The final atomic parameters are given in Table 1, together with their standard deviations. The observed and calculated structure factors are listed in Table 2.

Description of the structure

The general arrangement of the atoms in pirssonite is shown in Fig. 1. The bond lengths and angles are listed in Tables 3 and 4.

The carbonate group is triangular and planar, with a mean C–O distance of 1·285 Å. The distances C–O(1) and C–O(2) are equal, whilst the C–O(3) distance is slightly longer. The corresponding angle O(1)–C–O(2) is narrower than the other two.

The calcium atom lies on the twofold axis and it is coordinated by eight oxygen atoms, at a mean distance of 2·467 Å, in an almost regular polyhedron, resembling a square antiprism. The Ca polyhedra, eight per unit cell, are independent from each other.

The coordination of Na is sixfold, in a somewhat irregular octahedron. These polyhedra are connected to each other by the sharing of one edge O(1)–O(2), so as to form an infinite diagonal chain, and by the sharing of one corner O(4) in the **b** direction. In the structure there are two sets of these chains, elongated parallel to the *ac* diagonals, that is along the directions of the two series of 'diamond' glide planes. The connexions between one chain and its two adjacent parallel ones are provided by the carbon atoms in the **c** direction, whilst along the **b** direction the connexions are through the Ca polyhedra and directly through the O(4) oxygen atoms. On the whole it can be said that the complex of Na coordination polyhedra forms a three-dimensional network, whose strength is increased by the Ca polyhedra and the CO_3 groups.

The oxygen of the water molecule is O(4), the only one not bound to the carbon atom, and its hydrogen atoms make indirect connexions between neighbour Ca atoms, by O(4)–H···O(3) hydrogen bridges. The distances from O(4) and its nearest neighbour oxygens, bound by the hydrogen atoms, are of 2·70 and 2·83 Å.

In conclusion, arising from the above considerations, a noteworthy feature of pirssonite is the massiveness of its structure. Indeed, the lack of any observed cleavage can be explained by the presence of two series of Na chains parallel to the *ac* plane, running in cross diagonal directions, by the connexions of Na polyhedra with carbon triangles in the **c** direction, and by Na–O(4)–Na and Na–O(2)–Ca bonds in the **b** direction. Also in the **b** direction there are indirect Na–Ca–Na connexions through the O(1)–O(4) edges.

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Crystal Structure of Tetramethylammonium Manganese(II) Chloride*

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The crystal structure of tetramethylammonium manganese(II) chloride has been determined by full-matrix least-squares refinement of three-dimensional Mo $K\alpha$ intensity data. The space group is $P6_3/m$ with lattice constants $a_0 = 9{\cdot}1510$, $c_0 = 6{\cdot}4940$ Å. The structure consists of infinite linear chains composed of manganese atoms bridged by three chlorine atoms, $-MnCl_3^-$–, and of disordered $[N(CH_3)_4]^+$ ions.

Introduction

The evaporation of aqueous solutions of tetramethylammonium chloride and manganous chloride (as well as the corresponding bromides) yields two differently colored crystals; the light green prisms, $[(CH_3)_4N]_2$-$MnCl_4$, are isomorphous with the zinc and cobalt compounds reported by Morosin & Lingafelter (1959; also Wiesner, Srivastava, Kennard, DiVaira & Lingafelter, 1967) which contain discrete $MnCl_4^{2-}$ ions while the rose pink rods, $(CH_3)_4NMnCl_3$, contain infinite linear chains composed of manganese atoms bridged by three chlorine atoms, $-MnCl_3^-$–. Under ultraviolet light, both of these materials fluoresce brightly. The crystal structure of the latter compound is reported here.

Experimental

The lattice constants for tetramethylammonium manganese chloride [$a_0 = 9{\cdot}1510(9)$, $c_0 = 6{\cdot}4940(9)$] were obtained with Cu $K\alpha$ radiation (λ for $K\alpha_1 = 1{\cdot}54050$ Å) by least-squares fit of 14 high 2θ values measured on films taken with a 115 mm diameter Weissenberg

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camera utilizing Straumanis film loading. 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 $P6_3/m$. The experimentally determined density by the flotation technique is 1·678(6) g.cm^{-3} compared with the value of 1·660 g.cm^{-3} calculated from the above lattice constants and two formula-weights of $\mathrm{N(CH_3)_4MnCl_3}$ per cell.

The rose-colored crystals are prismatic in habit, the hexagonal prism $\{10\bar{1}0\}$ being terminated by the hexagonal pyramid $\{10\bar{1}0\}$. Doubly terminated crystals show equal development of the pyramid terminations. Optically, the crystals are uniaxial positive, $N_o=$ 1·588(5) and $N_e=$ 1·616(5) (5893 Å, 25 °C). Pleochroism is distinct in larger fragments with $\theta=$rose and $E=$ colorless. No evidence of piezoelectricity was observed.

Three-dimensional Mo $K\alpha$ intensity data were measured by using the θ–2θ scan technique on a Picker diffractometer equipped with a Datex automatic control module for setting the angles on the E & A full-circle Eulerian orienter and with a scintillation counter employing pulse-height discrimination. A unique set of 606 reflections (112 were considered unobserved) was obtained by averaging three symmetry-related (positive l) sets after absorption corrections ranging from 2·05 to 2·57 had been applied ($\mu=27{\cdot}4$ cm^{-1}; crystal bound by 8 faces of the forms $\{0001\}$ and $\{10\bar{1}0\}$ and of approximate size 0·34 × 0·32 × 0·33 mm).

Since the anomalous dispersion effect would be greater with Cu than Mo radiation, upper level Weissenberg Cu $K\alpha$ photographs were taken about the c axis and the intensities of reflections indexed hkl were carefully compared with those for $hk\bar{l}$. No visual differences were noted, implying that, should the structure be noncentrosymmetric, the contribution to the intensities from dispersion must be small enough to escape visual detection.

Lorentz and polarization factors were applied and structure factors calculated with $\mathrm{Mn^{2+}}$, $\mathrm{Cl^-}$, N and C scattering factors from Table 3.3.1A and dispersion corrections from Table 3.3.2C of *International Tables for X-ray Crystallography* (1962).

Structure determination

With two formula units in either space group $P6_3$ or $P6_3/m$, some of the atomic positions must be located on special positions unless there is disordering of particular atoms (or groups of atoms). A statistical analysis of the intensity data indicated that this compound belongs to a centrosymmetric space group; however, the few atomic positions not located on special positions of the noncentrosymmetric space group (which are therefore themselves centrosymmetric) may not greatly influence the statistical distribution of the normalized observed structure factors.

Two alternative structures, case I for $P6_3$ and case II for $P6_3/m$, were suggested by packing and symmetry arguments.* A three-dimensional Patterson synthesis verified these alternative arrangements and the chain-like $-\mathrm{MnCl_3^-}-$ structure. For case I the position of the chlorine atom is not required to be situated exactly at $\frac{1}{4}$ of a unit cell along z from the origin defining manganese atom, and the tetramethylammonium ion was considered situated on the threefold axis, $\frac{1}{3},\frac{2}{3},z$ (both the nitrogen atom and one carbon atom occupying such a position). Since anomalous dispersion effects could possibly be present and escaped visual detection on Cu $K\alpha$ photographs and since the Mo $K\alpha$ intensity data exceed the 'copper sphere', the alternative configuration (with $-z$) must be considered as part of case I. For case II, the manganese atom is located at the origin, chlorine atoms are on the mirror planes at $\frac{1}{4}$ along z. In this case the tetramethylammonium ions are statistically disordered, with the nitrogen atoms located on the mirror and the carbon atoms situated above and below this mirror in accord with the threefold axis and an occupation site equal to $\frac{1}{2}$. (Recently, the structure of $\mathrm{N(CH_3)_4NiBr_3}$ (Stucky, D'Agostino & McPherson, 1966) appeared as a case I with $R\simeq0{\cdot}10$). Both cases were refined by full-matrix least-squares methods using anisotropic thermal parameters to a reliability index, $R=\Sigma\,||F_{\text{obs}}|-|F_{\text{calc}}||/\Sigma\,|F_{\text{obs}}|$, of 0·036. The function, $\Sigma w(F_o-F_c)^2$, was minimized; weights were assigned to

Table 1. *Atomic positional and anisotropic thermal parameters for tetramethylammonium manganese*(II) *chloride*

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mn	0	0	0	2·61 (2)		1·64 (2)			
Cl	0·1499 (1)	0·2481 (1)	$\frac{1}{4}$	3·12 (2)	2·10 (2)	2·21 (2)	0·83 (2)		
N	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	2·22 (13)		2·93 (17)			
C(1)	$\frac{2}{3}$	$\frac{1}{3}$	0·4735 (37)	20·41 (305)		4·23 (88)			
C(2)	0·6193 (13)	0·4571 (13)	0·1872 (34)	7·55 (48)	7·17 (46)	23·14 (235)	5·15 (42)	1·75 (77)	8·30 (94)

Thermal parameters are of the form: $\exp\left(-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ij}h_ih_ja_i^*a_j^*\right)$;

$B_{11}=B_{22}=2B_{12}$ for Mn, N and C(1); and $B_{13}=B_{23}=0{\cdot}0$ for all except C(2) as required by symmetry.

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* The referee correctly points out that two other possibilities exist. One (case III) the intimate twinning of the two noncentrosymmetric structures and two (case IV) structures of short-range order which are intermediate between case II and case III. Very carefully measured intensities might resolve these cases since it is true that $I_{hkl}{}^{\text{case I}}\neq I_{hk\bar{l}}{}^{\text{case I}}$, $I_{hkl}{}^{\text{case II}}\neq I_{hkl}{}^{\text{case I}}$, $I_{hkl}{}^{\text{case III}}\neq\frac{1}{2}[I_{hkl}{}^{\text{case I}}+I_{hkl}{}^{\text{case II}}]$ for $\pm l$. Case IV would demand the detection of very small differences in intensities resulting from different proportions of case II and case III. Differences in intensities could be enhanced by proper selection of radiation; Cu or Co $K\alpha$ would probably be a better choice than Mo $K\alpha$.

Table 2. *Observed and calculated structure factors*

An asterisk denotes 'less than'.

H	10FO	10FC
K= 0 L= 0		
1	473	674
2	111	78
3	127	131
4	123	120
5	120	115
6	131	125
7	197	187
8	226	223
9	111	111
10*	18	-5
11	44	45
K= 1 L= 0		
1	544	558
2	165	137
3	467	462
4	552	562
5	168	157
6	25	16
7	130	127
8	64	69
9*	20	10
10	41	38
11	89	87
K= 2 L= 0		
1	96	-75
2	492	501
3	696	730
4	448	441
5	192	192
6	11	-4
7	70	65
8	65	67
9*	21	10
10	49	49
K= 3 L= 0		
1	294	272
2	397	395
3	539	536
4	148	144
5*	19	9
6	157	155
7	173	173
8	87	86
9	32	32
10	27	26
K= 4 L= 0		
1	189	157
2	200	182
3	104	102
4	55	62
5	99	97
6	226	227
7	193	197
8	48	48
9*	16	-3
K= 5 L= 0		
1*	16	6
2	109	104
3*	16	16
4	58	58
5	170	175
6	181	183
7	65	69
8*	24	9
K= 6 L= 0		
1	159	137
2	233	229
3	127	131
4	62	56
5	62	64
6	63	61
7*	0	-1
K= 7 L= 0		
1	352	348
2	240	236
3	70	72
4	25	23
5*	23	18
6*	24	11
K= 8 L= 0		
1	241	245
2	119	119
3*	15	3
4*	24	20
5	77	74
K= 9 L= 0		
1	54	55
2*	15	-4
3	55	54
4	84	87
K= 10 L= 0		
1*	24	18
2*	25	21
3	71	69
K= 11 L= 0		
1	38	37
K= 0 L= 1		
1	200	143
2	532	-613
3	402	-408
4*	14	-10
5	218	211
6	121	114
7	26	-21
8	31	-26
9	66	63
10*	24	16
11	45	-43
K= 1 L= 1		
1	109	112
2	97	-68
3	154	-154
4	85	80
5	87	87
6	215	-212
7	140	-138
8	65	62
9	99	99
10	37	36
11*	24	-2
K= 2 L= 1		
1	482	480
2	43	48
3	62	58
4	78	-80
5	151	-146
6	165	-164
7	64	-63
8	108	106
9	70	72
10	30	-27
K= 3 L= 1		
1	300	277
2	57	-47
3*	16	-11
4	95	96
5	90	-86
6	61	-61
7	38	39
8	36	34
9	32	-33
10	44	-43
K= 4 L= 1		
1	296	-283
2	105	-111
3	94	85
4	204	200
5	81	81
6*	22	-6
7*	22	2
8*	25	-19
9	73	-70
K= 5 L= 1		
1	326	-321
2*	18	13
3	206	205
4	107	106
5	25	-16
6*	23	-8
7*	22	1
8*	27	-11
K= 6 L= 1		
1	65	-62
2	45	41
3	67	66
4	57	-55
5	87	-88
6*	25	5
7	61	60
K= 7 L= 1		
1	26	27
2*	21	-5
3	100	-99
4	121	-120
5*	25	-13
6	44	47
K= 8 L= 1		
1	24	-24
2	26	-24
3	32	-31
4	43	-43
5	29	25
K= 9 L= 1		
1	40	40
2	44	45
3	30	29
4*	27	23
K= 10 L= 1		
1	69	74
2	78	77
3*	24	2
K= 11 L= 1		
1*	27	25
K= 0 L= 2		
0	463	-512
1	89	84
2	524	564
3	526	525
4	389	372
5	354	348
6	248	241
7	110	108
8*	14	4
9	64	64
10	130	133
11	54	56
K= 1 L= 2		
1	430	415
2	477	487
3	167	162
4	19	-25
5	235	225
6	292	287
7	132	136
8	128	129
9	131	136
10	70	72
11*	21	-3
K= 2 L= 2		
1	588	620
2	163	151
3	155	-153
4*	5	1
5	178	175
6	264	264
7	143	142
8	100	101
9	109	112
10	50	48
K= 3 L= 2		
1	364	361
2	119	107
3	63	-61
4	209	204
5	262	260
6	86	92
7*	20	11
8	55	55
9	69	68
K= 4 L= 2		
1	326	323
2	262	258
3	246	240
4	241	242
5	133	131
6	37	-31
7	43	-42
8	59	64
9	86	85
K= 5 L= 2		
1	372	361
2	244	239
3	259	256
4	175	177
5	29	27
6	30	-25
7	49	50
8	75	74
K= 6 L= 2		
1	180	181
2	60	60
3	101	102
4	125	125
5	87	88
6	54	54
7	88	92
K= 7 L= 2		
1	84	-78
2	26	-18
3	108	115
4	113	116
5	95	99
6	77	76
K= 8 L= 2		
1	35	-28
2	46	46
3	126	131
4	88	89
5*	25	15
K= 9 L= 2		
1	90	93
2	126	128
3	49	48
4*	18	1
K= 10 L= 2		
1	92	90
2	73	74
K= 11 L= 2		
1	48	44
K= 0 L= 3		
1	28	26
2	368	357
3	343	339
4	29	-25
5	164	-186
6	97	-93
7	22	28
8	26	27
9	57	-59
10*	25	-17
11	34	35
K= 1 L= 3		
1	92	-88
2	61	56
3	132	122
4	56	-49
5	68	-60
6	174	166
7	115	111
8	49	-50
9	87	-85
10	33	-27
K= 2 L= 3		
1	329	-319
2	74	-72
3	46	-42
4	59	52
5	124	122
6	153	159
7	49	48
8	88	-90
9	68	-67
10	29	24
K= 3 L= 3		
1	210	-197
2	71	67
3*	18	-5
4	65	-62
5	61	54
6	51	52
7	33	-31
8	30	-29
9	28	31
K= 4 L= 3		
1	197	186
2	101	99
3	80	-81
4	169	-166
5	64	-61
6*	24	1
7*	21	-1
8*	26	12
K= 5 L= 3		
1	282	274
2*	20	-8
3	177	-174
4	93	-100
5*	23	18
6*	23	4
7*	27	4
8*	27	8
K= 6 L= 3		
1	45	50
2	39	-40
3	46	-45
4	44	43
5	79	80
6*	26	-8
7	53	-53
K= 7 L= 3		
1*	21	-10
2*	23	-6
3	87	87
4	104	104
5*	25	10
6	39	-37
K= 8 L= 3		
1*	23	20
2	24	26
3	28	23
4	38	40
5*	28	-26
K= 9 L= 3		
1	36	-40
2	44	-36
3	32	-28
K= 10 L= 3		
1	65	-67
2	64	-64
K= 0 L= 4		
0	753	798
1	445	438
2	90	81
3	119	112
4	125	122
5	59	60
6	84	78
7	130	133
8	172	177
9	85	89
10*	13	1
K= 1 L= 4		
1	264	247
2	104	97
3	284	277
4	380	371
5	129	130
6	27	30
7	81	82
8	52	52
9*	20	5
10	37	33
K= 2 L= 4		
1	41	38
2	348	336
3	468	465
4	322	322
5	109	105
6*	16	7
7	55	57
8	52	53
9*	24	13
K= 3 L= 4		
1	112	104
2	306	298
3	367	361
4	117	119
5*	20	22
6	99	102
7	133	133
8	63	62
9	35	31
K= 4 L= 4		
1	132	123
2	110	110
3	80	80
4	31	28
5	81	84
6	169	172
7	150	155
8	32	35
K= 5 L= 4		
1	18	18
2	77	75
3	24	29
4	38	38
5	128	132
6	133	135
7	51	53
K= 6 L= 4		
1	109	112
2	152	153
3	100	103
4	45	47
5	48	49
6	50	53
K= 7 L= 4		
1	259	263
2	183	187
3	49	46
4	28	25
5*	23	8
K= 8 L= 4		
1	171	173
2	91	98
3*	13	1
4*	26	21
K= 9 L= 4		
1	45	42
2*	9	0
3	44	41
K= 10 L= 4		
1*	26	16
K= 0 L= 5		
1*	16	-6
2	251	-241
3	242	-234
4	23	20
5	140	138
6	76	75
7	28	-25
8*	24	-20
9	39	39
10*	27	14
K= 1 L= 5		
1	62	60
2	29	-26
3	93	-90
4	38	38
5	32	32
6	113	-117
7	84	-84
8	36	41
9	65	65
K= 2 L= 5		
1	200	191
2	62	60
3	28	24
4	28	-28
5	89	-90
6	121	-121
7	34	-37
8	64	65
9	54	52
K= 3 L= 5		
1	141	137
2	50	-51
3*	21	3
4	39	41
5	32	-36
6	43	-40
7	28	27
K= 4 L= 5		
1	133	-131
2	74	-71
3	67	64
4	117	118
5	46	48
6*	26	-6
7*	26	3
K= 5 L= 5		
1	194	-193
2*	22	-3
3	132	136
4	69	72
5*	25	-11
6*	25	-3
K= 6 L= 5		
1	36	-34
2	33	30
3	31	32
4	29	-30
5	61	-62
K= 7 L= 5		
1*	23	5
2*	25	7
3	63	-67
4	75	-75
K= 8 L= 5		
1*	25	-18
2*	26	-16
3*	27	-21
K= 9 L= 5		
1*	27	26
2	36	29
K= 0 L= 6		
0	139	-127
1	50	44
2	262	256
3	240	235
4	176	177
5	175	179
6	145	145
7	67	66
8*	21	8
9	40	38
K= 1 L= 6		
1	189	188
2	237	234
3	85	83
4*	10	3
5	112	116
6	145	151
7	83	83
8	75	74
K= 2 L= 6		
1	275	268
2	74	70
3	78	-67
4*	20	-7
5	116	116
6	140	146
7	85	85
8	56	57
K= 3 L= 6		
1	202	202
2	46	46
3*	24	-19
4	98	104
5	142	145
6	54	55
7*	24	13
K= 4 L= 6		
1	172	169
2	130	136
3	133	138
4	142	140
5	77	77
6*	28	-13
K= 5 L= 6		
1	195	198
2	134	133
3	133	138
4	105	107
5*	24	15
K= 6 L= 6		
1	90	92
2	50	48
3	59	56
4	79	77
K= 7 L= 6		
1	40	-42
2*	25	-6
3	68	68
K= 8 L= 6		
1*	28	-12
2	32	30
K= 0 L= 7		
1	30	22
2	139	137
3	147	147
4*	24	-5
5	91	-93
6	50	-49
7*	26	16
8*	27	12
K= 1 L= 7		
1	37	-38
2	31	28
3	49	49
4*	24	-25
5*	25	-17
6	75	74
7	54	56
K= 2 L= 7		
1	133	-131
2	41	-39
3*	24	-9
4*	24	14
5	59	59
6	76	77
7*	27	25
K= 3 L= 7		
1	80	-79
2	30	26
3*	25	-0
4	27	-26
5	27	24
6*	27	25
K= 4 L= 7		
1	86	86
2	49	47
3	42	-43
4	76	-76
5	34	-32
K= 5 L= 7		
1	121	121
2*	25	4
3	85	-89
4	40	-45
K= 6 L= 7		
1*	25	23
2*	26	-20
3*	27	-22
K= 7 L= 7		
1*	26	-5
2*	28	-3
K= 0 L= 8		
0	285	286
1	178	176
2	41	41
3	43	42
4	55	57
5	38	36
6	37	34
K= 1 L= 8		
1	89	89
2	45	46
3	117	121
4	151	149
5	65	62
6*	25	20
K= 2 L= 8		
1	24	26
2	129	132
3	194	197
4	141	141
5	53	47
K= 3 L= 8		
1	44	50
2	126	128
3	150	150
4	58	58
K= 4 L= 8		
1	52	50
2	57	56
3	38	37
4*	26	19
K= 5 L= 8		
1*	23	12
2	41	37
K= 6 L= 8		
1	55	55
K= 0 L= 9		
1*	25	-6
2	80	-81
3	81	-82
4*	28	4
K= 1 L= 9		
1	27	21
2*	26	-12
3	32	-29
4*	27	14
K= 2 L= 9		
1	71	70
2*	27	22
3*	28	6
K= 3 L= 9		
1	50	46
2*	27	-16
K= 4 L= 9		
1	45	-48

the observed reflection from counting statistics while the unobserved and the 100 were assigned zero weights. For case I the z parameter for the chlorine atoms differed by less than 1σ from the $z=0{\cdot}25$ value required for them to be located exactly between the metal atoms in the $-MX_3^-$– chains. The model with negative values of z appeared to be nearly a mirror image (not exactly, but within 3σ) to that with plus values of z and gave the same fit to the intensity data. This strongly suggests that the $-MX_3^-$– chains contain an inversion center irrespective of the remainder of the structure. The magnitude of the anisotropic thermal parameters for the carbon atoms was larger for case I than for case II, although the directions of the principal axes of the thermal ellipsoids were the same. However, the three-dimensional difference synthesis, calculated for verification of the final refined structures, contained small peaks for case I corresponding to the mirroring of carbon atoms but was nearly flat for case II (the entire region, though flat, was not equal to zero; this was attributed to the lack of inclusion of hydrogen atoms).

The results of the two parallel refinements suggest that the centrosymmetric space group probably is the correct one and that the $[N(CH_3)_4]^+$ ions are statistically as well as positionally disordered about the mirror. Table 1 lists the positional and anisotropic thermal parameters for case II and Table 2 lists the observed and calculated structure factors obtained with these parameters.

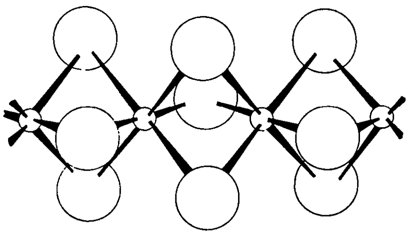

Fig. 1. A sketch of the linear chains found in $N(CH_3)_4MnCl_3$. The octahedral environment about the manganese atom is slightly distorted, corresponding to a lengthening along the chain.

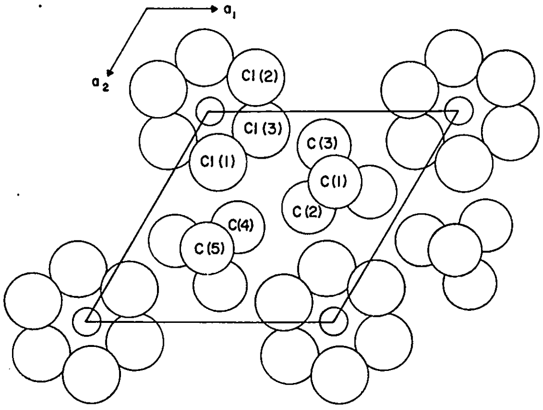

Fig. 2. A representation of the crystal structure of $N(CH_3)_4MnCl_3$ viewed along the c axis. Chains which are shown in Fig. 1 parallel the **c** direction and pass through the origin; $[N(CH_3)_4]^+$ ions are located between these chains in a statistical (orientation) and positional disordered manner.

Discussion

As mentioned in the preceding section, the case II structure consists of infinite $-MnCl_3^-$– chains (Fig. 1) and discrete but disordered $[N(CH_3)_4]^+$ ions located on the threefold axes (Fig. 2). The chlorine–manganese–chlorine angles in the chain are 84·09 and 95·91° (Table 3) indicating a slight trigonal elongation of the octahedron about the manganese atom.[*] The 2·560 Å Mn–Cl separation (Table 3) is similar to the 2·553(3) Å average separation found in $MnCl_2.2H_2O$. The average observed N–C distance of 1·46 Å is in good agreement with the accepted single bond distance of 1·47 Å.

The anisotropic thermal parameters for the carbon atoms are quite large and imply small disordering of the $[N(CH_3)_4]^+$ ions about the central nitrogen atom.[†] This oscillation of the tetrahedral ion is such as to tip the carbon on the threefold axis away from this axis. A model built with hard spheres using van der Waals contact distances from Pauling (1960) was compatible with such a tipping of the tetrahedral ions. The shorter 3·641 and 3·749 Å chlorine–carbon separations (Table 3) indicate a crowding effect, in agreement with the hard sphere model (the accepted values for the van der Waals radii of Cl^- and $-CH_3$ groups are 1·8 and 2·0 Å)

Table 3. *Interatomic separations and angles in* $N(CH_3)_4MnCl_3$

(a) Involving chemically bonded atoms (for labeling, see Fig. 2)

Mn–Cl(1)	2·560 (2) Å	Cl(1)–Mn–Cl(2)	84·09°
		Cl(1)–Mn–Cl(3)	95·91
N —C(1)	1·451 (24)	C(1) -N —C(2)	106·25
N —C(2)	1·459 (25)	C(2) -N —C(3)	112·50

(b) Involving near-neighbor contact separations within chain and $[N(CH_3)_4]^+$ ion

Cl(1)–Cl(2)	3·429 (2) Å
Cl(1)–Cl(3)	3·803 (2)
C(1) -C(2)	2·328 (34)
C(2) -C(3)	2·560 (34)

(c) Involving near-neighbor contact separation between chain and/or $[N(CH_3)_4]^+$ ions

Cl(2)–C(3)	3·641 (25) Å	C(1)–C(4)	4·179 Å
Cl(1)–C(2)	3·749 (25)	C(2)–C(4)	4·199
Cl(1)–C(4)	3·754 (25)		
Cl(1)–C(5)	3·779 (24)		

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[*] In compounds containing infinite chains the neighboring halide atoms along the chain are usually found to be a bit more distant than those in adjacent positions on the chain. In our case, the distances are 3·429 and 3·803 Å; other examples of such behavior are found in $CH_3NH_3NiCl_3$ (Willett, 1966), $N(CH_3)_4NiBr_3$ and iron-group halide dihydrates (Morosin & Graeber, 1965).

[†] More recently, Wiesner, Srivastava, Kennard, DiVaira and Lingafelter have found a disordering of both tetrahedral MCl_4^{2-} and $[N(CH_3)_4]^+$ ions in $[N(CH_3)_4]_2MCl_4$, where M = Co, Ni and Zn.

when the carbon atoms are situated at the equilibrium sites (Table 1). A B_{ij} value near 20·0 Å^2 implies an r.m.s. amplitude of vibration of about 0·5 Å which would be similar to a displacement of 0·16 Å off the axis (to relieve crowding) and a B_{ij} value near 7·0 Å^2. Further evidence that the large thermal parameters for the carbon atoms result from disordering rather than from large thermal motion may be obtained by noting any decrease in thermal diffuse scattering when the crystals are cooled. However, no change was noted in diffraction photographs when the crystals were cooled to 77°K. In addition, if the large thermal parameters were due to thermal motion, a phase change might occur upon cooling as this motion is restricted or frozen into the lowest energy state (unless this would result in statistical ordering). However, no phase change is observed by diffraction to 77°K or by changes in the electron absorption spectra to 5°K (Lawson, 1967). This suggests that the interpretation that the high carbon thermal parameters result from the statistical and positional disordering of the $[N(CH_3)_4]^+$ ion is correct.

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The Structure of Molybdenum Pentachloride-Graphite by Single-Crystal Electron and X-ray Diffraction*

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The structures found in the 4th stage graphite lamellar compound containing 24·8 % $MoCl_5$ have been determined by a combination of single-crystal electron-diffraction and X-ray-diffraction methods. The use of the latter technique showed sets of four adjacent graphite sheets to retain the normal *ABAB* stacking and interlayer spacing of free graphite. Electron diffraction showed the lateral structure within each graphite sheet to be unchanged and the intercalated molybdenum pentachloride layers to exist in two or more phases. In the most clearly characterized of these phases the dimer molecular structure of the free pentachloride is preserved, the molecules lying in a close-packed array having a precise orientation to the adjacent graphite sheets. The measurable intramolecular atomic distances of the dimer molecule remain unchanged from those in the free chloride but owing to interaction with the graphite the molecular symmetry is lower than that possessed by non-intercalated molecules. The other reactant layer phases are characterized by hexagonal and disordered cation distributions, the dimeric relationship no longer being distinguishable. A substructure consisting of two adjacent pseudo close-packed chlorine layers is common to all phases, individual phases being distinguished by the cation distribution within the octahedral sites. Certain orientations of the substructure relative to the graphite are more highly favoured, the reactant at other orientations being characterized by a disordered cation distribution and an increase in the mean chlorine–chlorine distance measured parallel to the layer plane.

Introduction

Generally the mechanism of formation of a lamellar graphite compound, that is the penetration of a graphite crystal at many independent points on its prismatic faces by the reactant atoms or molecules, automatically results in a disordered and multiply twinned condition of the intercalated crystal. Consequently structural knowledge of these compounds is difficult to obtain by single-crystal X-ray methods. The greater resolving power of microbeam electron diffraction and its ability to select minute ordered regions of the crystal avoids

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