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catena-Poly[4-methylmorpholin-4-ium [[dichloridobismuth(III)]-di-μ-chlorido]]

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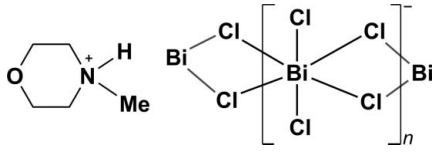
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.013 Å; R factor = 0.037; wR factor = 0.088; data-to-parameter ratio = 25.5.

The asymmetric unit of the title complex, $\{(C_5H_{12}NO)[BiCl_4]\}_n$, contains two bridging and two *cis* non-bridging chloride ligands coordinated to a central Bi^{III} atom, and one 4-methylmorpholin-4-ium cation. The Bi^{III} atoms are linked by the bridging chloride ligands into linear chains parallel to the *c* axis. The chloride ions create a pseudo-octahedral geometry about each Bi^{III} atom. Bifurcated N—H···Cl hydrogen bonds link the cations to the anionic chains.

Related literature

For the structures of related amino compounds, see: Turnbull (2007). For the ferroelectric properties of related amino derivatives, see: Fu *et al.* (2011*a*,*b*,*c*).



Experimental

Crystal data

$(C_5H_{12}NO)[BiCl_4]$
M_r = 452.94
Monoclinic, $C2/c$
a = 18.166 (4) Å
b = 9.801 (2) Å
c = 13.915 (3) Å
β = 93.36 (3)°
V = 2473.2 (9) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 15.08 mm^{-1}
T = 298 K
0.10 × 0.05 × 0.05 mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.428, T_{max} = 0.470
12468 measured reflections
2830 independent reflections
2437 reflections with $I > 2\sigma(I)$
R_{int} = 0.090

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.088
S = 1.14
2830 reflections
111 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 2.45 e Å^{-3}
$\Delta\rho_{min}$ = −1.44 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl3^{i}	0.90	2.76	3.434 (6)	133
N1—H1···Cl2^{i}	0.90	2.85	3.410 (6)	122

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

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: PK2380).

References

Fu, D.-W., Zhang, W., Cai, H.-L., Ge, J.-Z., Zhang, Y. & Xiong, R.-G. (2011*c*). *Adv. Mater.* **23**, 5658–5662.
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supporting information

Acta Cryst. (2012). E**68**, m181 [doi:10.1107/S1600536812001717]

catena-Poly[4-methylmorpholin-4-ium [[dichloridobismuth(III)]-di-μ-chlorido]]

Ying-Chun Wang

S1. Comment

Simple organic salts containing amino cations have attracted attention as materials that display ferroelectric-paraelectric phase transitions (Fu *et al.*, 2011*a*,*b*,*c*). In this study, we describe the crystal structure of the title compound, *N*-methylmorpholinium *catena*-Poly[(di-μ_2-chloro)-dichloro Bi^{III}]

The asymmetric unit contains four independent Cl atoms, one Bi^{III} atom and one organic cation (Fig. 1). All bond lengths and angles are normal and comparable with those reported for the cation in a related Ni(III) compound (Turnbull, 2007). The non-bridging (Cl1 & Cl2) and bridging Cl (Cl3 & Cl4) atoms create a pseudo-octahedral geometry about each Bi (III) atom. The Bi^{III} atoms are linked *via* bridging Cl ions into linear chains that propagate parallel to the *c* axis.

In the crystal structure, the amino N1 atom is involved in hydrogen bonds with the Cl atoms (Cl2 and Cl3) with the N—H···Cl distance of 3.434 (6) and 3.410 (6) Å, respectively. The bifurcated N—H···Cl H-bonds link the cations to the inorganic anion chain. (Fig. 2, Table 1).

S2. Experimental

A mixture of N-methylmorpholine (0.4 mmol), $BiCl_3$ (0.4 mmol) and HCl/distilled water (10ml, 1:4) sealed in a Teflon-lined stainless steel vessel was maintained at 100 °C. Colorless block 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). Positional parameters of the N-bound H atom were intially refined freely, but subsequently restrained using a distance of 0.90 Å and, in the final refinements treated as riding on their parent nitrogen atoms with U_{iso}(H)=1.2U_{eq}(N).

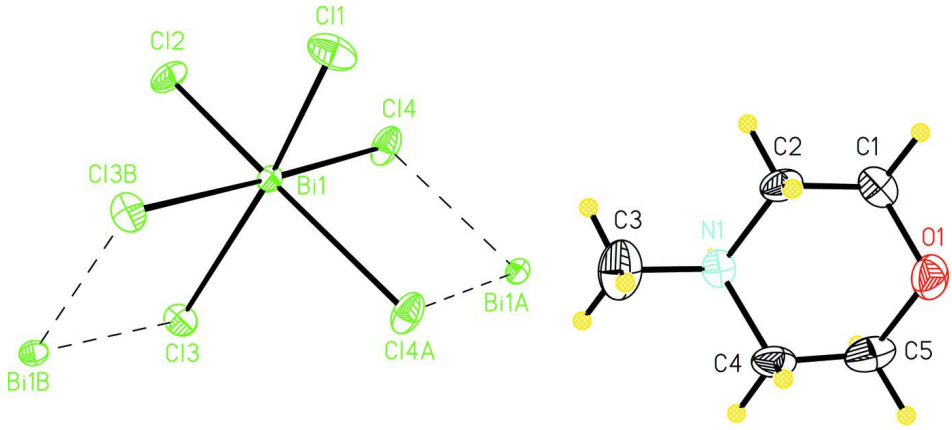

Figure 1

A view of the title compound. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii.

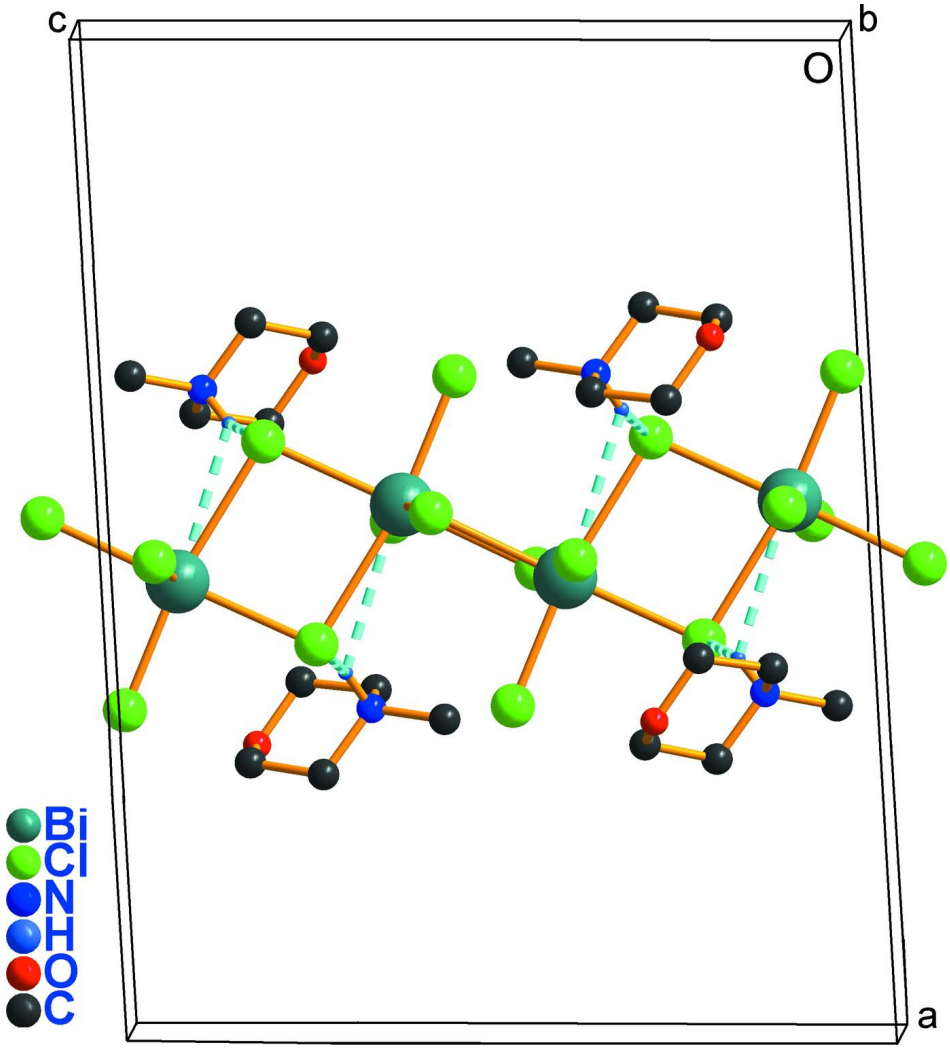

Figure 2

The crystal packing of the title compound showing the one-dimensional chain. Hydrogen atoms not involved in hydrogen bonding have been omitted for clarity.

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$c = 13.915\ (3)$ Å
$\beta = 93.36\ (3)°$
$V = 2473.2\ (9)$ Å^3
$Z = 8$
$F(000) = 1664$
$D_x = 2.433$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2830 reflections
$\theta = 3.6–27.5°$
$\mu = 15.08$ mm^{-1}
$T = 298$ K
Block, colorless
0.10 × 0.05 × 0.05 mm

Data collection

Rigaku Mercury2 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 13.7 pixels mm^{-1}
CCD profile fitting scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
T_{min} = 0.428, T_{max} = 0.470

12468 measured reflections
2830 independent reflections
2437 reflections with $I > 2\sigma(I)$
R_{int} = 0.090
θ_{max} = 27.5°, θ_{min} = 3.6°
h = −23→23
k = −12→12
l = −18→18

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.088
S = 1.14
2830 reflections
111 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
$w = 1/[\sigma^2(F_o^2) + (0.015P)^2 + 5.1391P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 2.45 e Å^{-3}
$\Delta\rho_{min}$ = −1.44 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.0095 (2)

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 $F^2 > 2\text{sigma}(F^2)$ 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}
Bi1	0.038523 (12)	0.36337 (2)	−0.101352 (17)	0.02581 (15)
Cl4	−0.02461 (14)	0.3417 (2)	0.06880 (17)	0.0494 (6)
Cl3	−0.10115 (11)	0.3718 (2)	−0.22296 (15)	0.0407 (5)
Cl2	0.02635 (11)	0.1057 (2)	−0.11236 (16)	0.0438 (5)
Cl1	0.16693 (12)	0.3571 (2)	−0.02381 (18)	0.0568 (7)
N1	0.1587 (3)	0.9444 (6)	0.1521 (4)	0.0342 (14)
H1	0.1239	0.9003	0.1835	0.041*
O1	0.1918 (3)	1.1380 (6)	0.3004 (5)	0.0564 (18)
C2	0.2251 (4)	0.9334 (8)	0.2192 (6)	0.045 (2)
H2A	0.2371	0.8380	0.2299	0.054*
H2B	0.2667	0.9766	0.1907	0.054*
C1	0.2122 (4)	0.9995 (9)	0.3123 (5)	0.046 (2)
H1B	0.1735	0.9510	0.3432	0.055*
H1C	0.2568	0.9938	0.3540	0.055*

C4	0.1376 (5)	1.0896 (9)	0.1428 (6)	0.049 (2)
H4A	0.1754	1.1389	0.1106	0.058*
H4B	0.0917	1.0974	0.1040	0.058*
C5	0.1287 (5)	1.1502 (9)	0.2384 (8)	0.059 (3)
H5A	0.1166	1.2461	0.2305	0.070*
H5B	0.0878	1.1060	0.2675	0.070*
C3	0.1707 (6)	0.8803 (10)	0.0586 (8)	0.075 (3)
H3A	0.1258	0.8837	0.0185	0.113*
H3B	0.1852	0.7869	0.0685	0.113*
H3C	0.2088	0.9284	0.0277	0.113*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Bi1	0.0243 (2)	0.0229 (2)	0.0303 (2)	0.00046 (9)	0.00217 (12)	−0.00330 (11)
Cl4	0.0746 (15)	0.0284 (11)	0.0480 (12)	−0.0059 (9)	0.0276 (11)	−0.0025 (9)
Cl3	0.0254 (10)	0.0589 (15)	0.0384 (11)	0.0057 (7)	0.0067 (8)	0.0025 (9)
Cl2	0.0409 (11)	0.0212 (10)	0.0692 (15)	0.0001 (8)	0.0033 (10)	−0.0040 (10)
Cl1	0.0340 (12)	0.0697 (18)	0.0647 (15)	−0.0136 (9)	−0.0135 (10)	0.0200 (11)
N1	0.035 (3)	0.036 (4)	0.033 (3)	−0.012 (3)	0.010 (2)	0.003 (3)
O1	0.052 (4)	0.049 (4)	0.068 (4)	−0.010 (3)	−0.003 (3)	−0.010 (3)
C2	0.029 (4)	0.033 (5)	0.071 (6)	0.001 (3)	−0.002 (4)	0.006 (4)
C1	0.040 (5)	0.058 (6)	0.040 (5)	−0.011 (4)	0.002 (3)	0.007 (4)
C4	0.050 (5)	0.037 (5)	0.058 (6)	−0.003 (4)	−0.004 (4)	0.021 (5)
C5	0.043 (6)	0.046 (6)	0.088 (8)	0.005 (4)	0.009 (5)	0.018 (5)
C3	0.080 (8)	0.070 (8)	0.078 (8)	−0.035 (5)	0.018 (6)	−0.012 (6)

Geometric parameters (Å, º)

Bi1—Cl1	2.513 (2)	C2—C1	1.480 (11)
Bi1—Cl2	2.539 (2)	C2—H2A	0.9700
Bi1—Cl4	2.699 (2)	C2—H2B	0.9700
Bi1—Cl3^{i}	2.758 (2)	C1—H1B	0.9700
Bi1—Cl4^{ii}	2.939 (2)	C1—H1C	0.9700
Bi1—Cl3	2.967 (2)	C4—C5	1.475 (13)
Cl4—Bi1^{ii}	2.939 (2)	C4—H4A	0.9700
Cl3—Bi1^{i}	2.758 (2)	C4—H4B	0.9700
N1—C3	1.473 (12)	C5—H5A	0.9700
N1—C4	1.476 (9)	C5—H5B	0.9700
N1—C2	1.486 (9)	C3—H3A	0.9600
N1—H1	0.9000	C3—H3B	0.9600
O1—C5	1.399 (11)	C3—H3C	0.9600
O1—C1	1.415 (10)		
Cl1—Bi1—Cl2	94.42 (7)	C1—C2—H2B	109.5
Cl1—Bi1—Cl4	93.03 (9)	N1—C2—H2B	109.5
Cl2—Bi1—Cl4	86.25 (6)	H2A—C2—H2B	108.1
Cl1—Bi1—Cl3^{i}	87.74 (8)	O1—C1—C2	111.8 (7)

Cl2—Bi1—Cl3^{i}	90.88 (6)	O1—C1—H1B	109.3
Cl4—Bi1—Cl3^{i}	177.08 (6)	C2—C1—H1B	109.3
Cl1—Bi1—Cl4^{ii}	92.51 (7)	O1—C1—H1C	109.3
Cl2—Bi1—Cl4^{ii}	168.41 (7)	C2—C1—H1C	109.3
Cl4—Bi1—Cl4^{ii}	84.11 (6)	H1B—C1—H1C	107.9
Cl3^{i}—Bi1—Cl4^{ii}	98.68 (6)	C5—C4—N1	110.5 (7)
Cl1—Bi1—Cl3	170.68 (7)	C5—C4—H4A	109.5
Cl2—Bi1—Cl3	85.68 (6)	N1—C4—H4A	109.5
Cl4—Bi1—Cl3	96.28 (7)	C5—C4—H4B	109.5
Cl3^{i}—Bi1—Cl3	82.94 (6)	N1—C4—H4B	109.5
Cl4^{ii}—Bi1—Cl3	88.98 (6)	H4A—C4—H4B	108.1
Bi1—Cl4—Bi1^{ii}	95.89 (6)	O1—C5—C4	113.1 (7)
Bi1^{i}—Cl3—Bi1	96.97 (6)	O1—C5—H5A	109.0
C3—N1—C4	112.6 (7)	C4—C5—H5A	109.0
C3—N1—C2	111.5 (7)	O1—C5—H5B	109.0
C4—N1—C2	108.8 (6)	C4—C5—H5B	109.0
C3—N1—H1	111.6	H5A—C5—H5B	107.8
C4—N1—H1	108.7	N1—C3—H3A	109.5
C2—N1—H1	103.1	N1—C3—H3B	109.5
C5—O1—C1	110.7 (6)	H3A—C3—H3B	109.5
C1—C2—N1	110.7 (6)	N1—C3—H3C	109.5
C1—C2—H2A	109.5	H3A—C3—H3C	109.5
N1—C2—H2A	109.5	H3B—C3—H3C	109.5

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl3^{ii}	0.90	2.76	3.434 (6)	133
N1—H1···Cl2^{ii}	0.90	2.85	3.410 (6)	122

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