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MOLECULAR STRUCTURE OF LOW TEMPERATURE FORM OF TRIAMINOGUANIDINIUM NITRATE (TAGN)

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A rigid-body motion study of triaminoguanidinium nitrate (TAGN) was initiated originally in order to determine if nitrate ion libration might be responsible for the TAGN fast burning rate. A low temperature polymorph of TAGN was discovered by this laboratory during the course of this rigid-body motion study. Continuation of this libration study in the lower temperature regime, however, necessitated understanding the molecular structure of the low temperature form of TAGN. To do this a signal-crystal x-ray diffraction structure determination of the low temperature form was undertaken. The crystal structure was determined including space group, lattice parameters, atomic coordinates and temperature factors, hydrogen bonding, and density.

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INTRODUCTION

Triaminoguanidinium nitrate (TAGN) has such an extremely fast burning rate that TAGN can be added to a solid propellant to enhance the overall burning rate of the propellant. For example, the burning rates of high energy RDX propellants can be increased markedly without substantial decrease in energy by the addition of TAGN. The mechanism, however, for this fast burning rate is not yet understood. In fact, there is speculation as to whether this property is a macroscopic, microscopic, or molecular phenomenon. A room temperature x-ray crystallographic study of TAGN was initiated by this laboratory (ref 1) in an attempt to ascertain if this behavior could be explained at the molecular level.

The resulting crystal structure determination revealed that the ions in TAGN formed a layered structure with electrostatic and hydrogen bonding forces operating within the layers, and weak molecular and hydrogen bonding forces holding the layers together. The interlayer distance is 3.3 A. These weakly bonded molecular layers result in macroscopic cleavage planes which are normal to the needle axis of the crystal. This molecular packing causes the TAGN crystal to be quite brittle.

Although this molecular arrangement explains the friability of TAGN crystals, it does not readily explain the burning rate. If burning rate varies inversely with particle size, one could certainly argue that easy crystal breakup into smaller fragments might enhance burning. However, not all oxidizers follow this inverse burning rate relationship. Certain organic orxidizers have burning rates which increase with particle size. Moreover, large single crystals of TAGN burn extremely fast. This suggests that something peculiar to TAGN itself is responsible for this effect.

It was also found in the structure determination that the thermal amplitudes of the nitrate ion oxygen atoms were excessively large. This indicated oxygen atom disorder in the nitrate ion which could be either static (positional) or dynamic disorder (rigid body motion). On the basis of both shortened N--O bond lengths and the large thermal amplitudes, it was suggested that the nitrate ion could be a hindered rigid rotor (ref 2). A simple analogy is a pinwheel that oscillates rather than freely rotates. A similar suggestion was also made in a subsequent neutron diffraction study (ref 3). If the hindered rotor model is correct at room temperature, then it is reasonable to expect free rotation to commence at some higher temperature and oscillatory motion to cease at some correspondingly lower temperature.

The TAGN crystal structure was later redetermined using positionally disordered nitrate ions in an effort to ascertain if quiescent nitrate ions would also account for the observed excessive thermal amplitudes. Although the results were not definitive, they did suggest that nitrate ion librational motion was probably the better explanation for the disorder observed at room temperature (ref 4).

In a subsequent low temperature examination of TAGN (ref 5) differential scanning calorimetry (DSC) and heat capacity measurements revealed a second order transition at -10°C. X-ray powder diffraction data revealed that TAGN undergoes a phase transition at approximately -10°C. Cessation of nitrate anion libration would produce a second order transition. Second order phase transitions can be caused by small structural changes.

It was also determined that the TAGN unit-cell volume below -10°C is four times larger than it is at room temperature. This could be a potential cause for concern, because if the low temperature form of TAGN has a different density, propellants formulated with TAGN could be adversely affected. Specifically, if the thermally induced TAGN phase transition results in a different density polymorph, thermal cycling of a TAGN propellant through the transition temperature could produce cracks in propellant grains. In addition, military propellants must be able to perform at -40°C which is well below the transition temperature.

To investigate the molecular structure of the low temperature polymorph, a single-crystal x-ray diffraction study of TAGN at -104°C was initiated. The effect of low temperature on the TAGN molecular and crystal structure and density is described in this report.

DATA COLLECTION

A colorless acicular crystal of TAGN, approximately 0.01 x 0.15 x 0.30 mm was mounted with it long axis parallel with the phi axis of the goniometer. All data were collected at 104(1)°C (169 K) using mo Kα x-radiation ($\lambda = 0.71073$ Å) on an Enraf-Nonius CAD computer controlled kappa axis diffractometer equipped with a graphite crystal incident-beam monochromater*.

The cell constants and orientation matrix for x-ray diffraction data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in the range of $4 < \theta < 8$.

A total of 2622 reflections were collected, of which 2140 were unique and systematically absent. Lorentz and polarization corrections were made to the data. Although no correction was made for absorption, a secondary extinction correction was made to each reflection (ref 6).

The heavy atom positions were determined with direct methods (ref 7) using 168 reflections. The hydrogen atoms were located with difference Fourier techniques. The structure was refined with full-matrix least squares until convergence was attained

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*X-ray diffraction collected by Molecular Structure Corporation, The Woodlands, TX.

using 994 reflections with intensity values equal or exceeding two times their standard deviations. The nonhydrogen atoms were refined anisotropically and the hydrogen atoms were refined with fixed isotropic thermal parameters.

DISCUSSION

The conformation of the triaminoguanidinium (TAG) cations and nitrate anions in the low temperature polymorph and their respective atoms numbering scheme are presented in figure 1. The disordered nitrate anion is compared to the ordered nitrate anion in figure 2. The molecular packing at room temperature viewed down the c axis of the unit cell and at low temperature viewed down the a axis of the unit cell are shown in figures 3 and 4, respectively. The similarity between the structures of the two polymorphs when viewed down the c axis by comparing the unit cell of low temperature polymorph with four room temperature TAGN unit cells stacked on the bc plane is illustrated in figure 5.

At -104°C, TAGN exists in the orthorhombic space group Pbca with a = 33.053(10), b = 12.573(2), and c = 6.573(4) Å (table 1). Above -10°C, TAGN transforms into the orthorhombic space group Pbcm with unit cell dimensions measured at 23°C of a = 8.366(2), b = 12.649(2), and c = 6.556(1) Å. The density of the low temperature form is 1.63 g/cm^3 and the density of the room temperature form is 1.60 g/cm^3 (ref 4). Despite the fact that the unit-cell volume at low temperature is almost quadruple the volume of the unit cell at room temperature, the densities of the two polymorphs are quite similar.

To understand why the density of TAGN remains virtually unchanged through this phase transition, one must examine and compare the molecular packing of both phases. The room temperature polymorph has an asymmetric group which contains one TAG cation and one nitrate anion. Four asymmetric groups are distributed over four special positions on mirror planes in the Pbcm space group for a total of four TAGN molecules per unit cell.

The low temperature polymorph contains eight asymmetric groups, each of which contains two TAG cations and two nitrate anions, which are distributed over eight general lattice positions in the Pbca space group for a total of 16 TAGN molecules per unit cell. Thus, at low temperature the unit cell volume increases by a factor of four, but the number of TAGN molecules filling the unit cell also increases by a factor of four. As a result, the density of both polymorphs is approximately the same.

Description of the TAG Cations

In the low temperature form of TAGN the asymmetric group contains two TAGN molecules (table 2) which will be referred to as TAGN(1) and TAGN(2). The bond lengths in table 3 reveal no significant differences between the respective heavy-atom bond lengths in the two TAG cations. These values are also consistent with the bond length reported for the room temperature polymorph (refs 1,2, and 4).

In TAG(1) the mean C--N and N--N bond lengths are 1.326(8) and 1.417(8) Å, respectively, and in TAG(2) these bond lengths are 1.324(9) and 1.417(8) Å, respectively. The mean N-C-N bond angle for both TAG(1) and TAG(2) is 120 deg(6) (table 4). The heavy atoms and imino hydrogen atoms in both TAG cations approach planarity with the largest heavy atom [N(5)] deviation from the least-squares plane of 0.018(5) Å and the largest imino hydrogen atom [H(7)] deviation of 0.16(6)Å for TAG(1). For TAG(2), the largest heavy atom [N(8)] deviation is 0.044(5) Å and the largest imino hydrogen atom deviation is 0.14(6) Å. The conformation of both planar cations (fig. 1) is approximately the same and approaches C_{3h} molecular symmetry displayed at room temperature. Thus, the two TAG cations in the asymmetric group are conformationally identical.

At room temperature the TAG cation is strictly planar displaying C_{3h} molecular symmetry with the heavy atoms and the imino hydrogen atoms constrained by space group symmetry to positions on mirror planes parallel to (001). Each amino hydrogen atom-pair is bisected by this mirror plane.

Description of the Nitrate Anions

In contrast to the TAG cations, the two nitrate planar anions in the asymmetric group are structurally different. These two structurally different nitrate anions referred to as N(1) and N(2) are depicted in figure 2. This is quite different from the room temperature polymorph which has only one nitrate anion.

The N-O bonds of N(1) (table 3) are equivalent with a mean value of 1.253(6). Furthermore, N(1) is not disordered. N(1) has D_{3h} molecular symmetry and none of its oxygen atoms display abnormally large thermal amplitudes (table 2). In addition, none of the N--O bond lengths are foreshortened as is observed at room temperature.

In contrast to N(1), N(2) does not exhibit D_{3h} molecular symmetry. There is, however, a pseudo 3-fold axis normal to the nitrogen atom which produces three nonequivalent N-O bonds with lengths of 1.269(7), 1.223(7), and 1.239(7) Å for N(14)-O(4), N(14)-O(5), and N(14)-O(6), respectively. In this case two N-O bonds are foreshortened, but not to the same extent as found at room temperature. N(2) is disordered as revealed by the large oxygen atoms thermal amplitudes (table 2). However, these thermal amplitudes are not as large as those observed at room temperature which indicates that the N(2) disorder is not as great as the disorder observed at room temperature. This suggests that disorder or libration decreases with falling temperature.

DESCRIPTION OF THE MOLECULAR STRUCTURE

In general, the low temperature form structure resembles the structure at room temperature. The most apparent differences between the two polymorphs are in the unit-cell volumes and nitrate anion disorder. The low temperature structure can best be understood by comparing it with the structure of the room temperature form.

Room Temperature Structure

The structure consists of layers of TAG cations and nitrate anions positioned in mirror planes normal to the c axis which are located at ±1/4 c. The planar TAG cation (heavy atoms and imino hydrogen atoms) is coplanar with the mirror plane and the planar, but disordered nitrate anion is bisected by the mirror plane with the central nitrogen atom and one oxygen atom located in the mirror plane. This structure is presented in figure 3 in which the nitrate anion disorder is represented by six statistical oxygen atoms distributed about the central nitrogen atom.

Within the layer, each ion has three oppositely charged nearest-neighbor ions. The plane of the TAG cation is oriented normal to the plane of nitrate anion. In addition to this ionic bonding scheme, each TAG cation is also hydrogen bonded through two imino hydrogen atoms to two nitrate anions. It must be emphasized that only one oxygen atom, which is located in the mirror plane, is involved in the imino group hydrogen bonding. This essentially forms hydrogen bond bridges between adjacent TAG cations.

In the interlayer packing scheme, TAG cations are stacked in adjacent layers almost directly over one another along the c axis separated by approximately 3.3 Å. The nitrate ions are also stacked over one another along the c axis, but in this case they are in alternate layers separated by 6.6 Å. Furthermore, each TAG cation is also hydrogen bonded through one amino hydrogen atom to one nitrate anion in the adjacent lower layer and one amino hydrogen atom to one nitrate anion in the adjacent higher layer. In this case, only oxygen atoms that are off the mirror plane are involved in the group amino hydrogen bonding.

Low Temperature Structure

At -104°C (fig. 4), TAGN consists of puckered layers of TAGN. The mean plane of each puckered layer is normal to the c axis. The planes of the TAG cations are not coplanar with the layer, but rather are tilted with respect to each other and to the layer mean plane. The nitrate anion N(1) is oriented 1.8 deg to N(2), while the TAG(1) and TAG(2) cations are tilted 19.7 deg with respect to each other. TAG(1) is oriented 91.6 deg to the plane of N(1) and 93.3 deg to N(2). Conversely, TAG(2) is oriented 84.6 deg to N(2) and 82.8 deg to N(1).

Within each layer both TAG cations are surrounded by three hydrogen bonded nitrate anions (table 5). TAG(1) is hydrogen bonded through imino group hydrogen atoms to one nearest-neighbor ordered nitrate anion [N(3)-H(4) . . .O(2), 2.882(7) Å] and to one nearest-neighbor disordered nitrate anion [N(1)-H(1) . . .O(4), 2.886(8) Å]. There is also a weaker TAG(1) imino group hydrogen bond interaction with the disordered nitrate anion [N(5)-H(7) . . .O(6), 2.959(8) Å]. Each TAG(2) is hydrogen bonded through imino group hydrogen atoms to one nearest-neighbor disordered nitrate anion [N(9)-H(13) . . .O(4), 2.861(8) Å] and to two nearest-neighbor ordered nitrate anions [N(7)-H(10) . . .O(2), 2.903(8) Å and N(11)-H(16) . . .O(1), 2.926(8) Å].

These imino group hydrogen/nitrate oxygen atom interactions, result in oxygen atom bridges between adjacent TAG cations. O(2) bridges TAG(1) and TAG(2) and O(4) bridges TAG(1) and TAG(2). This is the same hydrogen-bonded oxygen bridge scheme observed at room temperature.

Interlayer oxygen bridges are also formed between imino and amino hydrogen atoms of both TAG cations and both nitrate anions. O(6) from the disordered nitrate anion forms a hydrogen bonded oxygen bridge between the imino hydrogen atom of TAG(1) in one layer [N(5)-H(7) . . .O(6), 2.959(8) Å] and the amino hydrogen atom of TAG(1) in the other layer [N(6)-H(9) . . .O(6), 3.054(8) Å]. O(1) of the ordered nitrate anion forms an oxygen bridge with the imino hydrogen atom of TAG(2) in one layer [N(11)-H(16) . . .O(1), 2.926(8) Å] and an amino hydrogen atom of TAG(2) in the other layer [N(12)-H(18) . . .O(1), 3.120 Å]. O(5) of the disordered nitrate anion forms an oxygen bridge between a TAG(1) amino hydrogen atom in one layer [N(4)-H(6) . . .O(5), 3.098(8) Å] and TAG(1) amino hydrogen atom in the adjacent layer [N(6)-H(8) . . .O(5), 3.107(8) Å]. O(3) of the ordered nitrate anion also forms an interlayer oxygen bridge between the TAG(2) amino hydrogen atom [N(1)-H(14) . . .O(3), 3.102(8) Å] and TAG(2) amino hydrogen atom [N(12)-H(17) . . .O(3), 3.098(8) Å]. This results in an infinite three-dimensional network of hydrogen-bonded puckered layers of TAGN.

A comparison of a single unit cell at low temperature with four unit cells at room temperature stacked on top of each other on the bc plane is presented in figure 5. Nitrate anion disorder is depicted with six statistical oxygen atoms distributed around the central nitrogen atom. Visual inspection of figure 5 reveals a conspicuous similarity between the structures. The only apparent difference between the two structures is the lack of disorder in one half of the nitrate anions in the unit cell at low temperature. Since the TAG cation and nitrate anion orientation differences between the two forms are not obvious in this illustration, both structures in figure 5 would appear to be the same if all the nitrate ions in the low temperature form were disordered.

The degree of disordered in the disordered nitrate anion is less at low temperature than it is at room temperature. This indicates that the average degree of nitrate anion disorder decreases with decreasing temperature. If this disorder is due to rigid-body motion (libration) then the average oscillation amplitude should continually decrease with decreasing temperature. Assuming that this disorder is, indeed, librational and that there is a statistical distribution of disorder over TAGN crystal space, there will occur at some temperature a point where half the nitrate ions are quiescent (ordered) and half are librating with a smaller mean amplitude. At this point (-10°C), the TAGN space group symmetry changes because there are equal concentrations of two unique nitrate anions. These changes in disorder result in different hydrogen bonding interactions which cause small positional changes.

Carrying this thesis to its logical conclusions, there should be some lower temperature at which all the nitrate ions are quiescent. This would result in a different TAGN crystal structure containing only one unique nitrate anion.

Very small changes in the TAGN structure are responsible for the transition from Pbcm to Pbca symmetry observed at -10°C. This behavior, typical of a second order transition, agrees with the heat capacity data which also showed a second order transition at this temperature (ref 5).

CONCLUSIONS

1. The phase transition at -10°C is a second order transition.

2. At -10°C, half of the nitrate ions librate as rigid bodies and half are quiescent with their individual atoms vibrating independently with a smaller average thermal amplitude.

3. The densities of the two forms of triaminoguanidinium nitrate (TAGN) are approximately the same down to a temperature of -104°C. Therefore, this phase change should not cause propellant grain cracking or any other mechanical problems in TAGN propellant formulations with respect to temperature cycling.

Table 1. Crystal data with estimated standard deviations in parentheses

Molecular formula	CH9N703
Formula weight	167.13
Crystal system	Orthorhombic
Space group	Pbca
a	33.058(10) Å
b	12.573(2) Å
c	6.541(4) Å
V	2718.7 $Å^3$
Z	16
D	1.63 g/cm^3
λ (Mo Kα)	0.71072 A
u (M0 Kα)	1.6 cm^{-1}
F (000)	1408
T	169(1) K
R	0.053
Rw	0.061

Table 2. Atomic coordinates and equivalent temperature factors and their estimated standard deviations in paratheses

Atom	x/a	y/b	z/c	B (eqv)
C(1)	0.0717(2)	0.2618(5)	0.2354(8)	1.2(1)
N(1)	0.0972(1)	0.1815(4)	0.2146(7)	1.5(1)
N(2)	0.1384(1)	0.2045(4)	0.1756(8)	1.5(1)
N(3)	0.0841(1)	0.3612(4)	0.2215(8)	1.7(1)
N(4)	0.0533(1)	0.4445(4)	0.2402(8)	1.6(1)
N(5)	0.0226(1)	0.2415(4)	0.2475(7)	1.4(1)
N(6)	0.0199(1)	0.1342(4)	0.2858(7)	1.8(1)
H(1)	0.091(2)	0.120(5)	0.210(9)	3.0
H(2)	0.146(2)	0.162(5)	0.065(9)	3.0
H(3)	0.155(2)	0.167(5)	0.270(9)	3.0
H(4)	0.106(2)	0.384(5)	0.193(9)	3.0
H(5)	0.064(2)	0.490(5)	0.345(9)	3.0
H(6)	0.057(2)	0.470(5)	0.120(9)	3.0
H(7)	0.019(2)	0.290(5)	0.285(9)	3.0
H(8)	0.011(2)	0.130(5)	0.406(9)	3.0
H(9)	0.002(2)	0.138(5)	0.172(9)	3.0
C(2)	0.3200(2)	0.2569(5)	0.1893(8)	1.4(1)
N(7)	0.3457(1)	0.1758(4)	0.2109(7)	1.4(1)
N(8)	0.3872(1)	0.2024(4)	0.2331(8)	1.7(1)
N(9)	0.3328(1)	0.3551(4)	0.2082(8)	1.5(1)
N(10)	0.3046(1)	0.4377(4)	0.1784(8)	1.9(1)
N(11)	0.2814(1)	0.2367(4)	0.1521(8)	1.6(1)
N(12)	0.2687(1)	0.1292(4)	0.1380(8)	1.9(1)
H(10)	0.340(2)	0.100(9)	0.175(9)	3.0
H(11)	0.399(2)	0.180(5)	0.125(9)	3.0
H(12)	0.395(2)	0.167(5)	0.342(9)	3.0
H(13)	0.360(2)	0.369(5)	0.204(9)	3.0
H(14)	0.309(2)	0.476(5)	0.058(9)	3.0
H(15)	0.307(2)	0.489(5)	0.275(9)	3.0
H(16)	0.263(2)	0.284(5)	0.145(9)	3.0
H(17)	0.250(2)	0.117(5)	0.247(9)	3.0
H(18)	0.254(2)	0.118(5)	0.026(9)	3.0
N(13)	0.1894(1)	0.0965(4)	0.6435(7)	1.4(1)
O(1)	0.2114(1)	0.1408(4)	0.5121(6)	2.3(1)
O(2)	0.1590(1)	0.0453(3)	0.5852(6)	1.80(9)
O(3)	0.1973(1)	0.1049(4)	0.8297(6)	2.3(1)
N(14)	0.4413(1)	0.0997(4)	0.7174(8)	1.6(1)
O(4)	0.4103(1)	0.0459(4)	0.6676(9)	3.6(1)
O(5)	0.4505(1)	0.1134(4)	0.8966(7)	2.9(1)
O(6)	0.4616(1)	0.1380(4)	0.5763(7)	3.1(1

Table 3. Bond lengths in Å with estimated standard deviations in parentheses

Bond	Length, Å	Bond	Length, Å
C(1)--N(1)	1.323(9)	C(2)--N(7)	1.335(9)
C(1)--N(3)	1.319(8)	C(2)--N(9)	1.312(9)
C(1)--N(5)	1.340(8)	C(2)--N(11)	1.325(8)
N(1)--N(2)	1.416(8)	N(7)--N(8)	1.420(8)
N(3)--N(4)	1.419(8)	N(9)--N(10)	1.410(7)
N(5)--N(6)	1.415(8)	N(11)--N(12)	1.418(8)
N(1)--H(1)	0.80(8)	N(7)--H(10)	1.00(8)
N(3)--H(4)	0.79(4)	N(9)--H(13)	0.93(7)
N(5)--H(7)	0.76(7)	N(11)--H(16)	0.86(7)
N(2)--H(2)	0.94(7)	N(8)--H(12)	0.86(7)
N(2)--H(3)	0.94(7)	N(8)--H(12)	0.87(7)
N(4)--H(5)	0.94(7)	N(10)--H(14)	0.95(7)
N(4)--H(6)	0.85(7)	N(10)--H(15)	0.90(7)
N(6)--H(8)	0.85(7)	N(12)--H(17)	0.96(7)
N(6)--H(9)	0.94(7)	N(12)--H(18)	0.89(7)
N(13)--O(1)	1.257(7)	N(14)--O(4)	1.269(7)
N(13)--O(2)	1.253(6)	N(14)--O(5)	1.223(7)
N(13)--O(3)	1.1.250(6)	N(14)--O(6)	1.239(7)

Table 4. Bond angles in degrees and their estimated standard deviations in parentheses

Atom	Angle, deg	Atoms	Angle, deg
N(1)-C(1)-N(3)	121.2(6)	N(7)-C(2)-N(9)	120.2(6)
N(1)-C(1)-N(5)	119.3(6)	N(7)-C(2)-N(11)	119.2(7)
N(3)-C(1)-N(5)	119.5(6)	N(9)-C(2)-N(11)	120.7(6)
C(1)-N(1)-N(2)	118.5(6)	C(2)-N(7)-N(8)	116.5(6)
C(1)-N(3)-N(4)	119.1(6)	C(2)-N(9)-N(10)	117.8(6)
C(1)-N(5)-N(6)	118.5(6)	C(2)-N(11)-N(12)	118.7(6)
C(1)-N(1)-H(1)	125.(6)	C(2)-N(7)-H(10)	125.(4)
C(1)-N(3)-H(4)	130.(6)	C(2)-N(9)-H(13)	120.(5)
C(1)-N(5)-H(7)	112.(6)	C(2)-N(11)-H(16)	125.(5)
N(1)-N(2)-H(2)	106.(4)	N(7)-N(8)-H(11)	106.(5)
N(1)-N(2)-H(3)	109.(4)	N(7)-N(8)-H(12)	103.(5)
N(3)-N(4)-H(5)	108.(4)	N(9)-N(10)-H(14)	115.(4)
N(3)-N(4)-H(6)	99.(5)	N(9)-N(10)-H(15)	111.(5)
N(5)-N(6)-H(8)	103.(5)	N(11)-N(12)-H(17	107.(4)
N(5)-N(6)-H(9)	96.(5)	N(11)-N(12)-H(18)	112.(4)
H(2)-N(2)-H(3)	94.(6)	H(11)-N(8)-H(12)	112.(8)
H(5)-N(4)-H(6)	115.(7)	H(14)-N(10)-H(15)	100.(6)
H(8)-N(6) H(9)	121.(7)	H(17)-N(12)-H(18)	104.(6)
O(1)-N(13)-O(2)	118.9(6)	O(4)-N(14)-O(5)	121.4(6)
O(1)-N(13)-O(3)	120.5(6)	O(4)-N(14)-O(6)	116.9(6)
O(2)-N(13)-O(3)	120.5(6)	O(5)-N(14)-O(6)	121.6(6)

Table 5. Details of hydrogen bonding with bond lengths in Å, bond angles in degrees, and their estimated standard deviation in parentheses

N(x)-H(y)....O(z)	N(x)-H(y)	H(y)....C(z)	N(x)....O(Z)	Angle
Imino TAG(1) H Bonds				
N(1)-H(1)...O(4)	0.80(8)	2.10(8)	2.886(8)	167.(4)
N(3)-H(4)...O(2)	0.79(7)	2.10(8)	2.882(7)	170.(4)
N(5)-H(7)...O(6)	0.76(7)	2.37(7)	2.959(8)	135.(4)
Amino TAG(1) H Bonds				
N(4)-H(6)...O(5)	0.85(7)	2.33(8)	3.098(8)	150.(4)
N(6)-H(9)...O(6)	0.94(7)	2.11(7)	3.054(8)	161.(4)
N(6)-H(8)...O(5)	0.85(7)	2.38(7)	3.107(8)	143.(4)
Imino TAG(2) H Bonds				
N(7)-H(10)...O(2)	1.00(8)	1.92(8)	2.903(8)	155.(4)
N(9)-H(13)...O(4)	0.93(7)	1.98(7)	2.861(8)	157.(4)
N(11)-H(16)..O(1)	0.86(7)	2.12(7)	2.926(8)	155.(4)
AMINO TAG(2) H Bonds				
N(10)-H(14)..O(3)	0.95(7)	2.18(8)	3.102(8)	163.(4)
N(12)-H(18)..O(3)	0.89(7)	2.29(7)	3.120(8)	155.(4)
N(12)-H(17)..O(1)	0.96(7)	2.17(7)	3.098(8)	162.(4)

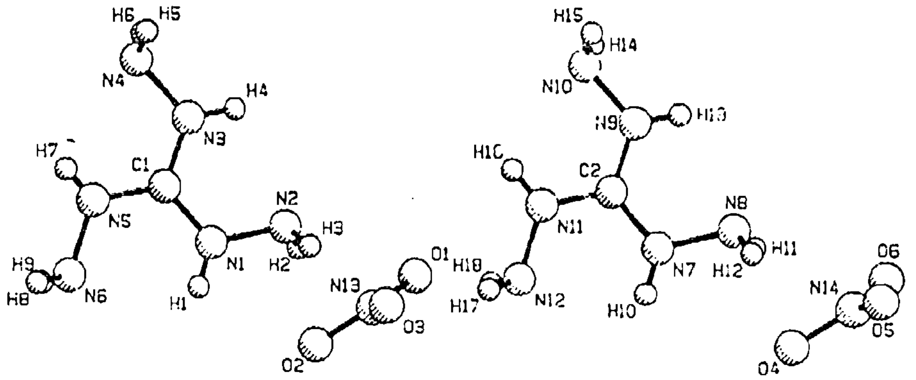
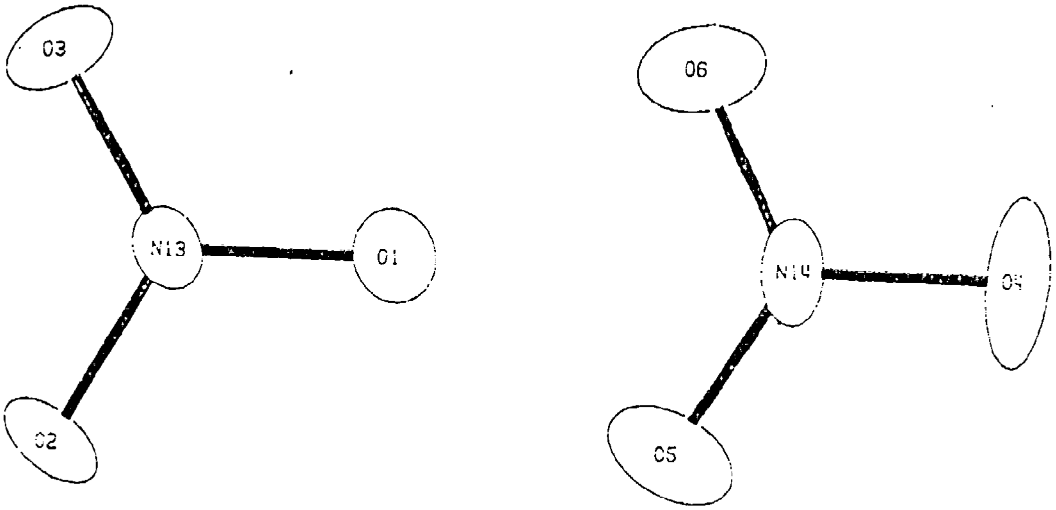


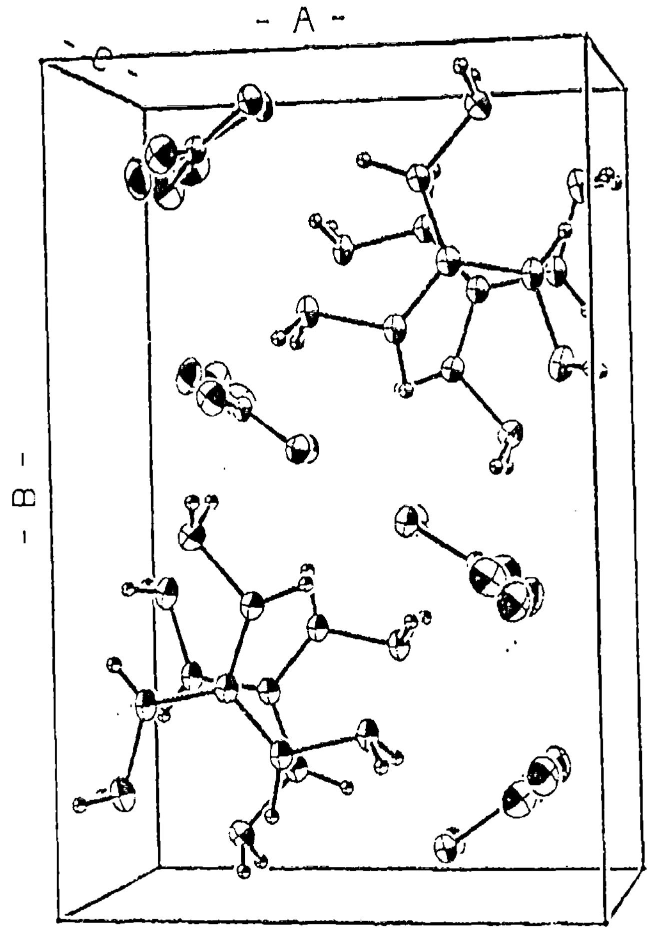
Figure 1. TAGN asymmetric group and atomic numbering scheme



(a) Nitrate anion N(1)

(b) Nitrate anion N(2)

Figure 2. Comparison of nitrate anions



Nitrate anion disorder shown in six statistical oxygen atoms distributed around central nitrogen atom.

Figure 3. Unit cell of room temperature TAGN polymorph viewed down the [illegible] axis

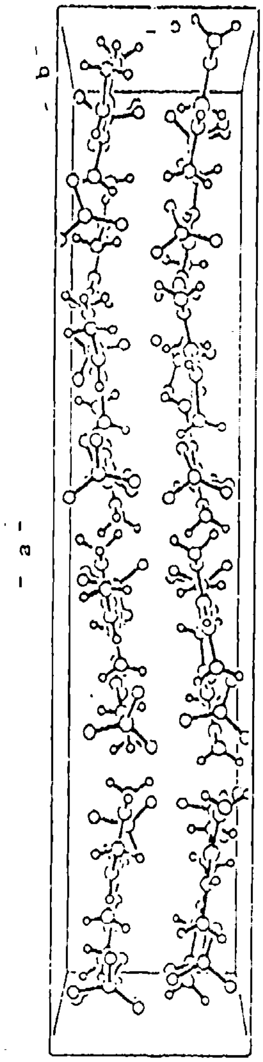
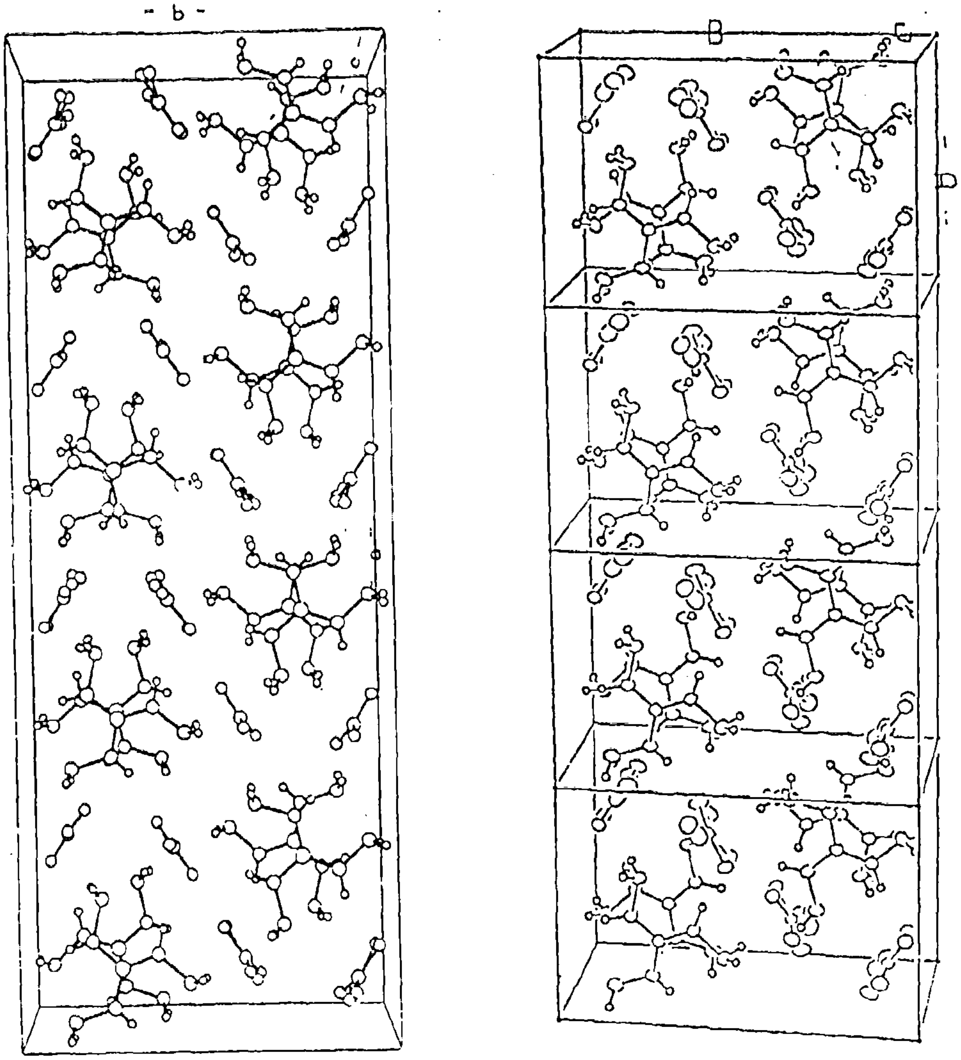


Figure 4. Unit cell of low temperature TAGN polymorph viewed down the a axis



(a) Low temperature polymorph viewed down the c axis. N(2) has six statistical oxygen atoms distributed around its central nitrogen atom.

(b) Four unit cells of room temperature polymorph stacked on the bc plane and viewed down the c axis.

Figure 5. Comparison of structures of TAGN polymorphs

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