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Dimethylammonium bis(4-methylmorpholin-4-ium) tetrachloridozincate

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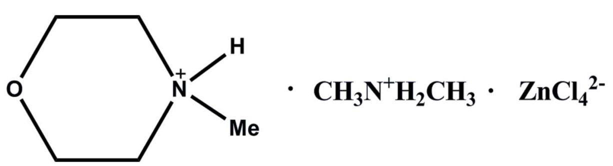
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.003 Å; R factor = 0.030; wR factor = 0.072; data-to-parameter ratio = 21.5.

The title compound, $(C_2H_8N)(C_5H_{12}NO)[ZnCl_4]$, was synthesized by hydrothermal reaction of $ZnCl_2$ with 4-methylmorpholine in a dimethylformamide solution. The asymmetric unit is composed of half a $[ZnCl_4]^{2-}$ anion, half a 4-methylmorpholin-4-ium cation and half a dimethylammonium cation, all located on mirror planes parallel to *ac*. All the amine H atoms are involved in intermolecular N—H⋯Cl hydrogen bonds, building up an infinite chain parallel to the *c* axis.

Related literature

For properties of amino compounds, see: Fu *et al.* (2009); Aminabhavi *et al.* (1986); Dai & Fu (2008*a*,*b*).



Experimental

Crystal data

$(C_2H_8N)(C_5H_{12}NO)[ZnCl_4]$
M_r = 355.42
Orthorhombic, *Pnma*
a = 20.272 (4) Å
b = 10.220 (2) Å
c = 7.3727 (15) Å
V = 1527.5 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.29 mm^{-1}
T = 298 K
0.30 × 0.05 × 0.05 mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.910, T_{max} = 1.000
15010 measured reflections
1851 independent reflections
1655 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.072
S = 1.14
1851 reflections
86 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.38 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1*C*⋯Cl1^{i}	0.81 (3)	2.78 (3)	3.435 (2)	139 (1)
N2—H2*D*⋯Cl3^{ii}	0.86 (4)	2.42 (4)	3.215 (3)	154 (3)
N1—H1*C*⋯Cl1	0.81 (3)	2.78 (3)	3.435 (2)	139 (1)
N2—H2*C*⋯Cl2	0.85 (4)	2.44 (4)	3.287 (3)	172 (4)

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

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*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZK2013).

References

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supplementary materials

Acta Cryst. (2011). E**67**, m1009 [doi:10.1107/S1600536811025049]

Dimethylammonium bis(4-methylmorpholin-4-ium) tetrachloridozincate

Y. Zhang and Y. Wang

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; Dai & Fu 2008*a*; Dai & Fu 2008*b*; Fu, *et al.* 2009). We report here the crystal structure of the title compound, *Bis*-(4-methylmorpholin-4-ium) (dimethylammonium) tetrachloride Zinc(II).

The asymmetric unit is composed of half $ZnCl_4^{2-}$ anion, half 4-methylmorpholin-4-ium cation and half dimethylammonium cation (Fig.1). The molecules are located in the *ac* mirror. 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···Cl hydrogen bonds building up an infinite one-dimensional chain parallel to the *c*-axis (Table 1 and Fig.2).

Experimental

A mixture of 4-methylmorpholine (0.4 mmol), $ZnCl_2$ (0.4 mmol) and DMF/distilled water (10ml,1:1) sealed in a Teflon-lined stainless steel vessel, was maintained at 100 °C. The dimethylamine was generated through the decomposition of DMF. Colorless block crystals suitable for X-ray analysis were obtained after 3 days (yield 31%, based on 4-methylmorpholine). elemental analysis: calcd. C 23.63, H 5.63, N 7.88; found C 23.49, H 5.51, N 7.75.

Refinement

All H atoms attached to C and N atoms were fixed geometrically and treated as riding with C-H = 0.97 Å(methylene), and C-H = 0.96 Å(methyl) N-H = 0.86 Å, with U_{iso}(H) = 1.2U_{eq}(methylene or N) and U_{iso}(H) = 1.5U_{eq}(methyl).

Figures

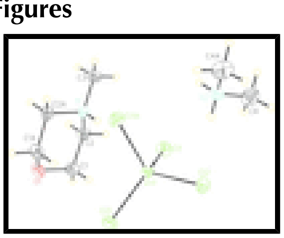

Fig. 1. Molecular view of the title compound with the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

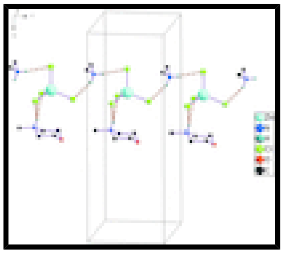

Fig. 2. The crystal packing of the title compound viewed along the *b* axis showing the one-dimensionnal hydrogen bondings chain (dashed line). Hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

Dimethylammonium bis(4-methylmorpholin-4-ium) tetrachloridozincate

Crystal data

$(C_2H_8N)(C_5H_{12}NO)[ZnCl_4]$	$F(000) = 728$
$M_r = 355.42$	$D_x = 1.546$ Mg m^{-3}
Orthorhombic, *Pnma*	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ac 2n	Cell parameters from 1851 reflections
$a = 20.272$ (4) Å	$\theta = 3.4$–27.5°
$b = 10.220$ (2) Å	$\mu = 2.29$ mm^{-1}
$c = 7.3727$ (15) Å	$T = 298$ K
$V = 1527.5$ (5) Å^3	Block, colorless
$Z = 4$	0.30 × 0.05 × 0.05 mm

Data collection

Rigaku Mercury2 diffractometer	1851 independent reflections
Radiation source: fine-focus sealed tube	1655 reflections with $I > 2\sigma(I)$
graphite	$R_{int} = 0.031$
Detector resolution: 13.6612 pixels mm^{-1}	$\theta_{max} = 27.5°$, $\theta_{min} = 3.4°$
CCD profile fitting scans	$h = -26 \rightarrow 25$
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)	$k = -13 \rightarrow 13$
$T_{min} = 0.910$, $T_{max} = 1.000$	$l = -9 \rightarrow 9$
15010 measured reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.030$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.072$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.14$	$w = 1/[\sigma^2(F_o^2) + (0.0307P)^2 + 0.7198P]$ where $P = (F_o^2 + 2F_c^2)/3$
1851 reflections	$(\Delta/\sigma)_{max} < 0.001$
86 parameters	$\Delta\rho_{max} = 0.38$ e Å^{-3}

0 restraints	$\Delta\rho_{min}$ = −0.42 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 > 2sigma(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	0.141654 (15)	0.2500	0.85173 (4)	0.03264 (11)
N1	−0.04000 (12)	0.2500	0.6307 (3)	0.0340 (5)
H1C	−0.0015 (17)	0.2500	0.663 (4)	0.041*
Cl2	0.25325 (4)	0.2500	0.84857 (11)	0.0495 (2)
O1	−0.09518 (12)	0.2500	0.9876 (3)	0.0541 (6)
Cl3	0.10112 (4)	0.2500	1.13530 (10)	0.0585 (3)
Cl1	0.10455 (3)	0.07882 (5)	0.68372 (8)	0.04847 (16)
C2	−0.06975 (11)	0.1302 (2)	0.7135 (3)	0.0402 (5)
H2A	−0.0472	0.0530	0.6686	0.048*
H2B	−0.1159	0.1240	0.6795	0.048*
C1	−0.06386 (13)	0.1363 (2)	0.9169 (3)	0.0507 (6)
H1A	−0.0839	0.0590	0.9695	0.061*
H1B	−0.0176	0.1370	0.9506	0.061*
C3	−0.0450 (2)	0.2500	0.4300 (4)	0.0532 (9)
H3A	−0.0240	0.3267	0.3821	0.080*
H3B	−0.0907	0.2500	0.3961	0.080*
N2	0.22432 (15)	0.2500	0.4099 (4)	0.0492 (7)
H2C	0.2277 (19)	0.2500	0.525 (5)	0.059*
H2D	0.184 (2)	0.2500	0.370 (5)	0.059*
C4	0.25540 (16)	0.1297 (3)	0.3477 (4)	0.0701 (8)
H4A	0.2331	0.0559	0.3998	0.105*
H4B	0.3008	0.1289	0.3844	0.105*
H4C	0.2528	0.1249	0.2178	0.105*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.02909 (17)	0.0403 (2)	0.02851 (17)	0.000	−0.00062 (12)	0.000
N1	0.0280 (11)	0.0368 (13)	0.0371 (13)	0.000	0.0001 (10)	0.000
Cl2	0.0281 (4)	0.0729 (6)	0.0476 (4)	0.000	−0.0013 (3)	0.000
O1	0.0637 (15)	0.0544 (14)	0.0441 (13)	0.000	0.0202 (11)	0.000

Cl3	0.0404 (4)	0.1060 (8)	0.0291 (4)	0.000	0.0030 (3)	0.000
Cl1	0.0547 (3)	0.0400 (3)	0.0508 (3)	−0.0067 (2)	−0.0042 (2)	−0.0089 (2)
C2	0.0421 (11)	0.0304 (10)	0.0479 (12)	−0.0014 (9)	0.0017 (9)	0.0011 (9)
C1	0.0591 (14)	0.0453 (13)	0.0476 (12)	0.0025 (11)	0.0076 (11)	0.0104 (11)
C3	0.072 (2)	0.054 (2)	0.0340 (16)	0.000	0.0016 (16)	0.000
N2	0.0449 (15)	0.0621 (18)	0.0405 (14)	0.000	0.0003 (13)	0.000
C4	0.0778 (19)	0.0614 (18)	0.0712 (18)	0.0134 (15)	−0.0120 (15)	−0.0059 (15)

Geometric parameters (Å, °)

Zn1—Cl3	2.2464 (9)	C2—H2B	0.9700
Zn1—Cl2	2.2625 (9)	C1—H1A	0.9700
Zn1—Cl1	2.2717 (6)	C1—H1B	0.9700
Zn1—Cl1^{i}	2.2717 (6)	C3—H3A	0.9597
N1—C3	1.483 (4)	C3—H3B	0.9597
N1—C2	1.495 (2)	N2—C4	1.456 (3)
N1—C2^{i}	1.495 (2)	N2—C4^{i}	1.456 (3)
N1—H1C	0.81 (3)	N2—H2C	0.85 (4)
O1—C1	1.423 (3)	N2—H2D	0.86 (4)
O1—C1^{i}	1.423 (3)	C4—H4A	0.9600
C2—C1	1.505 (3)	C4—H4B	0.9600
C2—H2A	0.9700	C4—H4C	0.9600
Cl3—Zn1—Cl2	112.05 (3)	O1—C1—H1A	109.4
Cl3—Zn1—Cl1	112.73 (2)	C2—C1—H1A	109.4
Cl2—Zn1—Cl1	108.99 (2)	O1—C1—H1B	109.4
Cl3—Zn1—Cl1^{i}	112.73 (2)	C2—C1—H1B	109.4
Cl2—Zn1—Cl1^{i}	108.99 (2)	H1A—C1—H1B	108.0
Cl1—Zn1—Cl1^{i}	100.72 (4)	N1—C3—H3A	109.7
C3—N1—C2	112.33 (16)	N1—C3—H3B	109.1
C3—N1—C2^{i}	112.33 (16)	H3A—C3—H3B	109.5
C2—N1—C2^{i}	109.9 (2)	C4—N2—C4^{i}	115.3 (3)
C3—N1—H1C	111 (2)	C4—N2—H2C	106.2 (13)
C2—N1—H1C	105.6 (12)	C4^{i}—N2—H2C	106.2 (13)
C2^{i}—N1—H1C	105.6 (12)	C4—N2—H2D	107.4 (12)
C1—O1—C1^{i}	109.5 (2)	C4^{i}—N2—H2D	107.4 (12)
N1—C2—C1	109.96 (19)	H2C—N2—H2D	115 (4)
N1—C2—H2A	109.7	N2—C4—H4A	109.5
C1—C2—H2A	109.7	N2—C4—H4B	109.5
N1—C2—H2B	109.7	H4A—C4—H4B	109.5
C1—C2—H2B	109.7	N2—C4—H4C	109.5
H2A—C2—H2B	108.2	H4A—C4—H4C	109.5
O1—C1—C2	111.3 (2)	H4B—C4—H4C	109.5
C3—N1—C2—C1	−179.4 (2)	C1^{i}—O1—C1—C2	−61.7 (3)
C2^{i}—N1—C2—C1	−53.6 (3)	N1—C2—C1—O1	58.1 (3)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1C···Cl1[i]	0.81 (3)	2.78 (3)	3.435 (2)	139.(1)
N2—H2D···Cl3[ii]	0.86 (4)	2.42 (4)	3.215 (3)	154 (3)
N1—H1C···Cl1	0.81 (3)	2.78 (3)	3.435 (2)	139.(1)
N2—H2C···Cl2	0.85 (4)	2.44 (4)	3.287 (3)	172 (4)

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

Fig. 1

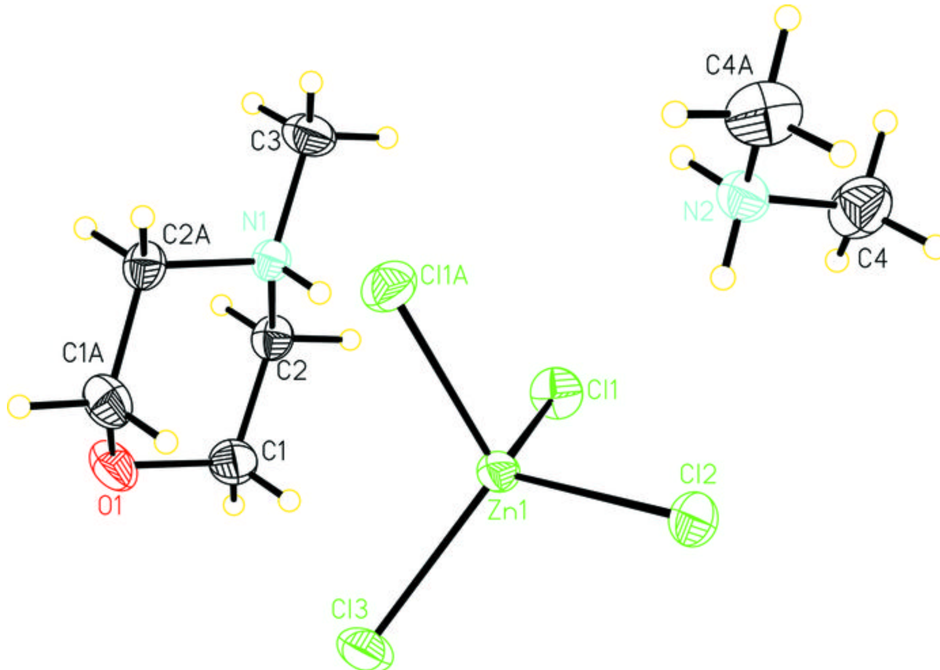

Fig. 2