1963), so that the changes are of similar order in both the fluorine and nitrate cases.

Atoji & Rundle (1958), and later Bacon (1963), have published graphical relationships between the O--H...O and O--H distances in a number of structures. The nature of the substances involved is varied, the experimental accuracy of the points on the graph is sometimes low, and the theoretical basis of the relationship is unexplained. Within these limitations, it is possible to deduce from the graph published by Bacon (1963) that the O--O distance of 2.45 \AA reported by Faithful & Wallwork (1967) corresponds to the hydrogen atom being almost symmetrically situated between the NO_3 groups in the $[\text{H}(\text{ONO}_2)_2]^-$ ion. By a similar argument, the O--O distance of 2.601 \AA in the present structure leads to an O--H distance of approximately 1 \AA . It seems clear that within the uncertainty of the above argument the hydrogen atom is asymmetrically situated between O(23) and O(12); electrostatic considerations of the type outlined above suggest that it will be closer to the outer NO_3 group than to the central one.

The N--O bond lengths can also be usefully compared with those in $[\text{H}(\text{ONO}_2)_2]^-$. It should be noted here that all the bond lengths quoted in this paragraph are uncorrected for librational motion, for purposes of comparison with the similarly uncorrected results given by Faithful & Wallwork (1967), and by Dobinson, Mason & Russell (1967). The N--O distance for the hydrogen bonded oxygen atom in the $[\text{H}(\text{ONO}_2)_2]^-$

ion is 1.29 \AA , and the other two N--O bond lengths average 1.21 \AA . In the present structure, the terminal N--O bonds in the outer NO_3 units have an almost identical average length of 1.22 \AA . The N--O(H) distance in each outer NO_3 unit is 1.34 \AA , to be compared with 1.26 \AA for N(1)--O(12) in the central NO_3 group. These values bracket the 1.29 \AA for the analogous N--O(H) bond in the $[\text{H}(\text{ONO}_2)_2]^-$ ion, which suggests that the hydrogen atom is appreciably closer to O(23), producing a weaker N(2)--O(23) bond than that at N(11)--O(12). The N(11)--O(12) bond is apparently slightly weaker than N(11)--O(11), due to the hydrogen bond at O(12). The terminal N--O bonds in the present structure, and in $[\text{H}(\text{ONO}_2)_2]^-$, are typical of those believed to involve N--O bonds of bond order > 1 .

In sum, the anion is best represented as $[\text{O}_2\text{NO--H}\cdots(\text{NO}_3)\cdots\text{H--ONO}_2]^-$, with an unsymmetrical O--H...O bond, with the range of N--O bond lengths then seen as one result of this unsymmetrical hydrogen bond. We believe that the description of the anion as a nitrate ion bonded to two nitric acid molecules is indeed an oversimplification, and that the properties of the hydrogen bond largely govern the structural arrangement.

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