H atom positions were all refineable and resulted in the following average values: C—H 0·984 Å, C—C—H 109·4°, and H—C—H 109·0°. The H in the short intramolecular hydrogen bond must be either on the mirror or disordered across the mirror. Difference-Fourier-map examination of the electron density revealed considerable variation in the appearance of the H atom. Using a cut-off of $\sin \theta/\lambda = 0.4$ Å^{-1} (which gave excellent resolution and a clean three-peak map for the methyl H atoms), the H atom appears to be on the mirror but to be somewhat elongated in the bonding direction (O—H = 1·219 Å from least squares).

An interesting feature of the structure in comparison with the Ni^{II} complex (Schlemper, Hamilton & LaPlaca, 1971) is the nearly planar nature of the five-membered chelate rings. The maximum deviation from the plane defined by the N atoms is only 0·07 Å [for C(1)] whereas in the Ni complex all the C atoms are well to one side of the metal–N plane (maximum 0·56 Å for the sp^3 C atoms). In this structure the methyl groups [C(4) and C(5)] are essentially equidistant from the plane of the four N atoms, whereas in the Ni complex one of these methyl groups is nearly in the plane while the other is about 2·00 Å out of the plane.

This difference in conformation is probably due to the *trans* chloro groups [Cl(2)—C(4) 3·62 Å, and Cl(1)—C(5) 3·74 Å]. This change in the chelate ring geometry allows the O···O distance to be nearly identical to that in the Ni complex without an increase in the N(amine)—Co—N(amine) angle [it actually decreases from 96·5 (1) to 95·8 (1)°]. This change in conformation is then sufficient to balance the lengthening in O···O distance which might have been anticipated as a result of the longer M—N distances in this Co complex. The hydrogen bond then remains among the shorter observed O···O hydrogen bonds.

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δ-Bis(n-Propylammonium) Tetrachloromanganate(II): A Neutron Refinement

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Abstract. δ-(C$_3$H$_7$NH$_3$)$_2$MnCl$_4$, orthorhombic, *Abma* (No. 64), $T = 182$ K, $a = 7.458$ (9), $b = 7.169$ (9), $c = 25.61$ (5) Å, $Z = 4$, $\lambda = 0.745$ Å. The MnCl$_6$ octahedra layer takes the $a^-a^-c^0$ tilt system, the n-propylammonium group is disordered, and the hydrogen-bonding scheme is a superposition of two symmetry-related schemes.

Introduction. Crystals suitable for neutron work were obtained by slow evaporation of a solution of MnCl$_2$ and C$_3$H$_7$NH$_3$Cl (molar ratio 1:1) in a mixture of water and ethanol. A crystal, 2·4 × 2·7 × 1·4 mm, was chosen and cooled to a set temperature of 182 K (17 K above the ε → δ phase transition). A Displex cryorefrigerator was used and the temperature was constant throughout the experiment. The cell dimensions and intensities were measured at the D9 diffractometer at the HFR of the Institut Laue–Langevin (Grenoble) with neutrons of wavelength 0·745 Å from a Cu(200) monochromator. Cell dimensions were obtained by least squares from the setting values of 11 reflexions. Data were collected by the ω/2θ-scan technique in the range $\theta < 30°$ yielding 910 unique reflexions of which about two-thirds had intensities >3σ. Transmission factors were estimated for two different crystal plates by their attenuation of a monochromatic beam. The

mean value of 2.15 cm^{-1} for the linear absorption coefficient corresponds to an incoherent cross-section for hydrogen of 36.7 barns (for $\lambda = 0.745$ Å and $T = 295$ K). Data reduction was carried out with the minimum $\sigma(I)/I$ method (Lehmann & Larsen, 1974) and the data were corrected for absorption. The structure was refined by full-matrix least squares minimizing $\Sigma w(|F_o| - |F_c|)^2$ with anisotropic temperature factors for all atoms. Neutron scattering lengths were $b(\text{Mn}) = -0.387$, $b(\text{Cl}) = 0.958$, $b(\text{N}) = 0.937$, $b(\text{C}) = 0.6648$, $b(\text{H}) = -0.3741 \times 10^{-12}$ cm. The weight was $0.009 \times 4F^2 \times [\sigma(F^2)^2 + (0.02F^2)^2]^{-1}$, where $\sigma(F^2)$ is based on counting statistics. As a result of the disorder of the propylammonium group and the relatively small number of reflexions the analysis suffered seriously from correlation. Therefore, the 142 parameters were divided into four groups, one of which varied in each refinement cycle while the other three varied alternately. In spite of this some temperature-factor coefficients in the propylammonium group refined to relatively dubious values and H(7) had to be taken from a difference Fourier map and held constant. However, the most important parts of the structure were clearly resolved. The final R_w ($= \Sigma w^{1/2}\Delta / \Sigma w^{1/2}|F_o|$) was 0.044 with a corresponding $R = 0.074$ for 910 reflexions including 219 with $F_o < 3\sigma(F_o)$.* The SHELX program was used throughout the refinement procedure.

Discussion. The structure of δ-$(\text{C}_3\text{H}_7\text{NH}_3)_2\text{MnCl}_4$ was first determined by Peterson & Willett (1972), but some questions concerning the propylammonium group and the hydrogen bonding remained unresolved. When we started a program to investigate the phase-transition behaviour of bis(n-alkylammonium) tetrachloromanganates(II) $[(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MnCl}_4]$ we found that the propyl compound is unique among the compounds with $n \leq 9$ in that it exhibits the greatest number of phase transitions (five) and the most unusual ones (Depmeier, Felsche & Wildermuth, 1977), e.g. the $\delta \rightarrow \gamma$ phase transition is marked by the formation of an incommensurate phase ($a_{\text{super}} = 5.7a_{\text{sub}}$), the $\delta \rightarrow \varepsilon$ phase transition leads to a commensurate superstructure with a triplication of the b axis, and $\gamma \rightarrow \beta$ is incommensurate to commensurate. To elucidate the mechanisms of these phase transitions it was necessary to know the structure of the δ-phase more exactly. Table 1 shows the atomic positions together with the results of the earlier X-ray work. It can be seen that the results for Mn and Cl are nearly identical, whereas the results for N and C differ appreciably with respect to the x and y parameters. The difference is mainly

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33099 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Refined positional parameters* ($\times 10^4$) *with standard deviations in parentheses*

For each nonhydrogen atom the X-ray results of Peterson & Willett (1972) are given (transformed) in the second row under the present neutron results.

	x	y	z
Mn	0	0	0
	0	0	0
Cl(1)	7500	7500	5107 (0)
	7500	7500	5101 (2)
Cl(2)	485 (2)	0	957 (1)
	467 (10)	0	944 (2)
N	−240 (2)	214 (46)	4147 (1)
	−172 (38)	0	4139 (7)
H(1)	−1520 (9)	−309 (16)	4136 (2)
H(2)	−274 (13)	1537 (12)	4207 (3)
H(3)	389 (11)	−450 (15)	4445 (3)
C(1)	721 (3)	−324 (5)	3658 (1)
	730 (70)	0	3680 (10)
H(4)	2009 (8)	484 (16)	3705 (3)
H(5)	885 (22)	−1765 (15)	3640 (4)
C(2)	−133 (5)	476 (6)	3191 (1)
	−50 (60)	0	3215 (12)
H(6)	−299 (28)	1862 (18)	3239 (4)
H(7)	−1420	325	3150
C(3)	918 (5)	−59 (25)	2700 (1)
	1004 (58)	0	2718 (10)
H(8)	266 (15)	526 (23)	2352 (3)
H(9)	2135 (15)	741 (19)	2724 (3)
H(10)	1171 (26)	−1368 (16)	2641 (5)

Table 2. *Bond angles* (°)

Cl(2)−Mn−Cl(1)	90.0 (0)	H(5)−C(1)−N	110.4 (5)
Cl(1)−Mn−Cl(1)′	87.1 (0)	C(1)−C(2)−C(3)	110.4 (3)
Mn−Cl(1)′−Mn	167.9 (0)	H(6)−C(2)−H(7)	114.2 (3)
H(1)−N−H(2)	109.9 (9)	H(6)−C(2)−C(3)	114.2 (5)
H(1)−N−H(3)	106.3 (6)	H(7)−C(2)−C(3)	103.4 (3)
H(2)−N−H(3)	110.7 (6)	H(8)−C(3)−H(9)	102.5 (6)
H(1)−N−C(1)	109.2 (4)	H(8)−C(3)−H(10)	109.2 (4)
H(2)−N−C(1)	113.7 (5)	H(9)−C(3)−H(10)	111.2 (5)
H(3)−N−C(1)	106.7 (4)	H(8)−C(3)−C(2)	110.1 (5)
N−C(1)−C(2)	111.9 (2)	H(9)−C(3)−C(2)	104.5 (4)
H(4)−C(1)−H(5)	114.4 (3)	H(10)−C(3)−C(2)	118.1 (3)
H(4)−C(1)−N	100.8 (4)		

because Peterson & Willet (1972) placed the propylammonium group at the average position on the mirror plane whereas in this work these atoms are split into two symmetry-related positions with an occupancy factor of 0.5.*

Such a split-atom model has also been used for the room-temperature phase of $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{MnCl}_4$ (Depmeier, 1976) and gave an improvement of the bond lengths and angles. In this work, too, the bond lengths

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* In a paper on $\text{NH}_3(\text{CH}_2)_3\text{NH}_3\text{MnCl}_4$ Willet & Riedel (1975) predicted this kind of disorder also for the room-temperature phase of $(\text{C}_3\text{H}_7\text{NH}_3)_2\text{MnCl}_4$.

Table 3. *Hydrogen bonds*

(1) H(1)···Cl(2)	2·26 Å	N···Cl(2)	3·20 Å	N—H···Cl	169°
(2) H(2)···Cl(2)'	2·52	N···Cl(2)'	3·45	N—H···Cl	161
(3) H(3)···Cl(1)	2·44	N···Cl(1)	3·24	N—H···Cl	147

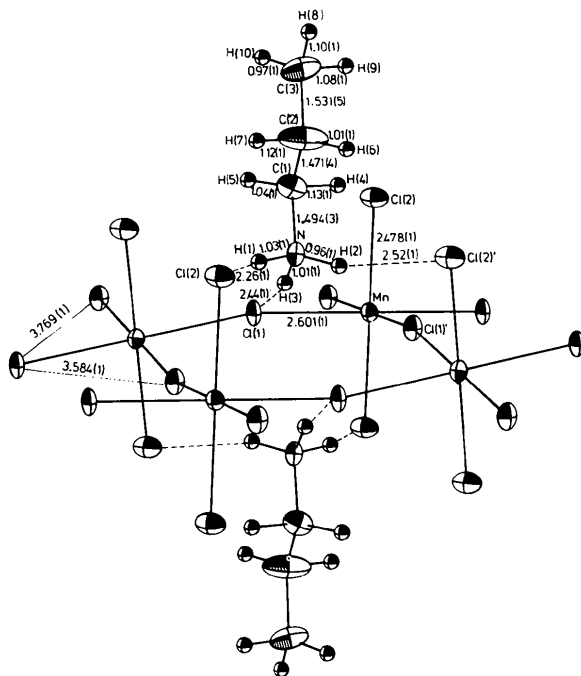
Fig. 1. *ORTEP* plot of δ-(C₃H₇NH₃)₂MnCl₄. The hydrogen atoms have been assigned a radius of 0·1 Å for clarity. Only one of the superposed propylammonium groups is shown above and below the octahedra layer around $z = 0.5$.

positions is shown in Fig. 1). The hydrogen-bonding system is monoclinic (Chapuis, Kind & Arend, 1976) and a superposition of that shown in Fig. 1 and its mirror image. Table 3 shows the distances and angles of the hydrogen bonds. Bond (1) is rather strong, whereas (3) has a short N—Cl distance, but is remarkably bent. The layer of MnCl₆ octahedra has an $a^-a^-c^0$ tilt system (Glazer, 1972; Depmeier, Felsche & Wildermuth, 1977) where the tilt angles about the pseudotetragonal (a-) axes are 6°. The octahedron itself, however, does not display its ideal symmetry but is distorted with two different Mn—Cl bonds [2·478 (1) and 2·601 (1) Å]. The shortening of the non-bridging Cl has been observed in related compounds (cf. Table 4 in Depmeier, 1977). Furthermore, the hydrogen bonding distorts the square base of the octahedron to a rectangle (see left side of Fig. 1).

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and angles are improved, as may be seen from Fig. 1 and Table 2. However, although there is an improvement, the lengths of the bonds involving C(1) are slightly anomalous. It is the dynamical disorder (Seliger, Blinc, Kind & Arend, 1976) of the propylammonium group (in spite of the low temperature used) which makes it impossible to locate this group correctly. However, the following most important features of the structure are clear. The propylammonium group is disordered (only one of the two