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Bis(triethylammonium) tetrabromidozincate

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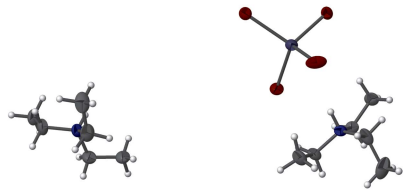
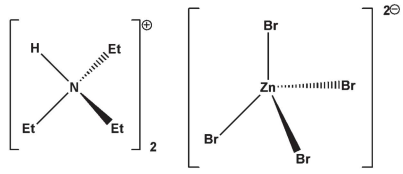
Structural data: full structural data are available from iucrdata.iucr.org

The title molecular salt, $(C_6H_{16}N)[ZnBr_4]$, consists of a tetrahedral tetrabromidozincate dianion and two triethylammonium cations linked by N—H···Br hydrogen bonds. In the crystal, these three-membered units are linked *via* C—H···Br hydrogen bonds, forming layers parallel to the *ab* plane.

3D view



Chemical scheme



Structure description

Many authors worldwide have synthesized ammonium salts of numerous acids for different purposes (Mouchaham *et al.*, 2015; Hamdouni *et al.*, 2015). A heterodinuclear complex containing $[ZnBr_4]^{2-}$ and triethylammonium ions with an Ru component has been reported (Mauthner *et al.*, 1999). The Senegalese group has used amines such as dipropylamine, diisopropylamine, monocyclohexylamine, dicyclohexylamine, dibutylamine, methyl-2-imidazole, ethylendiamine for obtaining the corresponding salts with sulfuric, oxalic and sulfonic acids and have reacted theirs salts with stannic organo- or halidostannate compounds or transition metal halides (Sarr *et al.*, 2014; Diop *et al.*, 2016). In this context, $(Et_3NH)_2{\cdot}C_2O_4$ has been allowed to react in ethanol with $ZnBr_2$ and crystals of the title molecular salt were obtained.

The molecular structure of the title molecular salt is shown in Fig. 1. It consists of a tetrahedral $[ZnBr_4]^{2-}$ dianion and two triethylammonium ions linked by N—H···Br hydrogen bonds (Table 1). The four Br atoms are non-equivalent; their distances range from 2.3945 (13) to 2.4408 (14) Å. Two of the Br atoms, Br3 and Br4, are involved in hydrogen bonds (Fig. 1 and Table 1) and their distances to the Zn atom are 2.4408 (14) and 2.4228 (13) Å, respectively. Atoms Br1 and Br2, which are not involved in N—H···Br hydrogen bonding, have shorter Zn—Br bond lengths [2.3945 (13) and 2.3947 (13) Å, respectively]. The Br—Zn—Br angles vary from 107.20 (2) to 112.91 (2)°, indicating a slightly distorted tetrahedron around the Zn atom with a τ_4 geometry index of 0.95 (for a perfect tetrahedron τ_4 is equal to 1; Yang *et al.*, 2007).

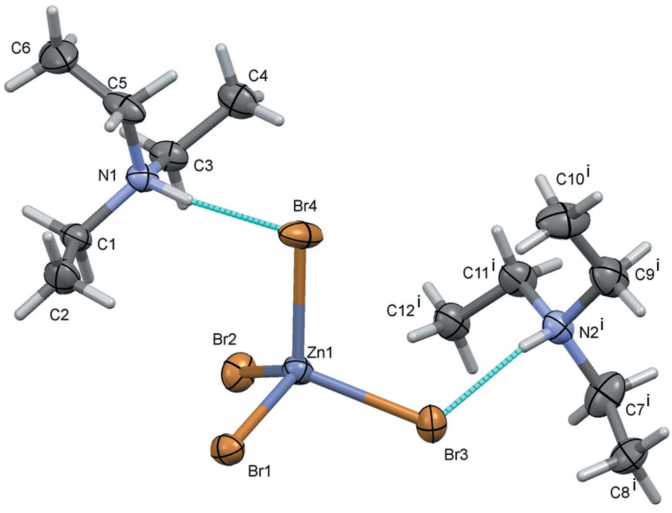


Figure 1
A view of the molecular structure of the title molecular salt, showing the atom labelling. Displacement ellipsoids are drawn at the 50% probability level. The N—H···Br hydrogen bonds are shown as dashed lines (see Table 1). [Symmetry code: (i) $x+\frac{1}{2}, y, -z+\frac{1}{2}$.]

In the crystal, the $(Et_3NH)_2{\cdot}ZnBr_4$ hydrogen-bonded species are connected to their neighbours through C—H···Br hydrogen bonds, forming layers parallel to the *ab* plane (Table 1 and Fig. 2).

Synthesis and crystallization

Oxalic acid was totally neutralized with Et_3NH in water giving $(Et_3NH)_2C_2O_4$, which was then mixed with $ZnBr_2$ in ethanol in a 1:1 ratio. A white precipitate was obtained and filtered.

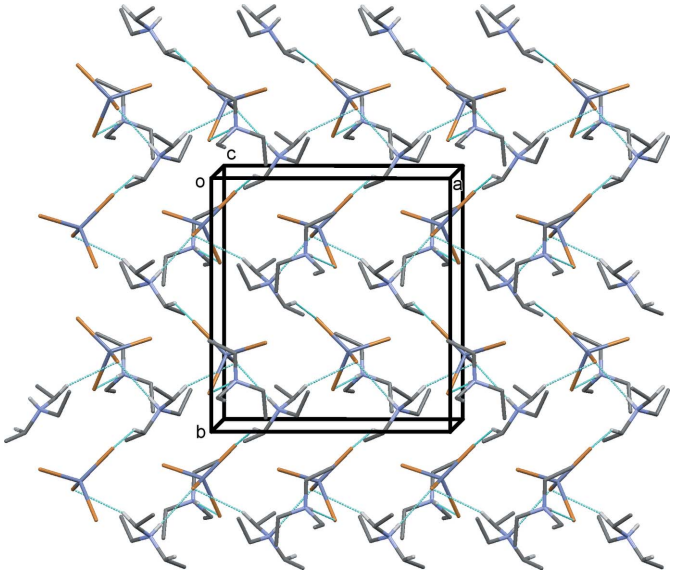


Figure 2
A view along the *c* axis of the crystal packing of the title molecular salt. Hydrogen bonds are shown as dashed lines (see Table 1) and H atoms not involved in these interactions have been omitted for clarity.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Br4	0.94 (3)	2.44 (3)	3.367 (3)	166 (3)
N2—H2···Br3^{i}	0.81 (4)	2.58 (4)	3.380 (3)	171 (3)
C7—H7*B*···Br3^{ii}	0.97	2.92	3.791 (5)	150
C9—H9*B*···Br1^{iii}	0.97	2.84	3.715 (5)	150

Symmetry codes: (i) $x-\frac{1}{2}, y, -z+\frac{1}{2}$; (ii) $x-1, y, z$; (iii) $-x+\frac{3}{2}, y+\frac{1}{2}, z$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$(C_6H_{16}N)_2[ZnBr_4]$
M_r	589.40
Crystal system, space group	Orthorhombic, *Pbca*
Temperature (K)	150
a, *b*, *c* (Å)	12.383 (6), 13.145 (6), 26.510 (11)
V (Å^3)	4315 (4)
Z	8
Radiation type	Mo *Kα*
μ (mm^{-1})	8.54
Crystal size (mm)	0.5 × 0.2 × 0.1
Data collection	
Diffractometer	Stoe *IPDS* 2T
Absorption correction	Integration (Coppens, 1970)
T_{min}, T_{max}	0.074, 0.135
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	35899, 4604, 3820
R_{int}	0.066
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.635
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.024, 0.045, 1.02
No. of reflections	4597
No. of parameters	186
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.69, −0.54

Computer programs: *X-AREA* (Stoe & Cie, 2009), *X-RED* (Stoe & Cie, 2009), *SHELXS97* (Sheldrick, 2008), *Mercury* (Macrae *et al.*, 2008), *SHELXL2014* (Sheldrick, 2015), *PLATON* (Spek, 2009) and *publCIF* (Westrip, 2010).

The filtrate was allowed to evaporate slowly at room temperature giving colourless crystals of the title molecular salt, suitable for X-ray diffraction analysis.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x161317 [doi:10.1107/S2414314616013171]

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Crystal data

$(C_6H_{16}N)_2[ZnBr_4]$
M_r = 589.40
Orthorhombic, *Pbca*
a = 12.383 (6) Å
b = 13.145 (6) Å
c = 26.510 (11) Å
V = 4315 (4) Å^3
Z = 8
F(000) = 2304
D_x = 1.814 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 707 reflections
θ = 2.8–24.4°
μ = 8.54 mm^{-1}
T = 150 K
Plate, colourless
0.5 × 0.2 × 0.1 mm

Data collection

Stoe IPDS 2T diffractometer
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus
Detector resolution: 6.67 pixels mm^{-1}
combination of /w– and /f–scans
Absorption correction: integration (Coppens, 1970)
T_{min} = 0.074, T_{max} = 0.135
35899 measured reflections
4604 independent reflections
3820 reflections with $I > 2\sigma(I)$
R_{int} = 0.066
θ_{max} = 26.8°, θ_{min} = 2.4°
h = −15→15
k = −16→16
l = −33→31

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.045
S = 1.02
4597 reflections
186 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0131P)^2 + 0.7809P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.69 e Å^{-3}
$\Delta\rho_{min}$ = −0.54 e Å^{-3}

Special details

Geometry. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	1.07931 (3)	0.07296 (3)	0.37735 (2)	0.0331 (1)
Br2	0.77855 (3)	0.15351 (3)	0.41392 (2)	0.0375 (1)
Br3	0.90854 (3)	0.23837 (3)	0.28535 (2)	0.0347 (1)
Br4	1.01299 (3)	0.35305 (3)	0.41642 (2)	0.0454 (1)
Zn1	0.94409 (3)	0.20302 (3)	0.37420 (2)	0.0270 (1)
N1	0.8953 (2)	0.2988 (2)	0.52772 (10)	0.0266 (8)
C1	0.8993 (3)	0.1880 (2)	0.54246 (13)	0.0300 (10)
C2	1.0072 (3)	0.1401 (3)	0.53058 (14)	0.0406 (11)
C3	0.7812 (2)	0.3369 (3)	0.52691 (14)	0.0323 (10)
C4	0.7718 (3)	0.4452 (3)	0.50953 (15)	0.0417 (12)
C5	0.9698 (3)	0.3640 (3)	0.55787 (15)	0.0379 (11)
C6	0.9399 (4)	0.3717 (3)	0.61273 (15)	0.0600 (14)
N2	0.2290 (2)	0.4253 (2)	0.23986 (11)	0.0305 (9)
C7	0.1726 (3)	0.3843 (4)	0.28569 (14)	0.0487 (13)
C8	0.2462 (3)	0.3374 (3)	0.32364 (13)	0.0419 (13)
C9	0.2943 (3)	0.5177 (3)	0.25324 (16)	0.0470 (12)
C10	0.3711 (3)	0.5483 (4)	0.21273 (17)	0.0563 (16)
C11	0.1516 (3)	0.4464 (3)	0.19735 (14)	0.0390 (11)
C12	0.1047 (3)	0.3521 (3)	0.17426 (14)	0.0407 (12)
H1	0.918 (3)	0.308 (2)	0.4941 (12)	0.023 (8)*
H1A	0.84290	0.15150	0.52470	0.0360*
H1B	0.88530	0.18190	0.57830	0.0360*
H2A	1.02130	0.14560	0.49510	0.0610*
H2B	1.00590	0.06960	0.54010	0.0610*
H2C	1.06300	0.17450	0.54900	0.0610*
H3A	0.75100	0.33130	0.56060	0.0390*
H3B	0.73880	0.29390	0.50470	0.0390*
H4A	0.80090	0.48960	0.53490	0.0620*
H4B	0.69720	0.46140	0.50390	0.0620*
H4C	0.81140	0.45380	0.47870	0.0620*
H5A	0.97060	0.43180	0.54340	0.0460*
H5B	1.04240	0.33670	0.55530	0.0460*
H6A	0.86730	0.39670	0.61570	0.0900*
H6B	0.98840	0.41770	0.62940	0.0900*
H6C	0.94480	0.30570	0.62810	0.0900*
H2	0.271 (3)	0.382 (3)	0.2304 (13)	0.027 (10)*
H7A	0.13310	0.43920	0.30170	0.0580*
H7B	0.12040	0.33360	0.27500	0.0580*
H8A	0.28780	0.28460	0.30790	0.0630*
H8B	0.20430	0.30900	0.35070	0.0630*
H8C	0.29400	0.38840	0.33680	0.0630*
H9A	0.24560	0.57390	0.26000	0.0560*
H9B	0.33460	0.50410	0.28390	0.0560*
H10A	0.41190	0.49010	0.20200	0.0840*
H10B	0.41940	0.59940	0.22540	0.0840*

H10C	0.33150	0.57520	0.18460	0.0840*
H11A	0.09320	0.48850	0.20990	0.0470*
H11B	0.18900	0.48470	0.17140	0.0470*
H12A	0.16200	0.31020	0.16140	0.0610*
H12B	0.05720	0.37060	0.14720	0.0610*
H12C	0.06510	0.31520	0.19940	0.0610*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0319 (2)	0.0318 (2)	0.0355 (2)	0.0054 (2)	−0.0045 (2)	−0.0037 (2)
Br2	0.0293 (2)	0.0476 (2)	0.0356 (2)	−0.0069 (2)	0.0061 (1)	0.0024 (2)
Br3	0.0343 (2)	0.0374 (2)	0.0324 (2)	0.0045 (2)	0.0021 (2)	0.0077 (2)
Br4	0.0590 (2)	0.0294 (2)	0.0479 (2)	−0.0174 (2)	0.0234 (2)	−0.0132 (2)
Zn1	0.0272 (2)	0.0244 (2)	0.0294 (2)	−0.0007 (2)	0.0036 (2)	−0.0002 (2)
N1	0.0255 (14)	0.0247 (14)	0.0297 (14)	−0.0031 (12)	0.0046 (11)	−0.0023 (12)
C1	0.0351 (18)	0.0218 (17)	0.0331 (17)	−0.0007 (15)	0.0026 (14)	−0.0016 (14)
C2	0.046 (2)	0.034 (2)	0.0419 (19)	0.0124 (18)	0.0048 (17)	0.0007 (18)
C3	0.0246 (16)	0.0295 (19)	0.0429 (19)	0.0007 (15)	0.0031 (15)	−0.0050 (16)
C4	0.034 (2)	0.036 (2)	0.055 (2)	0.0075 (17)	−0.0011 (17)	−0.0007 (19)
C5	0.0260 (17)	0.0247 (19)	0.063 (2)	−0.0015 (15)	−0.0083 (16)	−0.0043 (18)
C6	0.090 (3)	0.040 (2)	0.050 (2)	−0.006 (2)	−0.033 (2)	−0.006 (2)
N2	0.0283 (15)	0.0290 (16)	0.0341 (16)	−0.0002 (14)	−0.0049 (12)	−0.0020 (13)
C7	0.0312 (18)	0.074 (3)	0.041 (2)	−0.001 (2)	0.0059 (17)	0.002 (2)
C8	0.0378 (19)	0.053 (3)	0.0350 (17)	−0.0027 (19)	0.0076 (17)	0.0070 (19)
C9	0.049 (2)	0.041 (2)	0.051 (2)	−0.0059 (19)	−0.0137 (19)	−0.005 (2)
C10	0.046 (2)	0.056 (3)	0.067 (3)	−0.021 (2)	−0.015 (2)	0.020 (2)
C11	0.0360 (19)	0.036 (2)	0.045 (2)	0.0021 (17)	−0.0153 (17)	−0.0002 (17)
C12	0.042 (2)	0.038 (2)	0.042 (2)	−0.0006 (19)	−0.0147 (16)	−0.0030 (18)

Geometric parameters (Å, º)

Br1—Zn1	2.3945 (13)	C5—H5B	0.9700
Br2—Zn1	2.3947 (13)	C5—H5A	0.9700
Br3—Zn1	2.4408 (14)	C6—H6B	0.9600
Br4—Zn1	2.4228 (13)	C6—H6C	0.9600
N1—C5	1.492 (5)	C6—H6A	0.9600
N1—C1	1.509 (4)	N2—H2	0.81 (4)
N1—C3	1.499 (4)	C7—C8	1.491 (5)
N1—H1	0.94 (3)	C9—C10	1.490 (6)
C1—C2	1.510 (5)	C11—C12	1.500 (6)
C3—C4	1.501 (6)	C7—H7A	0.9700
C5—C6	1.504 (6)	C7—H7B	0.9700
C1—H1A	0.9700	C8—H8C	0.9600
C1—H1B	0.9700	C8—H8A	0.9600
C2—H2B	0.9600	C8—H8B	0.9600
C2—H2C	0.9600	C9—H9B	0.9700
C2—H2A	0.9600	C9—H9A	0.9700

N2—C11	1.505 (5)	C10—H10A	0.9600
N2—C7	1.501 (5)	C10—H10B	0.9600
N2—C9	1.502 (5)	C10—H10C	0.9600
C3—H3A	0.9700	C11—H11A	0.9700
C3—H3B	0.9700	C11—H11B	0.9700
C4—H4C	0.9600	C12—H12B	0.9600
C4—H4A	0.9600	C12—H12C	0.9600
C4—H4B	0.9600	C12—H12A	0.9600

Br1—Zn1—Br3	107.20 (2)	H6A—C6—H6C	109.00
Br1—Zn1—Br4	108.59 (2)	C5—C6—H6C	110.00
Br2—Zn1—Br3	108.77 (2)	H6A—C6—H6B	109.00
Br2—Zn1—Br4	108.64 (2)	C5—C6—H6B	109.00
Br3—Zn1—Br4	110.75 (2)	H6B—C6—H6C	110.00
Br1—Zn1—Br2	112.91 (2)	C5—C6—H6A	109.00
C1—N1—C5	113.3 (3)	C11—N2—H2	108 (2)
C1—N1—C3	110.9 (3)	C7—N2—H2	107 (3)
C3—N1—C5	113.5 (3)	C9—N2—H2	107 (3)
C1—N1—H1	111.0 (16)	N2—C7—C8	114.2 (3)
N1—C1—C2	112.2 (3)	N2—C9—C10	113.1 (3)
C3—N1—H1	103 (2)	N2—C11—C12	113.6 (3)
C5—N1—H1	104 (2)	N2—C7—H7B	109.00
N1—C3—C4	113.2 (3)	N2—C7—H7A	109.00
N1—C5—C6	113.9 (3)	C8—C7—H7A	109.00
C2—C1—H1B	109.00	C8—C7—H7B	109.00
H1A—C1—H1B	108.00	H7A—C7—H7B	108.00
N1—C1—H1A	109.00	H8A—C8—H8B	109.00
N1—C1—H1B	109.00	H8A—C8—H8C	109.00
C2—C1—H1A	109.00	H8B—C8—H8C	109.00
C7—N2—C9	110.5 (3)	C7—C8—H8A	109.00
C1—C2—H2A	110.00	C7—C8—H8B	110.00
C1—C2—H2B	109.00	C7—C8—H8C	109.00
C1—C2—H2C	110.00	C10—C9—H9A	109.00
H2A—C2—H2B	109.00	N2—C9—H9A	109.00
H2A—C2—H2C	109.00	N2—C9—H9B	109.00
H2B—C2—H2C	109.00	C10—C9—H9B	109.00
C7—N2—C11	112.1 (3)	H9A—C9—H9B	108.00
C9—N2—C11	111.8 (3)	C9—C10—H10B	110.00
N1—C3—H3A	109.00	C9—C10—H10A	110.00
C4—C3—H3B	109.00	H10A—C10—H10B	109.00
N1—C3—H3B	109.00	H10A—C10—H10C	109.00
C4—C3—H3A	109.00	C9—C10—H10C	109.00
H3A—C3—H3B	108.00	H10B—C10—H10C	109.00
H4B—C4—H4C	109.00	C12—C11—H11A	109.00
C3—C4—H4C	109.00	C12—C11—H11B	109.00
H4A—C4—H4B	110.00	N2—C11—H11A	109.00
H4A—C4—H4C	109.00	N2—C11—H11B	109.00
C3—C4—H4B	109.00	H11A—C11—H11B	108.00

C3—C4—H4A	109.00	H12B—C12—H12C	110.00
N1—C5—H5B	109.00	C11—C12—H12A	109.00
N1—C5—H5A	109.00	C11—C12—H12B	109.00
H5A—C5—H5B	108.00	C11—C12—H12C	109.00
C6—C5—H5A	109.00	H12A—C12—H12B	109.00
C6—C5—H5B	109.00	H12A—C12—H12C	110.00
C3—N1—C1—C2	164.9 (3)	C9—N2—C7—C8	−69.6 (4)
C5—N1—C1—C2	−66.1 (4)	C11—N2—C7—C8	165.0 (3)
C1—N1—C3—C4	−176.6 (3)	C7—N2—C9—C10	167.1 (3)
C5—N1—C3—C4	54.5 (4)	C11—N2—C9—C10	−67.4 (4)
C1—N1—C5—C6	−66.3 (4)	C7—N2—C11—C12	−69.5 (4)
C3—N1—C5—C6	61.4 (4)	C9—N2—C11—C12	165.8 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Br4	0.94 (3)	2.44 (3)	3.367 (3)	166 (3)
N2—H2···Br3^{i}	0.81 (4)	2.58 (4)	3.380 (3)	171 (3)
C7—H7*B*···Br3^{ii}	0.97	2.92	3.791 (5)	150
C9—H9*B*···Br1^{iii}	0.97	2.84	3.715 (5)	150

Symmetry codes: (i) $x-1/2, y, -z+1/2$; (ii) $x-1, y, z$; (iii) $-x+3/2, y+1/2, z$.