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Crystal structure of *N,N,N′,N′*-tetramethylethylenediammonium dinitrate

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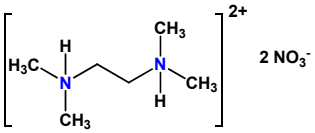
ABSTRACT

N,N,N′,N′-tetramethylethylenediammonium dinitrate has been synthesized. The crystal and molecular structure of the title compound has been determined from single crystal X-ray diffraction data. $C_6H_{18}N_4O_6$, M =242.24, Triclinic, a = 6.040(2) Å, b = 6.834(3) Å, c = 7.867(2) Å, α = 74.1120(10)°, β = 83.700(2)°, γ = 80.314(2)°, V = 307.12(19) Å^3, T = 298(2) K, space group P-1 (no. 2), Z = 1, μ(Mo-K$_\alpha$) = 0.115, 2383 reflections measured, 1342 unique (R_{int} = 0.0169) which were used in all calculations. The final $wR(F^2)$ was 0.1262 (all data). In the title compound, $C_6H_{18}N_2^{2+}.2NO_3^-$, both N atoms of the cationic moiety are protonated and linked via hydrogen bonds to two trigonal planar nitrate anions. Two types of classical hydrogen bonds are observed: N1-H...O1 and N1-H...O2. These bonds link the cations and the anions together, forming a one-dimensional network and reinforcing the cohesion of the ionic structure.

1. Introduction

Due to their application in many fields of chemistry, the preparation of nitrogen-containing ligands is still of great interest in synthetic chemistry. Recent investigations have proved the direct deprotonation of methylamines to be a synthetically very useful method for functionalizations and thus for the synthesis of nitrogen ligands [1-3]. In addition, it is well known that organic amines, such as ethylenediamine, 1,3-propanediamine, *N,N,N',N'*-tetramethylethylenediamine and piperazine have been widely used as structure-directing agents for the construction of novel supramolecular assemblies [4,5]. Here, a new member of this family, *N,N,N′,N′*-tetramethylethyl enediammoniume dinitrate, **I**, is presented. The synthesis and structure of the title compound is presented here (Scheme 1).



Scheme 1

2. Experimental

2.1. Synthesis

N,N,N',N'-Tetramethylethylenediamine (TMEDA) (0.076 mol) and an equivalent amount of $MnCl_2.4H_2O$ (1 mol) were dissolved in a mixture of methanol (5 mL) and nitric acid (2 M, 1 mL) and stored at room temperature for two month. After evaporation of the solvent, a crystalline solid which is suitable for X-ray single crystal structure diffraction studies remained.

2.2. Instrumentation

Data were collected using a crystal, size 0.03×0.02×0.01 mm, on an Enraf-Nonius CAD4 diffractometer. The cell parameters were determined and optimized by least-squares refinement based on 25 reflections in the range 9°≤ θ ≤ 15°. The crystal structure was solved and refined using full matrix least squares on F^2. All calculations were performed using the SHELX-97 [6] computer programs included in the WinGX software package [7]. Molecular graphics are made with Diamond 2.1 [8]. The relevant crystallographic data for the title compound are listed in Table 1.

3. Results and discussion

The molecular structure of *N,N,N′,N′*-tetramethylethylene diammonium dinitrate is depicted in Figure 1. Selected bond lengths and angles of the title compound are presented in Table 2 and 3, respectively. Atomic coordinates and equivalent isotopic displacement parameters for non-hydrogen atoms of the title compound are given in Table 4.

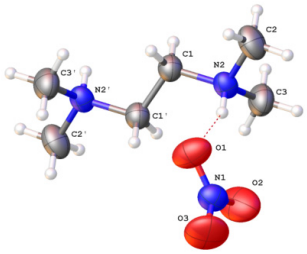


Figure 1. The molecular structure of the title compound. Thermal ellipsoids are shown at the 50% probability level.

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Table 1. Crystal data and structure refinement for the title compound.

Empirical formula	$C_6H_{18}N_2{\cdot}2(NO_3)$
Formula weight (g/mol)	242.24
Temperature (°C)	298 (2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	*a* = 6.040 (2) Å
	b = 6.834 (3) Å
	c = 7.867 (2) Å
	α = 74.1120 (10)°
	β = 83.700 (2)°
	γ = 80.314 (2)°
Volume	307.12 (19) Å^3
Z	1
Density (calculated) (Mg m^{-3})	1.310
Absorption coefficient (mm^{-1})	0.115
F(000)	130
Crystal size (mm^3)	0.03 × 0.02 × 0.01
Theta range for data collection °	2.70 to 26.96°
Index ranges	$-7 \le h \le 5$
	$-8 \le k \le 8$
	$-10 \le l \le 10$
Reflections collected	2383
Independent reflections	1342 [R(int) = 0.0169]
Absorption correction	psi-scan
Max. and min. transmission	0.999 and 0.997
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1342/0/80
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	$R1$= 0.0429, $wR2$ = 0.1160
R indices (all data)	$R1$= 0.0586, $wR2$ = 0.1262
Extinction coefficient	0.18 (2)
Largest diff. peak and hole (e Å^{-3})	0.211 and −0.119
Measurement	Enraf Nonius CAD4 diffractometer
Program system	Wingx
Structure determination	Direct methods (SHELXL-97, SHELXTL)
CCDC	798752

Table 2. Bond lengths for the title compound.

Atom-Atom	Bond length/Å
N1-O1	1.248(2)
N1-O2	1.231(2)
N1-O3	1.222(2)
N2-C1	1.496(2)
N2-C2	1.499(2)
N2-C3	1.488(2)
C1-C1^{i}	1.521(3)

Symmetry code: (*i*) −*x*, −*y*, −*z*+1.

Table 3. Bond angles for the title compound.

Atom-Atom-Atom	Bond Angle (°)
O2-N1-O1	117.28(15)
O3-N1-O1	119.69(17)
O3-N1-O2	123.02(18)
N2-C1-C1^{i}	110.67(16)
C1-N2-C2	110.83(14)
C3-N2-C1	112.56(13)
C3-N2-C2	110.66(13)

Symmetry code: (*i*) −*x*, −*y*, −*z*+1

Table 4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for the title compound. *U*(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	*x*	*y*	*z*	*U*(eq)
N1	5332(2)	-2342(2)	2398(2)	52.9(4)
O1	5148(2)	-1256(3)	3463(2)	75.9(5)
O2	3783(3)	-2062(3)	1425(3)	94.9(6)
O3	7012(3)	-3608(3)	2351(3)	103.8(7)
N2	1241(2)	1627(2)	2854.9(17)	42.8(4)
C1	218(3)	1111(2)	4715(2)	44.9(4)
C2	2288(3)	3554(3)	2466(3)	62.2(5)
C3	-401(3)	1798(3)	1525(2)	61.4(5)

In the title salt, $C_6H_{18}N_2^{+}.2NO_3^{-}$, (Figure 1) both N atoms of the cationic moiety are protonated and linked via hydrogen bonds to two trigonal planar nitrate anions. The components lie on centres of symmetry such that the asymmetric unit consists of half of the *N,N,N′,N′*-tetramethylethylenediammonium cation, which lies across an inversion center (C1-C1^{i} bond (*i*: -*x*, -*y*, -*z*+1)) and nitrate ion. Alternating nitrate anions and cationic ligands are observed parallel to the (010) plane (Figure 2).

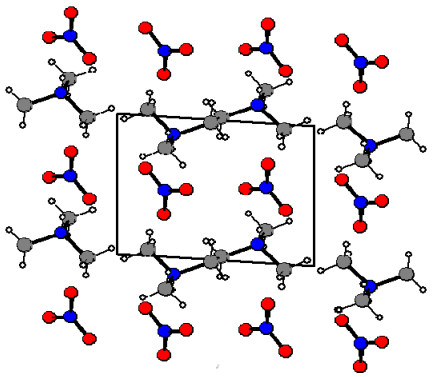


Figure 2. A projection of the title compound $C_6H_{18}N_2^{2+}.2NO_3^{-}$(I) along the *y* direction.

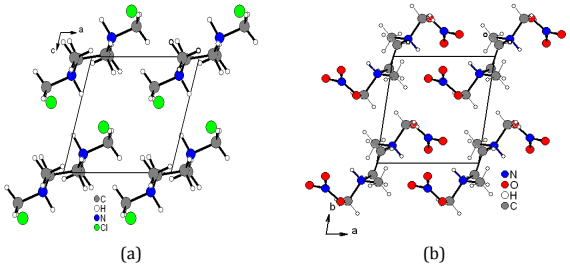
The structure is stabilized by two types of hydrogen-bonding interactions: (N2-H…O1) and (N2-H…O2)) contacts (Table 5).

Table 5. Hydrogen-bond geometry (Å, °)

D-H…A	d(D-H)	d(H..A)	d(D..A)	<DHA
N2-H2N…O1	0.862	1.995	2.801	154.95
N2-H2N…O2	0.862	2.375	3.138	147.65

The bond lengths and angles in the cation are not unusual (Table 2 and 3). The C-C and C-N bond lengths are in good agreement with those found in other compounds containing the TMEDA moiety [9-11]. The shortest distance between adjacent methyl is about 3.6441 (3) Å, which indicates the existence of stacking interactions.

The crystal structure of the title compound and *N,N,N′,N′*-tetramethylethylenediammonium dichloride [10] are isostructural. In both molecules, the asymmetric unit contains an organic cation, TMEDA, and X anions (X: dinitrate (in title compound); dichloride [10]). They are characterized by one-dimensional hydrogen-bonded networks (Figure 3). The major difference between the two structures is in the distinct orientations of the hydrogen atom of N2 atom. These relative orientations are due to interactions with the nearest neighbouring anions.



(a) (b)

Figure 3. A projection of *N,N,N′,N′*-tetramethylethylenediammonium dichloride [10] $C_6H_{18}N_2^{2+}.2Cl^{-}$ (a) along the *b* axis and the title compound $C_6H_{18}N_2^{2+}.2NO_3^{-}$ (I) along the *c* axis.

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Supplementary material

CCDC-798752 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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