Crystal structure and Hirshfeld surface analysis of 1,2,4-triazolium hydrogen oxalate

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The asymmetric unit of the title 1:1 salt 1,2,4-triazolium hydrogen oxalate, $C_2H_4N_3{}^+ \cdot C_2HO_4{}^-$ (**I**), comprises one 1,2,4-triazolium cation and one hydrogen oxalate anion. In the crystal, the hydrogen oxalate anions are linked by O—H⋯O hydrogen bonds into chains running parallel to [100]. In turn, the anionic chains are linked through the 1,2,4-triazolium cations by charge-assisted ${}^+$N—H⋯O${}^-$ hydrogen bonds into sheets aligned parallel to (01$\bar{1}$). The sheets are further stacked through π–π interactions between the 1,2,4-triazolium rings [centroid-to-centroid distance = 3.642 (3) Å, normal distance = 3.225 (3) Å, slippage 1.691 Å], resulting in the formation of a three-dimensional supramolecular network. Hirshfeld surface analysis of the title salt suggests that the most significant contributions to the crystal packing are by H⋯O/O⋯H and H⋯N/N⋯H contacts involving the hydrogen bonds.

1. Chemical context

The oxalate anion ($C_2O_4{}^{2-}$), *i.e.* the complete deprotonation product of oxalic acid ($C_2H_2O_4$), is a small, rigid, planar species and has been widely used as a ligand in the formation of coordination polymers (Gruselle *et al.*, 2006; Abraham *et al.*, 2014). This ligand possesses four electron-donating O atoms and can display versatile coordination modes upon metal complexation. As a result, a large number of compounds with multi-dimensional coordination networks with short inter-metallic distances have been synthesized along with the investigation of interesting properties (Clemente-León *et al.*, 2011). During our synthetic efforts to develop novel lanthanide coordination polymers with rigid, short, organic ligands including the oxalate anion, the title salt $C_2H_4N_3{}^+ \cdot C_2HO_4{}^-$ (**I**) was obtained unexpectedly from the reaction of terbium(III) chloride hexahydrate, oxalic acid, and 1,2,4-triazole in water at room temperature.
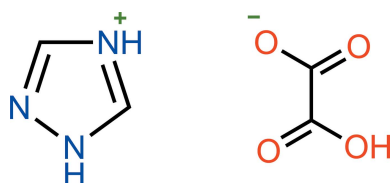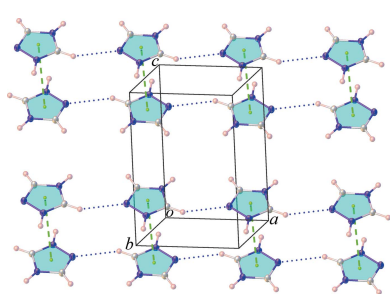
Herein, we describe the crystal structure and Hirshfeld surface analysis of the title salt (**I**).

2. Structural commentary

As shown in Fig. 1, the asymmetric unit consists of one 1,2,4-triazolium cation and one hydrogen oxalate anion. In the

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
O1—H1A$\cdots$O4^{i}	0.94 (2)	1.61 (2)	2.5447 (13)	175.0 (18)
N1—H1$\cdots$O3	0.91 (2)	1.81 (2)	2.7199 (15)	175.4 (18)
N2—H2$\cdots$O4^{ii}	0.96 (2)	1.80 (2)	2.7443 (15)	167.3 (19)
C3—H3$\cdots$O2^{iii}	0.93	2.40	3.1717 (17)	141
C3—H3$\cdots$N3^{iv}	0.93	2.58	3.3939 (18)	146
C4—H4$\cdots$O1	0.93	2.45	3.0289 (16)	120
C4—H4$\cdots$O3^{i}	0.93	2.30	3.1625 (17)	153

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

hydrogen oxalate anion, the C1—O1 bond to the O atom that carries the H atom is significantly longer [1.3066 (14) Å] than the C1—O2 bond [1.1976 (15) Å], whereas the C2—O3 and C2—O4 bond lengths of the carboxylate group show intermediate values [1.2370 (15) and 1.2586 (14) Å, respectively]. The hydrogen oxalate molecule is nearly planar with an O2—C1—C2—O4 torsion angle of 2.3 (2)°. The 1,2,4-triazolium molecule is perfectly planar with a root-mean-square (r.m.s.) deviation (excluding hydrogen atoms) of 0.001 Å. The cationic and anionic molecules are coplanar with an r.m.s. deviation of 0.020 Å.

3. Supramolecular features

Extensive hydrogen-bonding interactions in the crystal of the title salt (**I**) are observed, the numerical values of which are collated in Table 1. As shown in Fig. 2, each hydrogen oxalate anion is linked with another anion by O—H$\cdots$O hydrogen bonds into an infinite chain running parallel to [100]. The anionic chains are linked by charge-assisted $^{+}$N—H$\cdots$O^{-} hydrogen bonds involving the 1,2,4-triazolium cations into sheets extending parallel to (01$\bar{1}$). Additionally, intrasheet C—H$\cdots$O hydrogen and C—H$\cdots$N hydrogen bonds involving cationic molecules are also observed. The sheets are further stacked through π–π interactions between the 1,2,4-triazolium rings [centroid-to-centroid distance = 3.642 (3) Å, normal distance = 3.225 (3) Å, slippage 1.691 Å], Fig. 3, resulting in the formation of a three-dimensional supramolecular network.
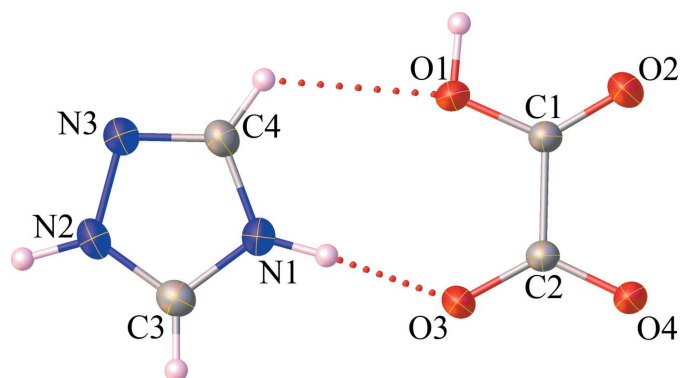

Figure 2
Partial view along [010] of the title salt (**I**), showing the O—H$\cdots$O and N—H$\cdots$O hydrogen-bonded sheet propagating parallel to (01$\bar{1}$). C—H$\cdots$O and C—H$\cdots$N hydrogen bonds are omitted for clarity.

4. Hirshfeld surface analysis

In order to quantify the nature of the intermolecular interactions present in the crystal structure, Hirshfeld surfaces (McKinnon et al., 2007) and their associated two-dimensional fingerprint plots (Spackman & McKinnon, 2002) were calculated using CrystalExplorer17 (Turner et al., 2017). The contribution of interatomic contacts to the d_{norm} surface of the title salt and the individual cations and anions are compared and shown in Fig. 4. In all cases, H$\cdots$O/O$\cdots$H contacts (i.e. $^{+}$N—H$\cdots$O^{-}, O—H$\cdots$O, C–H$\cdots$O) were found to be the major contributors towards the Hirshfeld surface, whereas H$\cdots$N/N$\cdots$H contacts (i.e. C—H$\cdots$N) between the 1,2,4-triazolium cations play a minor role in the stabilization of the crystal packing. The differences between the individual fingerprints of cations and anions result from different distributions of the C$\cdots$N/N$\cdots$C contacts (i.e. π–π stacking). It was found that the H$\cdots$H contacts have a relatively small contri-

Figure 1
The structures of the molecular entities in the title salt (**I**) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level, and hydrogen bonds are shown as dotted lines.
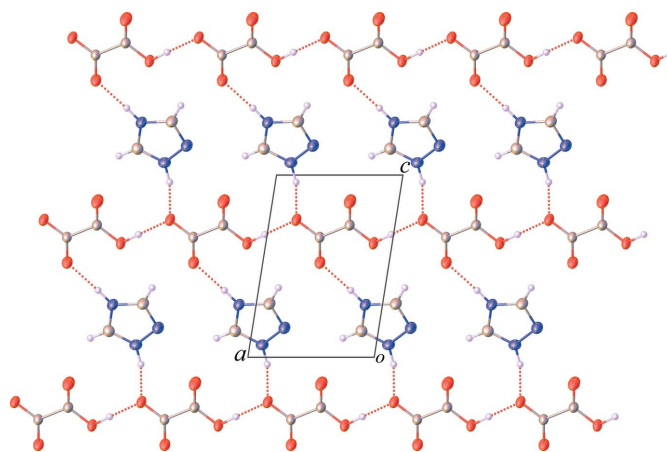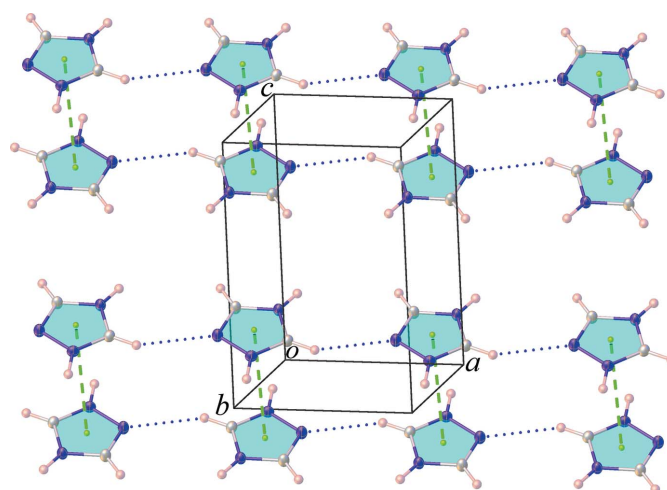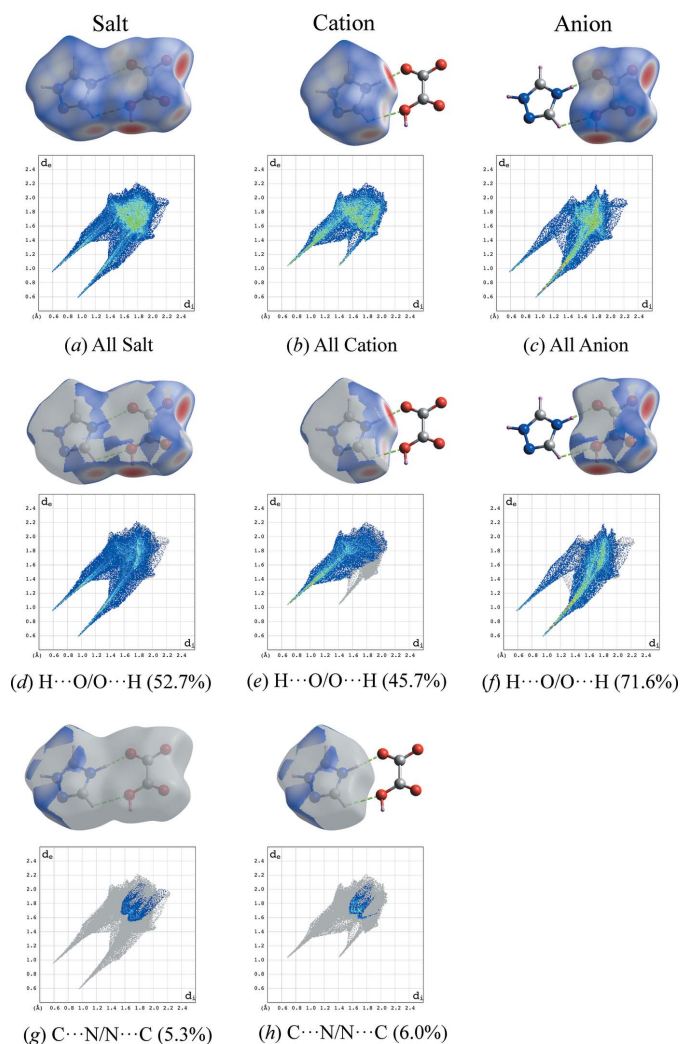

Figure 3
A view of the π–π stacking interactions along with the C—H$\cdots$N hydrogen bonds in the title salt (**I**).

Figure 4
Full two-dimensional fingerprint plots of the title salt (**I**) (*a*), and its cation (*b*) and anion (*c*); separate contact types for the salt are given in (*d*)–(*h*) with relative contributions. Hirshfeld surfaces mapped over d_{norm} are displayed in all plots.

bution of only 7.7% to the entire Hirshfeld surfaces of the title salt.

5. Database survey

A search of the Cambridge Structural Database (CSD version 5.40, August 2019 update; Groom *et al.*, 2016) for structures with hydrogen oxalate gave 666 hits of which five are hydrogen-bonded salts of triazolium, *viz*. AFIVAO (Essid *et al.*, 2013) and CIRXEH (Matulková *et al.*, 2008), or imidazolium, *viz*. EVAPEX (Zhu, 2011), MEQPAZ (MacDonald *et al.*, 2001) and MEQPAZ01 (Prasad *et al.*, 2002).

6. Synthesis and crystallization

An aqueous solution (5 ml) of oxalic acid (0.09 g, 0.01 mol) and 1,2,4-triazole (0.07 g, 0.01 mmol) was added dropwise to

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_2H_4N_3^+ \cdot C_2HO_4^-$
M_r	159.11
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	296
a, b, c (Å)	5.592 (1), 7.2162 (12), 8.4021 (13)
α, β, γ (°)	109.148 (6), 93.889 (7), 103.282 (6)
V (Å^3)	307.92 (9)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.16
Crystal size (mm)	$0.34 \times 0.22 \times 0.22$
Data collection	
Diffractometer	Bruker D8 Quest CMOS PHOTON II
Absorption correction	Multi-scan (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.638, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4805, 1524, 1278
R_{int}	0.038
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.668
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.037, 0.102, 1.07
No. of reflections	1524
No. of parameters	112
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å^{-3})	0.37, −0.20

Computer programs: *APEX3* and *SAINT* (Bruker, 2016), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

an aqueous solution (5 ml) of TbCl$_3$·6H$_2$O (0.37 g, 0.01 mol) under constant stirring for one h. The resulting solution was filtered to remove any undissolved solid. The filtrate was allowed to slowly evaporate at room temperature. After two weeks, colourless block-shaped crystals of the title salt (**I**) suitable for X-ray analysis were obtained.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The carboxyl and triazolium H atoms were located in difference-Fourier maps and were freely refined. Carbon-bound H atoms were placed in calculated positions and refined using a riding-model approximation with C—H = 0.93 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

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supporting information

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Computing details

Data collection: *APEX3* (Bruker, 2016); cell refinement: *SAINT* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

1,2,4-Triazolium hydrogen oxalate

Crystal data

$C_2H_4N_3{}^+ \cdot C_2HO_4{}^-$	$Z = 2$
$M_r = 159.11$	$F(000) = 164$
Triclinic, $P\bar{1}$	$D_x = 1.716$ Mg m^{-3}
$a = 5.592$ (1) Å	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$b = 7.2162$ (12) Å	Cell parameters from 2650 reflections
$c = 8.4021$ (13) Å	$\theta = 2.6$–28.3°
$\alpha = 109.148$ (6)°	$\mu = 0.16$ mm^{-1}
$\beta = 93.889$ (7)°	$T = 296$ K
$\gamma = 103.282$ (6)°	Block, light colourless
$V = 307.92$ (9) Å^3	$0.34 \times 0.22 \times 0.22$ mm

Data collection

Bruker D8 Quest CMOS PHOTON II diffractometer	4805 measured reflections
Radiation source: sealed x-ray tube	1524 independent reflections
Graphite monochromator	1278 reflections with $I > 2\sigma(I)$
Detector resolution: 7.39 pixels mm^{-1}	$R_{int} = 0.038$
ω and φ scans	$\theta_{max} = 28.4°$, $\theta_{min} = 2.6°$
Absorption correction: multi-scan (*SADABS*; Bruker, 2016)	$h = -6 \rightarrow 7$
	$k = -9 \rightarrow 8$
$T_{min} = 0.638$, $T_{max} = 0.746$	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent
$R[F^2 > 2\sigma(F^2)] = 0.037$	and constrained refinement
$wR(F^2) = 0.102$	$w = 1/[\sigma^2(F_o^2) + (0.0441P)^2 + 0.0686P]$
$S = 1.07$	where $P = (F_o^2 + 2F_c^2)/3$
1524 reflections	$(\Delta/\sigma)_{max} < 0.001$
112 parameters	$\Delta\rho_{max} = 0.37$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -0.20$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.14792 (16)	0.88282 (15)	0.62587 (12)	0.0335 (3)
H1A	0.020 (4)	0.935 (3)	0.674 (2)	0.069 (6)*
O2	0.38612 (19)	1.12875 (18)	0.85543 (14)	0.0506 (3)
O3	0.54794 (17)	0.76994 (15)	0.51985 (12)	0.0365 (3)
O4	0.78723 (16)	1.00344 (15)	0.75427 (12)	0.0345 (3)
N1	0.1358 (2)	0.53625 (17)	0.28813 (14)	0.0305 (3)
H1	0.270 (4)	0.620 (3)	0.367 (2)	0.057 (5)*
N2	−0.0976 (2)	0.30879 (17)	0.06817 (14)	0.0305 (3)
H2	−0.162 (4)	0.201 (3)	−0.039 (3)	0.063 (6)*
N3	−0.2527 (2)	0.40637 (18)	0.16122 (14)	0.0352 (3)
C1	0.3594 (2)	0.98777 (18)	0.72504 (15)	0.0264 (3)
C2	0.5818 (2)	0.91101 (18)	0.65830 (15)	0.0249 (3)
C3	0.1335 (2)	0.38679 (19)	0.14421 (16)	0.0304 (3)
H3	0.270783	0.345169	0.104695	0.036*
C4	−0.1040 (2)	0.5435 (2)	0.29349 (17)	0.0340 (3)
H4	−0.155357	0.635686	0.381391	0.041*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0174 (4)	0.0398 (5)	0.0303 (5)	0.0095 (4)	0.0014 (4)	−0.0054 (4)
O2	0.0280 (5)	0.0571 (7)	0.0392 (6)	0.0155 (5)	−0.0002 (4)	−0.0201 (5)
O3	0.0224 (5)	0.0396 (5)	0.0306 (5)	0.0093 (4)	0.0027 (4)	−0.0101 (4)
O4	0.0183 (4)	0.0414 (5)	0.0294 (5)	0.0093 (4)	−0.0003 (4)	−0.0064 (4)
N1	0.0231 (5)	0.0316 (6)	0.0269 (5)	0.0052 (4)	−0.0002 (4)	−0.0003 (4)
N2	0.0319 (6)	0.0286 (5)	0.0225 (5)	0.0072 (4)	0.0021 (4)	−0.0009 (4)
N3	0.0264 (6)	0.0380 (6)	0.0294 (6)	0.0091 (5)	0.0012 (5)	−0.0029 (5)
C1	0.0190 (6)	0.0304 (6)	0.0236 (6)	0.0083 (5)	0.0023 (4)	0.0004 (5)
C2	0.0183 (5)	0.0274 (6)	0.0238 (6)	0.0071 (4)	0.0033 (4)	0.0018 (5)
C3	0.0281 (6)	0.0313 (6)	0.0285 (6)	0.0103 (5)	0.0059 (5)	0.0046 (5)
C4	0.0273 (7)	0.0359 (7)	0.0275 (6)	0.0101 (5)	0.0014 (5)	−0.0038 (5)

Geometric parameters (Å, º)

O1—H1A	0.94 (2)	N2—H2	0.96 (2)
O1—C1	1.3066 (14)	N2—N3	1.3677 (16)
O2—C1	1.1976 (15)	N2—C3	1.3089 (17)
O3—C2	1.2370 (15)	N3—C4	1.2967 (17)
O4—C2	1.2586 (14)	C1—C2	1.5413 (17)

N1—H1	0.91 (2)	C3—H3	0.9300
N1—C3	1.3272 (16)	C4—H4	0.9300
N1—C4	1.3568 (18)		
C1—O1—H1A	109.1 (12)	O2—C1—C2	121.49 (11)
C3—N1—H1	127.8 (13)	O3—C2—O4	125.86 (11)
C3—N1—C4	106.09 (11)	O3—C2—C1	119.53 (11)
C4—N1—H1	126.1 (13)	O4—C2—C1	114.60 (10)
N3—N2—H2	120.4 (13)	N1—C3—H3	126.3
C3—N2—H2	128.5 (13)	N2—C3—N1	107.36 (12)
C3—N2—N3	111.11 (11)	N2—C3—H3	126.3
C4—N3—N2	103.62 (11)	N1—C4—H4	124.1
O1—C1—C2	112.90 (10)	N3—C4—N1	111.81 (12)
O2—C1—O1	125.61 (12)	N3—C4—H4	124.1
O1—C1—C2—O3	3.15 (18)	N3—N2—C3—N1	0.08 (15)
O1—C1—C2—O4	−177.26 (11)	C3—N1—C4—N3	0.23 (17)
O2—C1—C2—O3	−177.27 (13)	C3—N2—N3—C4	0.06 (15)
O2—C1—C2—O4	2.3 (2)	C4—N1—C3—N2	−0.18 (15)
N2—N3—C4—N1	−0.18 (16)		

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1*A*···O4[i]	0.94 (2)	1.61 (2)	2.5447 (13)	175.0 (18)
N1—H1···O3	0.91 (2)	1.81 (2)	2.7199 (15)	175.4 (18)
N2—H2···O4[ii]	0.96 (2)	1.80 (2)	2.7443 (15)	167.3 (19)
C3—H3···O2[iii]	0.93	2.40	3.1717 (17)	141
C3—H3···N3[iv]	0.93	2.58	3.3939 (18)	146
C4—H4···O1	0.93	2.45	3.0289 (16)	120
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