Table 3. *Torsion angles* (°)

C(16)—N(2)—C(15)—C(14)	83
C(20)—N(2)—C(15)—C(14)	−154
N(2)—C(15)—C(14)—C(13)	58
C(15)—C(14)—C(13)—N(1)	57
C(14)—C(13)—N(1)—C(2)	74
C(14)—C(13)—N(1)—C(7)	−122

and clopimozide (Van Opdenbosch, Evrard, Durant & Koch, 1977). The dimerization is due to the amide groups which are hydrogen-bonded: O—N(4)[−x,−y,−z] 2·82 Å.

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N-Methylphenethylammonium Trichloronickelate(II)

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Abstract. [$C_9H_{14}N$]NiCl$_3$, M_r = 301·29, orthorhombic, $P2_12_12_1$, Z = 4. At −35°C, a = 7·414 (1), b = 26·510 (5), c = 6·125 (1) Å, V = 1203·7 Å³, D_x = 1·662 g cm⁻³. Mo $K\alpha$ radiation, λ = 0·71069 Å, μ = 22·3 cm⁻¹. Full-matrix least-squares refinement using 1116 reflections [$I > 2\sigma(I)$] collected with ω scans on a Syntex diffractometer converged at a conventional R of 0·039. The structure consists of (NiCl$_3^-$)$_n$ infinite chains in which each of the chloride ions serves as a bridging ligand to effect octahedral coordination of the nickel ions. These chains interact weakly with the cations through N—H$\cdots$Cl hydrogen bonds.

Introduction. The structures of N-methylphenethylammonium trichlorocuprate(II) (Harlow, Wells, Watt & Simonsen, 1974a) and bis(N-methylphenethylammonium) tetrachlorocuprate(II) (Harlow, Wells, Watt & Simonsen, 1974b) contain Cu²⁺ ions with unusual coordination geometries. As an extension of these studies, other N-methylphenethylammonium [hereafter abbreviated as (nmpH)] chlorometallates are presently being investigated.

Light-orange crystals of the title compound were grown by slow evaporation of an acetone solution under a stream of dry N₂ gas. The crystal selected for this study was a cleaved section of a needle with approximate dimensions of 0·05, 0·1 and 0·5 mm. The crystal was mounted parallel to the needle axis (crystallographic c axis) and placed on a Syntex diffractometer equipped with a low-temperature apparatus which kept the crystal cooled to −35°C. The unit-cell parameters were refined using the Bragg angles of 30 low-angle (18 < 2θ < 27°) reflections.

Intensity data for 1635 unique reflections (4 < 2θ < 55°) were collected by the ω-scan technique. Scans of 1·0° were employed with scan rates which ranged from 1·5 to 5·0° min⁻¹ depending on the number of counts accumulated in a rapid preliminary scan. Background measurements were taken at both ends of the scan; the time for each measurement was one-half the scan time. The intensities of four standard reflections were monitored after every 96 reflections; only statistical variations were noted. The intensities were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods and Fourier syntheses. The full-matrix least-squares refinement of 127 variables using only those 1116 reflections for which $I > 2\sigma(I)$ converged at a conventional R of 0·039. Anomalous dispersion corrections for the scattering factors of Ni and Cl were included in the final stages of the refinement; the enantiomorphic structure converged at R = 0·042. The non-hydrogen atoms were refined with anisotropic thermal

Table 1. *Final atomic coordinates with the assigned isotropic thermal parameters of the hydrogen atoms (e.s.d.'s in parentheses)*

	x	y	z	U_{iso}
Ni	0·2492 (3)	0·00026 (3)	0·4433 (1)	
Cl(1)	0·0347 (3)	−0·03758 (7)	0·1968 (5)	
Cl(2)	0·4753 (3)	−0·03084 (7)	0·1958 (5)	
Cl(3)	0·2324 (3)	0·07042 (5)	0·1933 (3)	
C(1)	0·0865 (9)	0·2947 (2)	0·1470 (11)	
C(2)	0·0087 (11)	0·2921 (3)	0·3527 (12)	
C(3)	0·0021 (16)	0·2455 (4)	0·4661 (19)	
C(4)	0·0747 (11)	0·2036 (3)	0·3705 (15)	
C(5)	0·1530 (10)	0·2057 (3)	0·1687 (15)	
C(6)	0·1610 (10)	0·2515 (3)	0·0565 (12)	
C(7)	0·0913 (11)	0·3441 (3)	0·0206 (14)	
C(8)	0·2619 (13)	0·3727 (2)	0·0613 (10)	
N	0·2627 (13)	0·4224 (2)	−0·0574 (9)	
C(9)	0·2443 (17)	0·4187 (2)	−0·2971 (12)	
H(1)	−0·0428	0·3231	0·4212	0·068
H(2)	−0·0548	0·2433	0·6139	0·067
H(3)	0·0703	0·1707	0·4499	0·071
H(4)	0·2046	0·1745	0·1016	0·067
H(5)	0·2206	0·2531	−0·0898	0·058
H(6)	0·0819	0·3365	−0·1390	0·062
H(7)	−0·0134	0·3654	0·0665	0·062
H(8)	0·3665	0·3521	0·0100	0·052
H(9)	0·2738	0·3792	0·2215	0·052
H(10)	0·1704	0·4410	−0·0065	0·053
H(11)	0·3676	0·4380	−0·0279	0·053
H(12)	0·2460	0·4534	−0·3620	0·056
H(13)	0·3465	0·3986	−0·3578	0·056
H(14)	0·1275	0·4019	−0·3340	0·056

parameters. The positions of the H atoms were found in a difference map but failed to refine properly; the H positions were then calculated (C–H and N–H distances were set at 1·0 and 0·9 Å respectively) and were fixed during the refinement. Each H atom was assigned an isotropic thermal parameter, B_{iso}, equal to 2·0 Å^2 plus the value of the atom to which it was bonded. The final positional and (for H) thermal parameters are listed in Table 1.* (See Fig. 1 for the
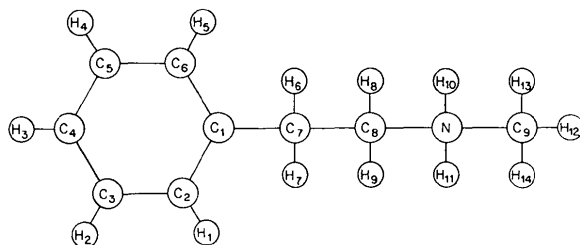
Fig. 1. Atom-numbering scheme for the *N*-methylphenethyl-ammonium cation.

atom numbering of the cation.) The largest peak in the final difference map had a magnitude of approximately 0·3 e Å^{-3} and was located midway between the Ni atoms of the infinite chain. The mathematical and computational details are noted elsewhere (Harlow & Simonsen, 1976).

Discussion. Structures of a large number of trichloro-cuprate(II) salts have shown that the Cu^{2+} ion exhibits a wide variety of coordination numbers and geometries when complexed with Cl$^-$ ions (see review by Smith, 1976). In contrast, the few trichloronickelate(II) structures that have been reported are all similar; the NiCl$_3^-$ units form one-dimensional chains in which all three Cl$^-$ ions serve as bridging ligands to effect octahedral coordination of the Ni^{2+} ions (Asmussen, Larsen & Soling, 1969; Stucky, 1968; Willett, 1966; and references therein). It was speculated, however, that (nmpH)NiCl$_3$ might possibly be isostructural with the CuCl$_3$ salt, which contains an unusual $(CuCl_3^-)_n$ infinite chain of five-coordinate Cu^{2+} ions in which two of the three Cl$^-$ ions serve as bridging ligands while the third is a terminal ligand. On the other hand, the NiCl$_3^-$ anions might form a novel dimeric or polymeric species (perhaps similar to those found for some CuCl$_3^-$ salts), particularly in view of the cation's ability to form strong N–H···Cl hydrogen bonds.

The geometry of the $(NiCl_3^-)_n$ chain in the structure of (nmpH)NiCl$_3$, shown in Fig. 2, is however identical with those reported for the Rb$^+$, (CH$_3$)$_4$N$^+$ and CH$_3$NH$_3^+$ salts (references noted above). The Ni–Cl bond lengths are given in Fig. 3 and are seen to be somewhat longer, in general, than those previously determined which ranged from 2·351 to 2·408 Å. The distortion of the Cl–Ni–Cl angles (Table 2) from 90° is apparently the result of Ni···Ni repulsions; this 'elongation' in the direction of the chain is found in all the NiCl$_3^-$ structures.

Table 2. *Bond angles (°) associated with Fig. 3*

(a) The polymeric anion

Cl(1)–Ni–Cl(2)	85·5 (1)	Cl(3)–Ni–Cl(1)′	97·2 (1)
Cl(1)–Ni–Cl(3)	83·6 (1)	Cl(3)–Ni–Cl(2)′	96·4 (1)
Cl(1)–Ni–Cl(1)′	179·1 (1)	Cl(3)–Ni–Cl(3)′	179·6 (1)
Cl(1)–Ni–Cl(2)′	95·0 (1)	Cl(1)′–Ni–Cl(2)′	84·8 (1)
Cl(1)–Ni–Cl(3)′	96·4 (1)	Cl(1)′–Ni–Cl(3)′	82·8 (1)
Cl(2)–Ni–Cl(3)	84·3 (1)	Cl(2)′–Ni–Cl(3)′	83·9 (1)
Cl(2)–Ni–Cl(1)′	94·7 (1)	Ni–Cl(1)–Ni″	78·3 (1)
Cl(2)–Ni–Cl(2)′	179·2 (1)	Ni–Cl(2)–Ni″	78·9 (1)
Cl(2)–Ni–Cl(3)′	95·4 (1)	Ni–Cl(3)–Ni″	78·6 (1)

(b) The N–H···Cl contacts

N–H(10)···Cl(1)	148	N–H(11)···Cl(2)	136
N–H(10)···Cl(2)′	132	N–H(11)···Cl(1)′	132
Cl(1)···H(10)···Cl(2)′	80	N–H(11)···Cl(3)′	135
		Cl(2)···H(11)···Cl(1)′	79
		Cl(2)···H(11)···Cl(3)′	83
		Cl(1)′···H(11)···Cl(3)′	65

Fig. 2. Packing diagram for *N*-methylphenethylammonium trichloronickelate(II). The three chloride ions of each $NiCl_3^-$ unit form bridges to produce chains (along crystallographic 2_1 screw axes) of octahedrally coordinated nickel ions.

Fig. 3. Bond distances (Å) for the $NiCl_3^-$ polymeric anion and for the N—H$\cdots$Cl contacts between the cation and the anion. The Ni$\cdots$Ni distance is 3·063 (1) Å.

Table 3. *Bond distances* (Å) *and angles* (°) *for the N-methylphenethylammonium cation*

C(1)—C(2)	1·388 (10)	C(2)—C(1)—C(6)	119·0 (6)
C(1)—C(6)	1·389 (10)	C(2)—C(1)—C(7)	121·1 (6)
C(1)—C(7)	1·521 (10)	C(6)—C(1)—C(7)	119·9 (6)
C(2)—C(3)	1·418 (14)	C(1)—C(2)—C(3)	120·3 (8)
C(3)—C(4)	1·366 (14)	C(2)—C(3)—C(4)	119·0 (10)
C(4)—C(5)	1·368 (13)	C(3)—C(4)—C(5)	121·5 (8)
C(5)—C(6)	1·396 (10)	C(4)—C(5)—C(6)	119·9 (7)
C(7)—C(8)	1·497 (11)	C(1)—C(6)—C(5)	120·3 (7)
C(8)—N	1·504 (8)	C(1)—C(7)—C(8)	111·8 (6)
N—C(9)	1·478 (9)	C(7)—C(8)—N	111·5 (6)
		C(8)—N—C(9)	115·0 (5)

for these two hydrogens, but most of the contacts are of the order of magnitude, 3·0 Å, of the sum of the van der Waals radii for H and Cl (Hamilton & Ibers, 1968). None of the N—H$\cdots$Cl angles is close to 180°.

The dimensions of the cation are shown in Table 3.

The details of the N$\cdots$Cl contacts are presented in Fig. 3 and Table 2. The positions of H(10) and H(11) appear to be the result of general cation–anion packing considerations. There are several H$\cdots$Cl interactions

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Bis(DL-proline)manganese(II) Dibromide Dihydrate

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Abstract. $C_{10}H_{22}N_2O_6Br_2Mn$, monoclinic, $P2_1/c$, $a = 9.375$ (1), $b = 9.195$ (2), $c = 10.122$ (2) Å, $\beta = 106.38$ (2)°, $M_r = 481.1$, $V = 837.1$ Å^3, $Z = 2$, $D_m = 1.91$, $D_x = 1.91$ g cm^{-3}, μ(Cu $K\alpha$) = 132.7 cm^{-1}, $\lambda = 1.5418$ Å. The proline molecule is a monodentate O-donor ligand. C^γ of the pyrrolidine ring is statistically situated on both sides of the $NC^\alpha C^\beta C^\delta$ plane. The structure was refined to an R of 0.038 for 1006 diffractometer data.

Introduction. The crystals grew as colourless plates from an aqueous solution of $MnBr_2$ and DL-proline in a molar ratio 1:2. All measurements for a crystal $0.12 \times 0.14 \times 0.15$ mm were made on a Syntex $P2_1$ computer-controlled four-circle diffractometer equipped with a scintillation counter and graphite monochromator. The cell parameters were determined by least-squares refinement of the setting angles of 15 reflexions given by the automatic centring program. Intensities of 1127 independent reflexions were measured up to $2\theta = 114.0°$ with the variable θ–2θ scan technique. The scan rate varied from 3.8 to 20.0° min^{-1} depending on the intensity. 1006 reflexions $I > 1.96\sigma(I)$ were used in the analysis. The intensities were corrected for Lorentz and polarization factors, but not for absorption.

The structure was solved by the heavy-atom method. Full-matrix refinement with isotropic thermal parameters to $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o| = 0.096$ and anisotropic thermal parameters to $R_1 = 0.050$ was performed. Deviations from the expected geometry of the pyrrolidine ring (C^β–C^γ was 1.407 Å) and very large thermal parameters of C^γ were found. A difference synthesis, excluding C^γ, showed two new maxima consistent with the pyrrolidine ring. The structure was again refined with isotropic thermal parameters to $R_1 = 0.092$ and with anisotropic

parameters to $R_1 = 0.048$. The occupancy factors, G, calculated for the new atoms were 0.60 and 0.40. The positions of the H atoms in the pyrrolidine ring were

Table 1. *The occupancy and positional* $(\times 10^4)$ *parameters with e.s.d.'s in parentheses*

	G	x	y	z
Mn	1.0	0	0	0
Br	1.0	2156 (1)	1712 (1)	−566 (1)
O(1)	1.0	1505 (5)	−1830 (5)	636 (5)
O(2)	1.0	1195 (7)	−3382 (5)	−1101 (5)
O(W)	1.0	697 (6)	633 (5)	2161 (4)
N	1.0	2434 (6)	−3814 (6)	2596 (6)
C'	1.0	1571 (7)	−3052 (8)	142 (7)
C$^\alpha$	1.0	2191 (7)	−4296 (7)	1146 (7)
C$^\beta$	1.0	3714 (10)	−4787 (11)	1085 (9)
C$^{\gamma_1}$	0.6	4744 (19)	−3863 (21)	2014 (17)
C$^{\gamma_2}$	0.4	4844 (27)	−4725 (43)	2564 (26)
C$^\delta$	1.0	4032 (9)	−3482 (11)	3178 (9)

	Atom bearing	G	x	y	z
H(1)*	C$^\alpha$	1.0	1435	−5114	879
H(2)	C$^\beta$	0.6	3821	−4678	120
H(3)	C$^\beta$	0.6	3921	−5830	1370
H(4)	C$^\beta$	0.4	3699	−5823	752
H(5)	C$^\beta$	0.4	4082	−4148	435
H(6)	C$^{\gamma_1}$	0.6	4916	−2957	1513
H(7)	C$^{\gamma_1}$	0.6	5726	−4371	2384
H(8)	C$^{\gamma_2}$	0.4	5812	−4361	2538
H(9)	C$^{\gamma_2}$	0.4	4850	−5599	3067
H(10)	C$^\delta$	0.6	4496	−4075	4029
H(11)	C$^\delta$	0.6	4192	−2416	3438
H(12)	C$^\delta$	0.4	4285	−2480	2907
H(13)	C$^\delta$	0.4	4357	−3536	4221
H(14)	N	1.0	2129	−4605	3159
H(15)	N	1.0	1813	−2927	2631
H(16)	O(W)	1.0	1300	−60	2870
H(17)	O(W)	1.0	940	1620	2520

* $B = 4.8$ Å^2 for the H atoms.