1,2,3-Triaminoguanidinium Nitrate

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Abstract. $CH_9N_6^+.NO_3^-$, orthorhombic, *Pbcm*, $a = 8.389$ (7), $b = 12.684$ (8), $c = 6.543$ (5) Å, $Z = 4$, $D_m = 1.60$, $D_x = 1.594$ Mg m^{-3}, $F(000) = 352$, μ(Mo $K\alpha$) = 0.1563 mm^{-1}, $M_r = 167.13$. The crystal structure consists of layers of ions parallel to (001). Each nitrate ion is hydrogen bonded to two cations within each layer, and also to two cations in alternate layers.

Introduction. Needle-like crystals ($0.5 \times 0.5 \times 0.7$ mm) were prepared by evaporation from aqueous solution. A total of 885 independent reflections were measured with an automated diffractometer utilizing graphite-monochromated Mo $K\alpha$ radiation, with 140 reflections rejected because of the imposed criterion $F \geq 2\sigma(F)$ where $\sigma(F)$ is the standard deviation based on counting statistics. The data were corrected for Lorentz and polarization effects, and absorption (transmission 0.952 to 0.928).

Systematic absences observed with Weissenberg photographs ($k = 2n + 1$ for $0kl$; $l = 2n + 1$ for $h0l$) are indicative of space groups *Pbcm* and *Pca2₁*. On the basis of intensity-distribution statistics, the centrosymmetric space group *Pbcm* was selected rather than the non-centrosymmetric space group *Pca2₁* reported by Keim (1944).

The structure was solved with *MULTAN* (Germain, Main & Woolfson, 1971) and refined by the full-matrix least-squares program *FLINUS*, a modification of the *ORFLS* program (Busing, Martin & Levy, 1962). The function minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$.

An E map calculated from a set of phases with the highest combined figure of merit (3·0) revealed the positions of the non-hydrogen atoms. The molecular shape of the nitrate ion was somewhat distorted and the weights of the O peaks were small suggesting the presence of disorder. The H atoms were located with a difference Fourier synthesis. All non-hydrogen atoms were refined anisotropically, while the temperature factors of the H atoms were constrained to equal those of the N atoms to which they were bonded. Also refined was an extinction parameter $g = 0.31 \times 10^{-3}$ mm (Coppens & Hamilton, 1970). Refinement converged with an R index of 0.083 $[R = \sum (|F_o| - |F_c|)/\sum |F_o|]$. The atomic coordinates are presented in Table 1; the

Table 1. *Atomic coordinates and their standard deviations*

Triaminoguanidinium cation	x	y	z
C	0.7188 (5)	0.7600 (3)	0.75
N(1)	0.6671 (5)	0.8586 (3)	0.75
N(2)	0.8740 (4)	0.7405 (3)	0.75
N(3)	0.6159 (4)	0.6814 (3)	0.75
N(4)	0.7800 (5)	0.9407 (3)	0.75
N(5)	0.9238 (4)	0.6340 (4)	0.75
N(6)	0.4530 (5)	0.7035 (3)	0.75
H(1)	0.562 (6)	0.873 (4)	0.75
H(2)	0.922 (6)	0.776 (5)	0.75
H(3)	0.645 (6)	0.624 (4)	0.75
H(4)	0.754 (4)	0.978 (3)	0.654 (6)
H(5)	0.996 (4)	0.631 (3)	0.652 (6)
H(6)	0.405 (4)	0.680 (3)	0.646 (6)

Nitrate anion	x	y	z
N	0.2405 (4)	0.9024 (3)	0.75
O(1)	0.3602 (4)	0.9549 (3)	0.75
O(2)	0.1808 (5)	0.8765 (3)	0.9092 (5)

molecular and crystal structure and the non-hydrogen bond lengths and angles are presented in Fig. 1.*

Discussion. The structure consists of layers of planar triaminoguanidinium cations and nitrate anions located on mirror planes at $\pm\frac{1}{4}c$. The cations are coplanar with the mirror planes (except for the amino H atoms), while each anion is bisected by the mirror plane with only the central N atom and one O atom on the mirror. The anions are stacked in alternate layers [6·543 (5) Å apart] directly over one another; the cations are packed over each other but in adjacent layers [3·272 (5) Å apart] and are hydrogen bonded [N(5)–H(5)···O(2) 3·103 (5) Å] to the anions in alternate layers. Within each layer, in addition to electrostatic forces, each cation is hydrogen bonded to two anions [N(1)–H(1)···O(1) 2·849 (5) Å; N(3)–H(3)···O(1) 2·880 (5) Å]. The
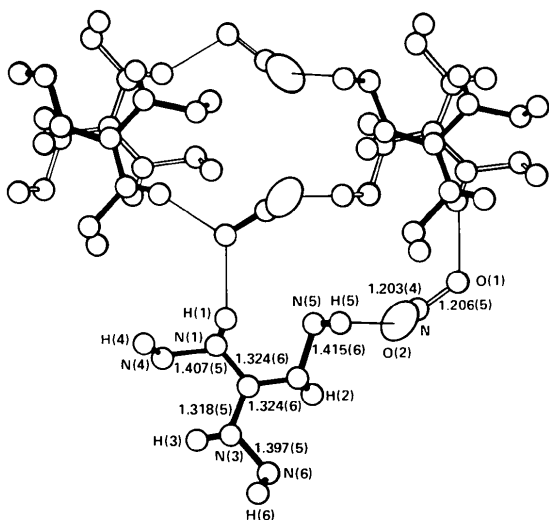

Fig. 1. Crystal structure projected on (001). Atoms with closed bonds are at $\frac{3}{4}c$ and atoms with open bonds are at $\frac{1}{4}c$. Hydrogen bonds are represented by single lines. The bond angles are: N(1)—C—N(2) 119·8 (4); N(2)—C—N(3) 120·1 (4); N(3)—C—N(1) 120·0 (4); O(1)—N—O(2) 120·0 (2); 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, $a = 8\cdot389$, $b = 12\cdot684$, $c = 6\cdot543$ Å, $Z = 4$, $D_m = 1\cdot60$, $D_c = 1\cdot594$ 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