131. Crystal Structure and Packing of 1-(4,6-Diamino-1,3,5-triazin-2-yl)guanidinium nitrate

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The title compound is a condensation product of four guanidinium ions formed during crystallization of guanidinium nitrate. The crystal structure consists of infinite molecular ribbons stacked into layers which are rotated 58.5° with respect to each other and connected by two different networks of hydrogen bonds.

Introduction. – Intermolecular interactions with directional preferences such as H-bonds provide a powerful tool to control solid-state structure. When used judiciously, well organised molecular assemblies such as 'molecular ribbons' or 'sheets' may be constructed [1–5]. We hypothesised that guanidinium nitrate could form stacks of molecular sheets in which each cation is surrounded by three anions across three pairs of H-bonds and *vice versa*. This has been confirmed [6]. During our crystallization experiments, crystals with a morphology different from that of guanidinium nitrate were observed and subjected to structural investigation. They were found to be the nitrate salt of a condensation product of four guanidinium ions (G4NO3) or, more specifically, of a melamine molecule and a guanidinium ion (*Fig. 1*, center).

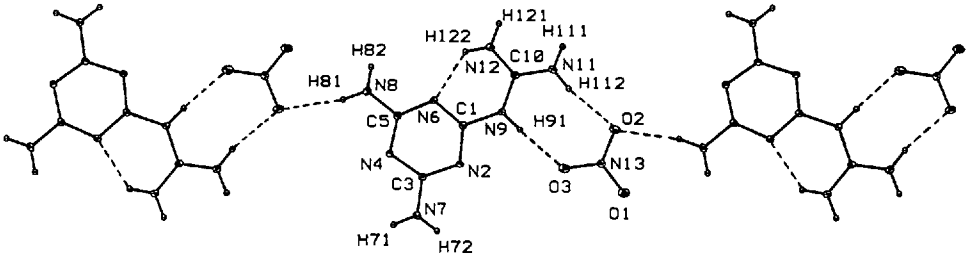

Fig. 1. *An infinite tape of alternating anions and cations of G4NO3 running along the [012] direction.* The central molecule shows the atomic numbering and the intramolecular H-bond.

Experimental. – Guanidinium nitrate was subjected to many crystallization attemps from EtOH/H_2O mixtures (20:80 vol-%). In this repeated crystallization process, a new crystal form with the appearance of flat prisms was found and subjected to X-ray structural analysis. Intensity data were collected at r.t. with an *Enraf-Nonius CAD4* diffractometer employing MoK_α radiation on a crystal of dimensions 0.36 × 0.21 × 0.11 mm. During data collection, three reflections used to monitor the stability and orientation of the crystal showed only an overall statistical fluctuation of 1.6%. Intensity controls were remeasured after every 7200 s of X-ray exposure time, and orientation standards were monitored after every 120 reflections. All other pertinent experimental details are recorded in *Table 1*.

Table 1. *Crystal Data and Experimental Details of G4NO3*

Molecular formula	$C_4H_9N_8^+ \cdot NO_3^-$	$(\mathrm{Sin}\ \theta/\lambda)_{max}$	0.6606
Molecular weight	231.20	No. of reflections measured	1570
Crystal system	Orthorhombic	No. of unique reflections	855
Space group	$Pna2_1$	R_{int}	0.013
Cell parameters a [Å]	12.561(2)	No. of significant reflections	$830(I > 2\sigma I)$
b [Å]	10.972(3)	Refinement on F^2	
c [Å]	6.613(2)	$R(F)$	0.0322
Volume [Å^3]	911.4(4)	$wR(F^2)$	0.0738
Z	4	$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2] + (0.0023P)^2$	where $P = (F_o^2 + F_c^2)/3$
D_c [g cm^{-3}]	1.685		
Radiation used	MoK_α	Goodness of fit	1.071
Wave length [Å]	0.71069	No. of parameters	145
μ [cm^{-1}]	1.43	$\Delta\rho$ (max), $\Delta\rho$ (min) in final difference *Fourier* [e Å^{-3}]	0.157, −0.201
Temp. [K]	295		
Scan mode	ω	$(\mathrm{Shift/e.s.d})_{max}$	≤ 0.001
No. of reflections for measuring lattice parameters, θ range [°]	15, 10.5–18.8		

The structure was solved by direct methods using the SHELXTL PC Package [7] and refined by least squares using SHELXL-93 [8]. H-Atoms were introduced at calculated positions (d(N–H) = 0.86 Å) and assigned a common isotropic temp. factor. A molecular diagram drawn with *Peanut* [9] and showing atomic numbering is given in *Fig. 1*. Positional coordinates with equivalent isotropic temp. factors, selected bond lengths and angles are recorded in *Table 2* and *3*, respectively.

Table 2. *Positional Coordinates and Isotropic Thermal Parameters of G4NO3* (e.s.d.'s in parenthesis)

Atom	x	y	z	U_{eq} [Å^2]
C(1)	0.2325(2)	0.1289(2)	0.8439(6)	0.0259(6)
N(2)	0.1271(2)	0.1162(2)	0.8373(6)	0.0277(5)
C(3)	0.0927(2)	0.0572(3)	0.6705(6)	0.0274(7)
N(4)	0.1549(2)	0.0125(2)	0.52290	0.0294(5)
C(5)	0.2588(2)	0.0325(2)	0.5498(7)	0.0261(6)
N(6)	0.3025(2)	0.0915(2)	0.7075(6)	0.0277(5)
N(7)	−0.0126(2)	0.0415(2)	0.6528(6)	0.0411(7)
N(8)	0.3270(2)	−0.0107(2)	0.4118(6)	0.0364(6)
N(9)	0.2693(2)	0.1868(2)	1.0167(6)	0.0303(6)
C(10)	0.3712(2)	0.2127(2)	1.0701(6)	0.0273(6)
N(11)	0.3865(2)	0.2615(2)	1.2488(6)	0.0357(7)
N(12)	0.4498(2)	0.1895(2)	0.9480(6)	0.0416(7)
N(13)	0.1301(2)	0.3419(2)	1.4530(6)	0.0328(6)
O(1)	0.0533(2)	0.3898(2)	1.5383(6)	0.0503(6)
O(2)	0.2224(2)	0.3575(2)	1.5181(6)	0.0457(6)
O(3)	0.1157(2)	0.2756(2)	1.3003(6)	0.0463(6)

Table 3. *Selected Bond Lengths* [Å] *and Angles* [°] *of G4NO3* (e.s.d.'s in parenthesis)

Atoms	Length	Atoms	Length	Atoms	Length
C(1)–N(2)	1.332(3)	C(3)–N(7)	1.339(3)	C(10)–N(11)	1.311(4)
C(1)–N(6)	1.325(4)	C(5)–N(4)	1.334(3)	C(10)–N(12)	1.301(4)
C(1)–N(9)	1.387(4)	C(5)–N(6)	1.345(4)	N(13)–O(1)	1.235(3)
C(3)–N(2)	1.350(4)	C(5)–N(8)	1.339(4)	N(13)–O(2)	1.248(3)
C(3)–N(4)	1.343(4)	C(10)–N(9)	1.357(3)	N(13)–O(3)	1.258(3)

Table 3 (cont.)

Atoms	Angle	Atoms	Angle
N(6)–C(1)–N(9)	118.8(2)	N(4)–C(5)–N(6)	125.6(3)
N(2)–C(1)–N(9)	114.0(3)	C(1)–N(6)–C(5)	114.0(2)
N(2)–C(1)–N(6)	127.2(3)	C(1)–N(9)–C(10)	128.7(3)
C(1)–N(2)–C(3)	113.3(3)	N(9)–C(10)–N(12)	120.9(3)
N(2)–C(3)–N(7)	116.7(3)	N(9)–C(10)–N(11)	117.3(3)
N(4)–C(3)–N(7)	117.7(3)	N(1)–C(10)–N(12)	121.9(3)
N(2)–C(3)–N(4)	125.6(3)	O(2)–N(13)–O(3)	119.3(3)
C(3)–N(4)–C(5)	114.3(2)	O(1)–N(13)–O(3)	120.0(2)
N(6)–C(5)–N(8)	116.0(3)	O(1)–N(13)–O(2)	120.7(3)
N(4)–C(5)–N(8)	118.5(3)		

Results and Discussion. – The six-membered ring of the triazine moiety is almost planar, the maximum deviation from the best plane through the ring atoms is only – 0.009(3) Å. The N-atoms of the amino groups attached to the triazine ring, N(9), N(8), and N(7), deviate from this plane by –0.049(3), –0.038(3), and 0.023(3) Å, respectively. The torsion angle C(1)–N(9)–C(10)–N(12) of 4.3(5)° shows that the terminal guanidinium part deviates slightly from the molecular plane of the triazine ring. As observed in triazine [10] and in many substituted triazine derivatives [11–14], the endocyclic angles at the N-atom are much smaller (113.9(3)°) than the corresponding angles at the C-atom (126.1(3)°).

The crystal structure of G4NO3 is based on the space group $Pna2_1$. It is built from infinite planar ribbons of alternating, H-bonded anions and cations (*Fig. 1*), generated by a combination of the *n*-glide and a translation operation along *c* and extending in the [0 1 ± 2] direction. These ribbons are connected by a pair of H-bonds N(9)···O(3), N(11)···O(2) on one side and a single H-bond N(8)···O(2) on the other side of the ions (*Table 4*). The intramolecular H-bond N(12)···N(6) further stabilizes the ribbon. The stacking of ribbons by translation along *c* leads to layers extending in the *b*, *c*

Table 4. *Planar Ribbon Contacts and Interlayer Contacts*

	D···A	H···A	D–H···A	Sym. code
Planar Ribbon Contacts				
N(12)···N(6)	2.667(4)	2.020	131.3	1
N(9)···O(3)	2.862(4)	2.004	175.1	1
N(11)···O(2)	2.921(4)	2.083	164.5	1
N(8)···O(2)	3.042(5)	2.196	167.7	6
Interlayer Contacts through Corrugated Ribbon				
N(7)···N(2)	3.068(5)	2.226	166.4	2
N(7)···N(4)	3.088(4)	2.403	137.1	3
Interlayer Contacts through NO_3				
N(11)···O(3)	2.927(3)	2.168	147.0	5
N(8)···O(1)	3.247(4)	2.444	155.6	4

1 x, y, z
2 $-x, -y, z-1/2$
3 $-x, -y, z+1/2$
4 $x+1/2, -y+1/2, z-1$
5 $x+1/2, -y+1/2, z$
6 $-x+1/2, y+1/2, z+1/2+1$

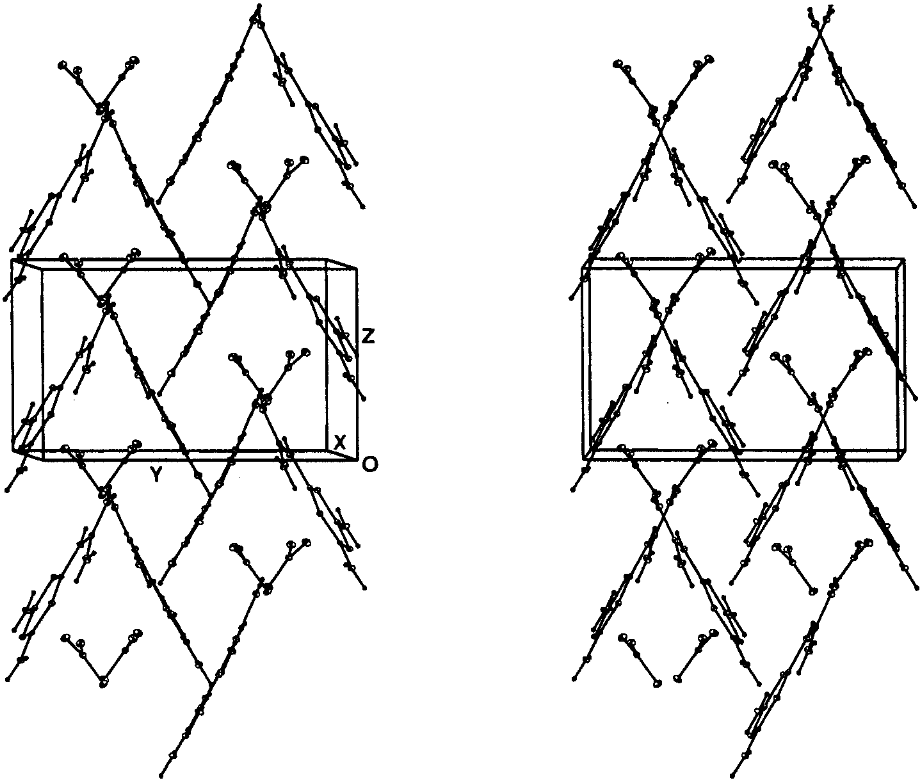

Fig. 2. *Stereoview of the stacking of the ribbons of G4NO3 viewed down the* a*-axis in the short direction of the molecular tape.* Consecutive stacks are inclined by 58.5°.

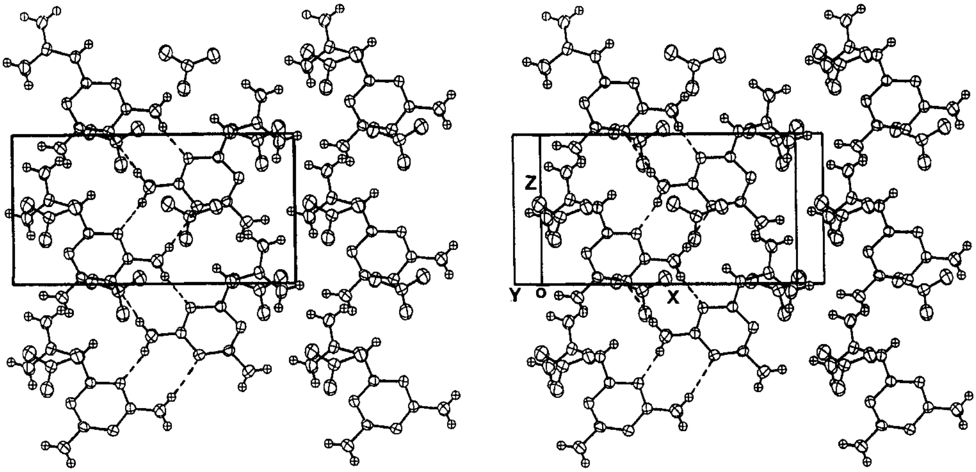

Fig. 3. *Stereoview of G4NO3 viewed down the* b*-axis, showing H-bond contacts between consecutive stacks of layers.* H-Bonds between the melamine fragments at $x \sim 0.5$ (dashed lines) and interlayer contacts mediated by NO_3^- at $x \sim 1.0$.

plane and to rows of melamine fragments and nitrate groups alternating in the [0 2 ∓ 1] direction (*Fig. 2*). In consecutive layers along *a*, the ribbons are inclined by 58.5°. *Fig. 2* depicts a projection of two such layers as viewed from the short direction of the molecular tape. The layers are connected by an intricate network of bonds. The contacts between neighbouring layers are essentially of two kinds, both localized about different 2_1 screw axes (*Fig. 3*). One kind involves H-bonds between N(7) and N(2) of one cation and N(4) and N(7), respectively, of the next. These H-bonds are repeated by the twofold screw operation along *c* leading to another, but this time corrugated ribbon of H-bonds (*Fig. 3*, $x \sim 0.5$). The same motif is found in the crystal packing of melamine itself [10]. The second type of contact between layers is mediated by H-bonds connecting the nitrate groups in one layer to amino groups in the other (N(8)···O(1) and N(11)···O(3); *Fig. 3*, $x \sim 1$).

In summary, the packing of G4NO3 displays features of both of its close relatives: *1*) a pair of H-bonds between NO_3^- and the guanidinium fragment and parallel stacking of these planar motifs as in guanidinium nitrate [6]. *2*) Corrugated ribbons of the melamine fragments as in melamine itself [10].

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