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catena-Poly[*N*-methylmorpholinium [nickelate(II)-tri-μ-chlorido]]

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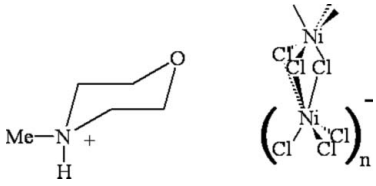
Key indicators: single-crystal X-ray study; T = 160 K; mean σ(C–C) = 0.006 Å; R factor = 0.050; wR factor = 0.106; data-to-parameter ratio = 23.1.

The structure of the title complex, $\{(C_5H_{12}NO)[NiCl_3]\}_n$, shows pseudo-octahedral geometry about the Ni^{II} ions with discrete *N*-methylmorpholinium cations. The cation has mirror symmetry; Ni and one Cl atom also lie on a mirror plane. The Ni atoms are linked *via* bridging Cl ions into a linear chain parallel to the *a* axis. The bridging Cl ions create a pseudo-octahedral geometry about each Ni atom with a Jahn–Teller compression. Bifurcated N—H···Cl hydrogen bonding occurs between the cations and anions.

Related literature

For related literature see: Harlow & Simonsen (1977); Stucky (1968); Willett (1966).



Experimental

Crystal data

$(C_5H_{12}NO)[NiCl_3]$
M_r = 267.22
Orthorhombic, *Pnma*
a = 6.119 (3) Å
b = 10.220 (6) Å
c = 14.401 (8) Å
V = 900.6 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 2.99 mm^{-1}
T = 160 (2) K
0.40 × 0.10 × 0.10 mm

Data collection

Siemens *P*4 diffractometer
Absorption correction: ψ scan (*SHELXTL*; Siemens, 1990)
T_{min} = 0.654, T_{max} = 0.742
2281 measured reflections
1384 independent reflections
888 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
3 standard reflections
every 97 reflections
intensity decay: 3.7%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.050
$wR(F^2)$ = 0.106
S = 1.02
1384 reflections
60 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.98 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl2^{i}	0.85 (6)	2.67 (5)	3.393 (4)	143.5 (9)

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

Data collection: *XSCANS* (Siemens, 1992); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

The author is grateful to the staff at the University of Canterbury, New Zealand, for their hospitality during his sabbatical visit.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2175).

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  doi:10.1107/S1600536807033788

supplementary materials

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Comment

The Ni(II) ions in (I), Fig. 1, exhibit a Jahn-Teller compression with two pairs of longer (2.448 (2) Å and 2.437 (2) Å) and one pair of shorter Ni—Cl bonds (2.346 (2) Å) in their octahedral Cl_6 environments. The Cl ions bridge Ni(II) ions to form tri-bridged chains parallel to the *a*-axis (Fig. 2). This type of trichloride-bridged chain has been previously reported for the tetramethylammonium (Stucky, 1968) and methylphenylethylammonium (Harlow and Simonsen, 1977) salts, although neither complex exhibits the Jahn-Teller distortion seen here. The methylammonium salt is also a tri-bridged chain, but which shows a typical Jahn-Teller elongation (Willett, 1966).

The *N*-methylmorpholinium ions pack in stacks parallel to the *c*-axis surrounding the chains and isolating them from each other. Bifurcated hydrogen bonds between the morpholinium N—H proton and Cl2 help stabilize the crystal structure (Fig. 2).

Experimental

The complex was prepared from a solution of one equivalent of $NiCl_2$ and two equivalents of *N*-methylmorpholine in 1 *M* HCl(aq). The solution was allowed to evaporate in air until a viscous syrup resulted whereupon it was transferred to a desiccator. After one week, green crystals of (*N*-methylmorpholinium)$_3$ClNiCl_4 grew along with yellow crystals of (I). The crystals are highly hygroscopic. Crystals were transferred in a drop of the mother liquor and then moved directly into an adjacent drop of fluorocarbon oil without exposure to the air. No attempt was made to maximize the yield.

Refinement

N—H atom was freely refined (N—H = 0.85 (6) Å. The C-bound H atoms were included in the riding model approximation with C—H = 0.96 Å, and with U_{iso}(H) = 1.2 U_{eq}(C).

Figures

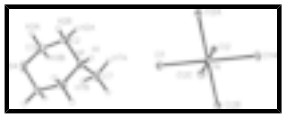

Fig. 1. Molecular structure of the *N*-methylmorpholinium cation (the cation has mirror symmetry) and the coordination sphere for the Ni cation (the Ni and Cl1 atoms lie on a mirror plane). Symmetry operations A: $x - 1/2, y, 0.5 - z$; B: $x, 0.5 - y, z$ and C: $x - 1/2, 0.5 - y, 0.5 - z$.

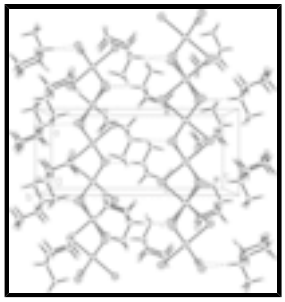

Fig. 2. Packing diagram of (I) viewed down the *b*-axis. Dotted lines represent hydrogen bonds.

catena-Poly[_N_-methylmorpholinium [nickelate(II)-tri-μ-chlorido]]

Crystal data

$(C_5H_{12}NO)[NiCl_3]$	F_{000} = 544
M_r = 267.22	D_x = 1.971 Mg m^{-3}
Orthorhombic, *Pnma*	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: -P 2ac 2n	Cell parameters from 21 reflections
a = 6.119 (3) Å	θ = 2.5–13.7º
b = 10.220 (6) Å	μ = 2.99 mm^{-1}
c = 14.401 (8) Å	*T* = 160 (2) K
V = 900.6 (9) Å^3	Rod, yellow
Z = 4	0.40 × 0.10 × 0.10 mm

Data collection

Siemens P4 diffractometer	R_{int} = 0.050
Radiation source: fine-focus sealed tube	θ_{max} = 30.0º
Monochromator: graphite	θ_{min} = 2.4º
T = 160(2) K	*h* = −8→3
ω scans	*k* = −1→14
Absorption correction: ψ scan (SHELXTL; Siemens, 1990)	*l* = −1→20
T_{min} = 0.654, T_{max} = 0.742	3 standard reflections
2281 measured reflections	every 97 reflections
1384 independent reflections	intensity decay: 3.7%
888 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.050	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.106	$w = 1/[\sigma^2(F_o^2) + (0.0431P)^2]$

	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
1384 reflections	$\Delta\rho_{max} = 0.61$ e Å^{-3}
60 parameters	$\Delta\rho_{min} = -0.98$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s 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 $F^2 > \sigma(F^2)$ 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}	Occ. (<1)
Ni	0.11686 (14)	0.2500	0.25034 (5)	0.01101 (17)	
Cl1	−0.1351 (2)	0.2500	0.37571 (8)	0.0147 (3)	
Cl2	0.36888 (16)	0.09476 (9)	0.32313 (6)	0.0131 (2)	
N1	−0.6499 (9)	0.2500	0.5313 (3)	0.0153 (10)	
H1	−0.641 (10)	0.2500	0.473 (4)	0.018*	
C2	−0.7788 (7)	0.1295 (4)	0.5539 (3)	0.0161 (8)	
H2A	−0.6865	0.0529	0.5473	0.019*	
H2B	−0.8998	0.1211	0.5108	0.019*	
C3	−0.8655 (7)	0.1365 (4)	0.6519 (3)	0.0189 (8)	
H3A	−0.9530	0.0594	0.6645	0.023*	
H3B	−0.7438	0.1370	0.6951	0.023*	
O4	−0.9946 (7)	0.2500	0.6661 (3)	0.0222 (10)	
C7	−0.4300 (10)	0.2500	0.5764 (4)	0.0199 (13)	
H7A	−0.4472	0.2500	0.6426	0.024*	
H7B	−0.3507	0.3267	0.5578	0.024*	0.50
H7C	−0.3507	0.1733	0.5578	0.024*	0.50

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni	0.0094 (3)	0.0142 (3)	0.0095 (3)	0.000	0.0004 (3)	0.000
Cl1	0.0113 (6)	0.0233 (7)	0.0096 (5)	0.000	−0.0013 (6)	0.000
Cl2	0.0127 (4)	0.0135 (4)	0.0132 (4)	0.0000 (4)	0.0001 (4)	0.0009 (3)
N1	0.015 (2)	0.023 (2)	0.0074 (19)	0.000	0.002 (2)	0.000
C2	0.0182 (19)	0.0114 (19)	0.0186 (19)	−0.0012 (17)	−0.0048 (17)	0.0011 (17)
C3	0.019 (2)	0.0194 (19)	0.0179 (18)	−0.004 (2)	0.0011 (19)	0.0057 (15)

O4	0.016 (2)	0.029 (3)	0.022 (2)	0.000	0.0073 (19)	0.000
C7	0.017 (3)	0.025 (3)	0.017 (3)	0.000	0.001 (2)	0.000

Geometric parameters (Å, °)

Ni—Cl1^{i}	2.3664 (18)	C2—H2A	0.9700
Ni—Cl1	2.3739 (19)	C2—H2B	0.9700
Ni—Cl2^{ii}	2.4371 (14)	C3—O4	1.418 (5)
Ni—Cl2	2.4483 (14)	C3—H3A	0.9700
N1—C7	1.494 (8)	C3—H3B	0.9700
N1—C2	1.499 (5)	C7—H7A	0.9600
N1—H1	0.85 (6)	C7—H7B	0.9600
C2—C3	1.510 (6)	C7—H7C	0.9600
Cl1^{i}—Ni—Cl1	179.41 (7)	C3—C2—H2A	109.6
Cl1^{i}—Ni—Cl2^{iii}	93.80 (5)	N1—C2—H2B	109.6
Cl1—Ni—Cl2^{ii}	85.75 (5)	C3—C2—H2B	109.6
Cl2^{iii}—Ni—Cl2^{ii}	81.24 (6)	H2A—C2—H2B	108.1
Cl1^{i}—Ni—Cl2	85.66 (5)	O4—C3—C2	111.7 (4)
Cl1—Ni—Cl2	94.78 (5)	O4—C3—H3A	109.3
Cl2^{iii}—Ni—Cl2	98.99 (5)	C2—C3—H3A	109.3
Cl2^{ii}—Ni—Cl2	179.43 (5)	O4—C3—H3B	109.3
Cl2^{iv}—Ni—Cl2	80.79 (6)	C2—C3—H3B	109.3
Ni^{iii}—Cl1—Ni	80.39 (6)	H3A—C3—H3B	107.9
Ni^{i}—Cl2—Ni	77.55 (5)	C3^{iv}—O4—C3	109.8 (4)
C7—N1—C2	112.3 (3)	N1—C7—H7A	109.5
C2—N1—C2^{iv}	110.5 (5)	N1—C7—H7B	109.5
C7—N1—H1	112 (5)	H7A—C7—H7B	109.5
C2—N1—H1	105 (2)	N1—C7—H7C	109.5
N1—C2—C3	110.4 (4)	H7A—C7—H7C	109.5
N1—C2—H2A	109.6	H7B—C7—H7C	109.5
Cl2^{iii}—Ni—Cl1—Ni^{iii}	−40.75 (3)	Cl2^{iii}—Ni—Cl2—Ni^{i}	132.91 (5)
Cl2^{ii}—Ni—Cl1—Ni^{iii}	40.75 (3)	Cl2^{iv}—Ni—Cl2—Ni^{i}	−46.57 (4)
Cl2^{iv}—Ni—Cl1—Ni^{iii}	139.44 (3)	C7—N1—C2—C3	75.1 (5)
Cl2—Ni—Cl1—Ni^{iii}	−139.44 (3)	C2^{iv}—N1—C2—C3	−51.2 (6)
Cl1^{i}—Ni—Cl2—Ni^{i}	39.73 (3)	N1—C2—C3—O4	56.8 (5)
Cl1—Ni—Cl2—Ni^{i}	−140.65 (4)	C2—C3—O4—C3^{iv}	−61.6 (5)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl2^{v}	0.85 (6)	2.67 (5)	3.393 (4)	143.5 (9)

Symmetry codes: (v) *x*−1, *y*, *z*.

Fig. 1

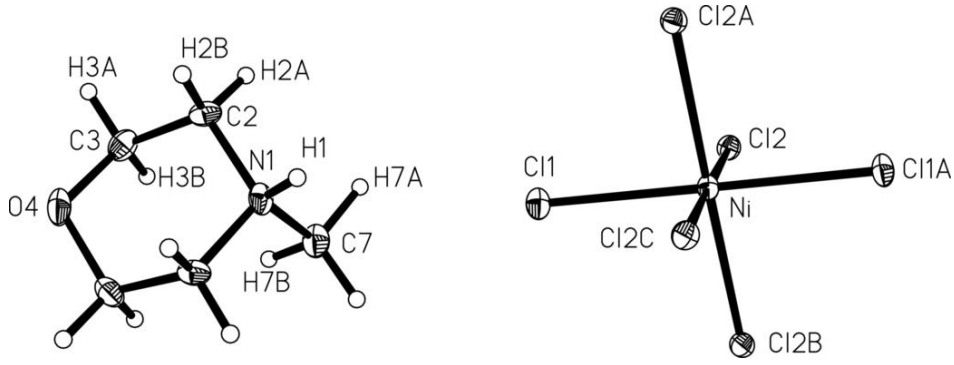
H2B
H3A
H2A
C2
C3
N1
H1
H7A
H3B
O4
C7
H7B
Cl2A
Cl2
Cl1
Cl1A
Ni
Cl2C
Cl2B

Fig. 2