

S(2), C(3) and S(2m), is  $37.6(2)^\circ$ . Such angles between least-squares planes do not appear to show trends with respect to formal charge and are probably due to packing forces. (For example, see Nigrey, Duesler, Wang & Williams, 1987; Nigrey, Morosin, Kwak, Venturini, Schirber & Baughman, 1986; KSKS, 1984.)

Ribbons of  $[\text{Ag}(\text{CN})_2]_\infty$  are formed by direct 2.103 (5) Å bonds to two  $\text{CN}^-$  ions as well as by more distant interactions with neighboring  $\text{CN}^-$  groups at about 3.3 Å. From the angles formed (Fig. 1) the interaction appears to be to the C—N bond rather than to either the C or N of the group. The  $\text{Ag}(\text{CN})_2$  are essentially linear considering the estimated error of the angle. The nearest contacts normal to the ribbons involve Ag and S, with each Ag having four S(1) atoms at 3.340 (1) Å, significantly shorter than the 3.57 Å van der Waals sum; these S contacts and the bond to C(4) form C(4)—Ag—S(1) angles of 81.7 (1) and 98.3 (1)°.

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## Structure of Bis(*n*-butylammonium) Tetrachlorocadmate(II)

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**Abstract.**  $2\text{C}_4\text{H}_{12}\text{N}^+ \cdot \text{CdCl}_4^{2-}$ ,  $M_r = 402.52$ , orthorhombic, *Abma*,  $Z = 4$ . At 295 K,  $a = 7.538$  (1),  $b = 7.416$  (3),  $c = 30.803$  (4) Å,  $V = 1722$  (1) Å<sup>3</sup>,  $D_x = 1.55$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.71069$  Å,  $\mu = 1.85$  mm<sup>-1</sup>,  $F(000) = 808$ ,  $R = 0.045$  for 1211 independent reflections with 46 refined parameters. This lamellar phase is similar to the  $\delta$  phase observed in parent compounds, with a tilting of the  $\text{CdCl}_6$  octahedra favouring one specific hydrogen bond to the ammonium end of the aliphatic chains. No simple model can convincingly explain the disorder affecting the chains, in contrast with the analogous manganese compound [Depmeier & Chapuis (1979). *Acta Cryst.* B35, 1081–1084]. The separation of successive aliphatic layers is probably too large for a modulated phase to occur. Phase transitions are observed around 200 K, at which temperature monocrystals are damaged.

**Introduction.** The family  $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MCl}_4$  (hereafter *C<sub>n</sub>M*) has been the subject of many studies during the last 15 years. These compounds contain  $\text{MCl}_4$  layers alternating with packed aliphatic chains

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(Fig. 1). Interesting two-dimensional magnetic properties (Yamasaki, 1979) have been detected. These substances have also been used as models of biological membranes (Needham, Willett & Franzen, 1984). The large number of phase transitions observed in these materials has created a rich area of structural research (see *e.g.* Kind, 1980). Surprisingly, the case  $n = 3$  exhibited modulated phases, the metallic atoms being Mn (see Depmeier, 1986, for a review), Cd (Doudin & Chapuis, 1988) or Cu (Jahn, Knorr & Ihringer, 1989; Doudin & Chapuis, 1990). The study of the butylammonium compound was motivated by the search for a similar phase. Our results revealed the existence of a commensurate phase  $\delta$ , similar to the one observed for the propylammonium compounds at ambient temperature. A phase transition was observed at approximately 210 K. It was accompanied by a splitting of the Bragg peaks, thus making a study on monocrystals more tedious.

C4Mn also exhibits the same symmetry. Depmeier & Chapuis (1979) showed that the terminal methyl group takes a *gauche* conformation. This effect has

not been observed in this refinement, but a disordered model for the butylammonium chain is discussed.

**Experimental.** The synthesis and growth of monocrystalline samples has been described earlier (Arend, Hofman & Waldner, 1974). A tabular crystal  $0.4 \times 0.4 \times 0.05$  mm was mounted directly from aqueous solution and measured on a CAD-4 diffractometer with graphite-monochromated  $\text{Mo } K\alpha$  radiation. Cell parameters were determined from setting angles of 15 centred reflections,  $12 < \theta < 19^\circ$ ;  $\omega$ - $2\theta$  scans with scan speed of  $1^\circ \text{ min}^{-1}$  and width of  $(0.8 + 0.5 \tan \theta)^\circ$ ; 3 check reflections were used every 100 measurements, a correction for a linear intensity decrease of approximately 10% was performed;  $(h, k, \pm l)$  with  $0 \leq h \leq 10$ ,  $0 \leq k \leq 11$ ,  $-49 \leq l \leq 49$  were measured up to  $(\sin \theta / \lambda)_{\text{max}} = 0.81 \text{ \AA}^{-1}$ , 3643 reflections. An absorption correction was applied (Gaussian integration method) with correction factors ranging from 1.13 to 1.56. Averaging ( $R_{\text{int}} = 0.10$ ) yielded 1766 reflections, of which only 845 had an intensity larger than  $3\sigma(I)$ . The XRAY72 system of programs (Stewart, Kundell & Baldwin, 1972) was used. Atomic scattering factors were taken from Cromer & Mann (1968). Anomalous-dispersion corrections for Cl and Cd atoms (Cromer & Liberman, 1970) were applied. The structure was solved from an initial model analogous to phase  $\delta$  of C3Cd. Refinement on  $F$  with  $w = 1/\sigma^2(F)$  converged with  $R(F) = 0.045$  and  $wR(F) = 0.032$  for 1211 contributing reflections [those with  $I > 3\sigma(I)$  or with  $F_{\text{calc}} > F_{\text{obs}}$ ]. The smaller values for the  $R$  factors compared to  $R_{\text{int}}$  can be explained by the large number of weak reflections. Maximum shift/e.s.d. value was 0.08. On a difference Fourier map, no peaks with an absolute value greater than  $0.4 \text{ e \AA}^{-3}$  were observed. No H atoms were included in the refinement; the large disorder affecting the organic chains (see below) justifies their absence. Anisotropic displacement factors for all atoms were included; 46 independent parameters; goodness-of-fit  $S = 3.5$ .\*

Phase transitions were detected by differential scanning calorimetry (Mettler DSC-30) measurements. Phase changes were observed at approximately 213, 201, 195 and 133 K on cooling. At 213 K splitting of Bragg peaks can be observed. On further cooling, splittings are subsequently observed around 130 K. The first transition appeared to be reversible (though with damage to the sample) whereas the last

one was not. On heating, the transition peaks appear at 143, 158, 197 and 213 K thus indicating strong hysteresis or irreversibility effects for the three lowest transitions.

**Discussion.** The non-standard space group setting  $Abma$  was chosen by analogy with the studies of related compounds and to keep the  $c$  axis perpendicular to the  $\text{CdCl}_4$  layers. The final atomic and displacement parameters are listed in Table 1, bond lengths and angles are in Table 2. Fig. 1 illustrates the packing of the structure. The corner-sharing  $\text{CdCl}_6$  octahedra form chessboard-like layers. The ammonium groups fill the cavities and are linked to the Cl atoms by hydrogen bonds. Soft non-bonded interactions between the methyl ends of the chains govern the packing of successive layers along  $c$ . The puckering of the  $\text{CdCl}_4$  layers can be explained by the existence of one particularly short  $\text{N} \cdots \text{Cl}$  distance (Fig. 1). On average, the butylammonium chains lie on a mirror plane perpendicular to  $\mathbf{b}$  (Fig. 1), allowing two possible hydrogen-bonding geometries. This is also true for the ambient phases of C3Cd, C3Mn and C4Mn.

The marked disorder affecting the C atoms is the most striking feature that can be deduced from Tables 1 and 2. The C—C distances are chemically unrealistic and must be considered as shortened average values. Surprisingly, the displacement ellipsoids exhibit a large component parallel to the covalent C—C bonds (Fig. 2). The refined parameters on the C atoms evidently reflect the superposition of various chain positions. Refinement of a model with half C atoms located on both sides of the mirror plane with restrained distances, did not give further insight into the disorder type. The displacement parameters remained large and the orientations of the ellipsoids were still unsatisfactory (Fig. 2). Despite the larger number of refined parameters, the  $R$  factor did not decrease. This is in contrast with the Mn compound (Depmeier & Chapuis, 1979) where the chain exhibits a *gauche* conformation for the terminal methyl group. This effect, illustrated by a large displacement of the C(4) atoms away from the mirror plane, is not present in this structure. This comparison suggests that the observed disorder could be a superposition of a splitting of the whole *trans* chain due to the two possible hydrogen bonds and the occurrence of *gauche* conformations.

In previous structural studies on propylammonium compounds and C4Mn, the resolution was lower with  $(\sin \theta / \lambda)_{\text{max}}$  varying from 0.5 to  $0.6 \text{ \AA}^{-1}$ . A refinement of the present structure using only reflections with  $\sin \theta / \lambda \leq 0.5 \text{ \AA}^{-1}$  produced no significant changes in the atomic parameters. The hypothesis of a result influenced by the resolution of the experiment is thus not realistic.

\* A list of structure factors, Tables 1(b) and 2(b) corresponding to the model with disordered C atoms and Fig. 3 have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54942 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0240]

Table 1. Fractional atomic coordinates and anisotropic displacement parameters  $U_{ij}$  ( $\times 100 \text{ \AA}^2$ ) with *e.s.d.*'s in parentheses

The last column indicates the displacement component  $U_{13}$  for all the atoms, except for Cl(2) atoms ( $U_{12}$ ). The other components are zero by symmetry constraints. The Debye-Waller factor  $T$  is given by:

$$T = \exp[-8\pi^2 \sum_{i,j} U_{ij} h_i h_j a_i^* a_j^*].$$

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{13(2)}$
Cd	0.00	0.00	0.00	3.01 (4)	2.43 (3)	9.01 (7)	-0.32 (6)
Cl(1)	0.25	0.25	-0.00945 (9)	4.18 (9)	3.53 (9)	11.7 (2)	-1.22 (8)
Cl(2)	0.0489 (2)	0.00	0.08121 (7)	5.5 (1)	8.6 (2)	8.8 (2)	-0.2 (1)
N	0.4712 (11)	0.00	0.0684 (3)	7.0 (6)	9.8 (6)	8.5 (7)	-1.8 (5)
C(1)	0.557 (3)	0.00	0.1046 (8)	14 (2)	13 (1)	27 (3)	12 (2)
C(2)	0.491 (5)	0.00	0.1391 (15)	40 (5)	38 (4)	42 (8)	-36 (6)
C(3)	0.545 (7)	0.00	0.1693 (16)	44 (5)	45 (5)	39 (7)	28 (5)
C(4)	0.490 (6)	0.00	0.2071 (8)	42 (5)	70 (4)	23 (3)	-7 (4)

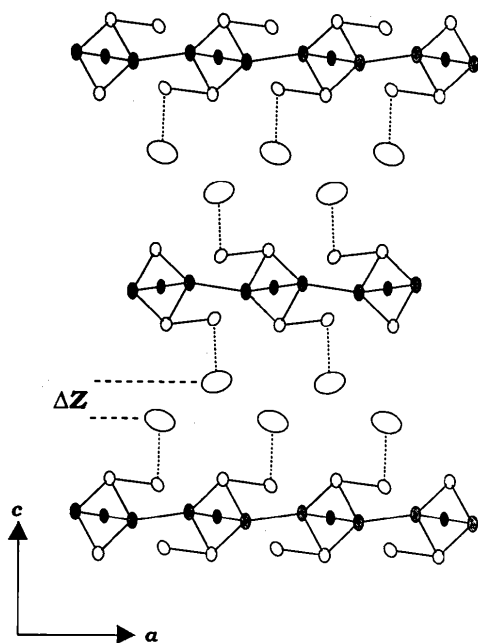


Fig. 1. ORTEP plot (Johnson, 1965) of the structure with *a* horizontal and *c* vertical. This *xz* cut illustrates the packing of the layers. The only atoms with a *y* value different from zero are the shaded Cl(1) atoms (and those generated by symmetry) at  $y = \pm 0.25$ , on a twofold axis parallel to *z*. The black Cd atoms have site symmetry  $2/m$ . The butylammonium chains are represented by broken lines between the terminal C(4) and N atoms, with the nitrogen connected by the preferred hydrogen bond to the Cl(2) atoms. Atoms represented in white lie on the mirror plane at  $y = 0$ . The ellipsoids correspond to 50% probability.

The separation  $\Delta Z$  between the terminal C(4) atoms of successive layers was also estimated. Its value of 2.64 Å is a measure of the van der Waals packing energy of the aliphatic layers (Doudin &

Table 2. Bond lengths (Å) and angles (°) including the preferred hydrogen bond

Cd—Cl(1)	2.660 (2)	Cl(1)—Cd—Cl(2)	90.29 (6)
Cd—Cl(2)	2.528 (2)	Cl(2)—N—C(1)	113 (1)
N—C(1)	1.29 (2)	N—C(1)—C(2)	124 (3)
C(1)—C(2)	1.18 (5)	C(1)—C(2)—C(3)	131 (5)
C(2)—C(3)	1.02 (7)	C(2)—C(3)—C(4)	137 (6)
C(3)—C(4)	1.24 (6)		
N...Cl(2)	3.21 (1)		

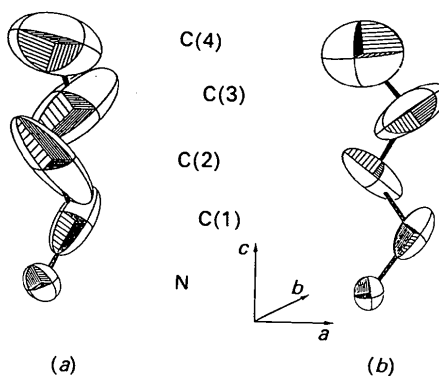


Fig. 2. ORTEP plot (Johnson, 1965) showing (a) a butylammonium chain with 30% probability ellipsoids (model refined in the text, with all atoms lying on a mirror plane); (b) the same chain after refining a disordered model (see text); a second half chain is generated by the mirror plane perpendicular to *b*.

Heine, 1990). If it is remembered that the value of  $Z$  is close to 1 Å for the propylammonium derivatives, this study confirms that a small value of  $\Delta Z$  is a necessary condition for the occurrence of modulated phases.

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