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Berkeley, California

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THE CRYSTAL STRUCTURE OF MANGANESE DICHLORIDE TETRAHYDRATE

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The Crystal Structure of Manganese Dichloride Tetrahydrate[1]

BY ALLAN ZALKIN, J. D. FORRESTER, AND DAVID H. TEMPLETON

The stable room temperature form of $MnC\ell_2 \cdot 4H_2O$ (α-form) has a monoclinic cell $\underline{a}$ = 11.186 Å, $\underline{b}$ = 9.513 Å, $\underline{c}$ = 6.186 Å, and β = 99.74°. The space group is $\underline{P2_1/n}$ with four formula units per unit cell and $\underline{d_x}$ = 2.03 g./cc. An X-ray diffraction study of this material yielded the positions of all of the atoms including the hydrogens. The structure consists of discrete octahedra of four oxygen atoms and two chlorine atoms about the manganese, and with the chlorine atoms adjacent to each other. The four Mn-O distances are nearly equidistant being 2.224 Å, 2.209 Å, 2.185 Å, and 2.206 Å; the two Mn-Cℓ distances are 2.475 Å and 2.500 Å. Only four of the eight hydrogen atoms make hydrogen bonds. Three of the hydrogen bonds are between oxygen and chlorine and one between two water molecules.

Introduction

Groth[2] reports two monoclinic crystal modifications of $MnC\ell_2 \cdot 4H_2O$. One form is metastable at room temperature (Dawson and Williams[3]), and is isomorphous with $FeC\ell_2 \cdot 4H_2O$, the structure of which has been described by Penfold and Grigor[4] with comments on the proton sites by Saffar and Murtz[5]. Our paper deals with the form that is stable at room temperatures, and in keeping with the nomenclature of Dawson and Williams[3] we refer to this

modification as the α-form, and to the metastable modification as the β-form. It should be noted here that Groth[2] in his publication has reversed the naming of these two forms from the above convention.

Delain[6] has reported the cell dimensions and space group of the α-form, and Gardner[7] has reported some preliminary results on the proton sites. We became interested in the structure of this crystal after learning of its use as a sample for low temperature magnetic measurements by Professor W. F. Giauque.

Experimental

An aqueous solution of manganous chloride was allowed to evaporate at room temperature and the tetrahydrate crystals grew readily in the form of approximately hexagonal plates. A suitable crystal with maximum dimension of 0.1 mm was mounted and used for collecting the intensity data. Intensities were measured with a General Electric XRD-5 equipped with a goniostat, a scintillation counter and a pulse height discriminator. Mo $K\alpha$ radiation was used and the unit cell dimensions are based on $\lambda = 0.70926$ Å for Mo $K\alpha_1$. No preliminary X-ray photographs were taken; the crystal was aligned on the goniostat using the cell dimensions reported in Donnay[8], together with the observations on the direction of extinction of polarized light. The systematic space group absences were carefully checked on the goniostat.

The 848 independent reflections permitted by the space group in the sphere with $\sin\theta/\lambda$ less than 0.538 (2θ less than 45°) were measured with counting times of 10 seconds each; of these, 49 were assigned zero intensity. The maximum intensity counted was 4200 counts/second, which was the 002 reflection.

No corrections were made for either absorption or extinction. The absorption factor μ for this crystal with Mo radiation is 28 cm^{-1}. μR is

about 0.14 or less, making the absorption very low.

Calculations were made with an IBM 7094 computer using a full matrix least squares refinement program written by P. K. Gantzell, R. A. Sparks, and K. N. Trueblood with minor changes and Fourier and distance programs written by A. Zalkin. We minimized the function $\sum \underline{w}(|\underline{F_o}| - |\underline{F_c}|)^2/\sum \underline{wF_o^2}$.

Atomic scattering factors were taken as the values by Ibers[9] for Mn^{+2}, $C\ell^{-1}$, neutral O and H. Dispersion corrections[10] of -0.4 and -0.1 electrons were added to the Mn^{+2} and $C\ell^{-1}$ scattering factors respectively. The imaginary part of the dispersion correction was neglected.

Results

Unit Cell and Space Group.—The primitive cell is monoclinic, contains four formula units ($MnC\ell_2 \cdot 4H_2O$) per unit cell and has the dimensions:

$\underline{a} = 11.186 \pm 0.006$ Å, $\underline{b} = 9.513 \pm 0.005$ Å, $\underline{c} = 6.186 \pm 0.002$ Å,

$\beta = 99.74 \pm 0.04^\circ$, $\underline{V} = 648.8$ Å^3, $\underline{a} : \underline{b} : \underline{c} = 1.1759 : 1 : 0.6503$.

These compare with values $\underline{a} = 11.3$, $\underline{b} = 9.55$ and $\underline{c} = 6.15$ Å and $\beta = 99.63^\circ$ reported by Delain[6] (after transformation from $\underline{P2_1/a}$) and the axial ratios of 1.1525 : 1 : 0.6445 with $\beta = 99.42^\circ$ by Groth[2].

From the X-ray data the calculated density is 2.03 g./cc. which compares with the value of 2.01 g./cc. reported in the Handbook of Chemistry and Physics[11].

Reflections $\underline{h0\ell}$ are absent unless $\underline{h} + \underline{\ell} = 2\underline{n}$ and $0\underline{k}0$ reflections are absent unless $\underline{k} = 2\underline{n}$. This is characteristic of the space group $\underline{P2_1/n}$ ($\underline{C_{2h}}^5$) and the success of our structure determination confirms this symmetry.

Determination of the Structure.—Projection data were collected initially and the Patterson functions for three projections $\underline{hk}0$, $\underline{h0\ell}$, and $0\underline{k\ell}$ were calculated from the observed intensities after correction for Lorentz and polarization effects. From these three projections, the positions of the Mn and the two independent $C\ell$ atoms required by the four formula units per

unit cell were obtained directly. These three atoms were all in 4 - fold general positions:

$$4(e) \pm (\underline{x}, \underline{y}, \underline{z}\ ;\ 1/2 + \underline{x}, 1/2 - \underline{y}, 1/2 + \underline{z}).$$

When all of the three dimensional data were available, a three dimensional Fourier was calculated with phases based on the positions of the Mn and two Cℓ atoms. In this Fourier, all four independent oxygen atoms were found in general positions.

The parameters of these 7 sets of atoms were refined by least squares using all the data, each with unit weight, and giving each atom an isotropic temperature factor of the form $\exp(-\underline{B}\lambda^{-2}\sin^2\theta)$. After 8 cycles of refinement the conventional reliability factor $\underline{R} = \sum||\underline{F_o}| - |\underline{F_c}||/\sum|\underline{F_o}|$ decreased to 0.083 . Correction of several blunders in the data taking and in the card punching and the introduction of anisotropic temperature factors of the form $\exp(-\beta_{11}\underline{h}^2 - \beta_{22}\underline{k}^2 - \beta_{33}\underline{\ell}^2 - 2\beta_{12}\underline{hk} - 2\beta_{13}\underline{h\ell} - 2\beta_{23}\underline{k\ell})$ for each of the 7 atoms reduced $\underline{R}$ to 0.047 after four more cycles of refinement.

An electron density difference function with all atoms subtracted out with the exception of hydrogen was calculated using the results of this anisotropic refinement and using the terms for which $\sin\theta/\lambda$ less than 0.48 . Eight out of the ten highest peaks in this function corresponded to reasonable positions for the eight independent hydrogen atoms in general positions. Four of these hydrogen atoms form hydrogen bonds, but the other four atoms have no suitable environment for forming bonds and remain unbonded.

Four cycles of least squares refinement with all eight hydrogen atoms each having isotropic temperature factors and the remaining seven heavier atoms having anisotropic temperature factors resulted in an $\underline{R}$ factor of 0.041 . The temperature factors of the four bonded hydrogen atoms remained normal, but those of two of the unbonded atoms, attached to O(3), had

higher values.

After four more cycles of refinement, the final R value was 0.039 . The final positional parameters and thermal parameters are listed in Table I and Table II respectively. The observed and calculated structure factors are listed in Table III.

TABLE I.

FINAL POSITIONAL PARAMETERS AND STANDARD DEVIATIONS FOR $MnC\ell_2 \cdot 4H_2O$

Atom	x	y	z	σ(x)	σ(y)	σ(z)
Mn	0.2329	0.1714	0.9865	0.0001	0.0001	0.0001
Cℓ(1)	.0610	.3076	.0938	.0001	.0001	.0002
Cℓ(2)	.3817	.3662	.0355	.0001	.0001	.0002
O(1)	.3010	.1127	.3334	.0004	.0005	.0006
O(2)	.1568	.2280	.6446	.0004	.0005	.0007
O(3)	.1323	.9736	.9590	.0005	.0006	.0011
O(4)	.3695	.0381	.8764	.0004	.0005	.0007
H(1)1 [a]	.39	.15	.37	.01	.01	.01
H(1)2	.30	.02	.35	.01	.01	.01
H(2)1	.08	.20	.62	.01	.01	.01
H(2)2	.19	.21	.56	.01	.01	.02
H(3)1	.11	.95	.87	.01	.01	.02
H(3)2	.10	.99	..01	..02	.02	.03
H(4)1	.43	.09	.81	.01	.01	.02
H(4)2	.35	.95	.86	.01	.01	.01

[a] H(i)j means that it is the j'th hydrogen of water oxygen O(i).

TABLE II.

THERMAL PARAMETERS [a] AND STANDARD DEVIATIONS.

Atom	B11 [b]	B22	B33	B12	B13	B23
Mn	1.98 ± .04	1.81 ± .04	1.50 ± .04	-0.02 ± .03	0.36 ± .03	0.01 ± .03
Cℓ(1)	2.16 ± .06	2.76 ± .07	2.51 ± .06	0.43 ± .05	0.65 ± .05	-0.29 ± .05
Cℓ(2)	2.22 ± .06	2.03 ± .06	2.38 ± .06	-0.29 ± .05	0.35 ± .05	0.00 ± .05
O(1)	3.3 ± .2	2.2 ± .2	2.0 ± .2	-0.1 ± .2	0.2 ± .1	0.1 ± .1
O(2)	2.5 ± .2	3.2 ± .2	2.2 ± .2	-0.2 ± .2	0.5 ± .2	0.3 ± .2
O(3)	4.1 ± .2	3.1 ± .2	3.4 ± .3	-1.2 ± .2	1.0 ± .2	-0.6 ± .2
O(4)	3.5 ± .2	2.6 ± .2	3.7 ± .2	0.1 ± .2	1.5 ± .2	-0.1 ± .2

Atom	B [c]	Atom	B	Atom	B
H(1)1	2 ± 2	H(2)2	5 ± 3	H(4)1	6 ± 3
H(1)2	3 ± 2	H(3)1	6 ± 5	H(4)2	5 ± 2
H(2)1	1 ± 1	H(3)2	21 ± 9		

[a] Units are $Å^2$.

[b] The anisotropic values $B_{ij} = 4\beta_{ij}/a_i^* a_j^*$ where a_i^* is the ith reciprocal cell length.

[c] Isotropic .

TABLE III.

OBSERVED STRUCTURE FACTOR MAGNITUDES (FOBx5) AND CALCULATED STRUCTURE FACTORS (FCAx5).

(Table submitted as photographic print)

Standard deviations of the parameters of the atoms were calculated assuming that the discrepancies in the structure factors represent random errors. The high standard deviations of the parameters of the hydrogen atoms illustrate that we are at the limit of our data's accuracy in determining these values.

H,K= 0, 0
L FOB FCA
2 694 696
4 118 109
6 133 138

H,K= 0, 1
L FOB FCA
1 102 79
2 260-270
3 133 128
4 110-112
5 69 69
6 49 49

H,K= 0, 2
L FOB FCA
0 333-322
1 140 136
2 201-174
3 291 287
4 42 -40
5 179 175
6 20 -31

H,K= 0, 3
L FOB FCA
1 225 236
2 231 224
3 255-253
4 105-106
5 216-212
6 101-100

H,K= 0, 4
L FOB FCA
0 196-191
1 170-173
2 193-191
3 223-224
4 168-177
5 98-105
6 76 -77

H,K= 0, 5
L FOB FCA
1 171 186
2 15 15
3 207 198
4 40 43
5 201 198

H,K= 0, 6
L FOB FCA
0 356 350
1 146 143
2 338 328
3 46 43
4 174 169
5 115-115

H,K= 0, 7
L FOB FCA
1 29 34
2 18 -21
3 26 -37
4 20 22

H,K= 0, 8
L FOB FCA
0 85 -82
1 26 16
2 76 -77
3 20 21
4 0 -9

H,K= 0, 9
L FOB FCA
1 204-200
2 29 33
3 82 -86

H,K= 0,10
L FOB FCA
0 0 -17
1 0 -6

H,K= 1, 0
L FOB FCA
1 314-313
2 162 163
3 162-160
4 64 63

H,K= 1, 1
L FOB FCA
-6 34 -41
-5 150-150
-4 52 53
-3 360-355
-2 124-110
-1 452-433
0 45 48
1 497-482
2 476 472
3 471-470
4 214 212
5 120-118
6 95 99

H,K= 1, 2
L FOB FCA
-6 88 -88
-5 60 66
-4 105 -98
-3 14 -3
-2 26 -7
-1 90 -86
0 258-252
1 61 -58
2 98 -93
3 91 84
4 94 -87
5 74 76
6 197-199

H,K= 1, 3
L FOB FCA
-6 20 24
-5 49 -42
-4 23 24
-3 69 -63
-2 54 51
-1 34 -36
0 0 16
1 11 -17
2 121-117
3 59 56
4 216-212
5 62 62
6 171-179

H,K= 1, 4
L FOB FCA
-6 101 105
-5 33 33
-4 289 292
-3 59 61
-2 437 431
-1 55 -50
0 207 214
1 296 297
2 99 91
3 219 217
4 143 139
5 0 4

H,K= 1, 5
L FOB FCA
-5 188 186
-4 40 -38
-3 322 316
-2 72 -70
-1 398 388
0 118-118
1 319 309
2 65 -65
3 201 200
4 128 129
5 75 74

H,K= 1, 6
L FOB FCA
-5 80 -81
-4 144-141
-3 25 -22
-2 168-161
-1 74 75
0 88 -88
1 77 76
2 16 -15
3 18 9
4 27 29
5 0 16

H,K= 1, 7
L FOB FCA
-4 0 -20
-3 59 52
-2 53 46
-1 116-117
0 140 143
1 314-313
2 162 163
3 162-160
4 64 63

H,K= 1, 8
L FOB FCA
-4 21 -31
-3 20 -20
-2 53 -49
-1 108-111
0 65 -63
1 166-164
2 126-126
3 78 -78

H,K= 1, 9
L FOB FCA
-3 76 -76
-2 29 31
-1 34 -26
0 34 28
1 63 59
2 0 -14

H,K= 1,10
L FOB FCA
-1 99 112
0 120 130
1 42 48

H,K= 2, 0
L FOB FCA
-6 403-407
-4 423-423
-2 54 62
0 367-355
2 480-471
4 91 -77
6 29 -39

H,K= 2, 1
L FOB FCA
-6 82 89
-5 43 -37
-4 241 236
-3 192-192
-2 255 257
-1 240-235
0 70 -68
1 211-204
2 169-158
3 192-182
4 16 -13
5 69 -63
6 21 -23

H,K= 2, 2
L FOB FCA
-6 126 130
-5 70 -71
-4 103 103
-3 199-198
-2 0 4
-1 277-286
0 85 68
1 33 -35
2 249 246
3 144-139
4 197 194
5 189-187
6 69 83

H,K= 2, 3
L FOB FCA
-6 29 26
-5 26 -11
-4 120-118
-3 329 320
-2 144 136
-1 585 582
0 483 508
1 288 287
2 90 90
3 239 231
4 24 25
5 193 189

H,K= 2, 4
L FOB FCA
-6 70 86
-5 60 58
-4 127 128
-3 150 150
-2 202 195
-1 77 71
0 154 152
1 44 38
2 38 -33
3 77 76
4 25 -18
5 123 123

H,K= 2, 5
L FOB FCA
-5 117-118
-4 82 -83
-3 242-235
-2 102-101
-1 347-346
0 14 -22
1 184-187
2 72 71
3 66 61
4 32 30
5 29 28

H,K= 2, 6
L FOB FCA
-6 79 -75
-5 121-118
-4 81 -83
-3 281-277
-2 293-286
-1 36 -44
0 430-443
1 28 27
2 298-299
3 57 52
4 168-168
5 0 3

H,K= 2, 7
L FOB FCA
-4 53 59
-3 26 20
-2 18 -4
-1 17 19
0 79 -79
1 86 -89
2 130-130
3 144-143
4 125-115

H,K= 2, 8
L FOB FCA
-4 36 34
-3 0 -6
-2 27 27
-1 18 -15
0 26 35
1 62 -69
2 178 178
3 70 -68

H,K= 2, 9
L FOB FCA
-3 112 107
-2 73 68
-1 131 132
0 183 191
1 194 190
2 165 162

H,K= 2,10
L FOB FCA
-1 21 -32
0 56 56

H,K= 3, 0
L FOB FCA
-5 83 83
-3 131 133
-1 150 160
1 70 71
3 296-305
6 265-264

H,K= 3, 1
L FOB FCA
-6 20 5
-5 216 220
-4 218-218
-3 374 367
-2 401-401
-1 227 209
0 133-140
1 206-216
2 104 -99
3 56 54
4 29 -27
5 157 155
6 0 2

H,K= 3, 2
L FOB FCA
-6 67 76
-5 0 -23
-4 167 164
-3 150-153
-2 226 222
-1 292-295
0 625 668
1 52 53
2 595 595
3 220 216
4 195 194
5 100 99

H,K= 3, 3
L FOB FCA
-6 21 -19
-5 37 -34
-4 80 84
-3 70 -68
-2 206 213
-1 140-140
0 275 282
1 26 -30
2 103 101
3 16 26
4 18 -18
5 98 -93

H,K= 3, 4
L FOB FCA
3 42 -40
4 31 -29
5 0 5

H,K= 3, 5
L FOB FCA
-5 151-154
-4 36 38
-3 161-158
-2 129-130
-1 103-101
0 167-167
1 0 -2
2 74 70
3 18 6
4 27 19
5 0 -12

H,K= 3, 6
L FOB FCA
-4 98 -97
-3 0 -9
1 111-118
2 65 59
3 144-140
4 35 -33

H,K= 3, 7
L FOB FCA
0 183 191
1 194 190
2 163-168
3 104 108
4 170-171

H,K= 3, 8
L FOB FCA
-4 102 106
-3 28 32
-2 168 166
-1 19 1
0 128 127
1 102 98
2 132 132
3 132 130

H,K= 3, 9
L FOB FCA
-3 41 39
-2 285-291
-1 27 15
0 178-187
1 19 17
2 60 -61
3 42 42

H,K= 4, 1
L FOB FCA
-6 0 6
-5 106 108
-4 51 49
-3 194 191
-2 80 -81
-1 157 156
0 40 -47
1 78 85
2 218 212
3 204 203
4 229 231
5 88 88

H,K= 4, 2
L FOB FCA
-6 50 -49
-5 0 -2
-4 187-186
-3 44 41
-2 316-318
-1 299 299
0 255-260
1 134 136
2 95 -93
3 42 -40
4 31 -29
5 0 5

H,K= 4, 3
L FOB FCA
-6 134-134
-5 166-165
-4 68 -74
-3 227-219
-2 78 76
-1 528-530
0 47 -43
1 512-526
2 42 43
3 333-326
4 58 59
5 147-144

H,K= 4, 4
L FOB FCA
-6 30 -40
-5 91 90
-4 31 23
-3 60 -59
-2 45 47
-1 188-183
0 87 -86
1 219-227
2 16 -5
3 108-105
4 19 29
5 0 4

H,K= 4, 5
L FOB FCA
-5 72 77
-4 26 -6
-3 57 -54
-2 23 -18
-1 60 -60
0 40 -35
1 131 133
2 163-168
3 104 108
4 170-171

H,K= 4, 6
L FOB FCA
-5 164-162
-4 138 144
-3 0 -11
-2 221 225
-1 70 68
0 138 136
1 70 68
2 36 25
3 108 104
4 65 65

H,K= 4, 7
L FOB FCA
-4 41 44
-3 172 173
-2 48 49
-1 166 163
0 0 -4
1 53 -57
2 0 -9
3 57 57

H,K= 4, 8
L FOB FCA
-3 41 39
-2 285-291
-1 27 15
0 178-187
1 19 17
2 60 -61
3 42 42

H,K= 4, 9
L FOB FCA
-2 0 -6
-1 54 -58
0 68 66
1 111-117

H,K= 5, 0
L FOB FCA
-5 18 34
-3 261 260
-1 467 480
1 90 95
3 37 41
5 216 227

H,K= 5, 1
L FOB FCA
-6 0 6
-5 0 20
-4 17 -21
-3 111-106
-2 24 24
-1 440-452
0 68 -73
1 243-251
2 33 -34
3 47 -46
4 0 -8
5 54 -55

H,K= 5, 2
L FOB FCA
-6 225-234
-5 27 -22
-4 390-392
-3 183-179
-2 274-272
-1 112-115
0 178-180
1 14 -4
2 224-224
3 68 -86
4 107-108
5 118-109

H,K= 5, 3
L FOB FCA
-6 0 -16
-5 38 33
-4 46 43
-3 0 5
-2 111 110
-1 126 127
0 72 -64
1 180 183
2 349-253
3 67 -64
4 113-115
5 69 -72

H,K= 5, 4
L FOB FCA
-5 44 -37
-4 206 206
-3 24 26
-2 98 93
-1 104-103
0 54 53
1 290-302
2 142 142
3 183-177
4 156 157

H,K= 5, 5
L FOB FCA
-5 0 22
-4 68 -66
-3 35 33
-2 55 -50
-1 68 64
0 204 205
1 101 101
2 208 204
3 103 100
4 109 101

H,K= 5, 6
L FOB FCA
-5 56 54
-4 0 -11
-3 122 120
-2 35 31
-1 94 92
0 146 146
1 88 89
2 0 12
3 100 90
4 137-129

H,K= 5, 7
L FOB FCA
-4 36 37
-3 262-254
-2 38 34
-1 237-239
0 94 -94
1 187-198
2 120-123
3 83 -85

H,K= 5, 8
L FOB FCA
-3 85 -89
-2 179-184
-1 0 -3
0 153-154
1 72 71
2 55 -58

H,K= 5, 9
L FOB FCA
-2 67 -68
-1 130 129
0 118-119
1 87 91

H,K= 6, 0
L FOB FCA
-6 0 20
-4 46 -44
-2 160-156
0 253-262
2 380-382
4 205-211

H,K= 6, 1
L FOB FCA
-6 29 30
-5 100 -93
-4 142-142
-3 159-159
-2 340-337
-1 165-162
0 340-347
1 71 77
2 248-244
3 30 34
4 77 -76
5 30 -35

H,K= 6, 2
L FOB FCA
-6 60 68
-5 19 -12
-4 98 61
-3 180 142
-2 97 97
-1 77 81
0 161 172
1 55 -53
2 190 189
3 67 -69
4 70 70

H,K= 6, 3
L FOB FCA
-5 294 301
-4 18 -8
-3 317 310
-2 106-102
-1 213 214
0 46 -47
1 35 37
2 34 -37
3 26 -27
4 63 -66

H,K= 6, 4
L FOB FCA
-5 60 60
-4 62 53
-3 17 16
-2 16 12
-1 83 -82
0 134 136
1 0 9
2 158 155
3 181 182
4 46 51

H,K= 6, 5
L FOB FCA
-5 93-108
-4 118 116
-3 149-153
-2 214 211
-1 61 -62
0 148 149
1 49 -45
2 111 119
3 52 -49
4 103 104

H,K= 6, 6
L FOB FCA
-4 40 -46
-3 76 -74
-2 132-127
-1 100-103
0 224-228
1 88 -91
2 164-168
3 132-122

H,K= 6, 7
L FOB FCA
-4 0 11
-3 40 -38
-2 108-110
-1 33 -33
0 189-189
1 34 -25
2 45 -41

H,K= 6, 8
L FOB FCA
-2 315 316
0 168 168
2 131 134
4 121 126

H,K= 6, 9
L FOB FCA
-3 0 -7
-2 87 84
-1 49 -52
0 116 121
1 77 -71

H,K= 7, 0
L FOB FCA
-5 34 -37
-3 0 8
-1 330-331
1 388-392
3 66 -75

H,K= 7, 1
L FOB FCA
-5 171 167
-4 54 49
-3 63 61
-2 55 57
-1 163 165
0 53 52
1 274 276
2 38 -40
3 216 211
4 96 -95

H,K= 7, 2
L FOB FCA
-5 28 -34
-4 182 176
-3 61 68
-2 182 183
-1 220 224
0 27 29
1 161 165
2 92 -49
3 80 81
4 81 -78

H,K= 7, 3
L FOB FCA
-5 64 -64
-4 131 125
-3 68 66
-2 113 109
-1 169 174
0 36 -27
1 17 -16
2 96 91
3 19 -24
4 189 189

H,K= 7, 4
L FOB FCA
-5 145 142
-4 161-159
-3 188 180
-2 241-238
-1 107 110
0 144-146
1 98 99
2 18 -19
3 39 39
4 0 -3

H,K= 7, 5
L FOB FCA
-4 159-155
-3 127-130
-2 44 -48
-1 160-161
0 18 -21
1 173-174
2 38 -36
3 178-170

H,K= 7, 6
L FOB FCA
-4 29 27
-3 66 -76
-2 200 205
-1 120-124
0 151 150
1 145-147
2 0 -6
3 127-123

H,K= 7, 7
L FOB FCA
-3 85 84
-2 45 44
-1 40 36
0 20 -35
1 50 48
2 47 -48

H,K= 7, 8
L FOB FCA
0 165 158
1 32 -35
2 150 147
3 46 35

H,K= 8, 0
L FOB FCA
-4 287 290
-2 315 316
0 168 168
2 131 134
4 121 126

H,K= 8, 1
L FOB FCA
-5 29 -22
-4 78 76
-3 35 -34
-2 48 44
-1 125 127
0 53 44
1 71 73
2 173 170
3 19 -21
4 133 132

H,K= 8, 2
L FOB FCA
-5 35 39
-4 154-151
-3 98 97
-2 82 -81
-1 171 174
0 70 67
1 209 206
2 32 29
3 108 111

H,K= 8, 3
L FOB FCA
-5 29 -32
-4 28 22
-3 37 -31
-2 68 65
-1 83 -84
0 0 8
1 86 -87
2 89 -92
3 20 -9

H,K= 8, 4
L FOB FCA
-4 153-147
-3 176-172
-2 100 -98
-1 202-210
0 95 -92
1 64 -66
2 140-137
3 51 -43

H,K= 8, 5
L FOB FCA
-4 36 -35
-3 108 105
-2 83 -81
-1 191 186
0 73 -72
1 204 202
2 35 -33

H,K= 8, 6
L FOB FCA
-3 98 97
-2 116 110
-1 85 82
0 94 98
1 45 -39
2 73 78

H,K= 8, 7
L FOB FCA
-2 21 -18
0 135 137
1 79 -81

H,K= 9, 0
L FOB FCA
-5 170 171
-3 19 -7

H,K= 8, 7
L FOB FCA
-1 41 -48

H,K= 9, 0
L FOB FCA
-1 103-100
3 69 91

H,K= 9, 1
L FOB FCA
-5 202-212
-4 34 36
-3 253-248
-2 124-127
-1 164-157
0 165 158
1 32 -35
2 150 147
3 46 35

H,K= 9, 2
L FOB FCA
-4 88 -86
-4 40 36
-3 38 -34
-2 36 29
-1 25 -23
0 40 -41
1 32 -22
2 122-122
3 42 -48

H,K= 9, 3
L FOB FCA
-4 64 -70
-3 61 61
-2 280-278
-1 45 -49
0 287-278
1 38 -37
2 169-166
3 30 25

H,K= 9, 4
L FOB FCA
-4 21 22
-3 20 -15
-2 58 53
-1 33 27
0 113 118
1 44 39
2 130 117

H,K= 9, 5
L FOB FCA
-3 183 181
-2 75 75
-1 153 153
0 119 111
1 29 37
2 70 69

H,K= 9, 6
L FOB FCA
-2 0 -2
-1 35 42
0 88 -85
1 37 48

H,K=10, 0
L FOB FCA
-4 127-128
-2 208-202
0 129-130
2 29 34

H,K=10, 1
L FOB FCA
-4 97-101
-3 0 2
-2 121-126
-1 33 -29
0 19 21
1 92 -88
2 35 28

H,K=10, 2
L FOB FCA
-4 0 10
-3 116-119
-2 125 121
-1 172-170
0 104 102
1 252-251
2 21 -27

H,K=10, 3
L FOB FCA
-3 29 36
-2 97 101
-1 19 11
0 52 46
1 70 69
2 0 11

H,K=10, 4
L FOB FCA
-3 0 15
-2 40 40
-1 164 160
0 70 -66
1 218 213

H,K=10, 5
L FOB FCA
-2 0 10
-1 55 53
0 42 40

H,K=11, 0
L FOB FCA
-3 146-142
-1 123-124
1 137-134

H,K=11, 1
L FOB FCA
-3 0 -4
-2 114-105
-1 20 23
0 73 -69
1 46 43

H,K=11, 2
L FOB FCA
-3 55 55
-2 124 121
-1 101 93
0 54 53
1 79 77

H,K=11, 3
L FOB FCA
-2 72 74
-1 55 -57
0 108 107

H,K=11, 4
L FOB FCA
-1 0 -16

Description of the Structure.—The structure consists of discrete octahedral groups with each manganese atom co-ordinated to two chlorine atoms at an average distance of 2.488 Å and to four oxygen atoms at an average distance of 2.206 Å. Of the eight hydrogen atoms only four are involved in hydrogen bonding which is discussed below. The over-all packing is illustrated in Fig. 1 and the dimensions of the octahedron shown in Table IV. A complete list of distances less than 4.0 Å is shown in Table V; the hydrogen atom distances are excluded.

TABLE IV

DIMENSIONS OF THE OCTAHEDRON AROUND MANGANESE IN $MnCl_2 \cdot 4H_2O$.

Atoms	Distance, Å	
Mn - Cl(1)	2.500 ± .002	(2.506)[a]
- Cl(2)	2.475 ± .002	(2.478)
- O(1)	2.224 ± .004	(2.229)
- O(2)	2.209 ± .004	(2.215)
- O(3)	2.185 ± .006	(2.198)
- O(4)	2.206 ± .005	(2.216)

Atoms	Angles	Atoms	Angles
Cl(1) - Mn - Cl(2)	96°	O(1) - Mn - O(2)	177°
- O(1)	92°	- O(3)	87°
- O(2)	87°	- O(4)	92°
- O(3)	93°	O(2) - Mn - O(3)	92°
- O(4)	174°	- O(4)	90°
Cl(2) - Mn - O(1)	88°	O(3) - Mn - O(4)	82°
- O(2)	94°		
- O(3)	169°		
- O(4)	89°		

[a]Distances in parentheses are values corrected for thermal motion assuming that the O anc Cl atoms "ride" on the Mn.

TABLE V

DISTANCES UNDER 4.0 Å WITH STANDARD DEVIATIONS IN $MnCl_2 \cdot 4H_2O$. [a]

Atom		Distance, Å	
Mn	- O(1)	2.224 ± .004	
	- O(2)	2.209 ± .004	
	- O(3)	2.185 ± .006	
	- O(4)	2.206 ± .005	
	- Cl(1)	2.500 ± .002	
	- Cl(2)	2.475 ± .002	
Cl(1)	- Mn	2.500 ± .002	
	- O(2)	3.233 ± .005	b
	- O(1)	3.391 ± .005	b
	- O(3)	3.414 ± .006	b
	- Cl(2)	3.708 ± .003	b
	- O(1)	3.169 ± .005	c
	- O(4)	3.292 ± .005	c
	- O(2)	3.477 ± .005	
Cl(2)	- Mn	2.475 ± .002	
	- O(1)	3.254 ± .005	b
	- O(4)	3.285 ± .005	b
	- O(2)	3.442 ± .005	b
	- Cl(1)	3.708 ± .003	b
	- O(2)	3.166 ± .005	c
	- O(3)	3.815 ± .007	
O(1)	- Mn	2.224 ± .004	
	- O(3)	3.033 ± .008	b
	- O(4)	3.185 ± .006	b
	- Cl(2)	3.254 ± .005	b
O(2)	- Mn	2.209 ± .004	
	- O(4)	3.117 ± .007	b
	- O(3)	3.146 ± .008	b
	- Cl(1)	3.233 ± .005	b
	- Cl(2)	3.442 ± .005	b
	- O(1)	2.926 ± .006	c
	- Cl(2)	3.166 ± .005	c
	- Cl(1)	3.477 ± .005	
O(3)	- Mn	2.185 ± .006	
	- O(4)	2.872 ± .008	b
	- O(1)	3.033 ± .008	b
	- O(2)	3.146 ± .008	b
	- Cl(1)	3.414 ± .006	b
	- Cl(2)	3.815 ± .007	
O(4)	- Mn	2.206 ± .005	
	- O(3)	2.872 ± .008	b
	- O(2)	3.117 ± .007	b
	- O(1)	3.185 ± .006	b
	- Cl(2)	3.285 ± .005	b
	- Cl(1)	3.292 ± .005	c
	- O(1)	3.339 ± .006	
O(1)	- Cl(1)	3.391 ± .005	b
	- O(2)	2.926 ± .006	c
	- Cl(1)	3.169 ± .005	c
	- O(4)	3.339 ± .006	

TABLE V (continued)

[a]Hydrogen atom distances are not included.

[b]Octahedral edge.

[c]Hydrogen bond.

The octahedron is only slightly distorted with the primary distortion due to the packing of the two larger chlorine atoms with the four somewhat smaller oxygen atoms. The chlorine atoms are adjacent in each octahedron, and not opposite as in the $FeC\ell_2 \cdot 4H_2O$ structure[4] although both structures have discrete octahedra. Also in the $FeC\ell_2 \cdot 4H_2O$ structure there are two different octahedral Fe-O distances (2.09 Å and 2.59 Å), whereas in the $MnC\ell_2 \cdot 4H_2O$ all four Mn-O distances are almost equivalent (2.19 Å to 2.22 Å). The densities of the two substances are very similar (2.03 g./cc. for the Mn compound, 1.98 g./cc. for the Fe compound), indicating that the efficiency of packing is also comparable. These comparisons suggest a rather interesting phase transformation if the metastable β-form of $MnC\ell_2 \cdot 4H_2O$ is indeed isomorphous with $FeC\ell_2 \cdot 4H_2O$ as is suggested by Groth[2].

According to Groth[2] $MnBr_2 \cdot 4H_2O$ has axial cell ratios, and β angle very close to $MnC\ell_2 \cdot 4H_2O$ and is presumably isostructural with the structure described in this paper.

There is a similarity between the $MnC\ell_2 \cdot 4H_2O$ structure and that reported by Culot *et al*[12] for $NaBr \cdot 2H_2O$. Dawson and Williams[3] remark that $MnC\ell_2 \cdot 4H_2O$ and $NaC\ell \cdot 2H_2O$ are isomorphous, and the relation is further expanded by Groth[2] who states that $NaC\ell \cdot 2H_2O$ and $NaBr \cdot 2H_2O$ are isomorphous. If the monoclinic cell for $NaBr \cdot 2H_2O$ is doubled along its *a* axis and a different setting chosen, the resulting cell has axial ratios and β angle as follows, $a : b : c = 1.171 : 1 : 0.653$ with $\beta = 97.3^\circ$; this is quite similar to the values for $MnC\ell_2 \cdot 4H_2O$ reported here. The $NaBr \cdot 2H_2O$ structure also consists of octahedra with the halide atoms adjacent. These octahedra

however, each share an edge with each of three adjacent octahedra, consistent with one extra anion in the formula, and form sheets in contrast with discrete octahedra in $MnC\ell_2 \cdot 4H_2O$.

Hydrogen Bonding.—All eight independent H atoms were located from the difference function calculated after an anisotropic refinement of the seven heavier atoms. Four of these are in a suitable environment to participate in hydrogen bonding, but the other four have no close neighbors that would indicate such bonding. A representative of each independent H atom is shown in Fig. 1 and appropriate distances for the four bonded hydrogens are indicated in Table V. The four hydrogen bonds are as follows.

O(1)——H(1)1·····Cℓ(1)	3.17 Å
O(2)——H(2)1·····Cℓ(2)	3.17 Å
O(2)——H(2)2·····O(1)	2.93 Å
O(4)——H(4)1·····Cℓ(1)	3.29 Å.

All of the distances above represent hydrogen bonding between atoms in different octahedra.

The distances calculated for the O-H distances in water from the parameters listed in Table I are .8 and 1.0 Å for O(1); .8 and .9 Å for O(2); .5 and .6 Å for O(3); and .9 and 1.0 Å for O(4). It is because of the limited accuracy of our hydrogen parameters that we have not presented a detailed list of distances to the hydrogen atoms.

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(1) Work done under the auspices of the U. S. Atomic Energy Commission.

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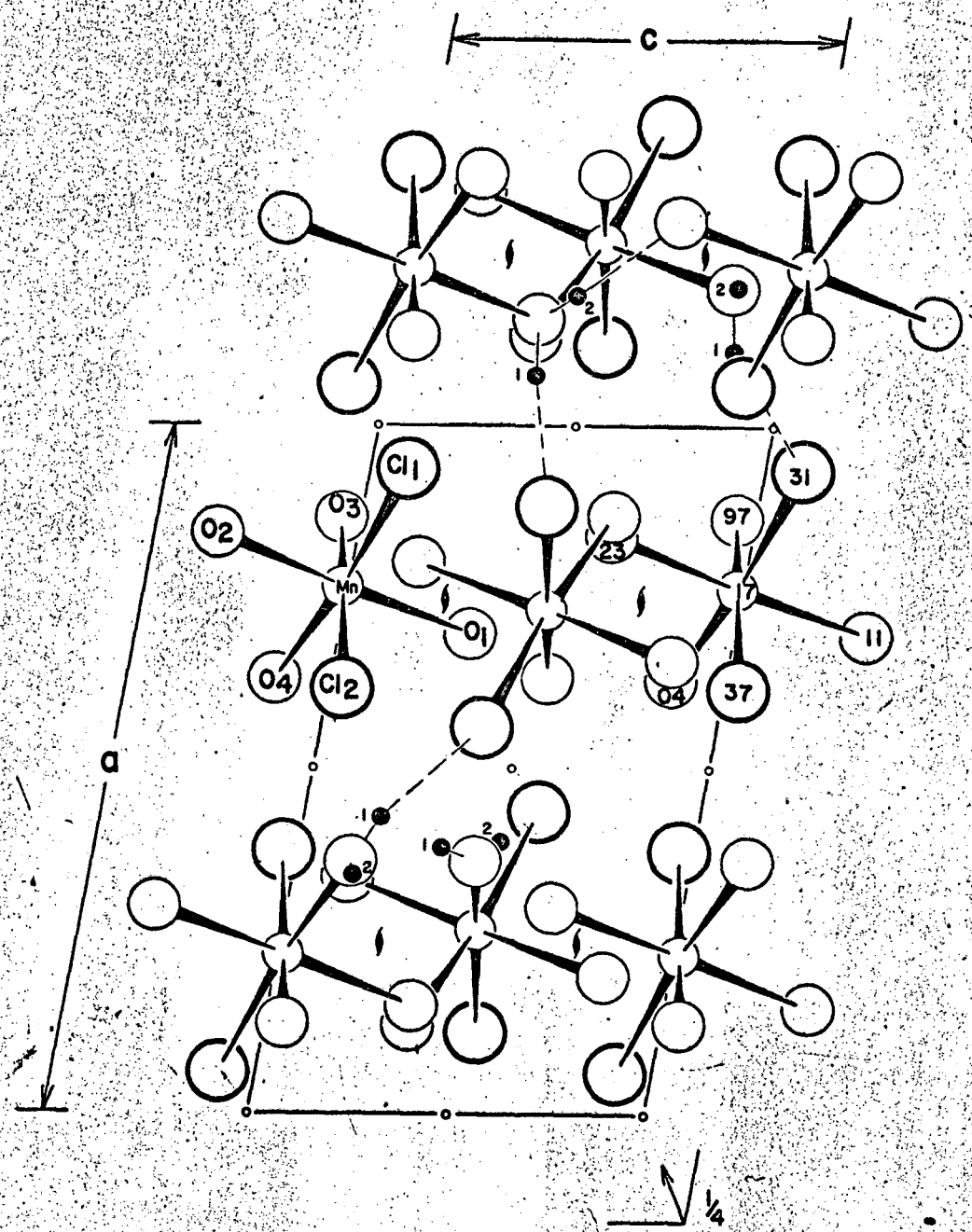
Figure Caption

Fig. 1.—Atomic arrangement in $MnC\ell_2 \cdot 4H_2O$. Y coordinates (x100) are indicated as numbers inside some of the circles. The small solid circles represent hydrogen atoms, and only one of each type is shown.



$MnCl_2 \cdot 4H_2O$

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