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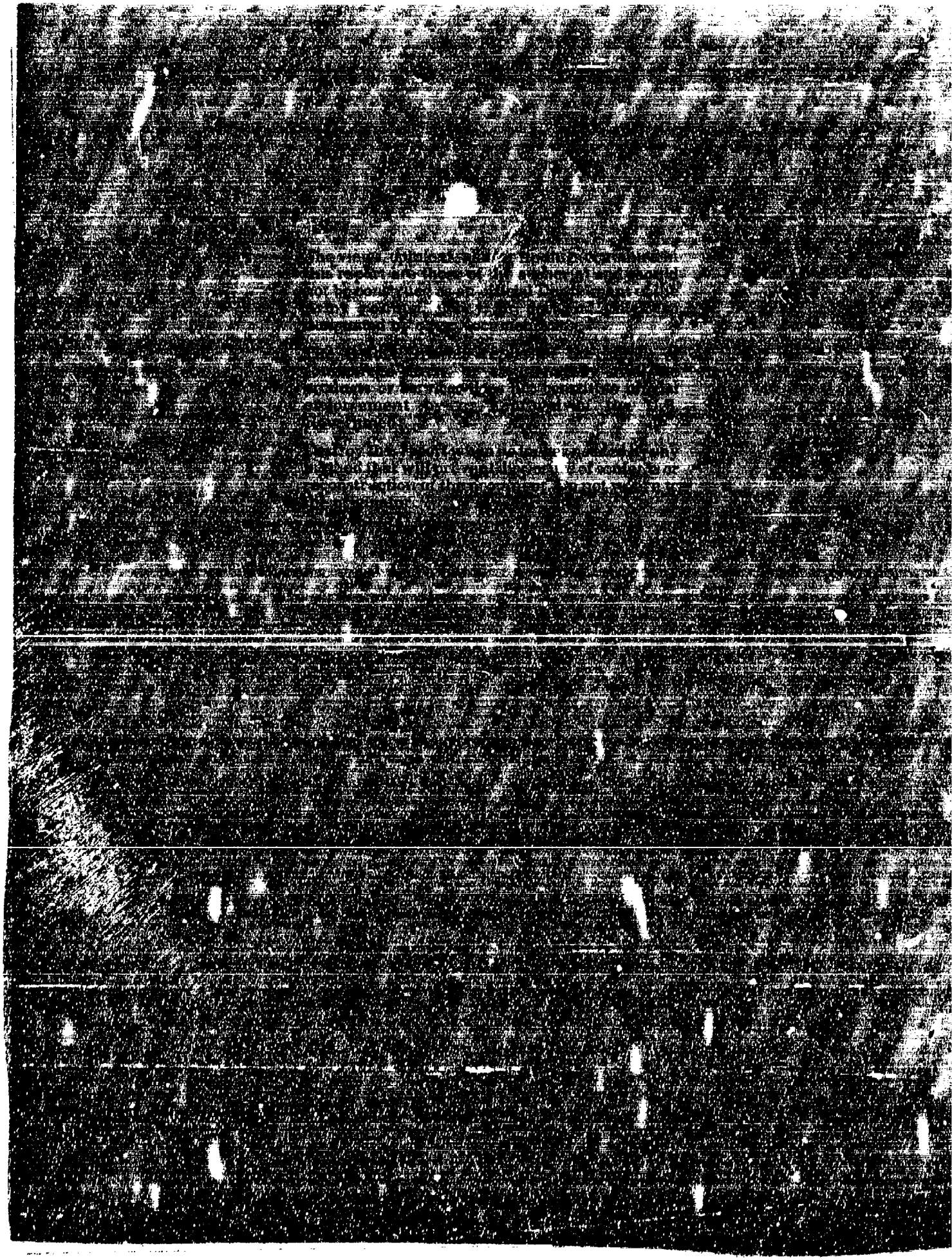

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
A new high nitrogen propellant compound, triaminoguanidinium azide nitrate (TAZN), has been discovered. Single crystal x-ray diffraction data were obtained. The crystal and molecular structure of this orthorhombic (Pbca) compound was determined. Comparisons between the structures of TAGN and TAZN are discussed with emphasis on possible hydrogen bonding.
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INTRODUCTION

Triaminoguanidinium salts (TAGX) apparently accelerate the burning rates of cyclonitramine (RDX, HMX) based propellants. The nitrate (TAGN) with its relatively low flame temperature (2600 K) has been used with RDX formulations not only to accelerate burning rates but to reduce flash and erosion. Over the years, interest in triaminoguanidinium azide (TAZ) with its low flame temperature (2308 K) has inspired propellant chemists to synthesize it.

In a metathetical method, sodium azide was reacted with $(TAG)_2\ SO_4$ to form TAZ according to the reaction

$$(TAG)_2SO_4 + 2NaN_3 \longrightarrow 2TAZ + NA_2SO_4 \qquad (1)$$

Alternately, TAZ also was prepared by reacting hydrazoic acid (HN_3) with TAGOH or TAG according to the reactions:

$$HN_3 + TAGOH \longrightarrow TAZ + H_2O \qquad (2)$$

$$HN_3 + TAG(S) \longrightarrow TAZ + H_2O \qquad (3)$$

These reactions can be safely accomplished by eluting sodium azide (NaN_3) through a protonated cation exchange column to generate HN_3 according to the reaction

$$NaN_3 + HR \longrightarrow NaR + HN_3 \qquad (4)$$

and adding it directly to the appropriate TAG compound (ref 1).

Surprisingly, it was also reported (ref 1) that samples of TAZ made by the different techniques were not identical. Samples prepared by reaction (1) had a nitrogen content of 83.06% and a density of 1.432 g/ml as opposed to 85.5% nitrogen content and a density of 1.68 g/ml for samples freshly prepared by reactions (2) and (3). Upon standing in air, the nitrogen content of samples prepared by reactions (2) and (3) drops to 83.06%. To confound the issue, both freshly prepared samples had identical IR spectra. As a consequence, it was proposed (ref 2) that these two samples might be polymorphs, but this seems unlikely because of the difference in nitrogen content.

To resolve this conflict, a single crystal x-ray diffraction study was undertaken.

EXPERIMENTAL

Sample Preparation

The sample* used in this study was prepared by eluting HN_3, prepared as shown in reaction (3), directly into a solution of TAGN, NaOH, and DMF with subsequent cooling in an acetone dry ice bath. This was previously reported (ref 2) as a very simple and direct method to prepare triaminoguanidine (TAG). The formation of TAG probably proceeds stepwise initially with formation of TAGOH

$$TAGN + NaOH \longrightarrow TAGON + Na^+ + NO_3^- \qquad (5)$$

which upon cooling in DMF dehydrates to form the basic anhydride TAG (CH_6H_8)

$$TAGOH + NaNO_3 + \xrightarrow[DMF]{} TAG + NaNO_3 + DMF \qquad (6)$$

Therefore, in theory, the introduction of HN_3 should react with both TAG and TAGOH to form TAZ.

X-ray Data Collection

A pale pink acicular crystal having the dimensions of 0.40x0.07.0.07 mm was grown from ethanol and water and mounted on a glass fiber in a random orientation. All x-ray measurements were made with an Enraf-Nonius CAD4 computer controlled, kappa axis diffractometer using CuK radiation (λ = 1.54184 A) and equipped with a graphite crystal incident-beam monochromater. All measurements were made at 23+1°C. From the systematic absences of:

okℓ k=2n+1

h0ℓ ℓ=2n+1

hk0 h=2n+1

the space group was determined to be Pbca. The lattice parameters of this orthorhombic unit are: a = 12.647(3); b = 6.573(2); and c = 16.550(7)A. The calculated x-ray density is 1.52 g/ml.

RESULTS

Elemental analysis (table 1) indicated that this compound contained 9.53% carbon, 78.17% nitrogen, 5.78% hydrogen, and unexpectedly, 6.15% oxygen. In contrast, TAZ theoretically contains 8.16% carbon, 85.71% nitrogen, and no oxygen.

---

* Sample received from G. Clark, Aerojet TACTICAL, Sacramento, CA.

The x-ray data indicated that this material was not an orthodox binary salt or a simple mixture of binary salts, but rather a single compound containing the two distinctly different anions, azide and nitrate. This disorder was caused by the replacement of a given number of anions in the structure by an equivalent number of different anions. Although this is not an unusual phenomenon and, in fact, occurs quite frequently among isomorphic species, it was unexpected in this case because of the difference in ionic shape displayed by the linear azide ion and the planar trigonal nitrate ion.

Azide and nitrate ions are randomly distributed over eight general positions in the space group (Pbca). This is equivalent to having each position filled with a statistical composite anion having the same nitrate to azide ratio (with this crystal the ratio is 50:50).

The statistical anion, a modeling convenience containing the features of both ions, is graphically presented in figure 1. Since the centers of gravity of both ions are coincident and contain nitrogen atoms, the central position of the statistical ion is competely filled with a nitrogen atom and is designated N(1). Also, one oxygen atom from the nitrate and one azide nitrogen atom share the same atomic position. The statistical atom (50%N 50%O) at this site is designated NO. The remaining atomic positions dictated by the conformation of each respective ion are half filled with nitrogen [N(2)] from the azide and oxygen atoms [O(1) and O(2)] from the nitrate. The atomic coordinates are listed in table 2.

In monovalent ionic azides, the azide ion normally displays a center of symmetry resulting in equivalent N-N bond lengths. Typical N-N bond lengths (ref 3) for these azide ions range from 1.162(14) to 1.187(1)A. The azide ion in this structure is not strictly linear and has rather long nonequivalent N-N bond lengths of 1.23(14) and 1.203(7)A (table 3).

The molecular conformation of the TAG ion approaches C_{3h} symmetry (fig. 1). This is in agreement with the TAG conformation reported earlier in the TAGN study (ref 4). The mean C-N and N-N bond lengths are 1.335(7) and 1.434(6)A, respectively, which exceed the bond lengths observed in TAGN where C-N is 1.322(6) and N-N is 1.406(5)A.

The disorder observed in this compound adversely affected the quality of the x-ray data to such an extent that the hydrogen positions were not determined. In addition, thermal parameters and atomic positions of the heavy atoms were affected enough to account for the apparent elognation of the bond lengths and the loss of the center of symmetry in the azide anion.

The structures displayed in figures 3 and 4 consists of puckered sheets of TAG, nitrate, and azide ions which lie approximately parallel to the c axis. Between adjacent sheets, the closest interionic contacts occur among amino nitrogens of the TAG ion, the oxygen atoms of the nitrate ion, and the nitrogen of the azide ion. These distances are 3.138(11), 2.983(10), and 3.130(7)A for O(2)-N(6), O(2)-N(8), and NO-N(8), respectively. The closet intercation contact is 3.292(7)A occuring between N(7)-N(7). The distances are consistent with the interlayer distances observed in the TAGN structure, with a closest anion-cation contact of 3.103(55)A and an intercationic distance of 3.26(4)A. Although the

hydrogen positions were not determined, the magnitudes of the heavy atom separations and their close agreement with those in TAGN in which hydrogen bonding was evident suggest hydrogen bonding as well as van der Waals' forces operate between the sheets.

Within each sheet, each ion is surrounded by three oppositely charged ions. The close interionic contacts (N-O and N-N, table 3) are 2.905(9) and 2.943(19)A for O(1)-N(5) and N(2)-N(5), respectively; 2.910(9) 2.989(16)A for O(1)-N(3) and N(2)-N(3), respecitvely; and 2.988(7)A for NO-N(7). Again, the magnitudes of the heavy atom separations suggest the presence of hydrogen bonding comparable to that observed in TAGN.

CONCLUSIONS

The oxygen content of the single crystal was 15.29% compared to 6.15% for its parent batch sample. This suggests that the batch sample is not homogeneous, but rather contains a mixture of TAG compounds.

To insure production of pure TAZ, TAGN should be excluded from the reaction medium.

The difference between TAZ samples prepared by the two methods has not been resolved yet, but the results of this study indicate that structural determinations of samples prepared by these two methods in TAGN-free media will resolve this problem.

Table 1. Elemental composition of TAZ and TAZN

	Batch sample*	Single crystal	TAZ theoretical	TAGN theoretical
%C	9.53	7.64	8.16	7.19
%N	78.77	71.34	85.71	58.68
%H	5,78	5.73	6.12	5.39
%O	6.15	15.29	--	28.87

* Chemical analysis.

Table 2. Atomic cordinates and equivalent isotropic temperature factors and their estimated standard deviations

Triaminoguanidinium	x/a	y/b	z/c	B_{eq},(A^2)
Ion				
C(1)	0.2403(7)	0.276(1)	0.3881(5)	2.8(2)
N(3)	0.3221(5)	0.250(1)	0.4401(4)	3.3(2)
N(5)	0.1417(5)	0.258(1)	0.4170(5)	3.6(2)
N(7)	0.2571(6)	0.306(1)	0.3111(4)	3.5(2)
N(4)	0.2997(5)	0.220(1)	0.5240(4)	3.8(2)
N(6)	0.0580(6)	0.284(1)	0.0051(5)	3.9(2)
N(8)	0.3648(6)	0.315(1)	0.2841(5)	4.5(2)
Azide Ion				
N(1)	0.5959(5)	0.195(1)	0.6715(4)	8.1(5)
N(2)	0.5546(13)	0.315(3)	0.9197(13)	3.3(2)
N0	0.6339(6)	0.0581(1)	0.8332(5)	5.0(3)
Nitrate Ion				
O(1)	0.5446(8)	0.139(2)	0.9311(6)	3.4(3)
O(2)	0.6159(10)	0.377(2)	0.8475(7)	4.3(3)

Table 3. Bond lengths and angles with their estimated standard deviations

Triaminoguanidinium cation	Lengths, A	Angles, deg	
Bond			
C(1)-N(3)	1.357(7)	N(3)-C(1)-N(5)	118.1(5)
C(1)-N(5)	1.341(7)	N(3)-C(1)-N(7)	120.9(6)
C(1)-N(7)	1.306(6)	N(5)-C(1)-N(7)	120.9(6)
N(3)-N(4)	1.432(6)	C(1)-N(3)-N(4)	118.8(5)
N(5)-N(6)	1.435(6)	C(1)-N(5)-N(6)	115.9(5)
N(7)-N(8)	1.434(6)	C(1)-N(7)-N(8)	118.1(5)
Azide Anion			
N(1)-NO	1.203(7)	NO-N(1)-N(2)	170.(1)
N(1)-N(2)	1.234(14)		
Nitrate Anion			
N(1)-O(1)	1.237(9)	O(1)-N(1)-O(2)	128.9(9)
N(1)-N(2)	1.284(10)	O(2)-NO	117.1(8)
N(1)-NO	1.203(7)	O(1)-NO	114.0(9)

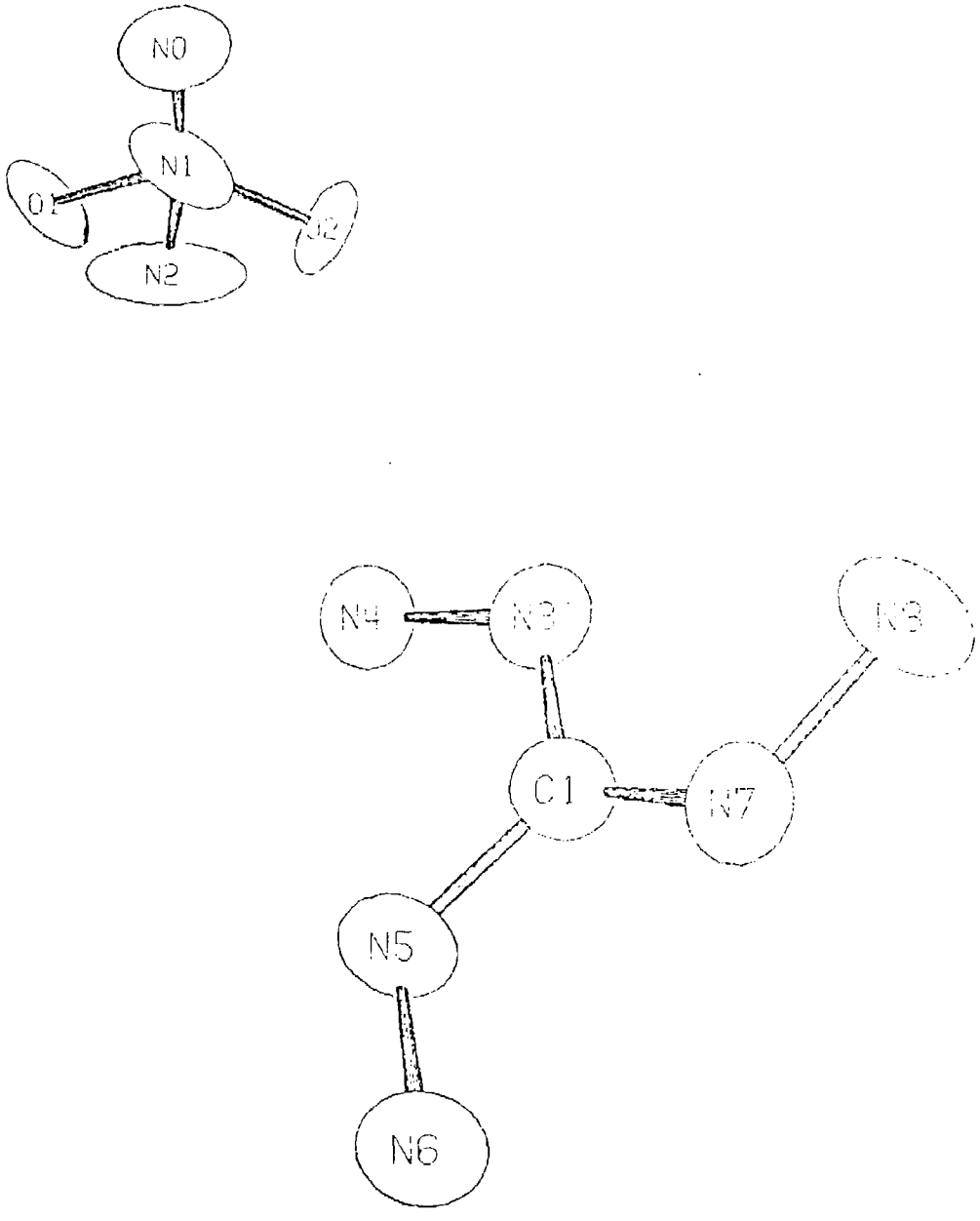

Figure 1. Molecular configurations and numbering schemes for triaminoguanidinium cation and statistical azide/nitrate anion

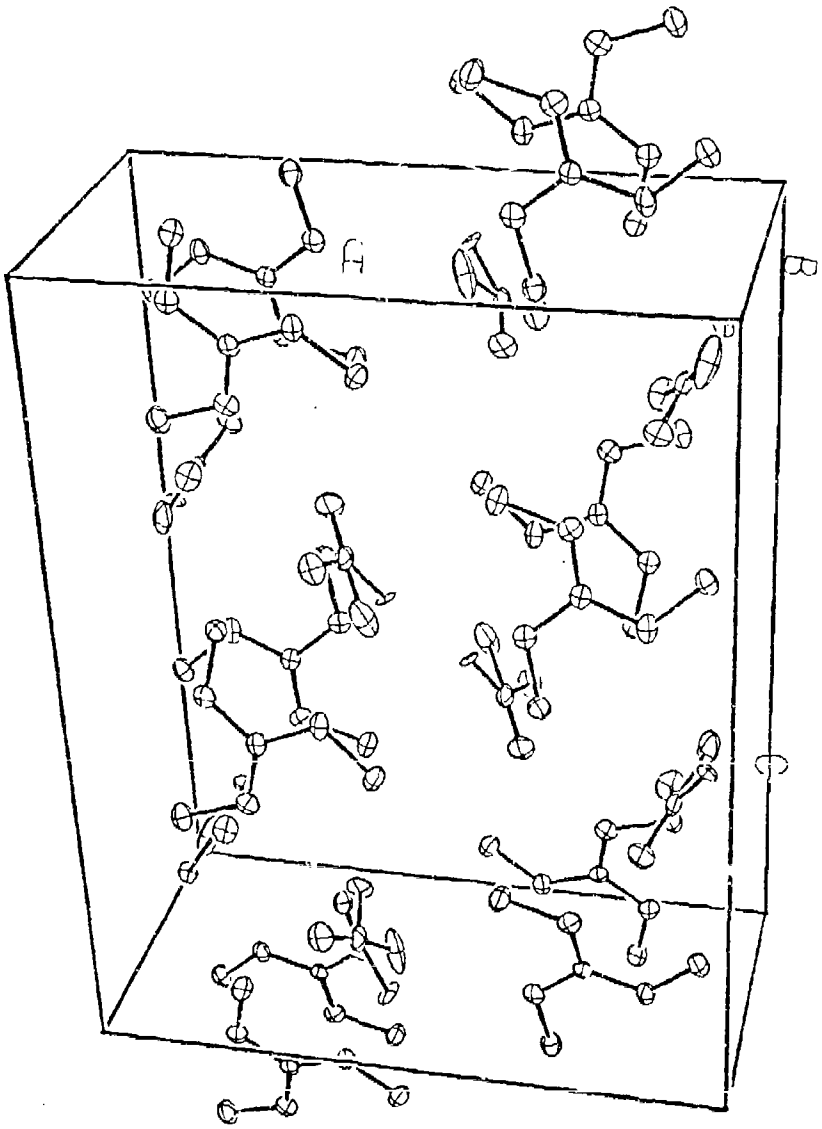

Figure 2. Unit cell of triaminoguanidinium azide nitrate viewed down the b axis

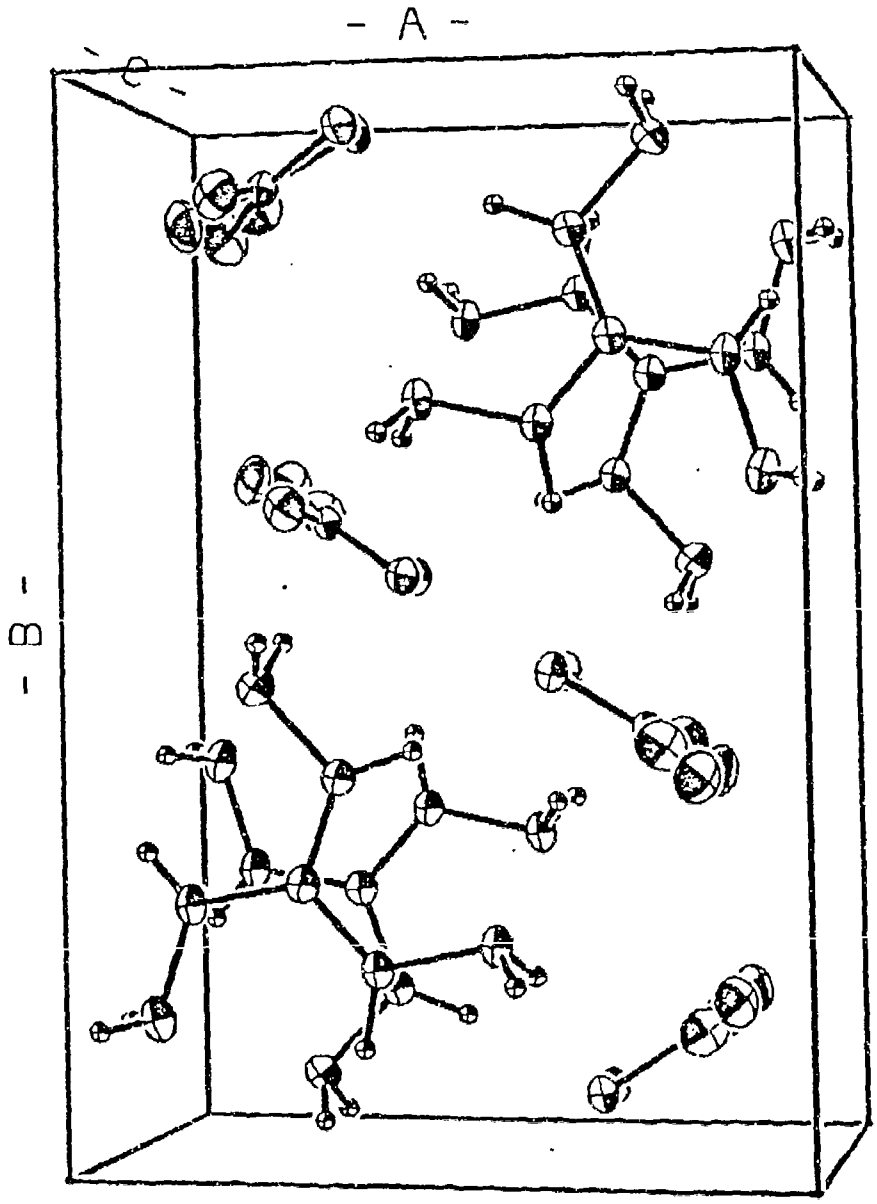

Figure 3. Unit cell of triaminoguanidinium azide nitrate viewed down the c axis

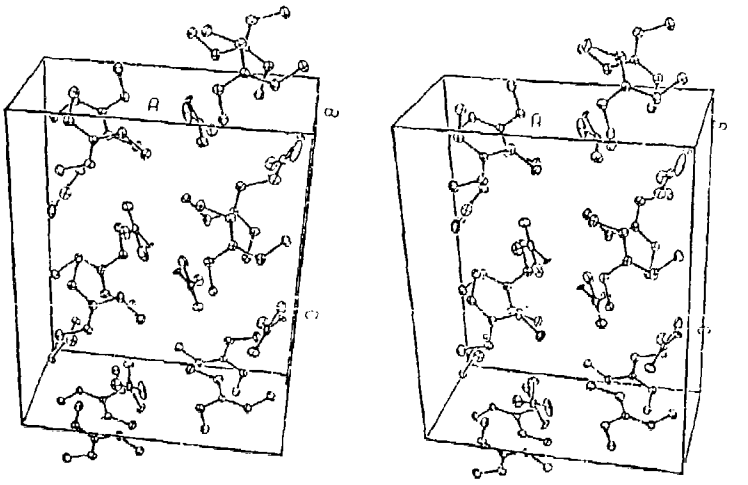

Figure 4. Stereo pair of triaminoguanidinium azide nitrate unit cells viewed down the b axis

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