

Computing Centre, University of Nottingham, for computing facilities.

References

SPEAKMAN, J. C. (1967). *Chem. Commun.* p. 32.
WALLWORK, S. C. (1962). *Acta Cryst.* **15**, 758.

WILLIAMS, J. M. (1969). *Nat. Bur. Stand. Special Publ. No.* 301, 237.

WILLIAMS, J. M. & PETERSON, S. W. (1971). *Spectroscopy in Inorganic Chemistry* Vol. 2, pp. 1–56, Edited by C. N. R. RAO & J. R. FERRARO. New York & London: Academic Press.

Acta Cryst. (1972). **B28**, 2303

Crystal structure of tetramethylammonium cadmium chloride.* By B. MOROSIN, *Sandia Laboratories, Albuquerque, New Mexico 87115, U.S.A.*

(Received 21 July 1971)

The crystal structure of tetramethylammonium cadmium chloride, $(\text{CH}_3)_4\text{NCdCl}_3$, has been refined using the full-matrix least-squares method on 506 Mo $K\alpha$ intensity data. The compound crystallizes in space group $P6_3/m$ with lattice constants $a_0=9.138$ and $c_0=6.723$ Å and a structure consisting of infinite linear chains formed from face-shared cadmium-chloride ion octahedra (Cd–Cl separation of 2.641 Å and Cl–Cd–Cl angle of 96.05° along the chain) and of disordered $[\text{N}(\text{CH}_3)_4]^+$ ions.

Introduction

Recent low-temperature neutron scattering experiments on tetramethylammonium manganese chloride (TMMC) have shown that the $-\text{MnCl}_3^-$ chains magnetically order at low temperature (Birgeneau, 1971). Attempts to grow a diamagnetic isomorphous analog as a host for resonance studies proved successful for only cadmium ions. The crystal structure of tetramethylammonium cadmium chloride (TMCC) proved to be very similar to that for TMMC (Morosin & Graeber, 1967) even to the extent of disorder of the $[\text{N}(\text{CH}_3)_4]^+$ ions.

Experimental

Colorless, hexagonal prismatic $\{10\bar{1}0\}$ crystals of TMCC were grown either by cooling hot aqueous saturated solutions, prepared with stoichiometric amounts of $\text{N}(\text{CH}_3)_4\text{Cl}$ and CdCl_2 , or by slow evaporation of similar room-temperature solutions.

The lattice constants for TMCC [$a_0=9.138$ (1), $c_0=6.723$ (1) Å] were obtained by least-squares fit of 12 high 2θ values measured on films taken with Cu $K\alpha$ radiation (λ for $K\alpha_1=1.54050$ Å) using a 115 mm diameter Straumanis loaded, Weissenberg camera. Systematic absences of $00l$ for l odd and the symmetry of the reciprocal lattice as recorded by the precession method indicate the space group to be either $P6_3$ or $P6_3/m$. Comparison of these photographs with those previously taken on TMMC indicated that these compounds are isomorphous. Similarly, the presence of a piezoelectric effect was not detected. There are two formula weights of $\text{N}(\text{CH}_3)_4\text{CdCl}_3$ per cell, yielding a calculated density of 2.07 g.cm $^{-3}$.

The θ - 2θ scan technique and a scintillation counter with pulse-height discrimination were used to measure the Mo $K\alpha$ intensity data on a crystal specimen mounted on $[11\bar{2}0]$. (A Datex automatic-control module was used for setting the angles on the Picker diffractometer and on the

E & A full-circle orienter.) Two symmetry-related sets for both positive and negative values of l were examined for differences that might imply the structure was noncentrosymmetric, or possibly that it consisted of an intimate twinning of two noncentrosymmetric structures (see TMMC). The number of pairs of reflections with the same sign for l which differed by more than 3σ (obtained from counting statistics)* was 64; however, only in five cases did the average value of the positive l differ from that for the negative l by 3σ . On the basis of this comparison of intensities, the presence or absence of the center of symmetry cannot be clearly established. Two data sets were considered for refinement: (1) 506 averaged intensities ($P6_3/m$) of which 116 were measured to be less than 3σ and, thus, considered to be unobserved,† and (2) 941 intensities with both positive and negative l index, of which 117 were correspondingly considered to be unobserved. No absorption corrections were applied to the data set ($\mu_{\text{Mo } K\alpha}=29.5$ cm $^{-1}$: crystal, hexagonal prism $0.19 \times 0.17 \times 0.18$ mm).

Refinement and results

Using the positional parameters determined for TMMC, the above data sets were subjected to full-matrix least-squares refinement using anisotropic thermal parameters. The function, $\sum w(F_o - F_c)^2$, was minimized; weights were assigned from counting statistics or set to zero for unobserved reflections when $F_o < F_c$. Structure factors were calculated with Cd, Cl $^-$, N, and C scattering factors from

* In the expression for σ [$\sigma=(N_{sc} + K^2 N_B)^{1/2}$, where N_{sc} , N_B , and dK are the total scan count, background counts, and the ratio of the scan to background times, respectively], K rather than K^2 was employed; further, no allowances for instability or other errors, which would be a function of intensity, were made.

† Only one particular measured value of a set needed to be less than 3σ for the intensity to be considered unobserved. For unobserved reflections with positive average values, I_{obs} set equal to the greater of either the average value or $3\sigma_{(\text{ave})}/\sqrt{n}$, where $\sigma_{(\text{ave})}$ is the average σ for n measurements; for negative average values, I_{obs} set to zero. Weights = $n/\sigma^2_{(\text{ave})}$.

* This work was supported by the U.S. Atomic Energy Commission.

Tables 3.3.1*A* and 3.3.1*B*, and dispersion corrections from Table 3.3.2*C* of *International Tables for X-ray Crystallography* (1962). The residual, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, are 0.031 and 0.029 for the $P6_3/m$ and $P6_3$ data sets, respectively.

If the carbon atoms are not included in the refinement, R is 0.052. A three-dimensional difference synthesis shows the density corresponding to the carbon atoms to be smeared as three arcs (or semicircles), with ends attached to the threefold axis and with density continuously varying from this widely spread minimum value at the threefold to a smaller cross section maximum value ($\sim 3 \times$ minimum) at the mirror. The carbon thermal parameters attempt to reflect this smeared shape, i.e. thin pancake for C(1) compared to egg shape for C(2). Clearly, the tetramethylammonium ions are disordered in the structure. If this Fourier synthesis is ignored and the separate refinements of

the two data sets are compared on the basis of the R factor ratio (Hamilton, 1965), the hypothesis that the structure is acentric cannot be rejected. The only significant positional parameter (change greater than 3σ) involves the nitrogen z parameter [$z=0.275$ (2) or -0.272 (2) with identical R values for the two absolute configurations]; however, because of the high-correlation interaction of this z parameter with U_{33} , whose value drops to 0.006 (7) \AA^2 , such a difference is highly suspect. (Because of thermal motion, the mean displacement in position of the nitrogen in the centric case is sufficiently large to be indistinguishable with the displacement of 0.17 \AA and the low U_{33} value as is obtained in the $P6_3$ refinement.)

The above results suggest that the centrosymmetric space group probably is the preferred one and that the $[\text{N}(\text{CH}_3)_4]^+$ ions are disordered. The positional and thermal

Table 1. Atomic positional and anisotropic thermal parameters ($\times 10^4$) for TMCC

Thermal parameters are of the form: $\exp(-2\pi^2 \sum U_{ij} h_i h_j a_i^* a_j^*)$; symmetry requires that $U_{11} = U_{22} = 2U_{12}$ for Mn, N, and C(1) and that $U_{13} = U_{23} = 0.0$ for all except C(2).

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cd	0	0	0	398 (3)		195 (3)			
Cl	1552 (2)	2560 (2)	$\frac{1}{2}^*$	459 (8)	319 (7)	306 (6)	130 (6)		
N	$\frac{2}{3}^*$	$\frac{1}{3}^*$	$\frac{1}{2}^*$	320 (20)		390 (50)			
C(1)	$\frac{2}{3}^*$	$\frac{1}{3}^*$		4500 (40)	5600 (900)	130 (90)			
C(2)	6260 (20)	4680 (20)	2080	1100 (100)	1200 (100)	3200 (400)	800 (100)	300 (200)	1400 (200)

* Fractional parameters are not multiplied by 10^4 .

Table 2. Observed and calculated structure factors for TMCC

* Unobserved reflections; F_o and F_c both $\times 10$.

0.0.L	1 327 -313	1.10.L	2 480 479	3.0.L	2 363 365	7 290 [*] -28	3 82 79	5.4.L	6 211 213	1 140 [*] -8	8.3.L
	2 565 553		3 82 79		3 158 -157	8 248 245	4 91 79		7 75 65	2 214 215	
2 153 -168	3 224 222	0 90 77	3 62 51	3 329 318	4 146 151			3 43 [*] -42		3 21 [*] 2	0 124 119
4 076 1106	4 302 300	1 62 66	4 255 257	4 366 353	5 117 122	4+2.L	4+8.L	4 203 205	6.3.L	4 145 149	1 35 [*] 6
6 56 65	5 153 -154	2 121 111	6 268 274	5 295 -221	6 209 212			5 28 [*] 31		5 35 [*] -2	2 128 124
8 422 415	6 311 315	3 61 -58	7 54 38	6 398 +02	7 76 -81	0 580 597	0 185 93	6 125 121	0 284 293	6 139 135	3 34 [*] -6
	7 97 100		8 136 137	7 136 139		1 90 -89	1 40 [*] -16		6 30 [*] -38		4 97 92
	8 150 146	2.0.L	8 169 165	9 83 -78	3+5.L	2 252 250	2 100 96	5.5.L	2 142 151	7.3.L	
01153 1084	1.5.L	0 469 450	2.5.L	0 221 235		3 62 65			3 30 [*] 31		8+4.L
1 203 146		1 634 -632	0 280 289	3+1.L	1 14 [*] 13	4 441 445	5.0.L	0 246 261	4 220 215	0 247 248	
2 499 493	0 199 223	2 903 942	1 44 [*] 51		2 194 199	5 35 [*] -37		5 40 [*] -43	5 40 [*] 39	1 49 [*] 49	0 76 65
3 46 38	1 287 -289	3 391 373	2 372 372	0 771 800	3 28 [*] -3	6 143 147	0 316 318	2 103 98	6 106 101	2 90 [*] 82	1 44 [*] -30
4 728 723	2 532 532	4 351 345	3 50 -44	1 121 -123	4 185 183	8 211 212	2 560 570	3 41 [*] 38		3 43 [*] -39	2 124 123
5 14 [*] 5	3 252 247	5 257 -259	4 222 223	2 417 405	5 16 [*] -0			4 203 208	6+4.L	5 20 [*] -28	
6 263 268	4 186 186	6 459 468	5 33 [*] 24	3 108 100	6 12 [*] 123	4.3.L	4 221 228	0 303 310		0 303 310	
7 411 32	5 169 -172	7 142 141	6 227 223	4 535 533			5 137 137	1 0 [*] -8		7+4.L	0 141 140
8 310 322	6 305 307	8 176 176	7 0 [*] -12	5 80 -74	3.7.L	0 128 123	6 306 317	2 42 [*] 42		2 42 [*] 42	
9 34 [*] -6	7 101 107	7 87 -85	8 244 248	6 230 232	4.2.L	1 102 95	7 91 -91	0 108 112	3 0 [*] 2	0 208 214	2 168 166
				7 39 [*] 41		2 196 206	2 416 413	1 67 -70	4 241 240	2 416 413	0 76 77
				8 244 248		3 88 88	4 99 91	2 165 155	5 12 [*] -5	2 155 155	4 126 120
						4 99 91	6 233 235	4 87 88		4 87 88	5 48 [*] 37
0 854 894	1.6.L	2+1.L	0 360 376	3+2.L	0 951 994	5 73 -68	7 44 [*] -30	5+1.L			9+1.L
1 121 115	0 349 348	1 83 -62	2 150 157		1 62 56						
2 827 782	1 35 [*] -21	2 790 784	3 22 [*] -35	0 951 994	4 99 91		0 321 322				
3 182 -94	2 266 275	3 58 56	4 277 279	1 62 56	5 73 -68		1 66 45	5.7.L	0 198 203	7.5.L	
4 523 500	3 23 [*] 19	4 377 372	5 22 [*] 27	2 81 82	3+8.L		2 445 443		1 25 [*] 2		9+1.L
5 59 66	4 268 270	5 39 [*] -24	6 117 113	3 46 -43			3 51 -29	0 85 73	2 74 67	1 60 [*] 79	0 70 72
6 381 388	5 15 [*] -12	6 406 415	7 25 [*] -17	4 665 670	0 71 65	0 193 202	4 259 261	1 44 [*] 16	3 33 [*] -6	0 60 [*] 60	2 182 189
7 46 [*] -41	6 156 161	7 28 [*] 28	8 180 182	5 31 [*] 23	1 20 [*] -6	1 196 190	6 248 250	2 125 126	4 165 159	2 123 119	3 75 -67
8 214 209	7 17 [*] -8	8 180 182	2.7.L	6 80 79	2 172 172	2 363 363	7 26 [*] -1	3 30 [*] -16		3 45 [*] -2	4 71 60
9 32 [*] 23		9 35 [*] -12		7 25 [*] -10	3 0 [*] 1	3 168 -160	8 143 136	6+0.L			9+2.L
				8 295 302	4 62 55	4 149 146					
						5 111 114	5+2.L	0 311 326	0 95 88	0 95 88	
						6 223 221		1 72 65	2 118 111	1 17 [*] 1	0 291 305
						7 73 -72		2 379 380	3 53 [*] -28	2 121 119	2 146 144
0 290 300	0 446 466	2.2.L	2 98 98	3+3.L	3+9.L			3 57 -50	7.0.L	3 26 [*] 1	3 35 [*] -32
1 527 490	2 39 [*] 30	1 22 [*] 24	4 24 24	0 682 680	0 120 112		0 304 311	4 239 237	5 48 [*] 42	4 235 243	9.3.L
2 936 947	3 18 [*] -6	2 413 383	5 35 [*] -5	1 17 [*] 14	1 41 [*] 29	4.5.L	3 362 362	5 48 [*] 42	0 337 346	6 93 83	
3 343 -331	4 355 356	3 58 -52	6 77 70	2 199 190	2 66 63		3 133 134	6 239 240	7 17 [*] -29	8+1.L	
4 304 299	5 34 [*] 2	4 597 585	3 27 [*] -20	4 485 489	0 408 419	0 180 188	4 216 216	8 239 240	8 239 240	8 239 240	
5 197 193	6 41 [*] 31	5 51 50	2.8.L	5 17 [*] 14	4.0.L	2 251 254	6 234 234				
6 449 455		6 218 216		4 485 489		2 637 625	3 73 67	7 17 [*] -29	2 206 209	2 206 209	
7 131 -132	1.8.L	7 39 [*] -33	0 148 149	6 140 134	3 34 [*] 34	0 408 419	3 48 [*] -55	7 65 65	6+1.L	3 34 [*] 33	
8 152 159		8 259 258	1 29 [*] -6	7 28 [*] -7	1 88 60	4 146 146	4 146 146		4 364 363	0 139 142	
9 71 70	0 265 271	3 140 148	8 222 223	2 148 148	8 222 223	6 223 311	5+3.L	0 176 181	1 294 -32	1 294 -32	10+0.L
	1 9 [*] 19	2.3.L	4 130 124	3+4.L	4 338 338	5 55 50		1 225 -227	6 139 135	2 219 218	
	2 96 102		5 30 [*] -6		5 55 50	6 223 205	4.6.L	2 417 423	7 21 [*] 19	3 84 -76	0 60 62
0 594 584	3 19 [*] 15	0 633 659	0 239 257	1 039 124	2 33 [*] 31	0 139 131	1 76 -70			4 121 113	1 37 [*] -2
1 241 218	4 204 203	1 84 -73	2 135 124	2 429 424	8 168 169	1 92 -81	2 363 366	4 153 157	7+1.L	5 65 59	2 184 166
2 632 621	5 17 [*] -14	2 389 354	2.9.L	3 105 -108	4.1.L	2 210 204	4 145 148	6 237 241		6 144 135	3 12 [*] 0
3 164 -150	6 80 71	4 493 491	0 68 56	3 105 -108		2 210 204	5 51 -31	7 82 82	0 240 247	8+2.L	4 68 60
4 344 344	1.9.L	5 63 -63	1 62 55	4 197 201		4 113 112	6 219 218		1 95 -93	10+1.L	
5 195 196		6 193 197	2 160 162	5 92 85		5 52 [*] -49	7 37 [*] 21	6+2.L	3 82 75	0 130 132	
6 357 363	0 84 90	7 40 [*] 36	3 56 -45	6 253 257	0 766 794				4 184 183	1 102 100	0 116 109
7 56 -61	1 44 [*] 58	8 224 231	3+0.L	7 64 -56	1 86 82				5 66 -55	3 91 -86	1 40 [*] 10
8 169 170	2 171 172	2.4.L	3+5.L		2 223 205	4.7.L	5+4.L	1 134 -139	6 155 151	2 172 169	2 94 83
	3 56 [*] -54				3 63 -56			0 247 251	2 354 359	4 111 105	3 0 [*] -6
	4 80 75				4 553 551	0 90 89	1 61 58	4 126 128	7+2.L	5 63 62	11+0.L
					5 35 [*] -42	1 87 -89	2 196 191	5 100 -103			0 102 102
0 497 392					6 152 149	2 169 164					1 39 [*] -32

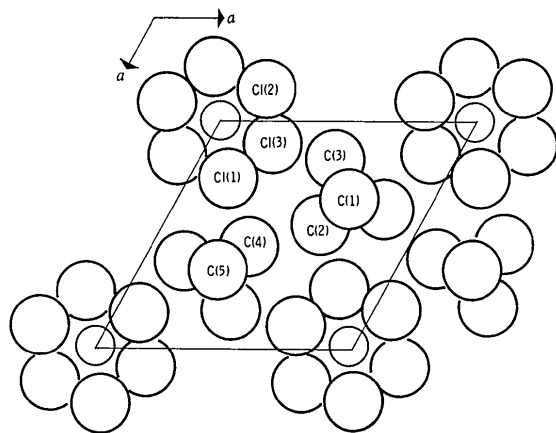


Fig. 1. A representation of the crystal structure of TMCC viewed along the c axis. Chains formed by face-sharing of octahedrally coordinated cadmium-chloride ion, $-\text{Cd}-\text{Cl}_3-\text{Cd}-$, are parallel to the 6_3 axis at the origin; $[\text{N}(\text{CH}_3)_4]^+$ ions are located between these chains in a disordered manner.

parameters for this case are given in Table 1. The observed and calculated structure factors obtained with these parameters are given in Table 2. The crystal structure of TMCC as viewed along the c axis is represented in Fig. 1.

The slight trigonal elongation (Table 3) of the octahedron about the cadmium ion is very similar to that observed in TMMC (84.09 and 95.91°). The longer Cd-Cl separation compared with Mn-Cl (2.560 Å) results in a slight elongation of the cell dimension along the c axis; this increased separation between the chloride ions along the chain allows the $[\text{N}(\text{CH}_3)_4]^+$ ions to fit closer to the chains, resulting in a slightly smaller a axis (for TMMC, $a_0 = 9.1510$ and $c_0 = 6.4940$ Å). Even though an improvement would be

Table 3. Interatomic separations and angles in TMCC

(a) Involving chemically bonded atoms (for labeling, see Fig. 1):			
Cd-Cl(1)	2.644 (1) Å	Cl(1)-Cd-Cl(2)	83.91 (3)°
N-C(1)	1.34 (3)	Cl(1)-Cd-Cl(3)	96.09 (3)
N-C(2)	1.47 (3)	C(1)-N-C(2)	101 (2)
		C(2)-N-C(3)	116 (1)
(b) Involving near-neighbor contact separations within chain and $[\text{N}(\text{CH}_3)_4]^+$ ion:			
Cl(1)-Cl(2)	3.535 (2) Å	C(1)-C(2)	2.17 (4) Å
Cl(1)-Cl(3)	3.933 (1)	C(2)-C(3)	2.50 (2)
(c) Involving near-neighbor contact separation between chain and/or $[\text{N}(\text{CH}_3)_4]^+$ ions:			
Cl(2)-C(3)	3.54 (2) Å	C(1)-C(4)	4.28 (3) Å
Cl(1)-C(2)	3.74 (2)	C(2)-C(4)	4.28 (5)
Cl(1)-Cl(4)	3.84 (4)		
Cl(1)-C(5)	3.83 (2)		

obtained for comparison of the carbon-carbon bond lengths with standard accepted values, those listed in Table 3 were not corrected for 'in phase' motion (Busing & Levy, 1964), because it is felt that the approximation of the model used (statistically disordered $[\text{N}(\text{CH}_3)_4]^+$ ions with atoms undergoing anisotropic harmonic thermal motion) is inadequate to describe the smeared electron density map mentioned above.

The assistance of R. A. Trudo is gratefully acknowledged.

References

- BIRGENEAU, R. J. (1971). *Bull. Amer. Phys. Soc.* **16**, 302.
 BUSING, W. R. & LEVY, A. A. (1964). *Acta Cryst.* **17**, 1420.
 HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502.
International Tables for X-ray Crystallography (1962). Vol. III, Birmingham: Kynoch Press.
 MOROSIN, B. & GRAEBER, E. J. (1967). *Acta Cryst.* **23**, 766.

Book Reviews

Works intended for notice in this column should be sent direct to the Book-Review Editor (M. M. Woolfson, Physics Department, University of York, Heslington, York YO1 5DD, England). As far as practicable books will be reviewed in a country different from that of publication.

Molecular structures and dimensions. Vol. 1. Bibliography 1935-69. General organic crystal structures. Edited by OLGA KENNARD and DAVID G. WATSON. Pp. xxiii + 413. Utrecht: Oosthoek's, 1970. Price f32 (\$10, £3.90), library copy: f45 (\$14, £5.40).

Molecular structures and dimensions. Vol. 2. Bibliography 1935-69. Complexes and organometallic structures. Edited by OLGA KENNARD and DAVID G. WATSON. Pp. xxiii + 364. Utrecht: Oosthoek's, 1970. Price f27 (\$8.50, £3.30), library copy: f35 (\$11, £4.30).

These two volumes are precisely what their titles claim, a list of titles and authors of some 4000 crystal structures

published between 1935 and 1 January 1969, together with some 500 of the structure analyses published during 1969. The bibliography refers to carbon-containing compounds, but omits what the authors describe as 'purely inorganic substances such as inorganic carbides, carbonyls, carbonates, cyanides and thiocyanates'. The omission of cyanides and thiocyanates is inconvenient but the omission of metal carbonyls I find quite extraordinary.

The criteria of a good bibliography must be its comprehensiveness within its declared criteria, its ease of use and its accuracy. On the first of these counts I must compliment the authors on their work. In some six months of use I have been able to fault the bibliography only once and that with a paper of obscure title in an obscure journal. Unfortunately the editors decided to have an indefinite termination date for the present section and I hope that the