Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

o-Phenylenediaminium chloride nitrate

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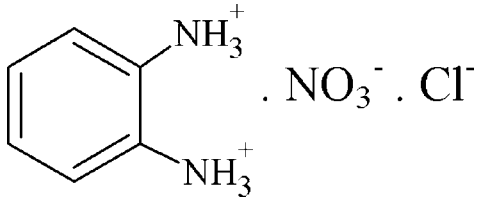
Received 4 March 2013; accepted 18 March 2013

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; R factor = 0.024; wR factor = 0.053; data-to-parameter ratio = 12.4.

In the title molecular salt, $C_6H_{10}N_2^{2+}\cdot NO_3^-\cdot Cl^-$, the complete cation is generated by a crystallographic mirror plane. The complete nitrate ion is also generated by reflection, with the N atom and one O atom lying on the mirror plane; the chloride ion also lies on the reflection plane. In the crystal, the components are linked by N—H···Cl and N—H···(N,O) hydrogen bonds, forming (001) layers with the benzene rings projecting into the interlayer regions. The layers are linked by weak C—H···O hydrogen bonds, generating a three-dimensional network.

Related literature

For background to inorganic–organic hybrid compounds, see: Bringley & Rajeswaram (2006); Dai *et al.* (2002). For reference structural data, see: Riahi *et al.* (2012); Engh & Huber (1991).



Experimental

Crystal data

$C_6H_{10}N_2^{2+}\cdot Cl^-\cdot NO_3^-$
M_r = 207.61
Orthorhombic, *Pnma*
a = 7.3695 (5) Å
b = 8.2367 (5) Å
c = 14.2398 (7) Å
V = 864.36 (8) Å^3
Z = 4
Ag $K\alpha$ radiation
λ = 0.56085 Å
μ = 0.22 mm^{-1}
T = 100 K
0.27 × 0.20 × 0.15 mm

Data collection

Bruker Photon100 CMOS detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
T_{min} = 0.751, T_{max} = 0.967
26823 measured reflections
812 independent reflections
812 reflections with $I > 2\sigma(I)$
R_{int} = 0.049

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.053
S = 0.80
812 reflections
66 parameters
12 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H34···O10	1.033 (4)	2.41 (1)	2.896 (2)	107.4 (9)
N3—H34···N1	1.033 (4)	2.429 (9)	3.263 (2)	137.1 (8)
N3—H31···Cl1^{i}	1.033 (4)	2.181 (4)	3.179 (2)	161.8 (5)
N3—H32···Cl1	1.033 (4)	2.183 (5)	3.156 (2)	156.2 (5)
C2—H2···O11	1.08	2.48	3.299 (2)	132
C1—H1···O10^{ii}	1.08	2.52	3.427 (2)	141

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x, -y+1, -z+1$.

Data collection: *COLLECT* (Bruker, 2004); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *MoPro* (Jelsch *et al.*, 2005); molecular graphics: *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *publCIF* (Westrip, 2010).

We thank the Secretary of State for Scientific Research and Technology of Tunisia for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB7052).

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supporting information

Acta Cryst. (2013). E**69**, o600 [doi:10.1107/S1600536813007447]

o-Phenylenediaminium chloride nitrate

Sarra Soudani, Riadh Kefi, Christian Jelsch, Emmanuel Wenger and Cherif Ben Nasr

S1. Comment

Inorganic-organic hybrid compounds provide a class of materials with interesting potential technological applications (Bringley & Rajeswaram 2006; Dai *et al.*, 2002). As part of our studies in this area, we report here the synthesis and the crystal structure of the title compound, (I), formed by the reaction between benzene-1,2-diamine, nitric acid and hydrochloric acid. The structure consists of one nitrate anion, one chloride anion and one benzene-1,2-diaminium dication (Fig. 1). In the crystal, the H atoms of the ammonium groups are involved in two kinds of hydrogen bonds: N—H···Cl and N3—H34···(N1, O10), which is a bifurcated H-bond interaction (Table 1). These hydrogen bonds link the ionic units (NH_3^+, Cl^- and NO_3^-) into layers parallel to (001) (Fig. 2) and situated at $z = n$ +/- 1/4 (Fig. 3). The chloride ion is actually located on a special position with y = 1/4. The phenyl groups of the benzene-1,2-diaminium dications are located alternatively on either side of the ionic layers *via* three weak C—H···O hydrogen bonds (Fig. 3) with the nitrate anion, which is perpendicular to the phenyl plane. No π-π stacking interactions between the organic rings or C—H···π interactions towards them are observed.

The geometrical parameters of the title compound are in the normal range. A N—O moiety of the nitrate is located on a special position y=3/4 and the two independant N—O bond distances are 1.243 (2) and 1.284 (1) Å. In addition, the O—N—O bond angle values are 118.6 (2)° and 122.8 (2), showing that the nitrate anion exhibits a slightly distorted C_{3h} geometry. These anionic geometrical features are comparable to those previously reported for 2-cyanoanilinium nitrate where the N—O bond length distances are in the range 1.228 (2)–1.273 (2) Å and the values of the O—N—O angles are between 117.52 (2) and 121,80 (15)° (Riahi *et al.*, 2012). For the organic cation, the mean value of the C—C bond lengths of the aromatic ring is 1.391 (2) Å which is close to the 1.382 (3) value between >CH aromatic atoms in the Engh & Huber (1991) stereochemical dictionary.

S2. Experimental

A mixture of an aqueous solution of benzene-1,2-diamine (3 mmol), nitric acid (3 mmol) and hydrochloric acid (3 mmol) was slowly evaporated at room temperature over several days leading to formation of transparent light brown prismatic crystals (yield 60%). The crystals are stable for months under normal conditions of temperature and humidity.

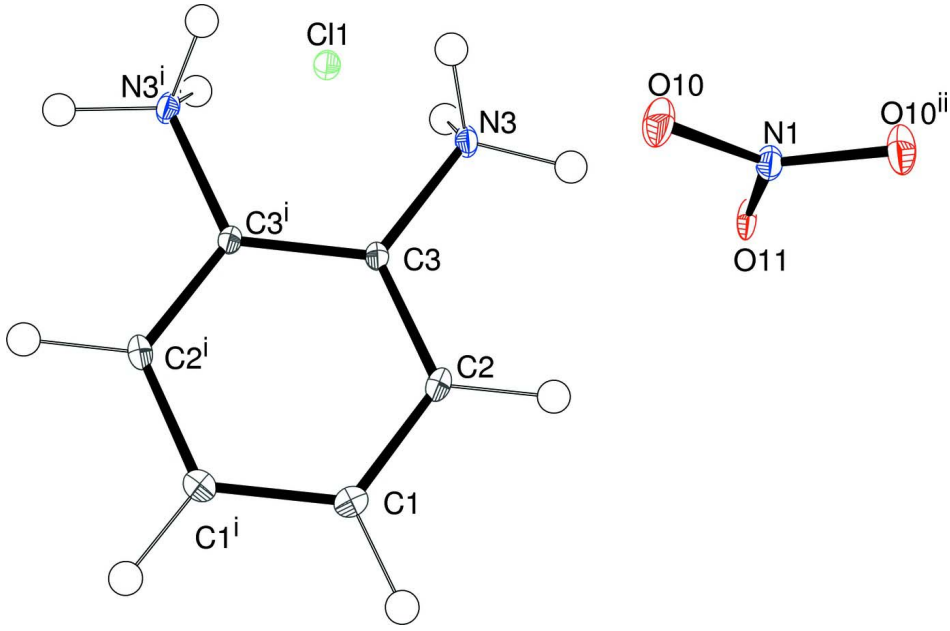

Figure 1

A view of the title compound, showing 50% probability displacement ellipsoids and spheres for the H atoms. Symmetry codes: (i) x, 1/2-y, z; (ii) x, 3/2-y, z.

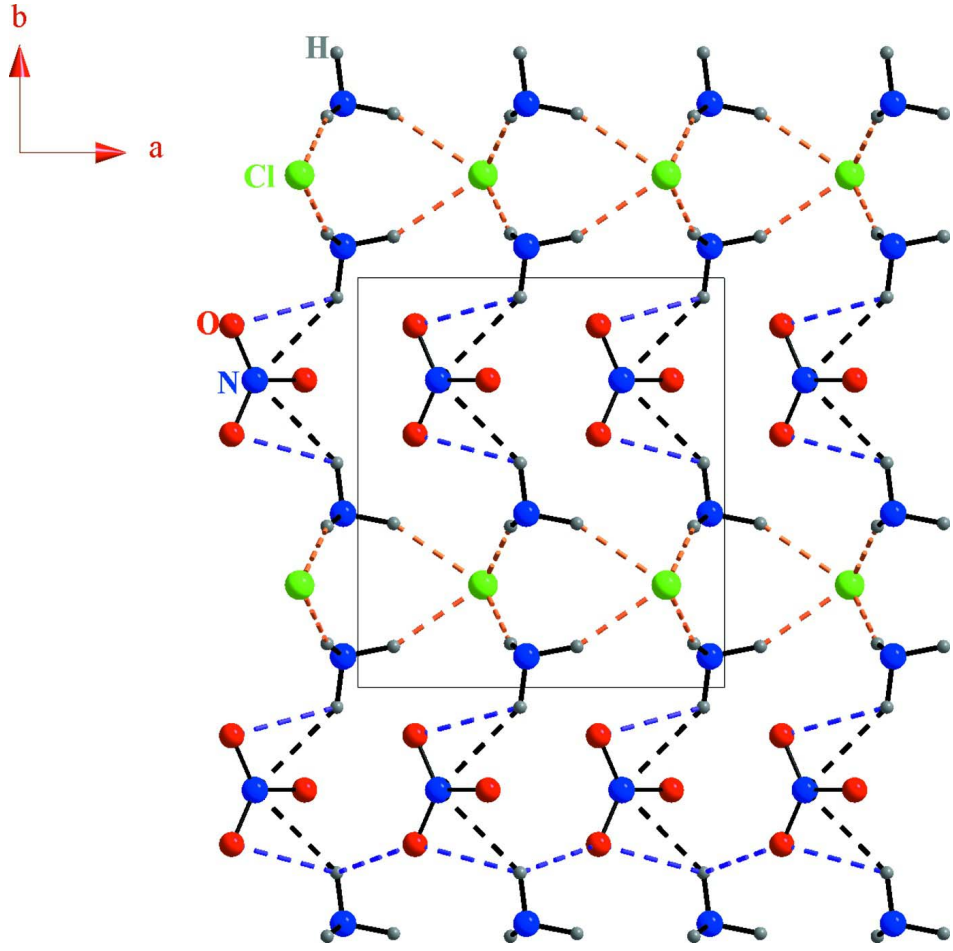

Figure 2

Projection along the *c*-axis of the inorganic layers in the structure of the title compound. Hydrogen bonds are shown as broken lines.

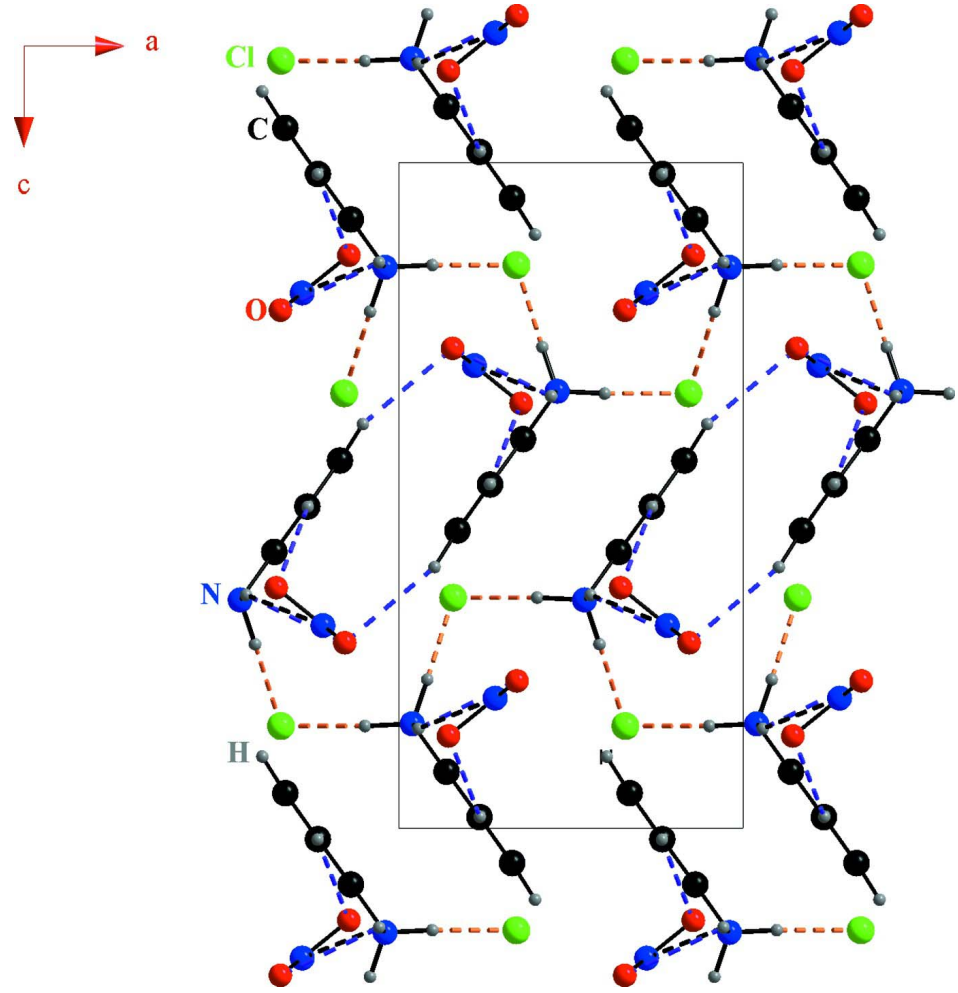

Figure 3

The packing diagram of the compound viewed down the *b*-axis. Hydrogen bonds are shown as broken lines.

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Crystal data

$C_6H_{10}N_2^{2+}\cdot Cl^-\cdot NO_3^-$
$M_r = 207.61$
Orthorhombic, *Pnma*
Hall symbol: -P 2ac 2n
$a = 7.3695\ (5)$ Å
$b = 8.2367\ (5)$ Å
$c = 14.2398\ (7)$ Å
$V = 864.36\ (8)$ Å^3
$Z = 4$
$F(000) = 432$
$D_x = 1.596$ Mg m^{-3}
Ag $K\alpha$ radiation, $\lambda = 0.56085$ Å
Cell parameters from 64 reflections
$\theta = 3.1$–$20.3°$
$\mu = 0.22$ mm^{-1}
$T = 100$ K
Prismatic, yellow
0.27 × 0.20 × 0.15 mm

Data collection

Bruker Photon100 CMOS detector diffractometer
Radiation source: fine-focus sealed tube
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2004)
$T_{min} = 0.751$, $T_{max} = 0.967$
26823 measured reflections
812 independent reflections

812 reflections with $I > 2\sigma(I)$
$R_{int} = 0.049$
$\theta_{max} = 19.5°$, $\theta_{min} = 2.5°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 9$
$l = 0 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.053$
$S = 0.80$
812 reflections
66 parameters
12 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.P)^2 + 2.3P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.002$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Special details

Refinement. Refinement of F^2 against reflections. The threshold expression of $F^2 > 2$sigma(F^2) is used for calculating R-factors(gt) and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.84182 (9)	0.25000	0.34646 (4)	0.00937 (9)
N1	0.2199 (3)	0.75000	0.3046 (2)	0.0091 (3)
O11	0.3554 (3)	0.75000	0.3614 (1)	0.0098 (3)
O10	0.1566 (2)	0.6174 (2)	0.27870 (9)	0.0143 (2)
C1	0.1707 (3)	0.3346 (2)	0.5526 (1)	0.0117 (3)
H1	0.10400	0.40337	0.60752	0.01410*
C2	0.2654 (3)	0.4193 (2)	0.4834 (1)	0.0100 (2)
H2	0.26439	0.55074	0.48291	0.01199*
C3	0.3611 (2)	0.3345 (2)	0.4152 (1)	0.0071 (2)
N3	0.4604 (2)	0.4241 (2)	0.3431 (1)	0.0083 (2)
H31	0.417 (1)	0.393 (1)	0.2766 (3)	0.01240*
H32	0.5979 (4)	0.400 (1)	0.3466 (10)	0.01240*
H34	0.443 (2)	0.5479 (3)	0.3506 (9)	0.01240*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0105 (3)	0.0079 (3)	0.0097 (3)	0	−0.0003 (3)	0
N1	0.011 (1)	0.006 (1)	0.010 (1)	0	−0.0011 (9)	0
O11	0.0117 (9)	0.0032 (9)	0.0145 (10)	0	−0.0032 (8)	0
O10	0.0168 (7)	0.0076 (6)	0.0184 (7)	−0.0016 (6)	−0.0052 (6)	−0.0023 (6)
C1	0.0149 (9)	0.0101 (10)	0.0102 (9)	0.0008 (8)	0.0030 (8)	−0.0012 (8)
C2	0.0128 (9)	0.0058 (9)	0.0113 (9)	0.0008 (8)	0.0011 (7)	−0.0014 (7)
C3	0.0084 (9)	0.0052 (9)	0.0079 (9)	−0.0001 (8)	0.0010 (7)	0.0003 (7)
N3	0.0099 (8)	0.0049 (7)	0.0100 (7)	−0.0008 (6)	0.0002 (6)	0.0008 (6)

Geometric parameters (Å, º)

N1—O10	1.243 (2)	C2—H2	1.083
N1—O11	1.284 (3)	C3—N3	1.461 (2)
C1—C2	1.395 (3)	N3—H32	1.033 (4)
C1—H1	1.083	N3—H34	1.033 (4)
C2—C3	1.389 (3)	N3—H31	1.033 (4)
O11—N1—O10	118.6 (2)	C3—N3—H32	111.2 (7)
O10—N1—O10^{i}	122.8 (2)	C3—N3—H34	111.3 (7)
C1—C2—C3	119.8 (2)	C3—N3—H31	111.1 (6)
C1—C2—H2	120.1	H31—N3—H32	107.7 (8)
H1—C1—C2	118.4	H31—N3—H34	107.6 (9)
C2—C3—N3	119.5 (2)	H32—N3—H34	107.7 (10)
H2—C2—C3	120.1		
C1—C2—C3—N3	−179.8 (2)	C2—C3—N3—H34	−2.1 (7)
H1—C1—C2—C3	176.3	C2—C3—N3—H31	−122.0 (7)
H1—C1—C2—H2	−3.7	H2—C2—C3—N3	0.2
C2—C3—N3—H32	118.0 (8)		

Symmetry code: (i) x, $-y+3/2$, z.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H34···O10	1.033 (4)	2.41 (1)	2.896 (2)	107.4 (9)
N3—H34···N1	1.033 (4)	2.429 (9)	3.263 (2)	137.1 (8)
N3—H31···Cl1^{ii}	1.033 (4)	2.181 (4)	3.179 (2)	161.8 (5)
N3—H32···Cl1	1.033 (4)	2.183 (5)	3.156 (2)	156.2 (5)
C2—H2···O11	1.08	2.48	3.299 (2)	132
C1—H1···O10^{iii}	1.08	2.52	3.427 (2)	141

Symmetry codes: (ii) $x-1/2$, $-y+1/2$, $-z+1/2$; (iii) $-x$, $-y+1$, $-z+1$.