Fig. 1. Crystal structure projected on (001). Atoms with closed bonds are at $\frac{3}{4}c$ and atoms with open bonds are at $\frac{1}{4}c$. Hydrogen bonds are represented by single lines. The bond angles are: N(1)–C–N(2) 119·8 (4); N(2)–C–N(3) 120·1 (4); N(3)–C–N(1) 120·0 (4); O(1)–N–O(2) 120·0 (2); O(2)–N–O(2) 120·1 (5)°. Thermal ellipsoids are scaled to enclose 50% probability.

configuration of the triaminoguanidinium ion (Fig. 1) approximates the C_{3h} symmetry described by Okaya & Pepinsky (1957) for the cation in the hexagonal triaminoguanidinium chloride. The C–N bonds are considered equivalent and agree with those found in triaminoguanidinium chloride [1·318 (9) Å]; guanidinium

chloride [1·318 (6), 1·325 (5), and 1·325 (5) Å; Haas, Harris & Mills (1965)]; and guanidinium oxalate dihydrate monoperhydrate [1·319 (9), 1·327 (10), and 1·325 (10) Å; Adams & Pritchard (1976)]. The N–N bond lengths display some variation and are shorter than the N–N bond length [1·450 (14) Å] observed in triaminoguanidinium chloride.

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1,2,3-Triaminoguanidinium Nitrate by Neutron Diffraction

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Abstract. $CH_9N_6^+.NO_3^-$, orthorhombic, *Pbcm*, $a = 8·389$, $b = 12·684$, $c = 6·543$ Å, $Z = 4$, $D_m = 1·60$, $D_c = 1·594$ Mg m^{-3}. The structure is made up of an infinite three-dimensional network of N–H···O hydrogen bonds linking the 1,2,3-triaminoguanidinium ions to the nitrate ions. The librational motions of the nitrate ion have a particularly large amplitude about an axis which is close to the perpendicular to the plane of the ion.

Introduction. The title compound (hereinafter referred to as TAG nitrate) is a strong oxidizer often used as a

constituent of propellants. Bracuti (1979), from whom unit-cell, measured-density and space-group information are taken, has recently determined the arrangement of the nonhydrogen atoms in the structure from X-ray diffraction data. He experienced difficulty in obtaining a satisfactory refinement because of the large-amplitude thermal motions of the O atoms in the nitrate groups. A neutron diffraction study was undertaken to determine the H positions accurately, and to study the thermal motion of the nitrate group in more detail.

A cylindrical crystal approximately 2 mm in diameter and 3 mm long was mounted on a computer-controlled four-circle diffractometer at the National Bureau of Standards Research Reactor, with the axis of the cylinder parallel to the φ axis of the diffractometer. The intensities of two symmetry-equivalent sets of reflections were measured using the procedure described previously (Prince, 1972). The agreement index $R = \sum |F(hkl) - F(\bar{h}kl)|/\sum [F(hkl) + F(\bar{h}kl)]$ was 0·026. Of 875 reflections within a sphere defined by a neutron wavelength of 1·230 Å and a maximum 2θ of 106°, 613 had observable intensities. Because the effect of absorption is small ($\mu r = 0·2$), no absorption corrections were applied.

All H atoms were located in a difference Fourier map using the positions found by Bracuti (1979) for the nonhydrogen atoms to determine the phases. The structure was then refined by least squares using the program *RFINE* (Finger & Prince, 1975). The function minimized was $\sum w(|F_o| - |F_c|)^2$, with the weights set by $w = [\sigma_s^2 + (0·005F)^2]^{-1}$, where σ_s is the estimated standard deviation computed from counting statistics. A conventional refinement using anisotropic temperature factors did not give satisfactory results because of the failure of the model to give an adequate description of the large-amplitude thermal motions of the O atoms in the nitrate group.

To accommodate such large-amplitude, and therefore markedly curvilinear, thermal motions, the nitrate group was constrained to be planar, and the thermal motions were treated as those of a rigid body, using the methods developed by Prince & Finger (1973). The parameters refined were the position of the N atom, the orientation of the plane of the groups, the N—O bond distances and the O—N—O bond angles, and the elements of the T, L, and S thermal-motion tensors. The number of parameters for the nitrate group in this model, which includes third-cumulant terms in the structure factor expression, is 18, as compared with 21 for the unconstrained two-cumulant model. A secondary-extinction parameter (Zachariasen, 1968) was included, with the path-length parameter $\bar{T}$ treated as a constant. Six very strong reflections with values of the extinction factor (F_{corr}/F_{calc}) less than 0·55 were excluded from the final stages of refinement. Refinement of the constrained model proceeded smoothly to the final R indices $R_w = 0·051$, $R = 0·055$. The final parameters are listed in Table 1.* Table 2 gives the final rigid-body thermal parameters for the nitrate group. Fig. 1 is a stereoscopic pair (Johnson, 1965) showing the structure. Selected interatomic distances and angles are listed in Table 3.

An attempt was made to refine the structure in the noncentrosymmetric space group $Pbc2_1$. However,

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33959 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional coordinates* ($\times 10^4$) *for* C(NHNH₂)₃NO₃ *with estimated standard errors in parentheses.*

	x	y	z
C	7197 (4)	7601 (3)	7500
N(1)	6668 (3)	8591 (2)	7500
N(2)	8747 (3)	7406 (3)	7500
N(3)	6163 (3)	6800 (3)	7500
N(4)	7781 (4)	9410 (3)	7500
N(5)	9264 (4)	6356 (3)	7500
N(6)	4517 (4)	7029 (2)	7500
H(1)	5494 (9)	8732 (7)	7500
H(2)	9513 (11)	8022 (9)	7500
H(3)	6556 (11)	6061 (7)	7500
H(4)	7591 (8)	9857 (5)	6280 (15)
H(5)	9926 (10)	6222 (6)	6291 (15)
H(6)	4016 (8)	6713 (6)	6286 (14)
N(7)	2396 (3)	9021 (2)	7500
O(1)	3575 (7)	9532 (5)	7500
O(2)	1832 (8)	8776 (5)	9030 (9)

Table 2. T ($Å^2$), L (rad^2), S (rad Å) *tensor elements allowed by symmetry*

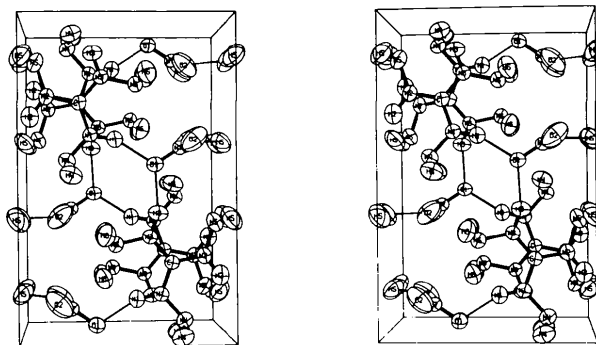| T_{11} | 0·0308 (12) | L_{11} | 0·013 (12) | S_{13} | −0·004 (3) |
T_{22}	0·0331 (12)	L_{22}	0·124 (4)	S_{23}	0·038 (3)
T_{33}	0·0642 (40)	L_{33}	0·018 (12)	S_{31}	0·004 (2)
T_{12}	−0·0007 (8)	L_{12}	−0·011 (3)	S_{32}	0·010 (7)

Fig. 1. Stereoscopic pair showing the structure of TAG nitrate as viewed down the c axis. The b axis is vertical.

Table 3. *Selected interatomic distances (Å) and angles (°) in TAG nitrate*

N—O distances are corrected for libration. Distances involving hydrogen bonds are marked by asterisks.

C—N(1)	1·332 (4)	N(1)—C—N(2)	120·2 (3)
C—N(2)	1·324 (4)	N(1)—C—N(3)	120·1 (3)
C—N(3)	1·336 (4)	N(2)—C—N(3)	119·7 (3)
N(1)—N(4)	1·396 (4)	C—N(1)—N(4)	118·6 (3)
N(1)—H(1)	1·00 (1)	C—N(1)—H(1)	119·8 (6)
N(4)—H(4)	0·99 (1)	H(1)—N(1)—N(4)	·121·6 (6)
N(2)—N(5)	1·401 (5)	C—N(2)—N(5)	118·8 (3)
N(2)—H(2)	1·01 (1)	C—N(2)—H(2)	118·6 (6)
N(5)—H(5)	0·98 (1)	H(2)—N(2)—N(5)	122·6 (6)
N(3)—N(6)	1·411 (9)	C—N(3)—N(6)	118·6 (3)
N(3)—H(3)	0·99 (1)	C—N(3)—H(3)	120·2 (6)
N(6)—H(6)	0·98 (1)	H(3)—N(3)—N(6)	121·2 (6)
N(7)—O(1)	1·256 (7)	N(1)—N(4)—H(4)	108·6 (4)
N(7)—O(2)	1·228 (7)	H(4)—N(4)—H(4′)	107 (1)
*H(1)—O(4)	1·847 (10)	N(2)—N(5)—H(5)	109·9 (5)
*O(1)—N(1)	2·793 (6)	H(5)—N(5)—H(5′)	107 (1)
*H(3)—O(1)	1·932 (10)	N(3)—N(6)—H(6)	109·5 (4)
*O(1)—N(3)	2·864 (7)	H(6)—N(6)—H(6′)	107 (1)
*H(5)—O(2)	2·104 (10)	O(1)—N(7)—O(2)	119·2 (5)
*O(2)—N(5)	3·058 (7)	O(2)—N(7)—O(2)	121·5 (5)
O(2)—H(4)	2·29 (1)	*N(1)—H(1)—O(1)	156 (1)
O(2)—H(2)	2·39 (1)	*N(3)—H(3)—O(1)	155 (1)
O(2)—H(6)	2·42 (1)	*N(5)—H(5)—O(2)	164 (1)

because this structure is very close to the centrosymmetric structure, this refinement did not converge to a stable solution.

Discussion. All of the atoms of the TAG cation, except for the H atoms in the amino group, lie in a mirror plane, and the atomic configuration differs insignificantly from threefold symmetry around an axis passing through the C atom. The mean C—N distance, 1·331 (3) Å, is indicative of a partial double bond, which is consistent with a model containing resonance among three equivalent structures (Pauling, 1960). The mean N—N bond length, 1·403 (6) Å, is much shorter than the 1·45 Å reported by Okaya & Pepinsky (1957) in TAG chloride. The plane of the nitrate anion is perpendicular to the mirror plane, with the central N atom and one O atom lying in the mirror plane. The ion

is somewhat distorted from trigonal symmetry: O(1), which accepts two hydrogen bonds, is 0·03 Å further away from the central N than O(2), which accepts only one.

The NO_3^- ion is surrounded by nine H atoms with contact distances of 2·42 Å or less. Four of these (see Table 2) participate in fairly strong N—H···O hydrogen bonds. The thermal motion of the ion is a highly anisotropic libration, with an r.m.s. amplitude of 20° around an axis tilted about 26° away from the normal to the plane of the ion and about 7° away from the *b* axis. The network of hydrogen bonds is three-dimensional, but it forms particularly strong chains (O···H distances less than 2·0 Å) parallel to this axis.

Note added in proof: The differences between the atomic coordinates reported in this paper and those reported by Bracuti (1979) are closely correlated with the amount of thermal motion. Atoms near the centers of molecular groups agree within two times the estimated standard deviation, but atoms on the peripheries of the groups and all hydrogen atoms differ by four to five times the standard deviation. Because of the much greater sensitivity of neutron data to hydrogen atom positions, our hydrogen atom parameters should be more accurate.

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