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Bis(4-methylmorpholin-4-ium) tetrabromidozincate(II)

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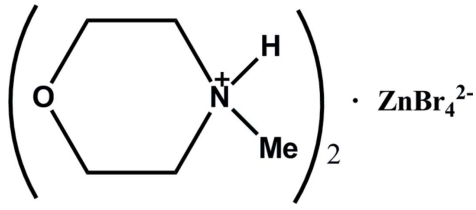
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.009 Å; R factor = 0.047; wR factor = 0.096; data-to-parameter ratio = 25.5.

The title compound, $(C_5H_{12}NO)_2[ZnBr_4]$, was synthesized by hydrothermal reaction of $ZnBr_2$ with 4-methylmorpholine in a HBr/distilled water solution. Each of the two independent cations exhibits a chair conformation; the anion deviates slightly from an tetrahedral configuration. The Zn—Br distances in the anion are in the range of 2.3996 (9)–2.4247 (9) Å. All of the amine H atoms are involved in bifurcated intermolecular N—H···Br hydrogen bonds, building up a trimer.

Related literature

For the preparation of amino coordination compounds, see: Fu *et al.* (2009); Aminabhavi *et al.* (1986).



Experimental

Crystal data

$(C_5H_{12}NO)_2[ZnBr_4]$ M_r = 589.32
Monoclinic, $P2_1/c$
a = 7.5000 (15) Å
b = 20.925 (4) Å
c = 12.670 (3) Å
β = 103.33 (3)°
V = 1934.8 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 9.53 mm^{-1}
T = 298 K
0.30 × 0.02 × 0.01 mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.810, T_{max} = 0.900
19809 measured reflections
4439 independent reflections
3118 reflections with $I > 2\sigma(I)$
R_{int} = 0.079

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.096
S = 1.07
4439 reflections
174 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.58 e Å^{-3}
$\Delta\rho_{min}$ = −0.78 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Br2^{i}	0.90	2.70	3.427 (4)	138
N1—H1···Br3^{i}	0.90	2.87	3.541 (4)	132
N2—H2···Br4	0.90	2.72	3.504 (4)	147
N2—H2···Br1	0.90	3.08	3.714 (4)	129

Symmetry code: (i) $-x, -y+1, -z+2$.

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

This work was supported by the start-up fund of Anyang Institute of Technology.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RU2007).

References

Aminabhavi, T. M., Biradar, N. S. & Patil, S. B. (1986). *Inorg. Chim. Acta*, **125**, 125–128.
Fu, D.-W., Ge, J.-Z., Dai, J., Ye, H.-Y. & Qu, Z.-R. (2009). *Inorg. Chem. Commun.* **12**, 994–997.
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supporting information

Acta Cryst. (2011). E**67**, m1056 [doi:10.1107/S1600536811026766]

Bis(4-methylmorpholin-4-ium) tetrabromidozincate(II)

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S1. Comment

The amino derivatives have found wide range of applications in material science, such as magnetic, fluorescent and dielectric behaviors. And there has been an increased interest in the preparation of amino coordination compound (Aminabhavi *et al.,* 1986; Fu, *et al.* 2009). We report here the crystal structure of the title compound, *Bis*-(4-methylmorpholin-4-ium) tetrabromidozincate(II).

The asymmetric unit is composed of one $ZnBr_4^{2-}$ anion and two 4-methylmorpholin-4-ium cations (Fig.1). Both the amine N atoms were protonated, thus indicating two positive charge in all. And the $ZnBr_4^{2-}$ anion was showing two negative charge to make the charge balance. The geometric parameters of the title compound are in the normal range.

In the crystal structure, all the H atoms of amine groups are involved in intermolecular N—H···Br hydrogen bonds building up a trimer (Table 1 and Fig.2).

S2. Experimental

A mixture of 4-methylmorpholine (0.4 mmol), $ZnBr_2$ (0.4 mmol) and HBr/distilled water (10ml,1:3) sealed in a Teflon-lined stainless steel vessel, was maintained at 100 °C. Colorless needle crystals suitable for X-ray analysis were obtained after 3 days.

S3. Refinement

All H atoms attached to C atoms were fixed geometrically and treated as riding with C-H = 0.97 Å(methylene) and C-H = 0.96 Å(methyl) with U_{iso}(H) = 1.2U_{eq}(methylene) and U_{iso}(H) = 1.5U_{eq}(methyl). The positional parameters of the H atoms (N1, N2) were refined freely. And in the last stage of the refinement, it were restrained with the H—N = 0.90 (2)Å), with U_{iso}(H)=1.2U_{eq}(N).

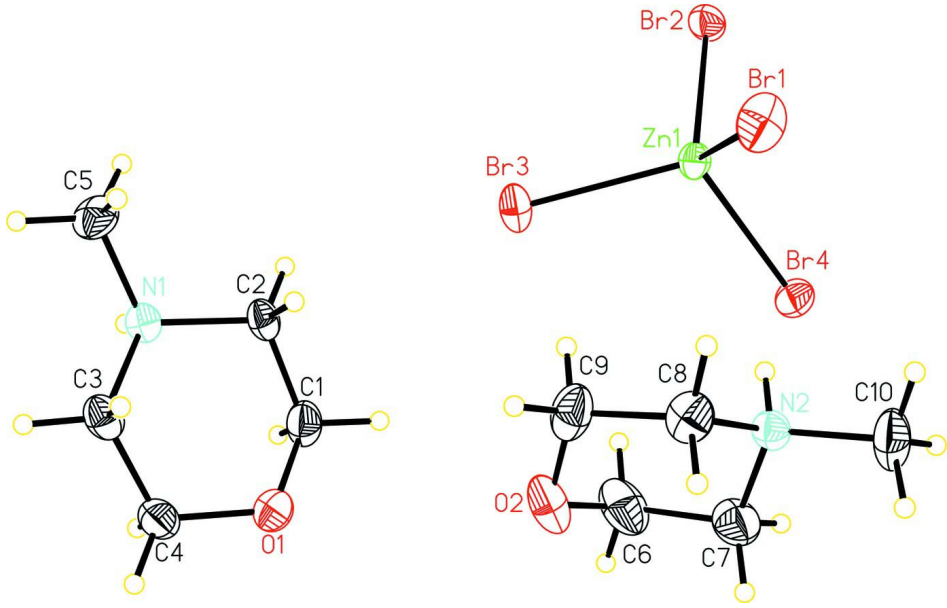

Figure 1

Molecular view of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

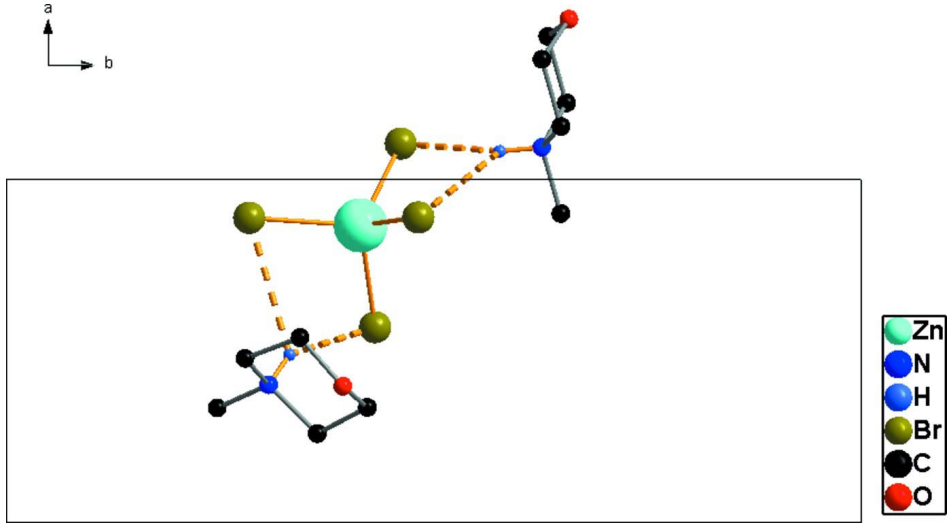

Figure 2

The crystal packing of the title compound viewed along the *c* axis showing the one-dimensionnal hydrogen bondings chain (dashed line). Hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

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Crystal data

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Hall symbol: -P 2ybc
a = 7.5000 (15) Å
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c = 12.670 (3) Å
β = 103.33 (3)°
V = 1934.8 (7) Å^3
Z = 4

$F(000) = 1136$
$D_x = 2.023$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 4439 reflections
$\theta = 3.1$–$27.5°$
$\mu = 9.53$ mm^{-1}
$T = 298$ K
Needle, colorless
0.30 × 0.02 × 0.01 mm

Data collection

Rigaku Mercury2 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 13.6612 pixels mm^{-1}
CCD profile fitting scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min} = 0.810$, $T_{max} = 0.900$
19809 measured reflections
4439 independent reflections
3118 reflections with $I > 2\sigma(I)$
$R_{int} = 0.079$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.1°$
$h = -9 \rightarrow 9$
$k = -27 \rightarrow 27$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.096$
$S = 1.07$
4439 reflections
174 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.024P)^2 + 1.999P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.78$ 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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2$sigma(F^2) is used only for calculating R-factors(gt) etc. 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}
Zn1	0.13367 (8)	0.63934 (3)	0.72630 (5)	0.03501 (16)
N1	0.0938 (5)	0.54509 (19)	1.2863 (3)	0.0349 (10)
H1	0.0825	0.5023	1.2819	0.042*
Br2	−0.10482 (8)	0.59847 (3)	0.58209 (4)	0.04782 (17)
Br3	0.11003 (9)	0.58049 (3)	0.88737 (4)	0.04937 (18)
C3	0.2234 (8)	0.5701 (3)	1.3845 (4)	0.0463 (14)
H3A	0.1917	0.5532	1.4491	0.056*
H3B	0.2144	0.6163	1.3864	0.056*
Br4	0.43069 (7)	0.62464 (3)	0.68930 (5)	0.04825 (17)
Br1	0.11182 (10)	0.75261 (3)	0.75420 (6)	0.0650 (2)
O1	0.4678 (5)	0.57277 (19)	1.2887 (3)	0.0552 (11)

C5	−0.0990 (8)	0.5644 (3)	1.2811 (5)	0.0537 (16)
H5A	−0.1349	0.5495	1.3448	0.081*
H5B	−0.1778	0.5459	1.2179	0.081*
H5C	−0.1086	0.6101	1.2772	0.081*
C4	0.4175 (8)	0.5510 (3)	1.3833 (4)	0.0507 (15)
H4A	0.5011	0.5688	1.4465	0.061*
H4B	0.4282	0.5049	1.3873	0.061*
C2	0.1551 (7)	0.5645 (2)	1.1864 (4)	0.0379 (13)
H2A	0.1432	0.6104	1.1768	0.045*
H2B	0.0780	0.5441	1.1233	0.045*
C1	0.3508 (8)	0.5452 (3)	1.1963 (5)	0.0505 (15)
H1A	0.3604	0.4990	1.2013	0.061*
H1B	0.3896	0.5585	1.1318	0.061*
N2	0.5985 (6)	0.7329 (2)	0.8998 (3)	0.0390 (10)
H2	0.5105	0.7118	0.8522	0.047*
O2	0.6025 (7)	0.6575 (2)	1.0880 (3)	0.0724 (14)
C8	0.5215 (9)	0.7569 (3)	0.9907 (5)	0.0528 (16)
H8A	0.4179	0.7847	0.9626	0.063*
H8B	0.6136	0.7814	1.0408	0.063*
C9	0.4608 (9)	0.7010 (3)	1.0494 (5)	0.0628 (19)
H9A	0.4146	0.7168	1.1099	0.075*
H9B	0.3613	0.6790	1.0004	0.075*
C7	0.7407 (9)	0.6834 (3)	0.9412 (5)	0.0641 (18)
H7A	0.7824	0.6648	0.8810	0.077*
H7B	0.8451	0.7031	0.9899	0.077*
C10	0.6659 (10)	0.7853 (3)	0.8407 (5)	0.0680 (19)
H10A	0.7112	0.7678	0.7819	0.102*
H10B	0.7628	0.8077	0.8893	0.102*
H10C	0.5673	0.8143	0.8126	0.102*
C6	0.6643 (11)	0.6325 (3)	0.9995 (6)	0.076 (2)
H6A	0.5630	0.6118	0.9498	0.091*
H6B	0.7578	0.6006	1.0254	0.091*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0398 (3)	0.0309 (3)	0.0357 (3)	−0.0033 (3)	0.0116 (3)	−0.0006 (3)
N1	0.043 (2)	0.029 (2)	0.033 (2)	−0.0024 (19)	0.0091 (19)	−0.0058 (19)
Br2	0.0445 (3)	0.0533 (4)	0.0409 (3)	−0.0084 (3)	0.0002 (3)	0.0049 (3)
Br3	0.0710 (4)	0.0452 (3)	0.0344 (3)	−0.0144 (3)	0.0171 (3)	0.0006 (3)
C3	0.058 (4)	0.045 (3)	0.034 (3)	−0.006 (3)	0.007 (3)	−0.004 (3)
Br4	0.0418 (3)	0.0538 (4)	0.0530 (4)	0.0060 (3)	0.0189 (3)	0.0008 (3)
Br1	0.0816 (5)	0.0295 (3)	0.0932 (5)	−0.0003 (3)	0.0392 (4)	−0.0060 (3)
O1	0.047 (2)	0.064 (3)	0.054 (3)	−0.016 (2)	0.011 (2)	0.010 (2)
C5	0.046 (3)	0.062 (4)	0.057 (4)	0.011 (3)	0.019 (3)	−0.010 (3)
C4	0.050 (4)	0.055 (4)	0.042 (3)	−0.008 (3)	0.001 (3)	0.010 (3)
C2	0.051 (3)	0.032 (3)	0.031 (3)	−0.007 (2)	0.009 (2)	0.004 (2)
C1	0.058 (4)	0.052 (4)	0.045 (3)	−0.009 (3)	0.018 (3)	0.005 (3)

N2	0.043 (3)	0.039 (3)	0.033 (2)	−0.004 (2)	0.007 (2)	−0.002 (2)
O2	0.102 (4)	0.071 (3)	0.043 (3)	−0.001 (3)	0.015 (3)	0.015 (2)
C8	0.060 (4)	0.053 (4)	0.049 (4)	−0.001 (3)	0.021 (3)	−0.014 (3)
C9	0.073 (5)	0.074 (5)	0.049 (4)	−0.025 (4)	0.029 (3)	−0.015 (4)
C7	0.058 (4)	0.075 (5)	0.062 (4)	0.024 (4)	0.018 (3)	0.012 (4)
C10	0.092 (5)	0.058 (4)	0.060 (4)	−0.023 (4)	0.029 (4)	0.010 (3)
C6	0.099 (6)	0.062 (5)	0.066 (5)	0.027 (4)	0.019 (4)	0.019 (4)

Geometric parameters (Å, º)

Zn1—Br4	2.3996 (9)	C1—H1A	0.9700
Zn1—Br2	2.4005 (11)	C1—H1B	0.9700
Zn1—Br1	2.4075 (9)	N2—C10	1.480 (7)
Zn1—Br3	2.4247 (9)	N2—C8	1.490 (6)
N1—C3	1.487 (6)	N2—C7	1.493 (7)
N1—C5	1.488 (7)	N2—H2	0.9002
N1—C2	1.499 (6)	O2—C9	1.398 (8)
N1—H1	0.9000	O2—C6	1.409 (8)
C3—C4	1.513 (8)	C8—C9	1.511 (8)
C3—H3A	0.9700	C8—H8A	0.9700
C3—H3B	0.9700	C8—H8B	0.9700
O1—C4	1.412 (6)	C9—H9A	0.9700
O1—C1	1.414 (7)	C9—H9B	0.9700
C5—H5A	0.9600	C7—C6	1.484 (9)
C5—H5B	0.9600	C7—H7A	0.9700
C5—H5C	0.9600	C7—H7B	0.9700
C4—H4A	0.9700	C10—H10A	0.9600
C4—H4B	0.9700	C10—H10B	0.9600
C2—C1	1.499 (7)	C10—H10C	0.9600
C2—H2A	0.9700	C6—H6A	0.9700
C2—H2B	0.9700	C6—H6B	0.9700
Br4—Zn1—Br2	111.59 (4)	O1—C1—H1B	109.3
Br4—Zn1—Br1	104.63 (3)	C2—C1—H1B	109.3
Br2—Zn1—Br1	113.48 (3)	H1A—C1—H1B	108.0
Br4—Zn1—Br3	110.52 (4)	C10—N2—C8	112.3 (5)
Br2—Zn1—Br3	105.87 (3)	C10—N2—C7	113.1 (5)
Br1—Zn1—Br3	110.84 (3)	C8—N2—C7	109.6 (4)
C3—N1—C5	112.5 (4)	C10—N2—H2	107.9
C3—N1—C2	110.1 (4)	C8—N2—H2	109.1
C5—N1—C2	111.9 (4)	C7—N2—H2	104.5
C3—N1—H1	115.9	C9—O2—C6	109.0 (5)
C5—N1—H1	101.0	N2—C8—C9	109.5 (5)
C2—N1—H1	105.0	N2—C8—H8A	109.8
N1—C3—C4	110.1 (4)	C9—C8—H8A	109.8
N1—C3—H3A	109.6	N2—C8—H8B	109.8
C4—C3—H3A	109.6	C9—C8—H8B	109.8
N1—C3—H3B	109.6	H8A—C8—H8B	108.2

C4—C3—H3B	109.6	O2—C9—C8	112.6 (5)
H3A—C3—H3B	108.2	O2—C9—H9A	109.1
C4—O1—C1	109.5 (4)	C8—C9—H9A	109.1
N1—C5—H5A	109.5	O2—C9—H9B	109.1
N1—C5—H5B	109.5	C8—C9—H9B	109.1
H5A—C5—H5B	109.5	H9A—C9—H9B	107.8
N1—C5—H5C	109.5	C6—C7—N2	110.3 (5)
H5A—C5—H5C	109.5	C6—C7—H7A	109.6
H5B—C5—H5C	109.5	N2—C7—H7A	109.6
O1—C4—C3	111.7 (4)	C6—C7—H7B	109.6
O1—C4—H4A	109.3	N2—C7—H7B	109.6
C3—C4—H4A	109.3	H7A—C7—H7B	108.1
O1—C4—H4B	109.3	N2—C10—H10A	109.5
C3—C4—H4B	109.3	N2—C10—H10B	109.5
H4A—C4—H4B	107.9	H10A—C10—H10B	109.5
N1—C2—C1	109.9 (4)	N2—C10—H10C	109.5
N1—C2—H2A	109.7	H10A—C10—H10C	109.5
C1—C2—H2A	109.7	H10B—C10—H10C	109.5
N1—C2—H2B	109.7	O2—C6—C7	111.4 (6)
C1—C2—H2B	109.7	O2—C6—H6A	109.3
H2A—C2—H2B	108.2	C7—C6—H6A	109.3
O1—C1—C2	111.6 (5)	O2—C6—H6B	109.3
O1—C1—H1A	109.3	C7—C6—H6B	109.3
C2—C1—H1A	109.3	H6A—C6—H6B	108.0

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Br2^{i}	0.90	2.70	3.427 (4)	138
N1—H1···Br3^{i}	0.90	2.87	3.541 (4)	132
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N2—H2···Br1	0.90	3.08	3.714 (4)	129

Symmetry code: (i) −*x*, −*y*+1, −*z*+2.