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Potassium 4-nitramino-1,2,4-triazolate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(N–C) = 0.003 Å
R factor = 0.048
wR factor = 0.124
Data-to-parameter ratio = 12.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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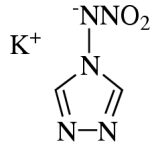
The title compound, $K^+ \cdot C_2H_2N_5O_2^-$, has an anion conformation similar to the reported conformation of 4-nitramino-1,2,4-triazole. Seven O and N atoms of six ligand molecules coordinate the potassium cation with short values of K···O and K···N interatomic distances.

Comment

The structure of 4-nitramino-1,2,4-triazole, (II), has a zwitterionic conformation and has been solved previously (Vasiliev *et al.*, 1999). To determine the influence of the transition from (II) to its anion on the molecular conformation and on its nitrimine fragment, the structure of the potassium salt of (II), *viz*. the title compound, (I), was investigated. The project arose from a search of structure–property relationships in a series of energetic nitramines. This knowledge is needed for an estimation of the properties of new hypothetical energetic molecules (Astachov, 1999).



(I)

The structural formula for (I) (see Scheme above) does not precisely reflect the true location of a negative charge in the anion of (I). However, as will be shown, the representation of (I) using the conventional principles of chemical structural formulae, which takes into consideration atom valence and experimental geometry parameters, was a difficult task.

As a whole, the transition from (II) to its anion does not affect the molecular geometry parameters. Like (II), the molecule in (I) is not planar, but consists of two planar fragments: a 1,2,4-triazole ring (all deviations < 0.001 Å) and an N—N—NO_2 nitrimide group [r.m.s. deviation 0.012 (1) Å and maximum deviation 0.019 (1) Å]. The N4—N6—N7—O2 torsion angle is 3.0 (3)° [−2.6° for (II)]. Maximum changes of valence angles are near 5° for the triazole ring and less than 2° for the nitrimide fragment.

The bond lengths of the nitrimide fragment of (I) are practically the same as in (II) [in brackets]: N4—N6 1.408 (2) Å [1.407 (2) Å], N6—N7 1.322 (3) Å [1.319 (2) Å], N7—O1 1.261 (2) Å [1.259 (2) Å] and N7—O2 1.243 (3) Å [1.235 (2) Å]. Some interatomic distances in the triazole ring changed rather more: N1—N2 1.393 (3) Å [1.362 (2) Å], N2—C3 1.295 (3) Å [1.300 (2) Å], C3—N4 1.351 (3) Å

[1.358 (2) Å], N4—C5 1.352 (3) Å [1.341 (2) Å] and C5—N1 1.299 (3) Å [1.308 (2) Å]. These data allow the assignment of single and double bonds more definitely than in the molecule of (II); this is reflected in the *Scheme*. The valence angles are given in Table 1.

In the crystal structure of (I), the seven atoms O1, O2, N1 and N2 of six anions coordinate the potassium cation (Fig. 1). It is worth noting that atom O1 has a tetrahedral environment, consisting of atom N7 and three potassium ions. Short values of K···O and K···N interatomic distances [2.788–2.934 (2) Å] (Table 1) do not allow exact location of a negative charge on some of the anion atoms. Taking account of atom valency and the non-variability of the nitrimide fragment geometrical parameters, atom N6 was assigned the negative charge in the structural formula of (I), but it does not coordinate the potassium ion.

The X-ray analysis, in particular, confirms the earlier proposal for the first step of thermolysis; namely, as in (II), it involves breaking the N4—N6 bond (Astachov, 1999). The established bond lengths show that the N4—N6 bond, which connects the nitrimine group and the triazole ring, is the weakest bond in the ligand of (I) and in the molecule of (II) (Vasiliev *et al.*, 1999).

Experimental

Several drops of water were added to a boiling suspension of 4-nitramino-1,2,4-triazole (1 g) in caustic alcohol (0.8 g potassium hydroxide in 20 ml of 95% ethanol) for solution homogenization. To the transparent solution was added diethyl ether (20 ml) and the mixture was cooled slowly to room temperature. A precipitae of fine needle-shaped crystals was separated by filtration, washed with ethanol and dried. The yield of (I) was 1.0 g (77%).

Crystal data

$K^+ \cdot C_2H_2N_5O_2^-$
M_r = 167.19
Monoclinic, $P2_1/c$
a = 7.9671 (6) Å
b = 4.8182 (4) Å
c = 16.812 (1) Å
β = 110.165 (7)°
V = 605.81 (8) Å^3
Z = 4
D_x = 1.833 Mg m^{-3}
Cu Kα radiation
Cell parameters from 25 reflections
θ = 22–28°
μ = 7.30 mm^{-1}
T = 293 (2) K
Lump, colourless
0.27 × 0.25 × 0.22 mm

Data collection

Kuma KM-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1230 measured reflections
1154 independent reflections
1039 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 70.0°
$h = -9 \rightarrow 0$
$k = 0 \rightarrow 5$
$l = -18 \rightarrow 20$
2 standard reflections
every 50 reflections
intensity variation: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.048
$wR(F^2)$ = 0.124
S = 1.01
1154 reflections
93 parameters
Only H-atom U's refined
$w = 1/[\sigma^2(F_o^2) + (0.1004P)^2 + 0.2012P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.80 e Å^{-3}
$\Delta\rho_{min}$ = −0.55 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0085 (17)

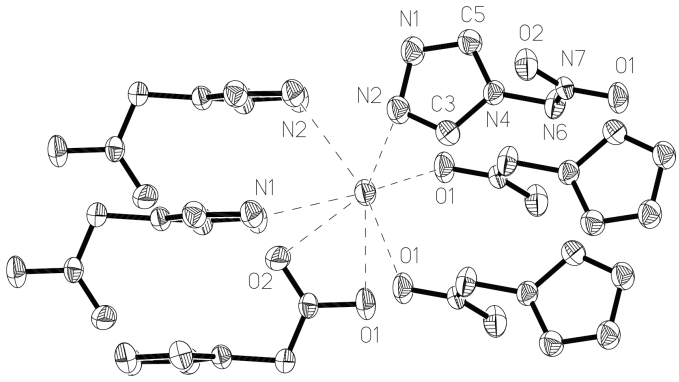


Figure 1
The arrangement of anions around the potassium ion in the crystal structure of (I), with the atomic numbering scheme (H atoms not shown). Dashed lines indicate K···O and K···N contacts.

Table 1
Selected geometric parameters (Å, °).

K···O1^{i}	2.7886 (18)	K···O1	2.923 (2)
K···N1^{ii}	2.862 (2)	K···O2	2.9257 (18)
K···O1^{iii}	2.9001 (18)	K···N2^{v}	2.934 (2)
K···N2^{iv}	2.914 (2)		
C5—N1—N2	107.3 (2)	N1—C5—N4	110.3 (2)
C3—N2—N1	106.4 (2)	N7—N6—N4	109.2 (2)
N2—C3—N4	111.2 (2)	O2—N7—O1	121.0 (2)
C3—N4—C5	104.9 (2)	O2—N7—N6	124.3 (2)
C3—N4—N6	126.7 (2)	O1—N7—N6	114.7 (2)
C5—N4—N6	128.1 (2)		

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

Two H atoms were found in a difference Fourier map and were refined as riding atoms with a common isotropic displacement parameter.

Data collection: *KM*-4 *Software* (Kuma, 1991); cell refinement: *KM*-4 *Software*; data reduction: *DATARED* in *KM*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1995); software used to prepare material for publication: *SHELXL*97.

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