title complex has larger cell dimensions, higher distortion of the central best plane and smaller *trans* N—Ni—N bond angles. These differences arise mainly from the steric effect of the two C-methyl groups.

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Structure of Dipiperidinium *catena*-Poly[nickel-tri-μ-chloro(1 −)] Chloride

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Abstract. $2C_5H_{12}N^+.NiCl_3^-.Cl^-$, $M_r = 372.84$, monoclinic, $P2_1/n$, $a = 10.131$ (1), $b = 6.1431$ (8), $c = 26.081$ (5) Å, $\beta = 98.01$ (1)°, $V = 1607.3$ (4) Å^3, $Z = 4$, $D_x = 1.54$ g cm^{-3}, λ(Cu $K\alpha$) = 1.5418 Å (graphite monochromator), $\mu = 78.8$ cm^{-1}, $F(000) = 776$, $T = 295$ K. Refinement of 186 least-squares parameters, $R = 0.0382$ for 1752 unique observed $[|F| > 3\sigma(|F|)]$ reflections. The compound is more properly formulated (piperidinium chloride).[piperidinium trichloronickelate(II)] and consists of anionic $(NiCl_3)_n^{n-}$ chains separated by the piperidinium cations and by an isolated lattice chloride anion. This new A_2NiX_4 structure type is constructed by *ABAB* stacking of hexagonal close packed (h.c.p.) A_2X_4 layers.

Introduction. The range of structural variation within the A_2NiX_4 family (A = monopositive cation, X = halide) is small. Nickel(II) assumes octahedral coordination with the small fluoride ion, as found in the familiar K_2NiF_4 (layer perovskite) structure (Muller & Roy, 1974) or in the Li_2NiF_4 (inverse spinel) structure (Rüdorff & Kandler, 1962). Tetrahedral coordination, on the other hand, should be stabilized by larger halide ions. This is indeed the case for a series of quaternary ammonium salts in which isolated tetrahedral NiX_4^{2-} ions (X = Cl, Br, I) are separated by large quaternary ammonium cations such as $(CH_3)_4N^+$ or $(CH_3)_3(C_6H_5)N^+$ (Gill & Nyholm, 1959; Stucky, Folkers & Kistenmacher, 1967). Structural behavior between these stereochemical extremes is found for several thermochromic $(R_xNH_{4-x})_2NiCl_4$ compounds (R = alky, $1 < x < 3$) in which low-temperature phases are yellow, the characteristic color of octahedral $NiCl_6^{4-}$ salts, but high-temperature phases are blue, the characteristic color of tetrahedral $NiCl_4^{2-}$ salts (Bloomquist & Willett, 1982). Spectroscopic, EPR and powder X-ray diffraction data verify this assignment of local Ni^{II} geometries in the two phases but the lack of reported single-crystal structure determinations leaves questions about their extended geometries unresolved, particularly concerning the bridging arrangements between octahedral Ni^{II} complexes in the polymeric low-temperature phase (Ferraro & Sherren, 1978).

In the course of our recent study (Bond & Willett, 1992; Bond, 1990) of the structural and magnetic properties of a series of ANiCl$_3$ hexagonal perovskites (A = organoammonium ion), we synthesized a yellow crystalline solid containing the piperidinium cation. Since the color of the compound indicates the presence of octahedral Ni^{II} we expected the crystal structure determination to reveal a distorted CsNiCl$_3$-type structure, *i.e.* parallel chains of face-sharing $NiCl_6^{4-}$ octahedra separated by the monopositive piperidinium cations. To our surprise we found an A_2NiCl_4 compound whose structure type, although similar in form to a distorted CsNiCl$_3$-type structure, is new to the A_2NiX_4 family.

Experimental. Yellow needle-like crystals obtained by slow evaporation of 6M HCl solution (maintained

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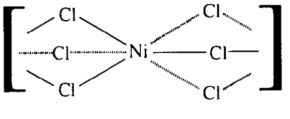
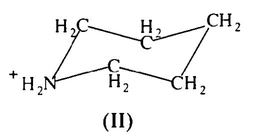
at 323–333 K and left open to the atmosphere) containing nickel chloride and a large molar excess of piperidinium chloride. Piperidinium chloride was prepared by reacting piperidine and HCl, then recrystallizing the product from water. Crystal with dimensions 0.07 × 0.12 × 0.66 mm was mounted on a Nicolet *R3m/E* diffractometer. Cell constants determined from angular settings of 25 well centered reflections in the range $73 \leq 2\theta \leq 95°$ (Campana, Shepard & Litchman, 1981). Data collected (1.1° ω scans; scan speed: 3.9–29.3° min^{-1}) in $0 \leq h \leq 11$, $0 \leq k \leq 7$, $-28 \leq l \leq 28$ quadrant to $(\sin\theta/\lambda)_{\text{max}} = 0.531\ \text{Å}^{-1}$. Three check reflections (105, 017, 204) measured every 93 reflections, variations within counting statistics. Lp, crystal decay, empirical absorption (ellipsoidal crystal shape, $T_{\text{max}} = 0.790$, $T_{\text{min}} = 0.477$) corrections and peak profile fitting procedure applied to data. 2394 reflections measured (12 rejected because of excessive background imbalance or asymmetric peak shape), 2016 unique (merging $R = 0.0167$) and 1752 observed $[|F| \geq 3\sigma(F)]$.

Structure solved by direct methods, refined using block-cascade least-squares technique within the *SHELXTL* crystallographic software package (Sheldrick, 1985) on a Data General Eclipse computer. Function minimized: $\sum w(F_o - F_c)^2$ where $w = [\sigma^2(F) + g|F|^2]^{-1}$ and $g = 0.00026$. Non-H-atom positions located on *E* map calculated from direct methods or on subsequent electron-density difference maps. N atoms identified as ring atoms with larger peaks on difference map and with favorable positions for hydrogen bonding to chloride ions. H-atom positions visible on difference map, but positions were calculated and constrained to C—H or N—H bond lengths of 0.96 Å and idealized geometry during refinement. Anisotropic thermal parameters for all non-H atoms, common isotropic thermal parameter for H atoms. Large thermal parameters of C atom in one piperidinium ring and of N and C atoms in another suggested a twofold disorder of atoms. In the first cation the disordered atom produces chair–boat conformational disorder of the ring with the chair conformation three times more probable than the boat conformation [refined site occupation factor: 0.72 (1) for C(12*A*)]. In the second cation, the presence of two disordered ring atoms obscures the nature of the disorder, *i.e.* whether there are different ring conformations or different ring orientations [refined site occupation factors: 0.49 (1) for C(23*A*), 0.47 (1) for N(2*A*)]. Isotropic secondary-extinction correction of the form $F^* = F_c/[1.0 + 0.002x|F|^2/\sin(2\theta)]^{0.25}$ [$x = 0.0034\ (3)$] included. Final refinement of 186 least-squares parameters gave $R = 0.0382$ and $wR = 0.0449$ (0.0450 and 0.0459, respectively, for all data), $S = 1.613$, $|\Delta/\sigma|(\text{mean}) = 0.004$, $|\Delta/\sigma|(\text{max.}) = 0.018$. Excursions on final difference map: -0.425 to $0.370\ \text{e Å}^{-3}$. Non-H-atom coordinates and isotropic thermal parameters are listed in Table 1,* bond lengths and angles in Table 2. A thermal-ellipsoid plot of the structure is presented in Fig. 1 and a stereoview of the structure is shown in Fig. 2.

Discussion. Parallel chains of face-sharing $NiCl_6^{4-}$ octahedra (I), separated from one another by two crystallographically independent piperidinium cations (II) and an isolated chloride anion, are the most prominent features of the structure. The inorganic chain axis is parallel to the monoclinic axis with nearest-neighbor chains related to one another by an *a*-axis translation. The chains are thus arranged into layers parallel to the *ab* plane of the crystal with the interlayer separation equal to d_{002}. An antiphase translational distortion (taken parallel to the *b* axis) of the hypothetical parent structure (see below) forces the chains in neighboring layers to move out of register with one another. This distortion, a common feature of $ANiCl_3$ salts by which close packing of aspherical cations is achieved, is measured by the parameter δ, the magnitude of this translation in terms of fractional cell coordinates [equal to $y(\text{Ni}) - \frac{1}{4} = 0.0446$ in the present structure (Bond & Willett, 1992; Bond, 1990)]. The organoammonium and isolated chloride ions lie primarily, but not entirely, between the inorganic layers. Fig. 2 shows that the environments of the independent piperidinium ions are dramatically different. The singly disordered cation lies between nearest-neighbor chains and is responsible for the large separation of the chains along the *a* axis. The doubly disordered cation, however, lies completely in the region between the layers of chains and forms alternating cation–anion rows parallel to **a** with the isolated chloride ion (Fig. 2).



(I)



(II)

These structural features suggest a simple model to describe the crystal chemistry of this new structure type. The close correspondence to the $CsNiCl_3$ structure type, which is built of stacks (*ABAB*) of close-packed AX_3 layers [(III), hexagonal *b* and *c* axes shown in layer], where the shaded circles represent

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* Lists of observed and calculated structure factors, anisotropic thermal parameters, and hydrogen-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55650 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST0567]

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* $(C_5H_{12}N)_2NiCl_4$

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ni	0.7492 (1)	0.2054 (1)	0.2497 (1)	0.029 (1)
Cl(1)	0.9161 (1)	0.4536 (2)	0.2900 (1)	0.038 (1)
Cl(2)	0.5951 (1)	0.4548 (2)	0.2807 (1)	0.036 (1)
Cl(3)	0.7325 (1)	0.4572 (2)	0.1760 (1)	0.036 (1)
Cl(4)	0.3624 (1)	0.8172 (2)	0.0594 (1)	0.066 (1)
N(1)	0.3915 (3)	0.5370 (6)	0.1631 (1)	0.049 (1)
C(11)	0.3550 (5)	0.3226 (9)	0.1387 (2)	0.074 (2)
C(12A)*	0.2106 (7)	0.3056 (13)	0.1184 (4)	0.065 (3)
C(12B)*	0.2473 (17)	0.2173 (27)	0.1586 (8)	0.077 (10)
C(13)	0.1244 (5)	0.3648 (10)	0.1602 (2)	0.071 (2)
C(14)	0.1650 (6)	0.5811 (11)	0.1835 (3)	0.094 (3)
C(15)	0.3015 (6)	0.6146 (13)	0.1976 (3)	0.116 (3)
N(2A)*	0.6797 (7)	0.8164 (12)	0.0837 (3)	0.060 (4)
N(2B)*	0.6483 (8)	0.8746 (14)	0.0400 (3)	0.054 (4)
C(21)	0.7014 (6)	0.6566 (10)	0.0383 (2)	0.078 (2)
C(22)	0.8413 (8)	0.6383 (14)	0.0339 (3)	0.126 (4)
C(23A)*	0.9141 (11)	0.8333 (21)	0.0333 (5)	0.077 (5)
C(23B)*	0.9268 (12)	0.7812 (20)	0.0659 (7)	0.135 (9)
C(24)	0.8839 (7)	0.9910 (11)	0.0757 (2)	0.099 (3)
C(25)	0.7385 (7)	1.0113 (10)	0.0798 (2)	0.088 (3)

*Site occupation factors for disordered atom pairs (constrained to s.o.f. [*A*] + s.o.f. [*B*] = 1) are as follows: s.o.f. [C(12*A*)] = 0.72 (1); s.o.f. [C(23*A*)] = 0.49 (1); s.o.f. [N(2*A*)] = 0.47 (1).

Table 2. *Bond lengths* (Å) *and angles* (°) *for* $(C_5H_{12}N)_2NiCl_4$

Ni—Cl(1)	2.407 (1)	Ni—Cl(2)	2.406 (1)
Ni—Cl(3)	2.455 (1)	Ni—Cl(1^i)	2.406 (1)
Ni—Cl(2^i)	2.415 (1)	Ni—Cl(3^i)	2.454 (1)
N(1)—C(11)	1.487 (7)	N(1)—C(15)	1.449 (8)
C(11)—C(12A)	1.488 (8)	C(11)—C(12B)	1.427 (20)
C(12A)—C(13)	1.533 (10)	C(12B)—C(13)	1.546 (18)
C(13)—C(14)	1.495 (9)	C(14)—C(15)	1.396 (8)
N(2A)—C(21)	1.577 (10)	N(2A)—C(25)	1.347 (10)
N(2B)—C(21)	1.446 (11)	N(2B)—C(25)	1.534 (10)
C(21)—C(22)	1.441 (10)	C(22)—C(23A)	1.408 (15)
C(22)—C(23B)	1.419 (16)	C(23A)—C(24)	1.533 (14)
C(23B)—C(24)	1.395 (14)	C(24)—C(25)	1.497 (10)
Cl(1)—Ni—Cl(2)	84.2 (1)	Cl(1)—Ni—Cl(3)	84.9 (1)
Cl(2)—Ni—Cl(3)	83.4 (1)	Cl(1)—Ni—Cl(1^i)	179.3 (1)
Cl(2)—Ni—Cl(1^i)	96.3 (1)	Cl(3)—Ni—Cl(1^i)	95.7 (1)
Cl(1)—Ni—Cl(2^i)	95.5 (1)	Cl(2)—Ni—Cl(2^i)	179.5 (1)
Cl(3)—Ni—Cl(2^i)	97.0 (1)	Cl(1^i)—Ni—Cl(2^i)	84.0 (1)
Cl(1)—Ni—Cl(3^i)	94.4 (1)	Cl(2)—Ni—Cl(3^i)	96.4 (1)
Cl(3)—Ni—Cl(3^i)	179.3 (1)	Cl(1^i)—Ni—Cl(3^i)	85.0 (1)
Cl(2^i)—Ni—Cl(3^i)	83.2 (1)	Ni—Cl(1)—Ni(^{i})	79.3 (1)
Ni—Cl(2)—Ni(^{i})	79.1 (1)	Ni—Cl(3)—Ni(^{i})	77.5 (1)
C(11)—N(1)—C(15)	114.6 (4)	N(1)—C(11)—C(12A)	112.8 (5)
N(1)—C(11)—C(12B)	113.8 (9)	C(11)—C(12A)—C(13)	111.1 (6)
C(11)—C(12B)—C(13)	113.8 (12)	C(12A)—C(13)—C(14)	110.4 (5)
C(12B)—C(13)—C(14)	110.8 (7)	C(13)—C(14)—C(15)	116.4 (6)
N(1)—C(15)—C(14)	118.2 (6)	C(21)—N(2A)—C(25)	112.8 (7)
C(21)—N(2B)—C(25)	109.8 (6)	N(2A)—C(21)—C(22)	110.4 (6)
N(2B)—C(21)—C(22)	116.7 (6)	C(21)—C(22)—C(23A)	117.2 (8)
C(21)—C(22)—C(23B)	115.6 (9)	C(22)—C(23A)—C(24)	111.8 (9)
C(22)—C(23B)—C(24)	119.9 (9)	C(23A)—C(24)—C(25)	113.6 (6)
C(23B)—C(24)—C(25)	115.1 (7)	N(2A)—C(25)—C(24)	112.4 (6)
N(2B)—C(25)—C(24)	114.0 (6)		

the *A* cations and the open circles represent the *X* cations, inspires a variant structure built of stacks (*ABAB*) of close-packed A_2X_4 layers (IV) with Ni^{II} ions filling all octahedral X_6 holes in both structures. The unit cell of the A_2X_4 layer-based structure is monoclinic $P2_1/m$. With the *b* axis directed out of the plane of the page, an outline of the unit cell in the layer is depicted on the right of (IV) with the *c* axis almost vertical and the *a* axis horizontal. In a structure composed of uniform spheres, *c* will equal $a \times 7^{1/2}/2$ and *b* will equal $a(\frac{2}{3})^{1/2}$ with a monoclinic angle of 100.9°. The large size and aspherical shape of the piperidinium cations in the present structure cause a substantial distortion away from the ideal. This principally consists of the antiphase translational distortion (see above) which doubles the length of the *c* axis. The symmetry of the system changes, upon distortion, to $P2_1/c$, a *klassengleiche* subgroup of index 2 of $P2_1/m$, with the $P2_1/n$ symmetry of the present structure obtained upon re-indexing the $P2_1/c$ cell. The outline of the $P2_1/n$ unit cell in the layer plane is depicted on the left in (IV) with the *b* axis directed out of the plane, the *a* axis horizontal and the *c* axis almost vertical. For an infinitesimal

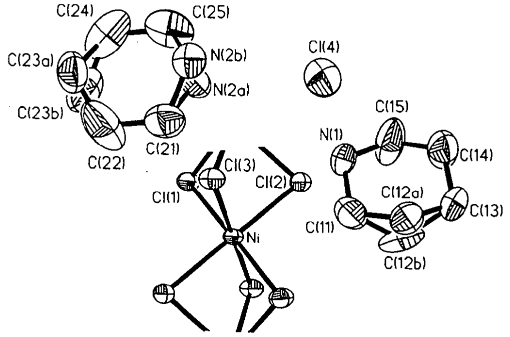


Fig. 1. View of the components of the $(C_5H_{12}N)_2NiCl_4$ structure (50% thermal ellipsoids, labels for all symmetrically inequivalent atoms, and omission of H atoms). The anionic $(NiCl_3)_n^{n-}$ chain axis (parallel to the crystallographic *b* axis) is vertical in the diagram.

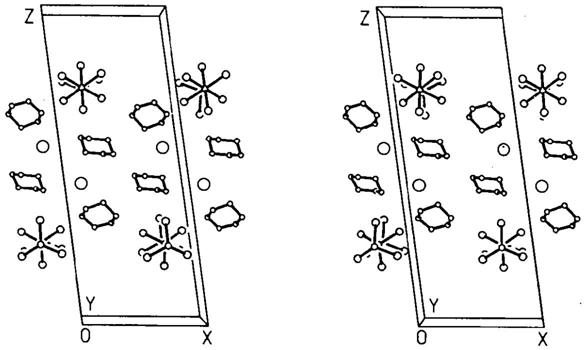
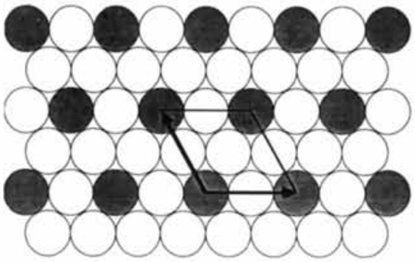
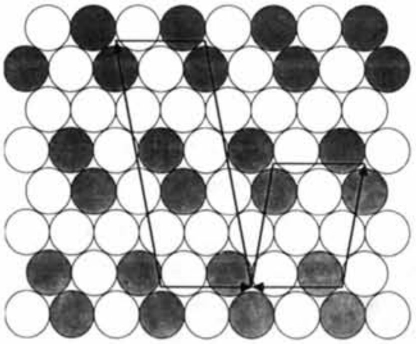


Fig. 2. Stereographic diagram of the bis(piperidinium) trichloronickelate(II) chloride structure including an outline of the unit-cell boundaries and labels for the cell axes. The piperidinium cations are shown only in the chair conformation to improve the clarity of the drawing. The isolated chloride ion is drawn slightly larger than the bridging chlorides in order to emphasize its position in the lattice.

distortion of the uniform sphere structure, c will equal $a \times 7^{1/2}$ with a monoclinic angle of 100.9°. The observed values of $c/(a \times 7^{1/2})$ (0.973) and β [98.01 (1)°] are in excellent agreement with this ideal while the deviation in the ratio $b/a(\frac{2}{3})^{1/2}$ (0.743) strongly reflects the presence of the lower-symmetry piperidinium cation.



(III)



(IV)

A more perfunctory analysis of the system is made by classifying it as a distorted variant of the $CsNiCl_3$ structure. Here a loosely defined aggregate of two piperidinium cations and a chloride anion comprise the 'monocation' of the structure. Distortions and characteristics of the isomorphic α-picolinium trichloronickelate structure (Bond & Willett, 1992; Bond, 1990) are, then, applicable to the description of the bis(piperidinium) tetrachloronickelate structure. Indeed, the average geometry of the inorganic chain is practically identical in the two structures: Ni—Cl (mean) = 2.42 (2) Å, Ni—Cl—Ni (mean) = 79 (1)°, Ni···Ni distance = 3.0716 (4) Å compared to 2.42 (3) Å, 78 (1)° and 3.040 (1) Å, respectively, for the α-picolinium salt. These chains have a nearest-neighbor distance of 10.17 Å compared to 9.37 Å in the α-picolinium derivative or 9.11 Å in the tetramethylammonium derivative, leading us to believe that this new class of A_2NiCl_4 compounds should prove to be good examples of one-dimensional magnetic systems.

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Structure of *trans*-[Re(CO)$_4$(PPh$_3$)I]

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Abstract. (*OC*-6-23)-Tetracarbonyliodo(triphenylphosphine)rhenium, $[ReI(C_{18}H_{15}P)(CO)_4]$, M_r = 687.4, monoclinic, $P2_1/c$, $a = 9.344$ (3), $b = 19.17$ (5), $c = 12.604$ (4) Å, $\beta = 90.13$ (2)°, $V = 2258$ (1) Å^3, $Z = 4$, $D_x = 2.0224$ g cm^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 88.2$ cm^{-1}, $F(000) = 1287.8$, $T = 293$ K, $R = 0.042$

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